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**Chiroptical probes to track spin & light polarization in space & time in emerging semiconductors**S. Feldmann<sup>1</sup><sup>1</sup>Laboratory for Energy Materials, EPFL Lausanne; sascha.feldmann@epfl.ch

Solution-processable semiconductors like halide perovskites and certain molecules are promising for next-generation spin-optoelectronic applications [1]. Yet, we don't fully understand what governs the excitation and spin dynamics in these materials, and even less how these are affected by chirality.

In this talk, I will give an overview of our recent efforts to understand the spin-optoelectronic performance of these materials through time-, space- and polarization-resolved spectroscopy and microscopy.

For halide perovskite films, I will first show that energetic disorder strongly modulates their charge dynamics [2,3]. By pushing broadband circular dichroism to diffraction-limited spatial and 15 fs time resolution, we then create a spin cinematography technique to witness the ultrafast formation of spin domains in these films due to local symmetry breaking and spin-momentum locking [4]. I will then briefly explain the fundamentals and artifacts involved in measuring circularly polarized luminescence (CPL) reliably and introduce an open-access methodology and code to do so [5], and finally show our most recent development of full Stokes-vector polarimetry with unprecedented time- and polarization resolution to track the emergence of chiral light emission [to be submitted].

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## Excited-State Symmetry Breaking and its Origins: Insights from Ultrafast Transient Two-Dimensional Infrared Spectroscopy

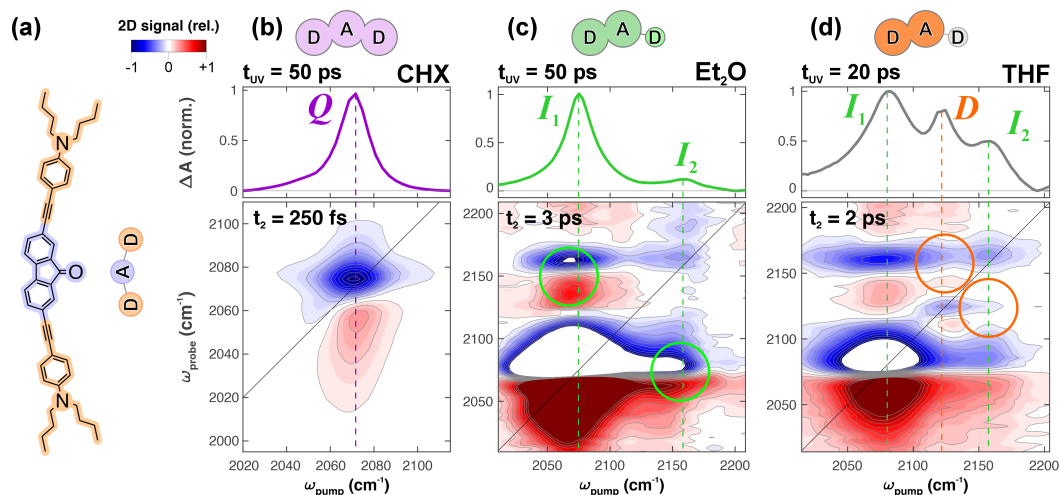
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Excited-state symmetry-breaking (ES-SB) is a fundamental phenomenon, which is being increasingly observed in multipolar molecules and leads to the localisation of the charge-transfer excitation. Harnessing this process is particularly relevant for the photoreactivity of conjugated optical materials.[1] Herein, we probe the excited-state dynamics of a D- $\pi$ -A- $\pi$ -D chromophore, which exhibits ES-SB upon photoexcitation (**Fig. 1A**).[2] Using transient 2D-IR (tr2DIR) spectroscopy, we examine the ultrafast relaxation dynamics, intramolecular vibrational couplings, and solvation effects, by focussing on the  $\nu(\text{C}\equiv\text{C})$  modes (2050–2250  $\text{cm}^{-1}$ ).

In cyclohexane, where symmetry is preserved, we only observe the fully delocalised quadrupolar state ( $Q$ ). This band exhibits ultrafast spectral diffusion within the IRF, leading to a motionally-narrowed 2D Lorentzian line shape (**Fig. 1B**). In  $\text{Et}_2\text{O}$ , we observe two bands, attributed to the intermediate state ( $I$ ), with partial exciton localisation. These two bands evolve and decay similarly, with cross peaks suggesting that they are anharmonically coupled (**Fig. 1C**). In the more polar THF, we observe three bands, pointing towards an equilibrium between the  $I$  and the dipolar ( $D$ ) states (**Fig. 1D**). In this case, cross peaks between the  $I$  and  $D$ -associated bands suggest either (i) ultrafast interconversion between these states within the vibrational lifetime; or (ii) transient promotion of the  $I \rightarrow D$  interconversion by vibrational excitation, which quickly relaxes back to equilibrium.

We will discuss these and other related results, and support our observations based on a newly developed methodology to simulate ES-SB using quantum-chemical calculations.



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**Real-time tracking of the ultrafast chirality and energy transfer in a chiral OLED complex with circularly-polarized luminescence**L. Müller<sup>1</sup>, F. Zinna<sup>2</sup>, G. Pescitelli<sup>2</sup>, M. Puppini<sup>3</sup>, M. Oppermann<sup>1\*</sup><sup>1</sup>Department of Chemistry, University of Basel, Switzerland, <sup>2</sup>Department of Chemistry and Industrial Chemistry, University of Pisa, Italy, <sup>3</sup>Lausanne Centre for Ultrafast Science, EPFL, Switzerland

Circularly-polarized luminescence (CPL) has promising applications in the fields of optical data storage, biomedical diagnosis and for the creation of more efficient OLED displays.<sup>1</sup> In this respect, chiral lanthanide complexes have gained a lot of attention as CPL emitters due to their sharp and intense emission lines, long emission lifetimes and above all, due to their high degree of circular polarization. However, despite the impressive progress in the synthesis of metallo-organic CPL complexes, the underlying excited state dynamics of their chiral luminescent states have thus far remained inaccessible due to a lack of ultrafast spectroscopic techniques with sufficient chiral sensitivity.

To address this gap, we have developed a novel ultrafast circular dichroism (CD) instrument that combines ultra-sensitive broadband detection with sub-picosecond time resolution.<sup>2</sup> We now apply this technique to resolve the CPL mechanism of the prototypical CsEu(+)-hfbc<sub>4</sub> (hfbc = 3-heptafluoro-butyrylcamphorate), which displays a record CPL emission with 85% of the photons being left-circularly polarized at 595 nm.<sup>3</sup> Although its luminescent transitions are metal-centered (MC), the chiral ligands play a crucial role in the CPL mechanism. First, they act as photosensitizers providing efficient energy transfer to the dipole-forbidden MC transition. Second, the CPL emission requires the coupling of the chiral ligands' electric transition dipoles to the MC magnetic transition dipoles, known as the dynamic coupling mechanism.<sup>4,5</sup>

Combining ultrafast CD with transient absorption and anisotropy measurements from the visible to the deep ultraviolet, we now present the first ultrafast spectroscopy study of a CPL complex. We found that the energy transfer proceeds via a chiral ligand-centered triplet state in 150 ps. Quite remarkably, we observe a change in optical activity of the ligand system upon energy transfer, which we attribute to an electronic coupling with the excited emissive MC states.

More generally, our results highlight that with ultrafast circular dichroism it is now possible to capture the evolution of chiral excited states in real-time, opening a new path to the direct investigation and optimization of CPL compounds.

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**Capturing site-selective chemical dynamics via time-resolved X-ray photoelectron spectroscopy**

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X-ray Photoelectron Spectroscopy (XPS) offers insight into a molecular system's chemical environment at a specific atomic site. Extending the concept of the chemical shifts to the femtosecond regime, photoinduced chemical dynamics could be traced with element selectivity, elucidating the complex interplay between electron rearrangement and nuclear motion.

Recently, the possibility of producing two intense femtosecond X-ray pulses with tunable time delay and color has been developed for X-ray Free Electron Lasers. Building on this capability, we demonstrated the potential of ultrafast time-resolved XPS (TR-XPS) with an X-ray pump/probe approach. In our study, we used carbon monoxide, i.e., a small heteronuclear molecule that can be well described with theoretical models. The pump pulse excites a core-electron resonantly at the oxygen K-edge, and then we probe the molecular response with photoemission from the carbon core levels. Using a combined experimental and theoretical approach, we could track and model the initial electronic core-excited state and hole localization, followed by the core-hole decay through the Auger-Meitner process, leading to the dissociation of the molecule [1].

The two-color X-ray pump/probe approaches can be further extended at SwissFEL. The widely tunable Athos undulator line allows the generation of two consecutive X-ray pulses in the soft X-ray spectral regime with variable photon energy, polarization, pulse duration, and time separation [2]. TR-XPS capability is offered to users at the Maloja endstation, where the excitation could be initiated by an X-ray or a UV/Vis/IR pulse.

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**Magnetic Deflection of Neutral Sodium Solvent Clusters: Na(H<sub>2</sub>O)<sub>n</sub>, Na(NH<sub>3</sub>)<sub>n</sub>, Na(MeOH)<sub>n</sub>, and Na(DME)<sub>n</sub>**D. P. Borgeaud dit Avocat<sup>1</sup>, J. V. Barnes<sup>1</sup>, E. Simmen<sup>1</sup>, B. L. Yoder<sup>1</sup>, R. Signorell<sup>1</sup><sup>1</sup>ETH Zürich, Department of Chemistry and Applied Biosciences, Zürich 8093, Switzerland

Since the discovery of concentration-dependent colors of alkali metal-ammonia solutions in the early 19th century<sup>[1]</sup>, excess electrons in alkali metal solutions have been found to be important in many areas. They are ubiquitous in liquid-phase chemistry<sup>[2]</sup> and play an essential role in several chemical reactions<sup>[3]</sup> and biology<sup>[4]</sup>. Extensive experimental and theoretical work has been performed on solvated electrons in alkali metal solutions<sup>[2]</sup> (and references therein). However, the underlying correlation effects of solvated electrons are still not well understood. While magnetic measurements have probed such effects in alkali metal solutions<sup>[5, 6]</sup>, diamagnetic and paramagnetic species have not yet been identified in such bulk phase experiments<sup>[2]</sup>. We present a study of the magnetic properties of sodium solvent (Solv) clusters (Na(Solv)<sub>n</sub>, n=1-10), where ammonia, water, dimethyl ether, and methanol were taken as model solvents<sup>[7, 8, 9]</sup>. Using a pulsed Stern-Gerlach deflector, we measure the magnetic deflection of a neutral cluster beam using both Velocity Map and Spatial Map Imaging detection. The experimental deflection is compared with molecular dynamics simulations based on the Zeeman interaction of a free spin ½ system. The comparison reveals unperturbed magnetic properties of a spin ½ system for both Na(NH<sub>3</sub>)<sub>1</sub> and Na(H<sub>2</sub>O)<sub>1</sub>. All other studied clusters, namely Na(NH<sub>3</sub>)<sub>n</sub> (n=2-10), Na<sub>3</sub>(NH<sub>3</sub>)<sub>n</sub> (n=1-2), Na(H<sub>2</sub>O)<sub>n</sub> (n=2-4), Na(DME)<sub>n</sub> (n=1-3) and Na(MeOH)<sub>n</sub> (n=1-4), by contrast, show reduced deflection compared with that of a spin ½ system or no deflection. These deviations from a spin ½ behavior are attributed to intra-cluster spin-relaxation effects occurring on time scales similar to or faster than the experiment. Determining spin relaxation times for these systems allows us to identify trends in their magnetic behavior. These trends are discussed in terms of coupling of thermally accessible rovibrational eigenstates.

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**Competition between product channels in ion-molecule reactions near 0 K:  $D_2^+ + CH_3F$  and  $D_2^+ + H_2O$** D. Schlander<sup>1</sup>, R. Hahn<sup>1</sup>, F. Merkt<sup>1\*</sup><sup>1</sup>Institute for Molecular Physical Science, ETH Zürich, 8093 Zürich, Switzerland

Ion-molecule reactions are essential steps of astrophysical and atmospheric chemical networks but are difficult to study at low energies ( $<k_B$  50 K) because stray fields heat the ions up. We circumvent this difficulty by replacing the ion (here  $D_2^+$ ) by a highly excited Rydberg molecule [1,2]. The distant Rydberg electron shields the ion core from external fields without influencing the ion-molecule reaction within its orbit. We use a Rydberg-Stark [3] deflector to merge a beam of  $D_2$  Rydberg molecules with supersonic beams of ground-state neutral molecules.

This deflector is also used to set the velocity of the Rydberg molecules ( $v_{Ryd}$ ). By tuning  $v_{Ryd}$  relative to the velocity of the ground-state molecules, we tune the collision energy  $E_{col}$  from  $\sim k_B$  100 mK to  $\sim k_B$  50 K. The product ions, the reaction rates and the branching ratios are measured as a function of  $E_{col}$ . Short ( $\sim 20$   $\mu$ s) gas pulses ensure a high collision-energy resolution.

We report here on the reactions of  $D_2^+$  with  $CH_3F$ ,  $H_2O$  and  $D_2O$  studied following the same procedure as used for the  $D_2^+ + NH_3$  reaction [4]. The rate coefficients of these reactions deviate strongly from Langevin rates and increase sharply below 2 K, as expected for reactions between ions and dipolar molecules. These observations are analyzed using a rotational adiabatic capture model including the Stark effect of the rotational states of the symmetric- or asymmetric-top molecules in the electric field of the ion [5,6,7].

Three products are observed for the reaction of  $D_2^+$  with  $CH_3F$ :  $CH_3F^+$ ,  $CH_3^+$  and  $CH_2F^+$ . The reaction with water produces  $H_2O^+$  and  $H_2DO^+$ . Both reactive systems exhibit a competition between charge transfer and short-range chemical processes. This competition results in a striking dependence of the reaction branching ratios on the collision energy, particularly at the lowest collision energies.

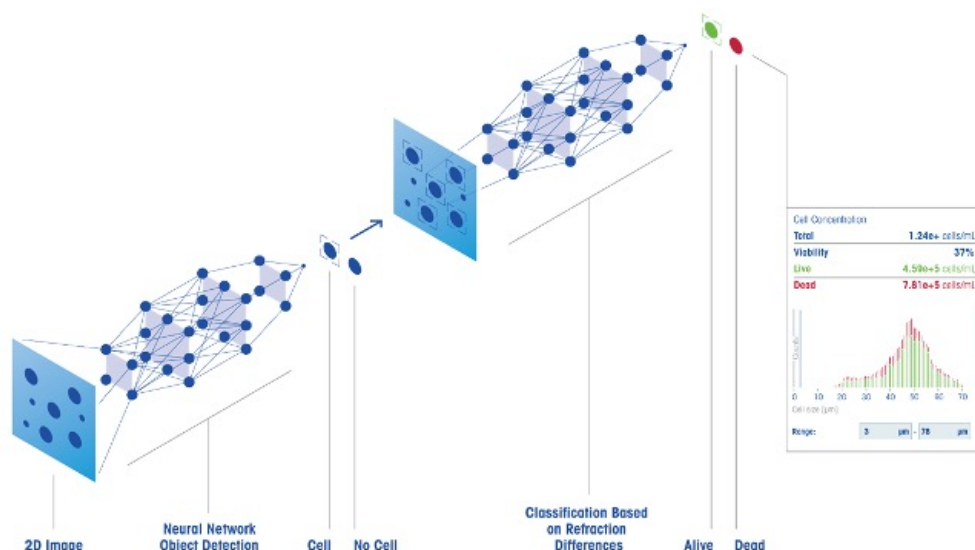
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## Holographic Microscopy and Machine Learning – Transforming Cellular Assays

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Cell counting is a critical step in cellular assays, enabling researchers to ensure a consistent number of cells for their experimental analyses. Recent advances in holographic microscopy and machine learning have transformed cellular assays development. This innovative technique provides a label-free and non-invasive approach for identifying and distinguishing healthy, dying, and dead eucaryotic cells. The integration of machine learning techniques allows for automatic cell classification, reducing result variability due to stain intensity, microscope settings, and user-dependent classification. This approach enhances the reliability of viability measurements between samples, while also addressing common issues present in other cellular analytical techniques. We will discuss the potential of holographic microscopy and machine learning in improving the accuracy and consistency of cellular assays.





**Multifunctional hybrid systems via self-organization of Janus nanoparticles and polymersomes for bio-applications**

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Nano-objects have the ability to self-organize into intricate architectures, forming novel systems with emergent properties and functionalities useful in fields such as electronics, technology and chemistry [1-3]. One way to achieve these advanced systems necessitates DNA hybridization among synthetic assemblies like polymersomes, nanoparticles, and micelles. The clusters between polymersomes are essential for developing interconnected artificial organelles, promoting cascade reactions between encapsulated catalytic compounds, and mimicking cellular signaling or interactions [4,5]. In this study, a new approach is proposed for developing a multifunctional hybrid system for specific bio-applications by investigating the self-organization of clusters between "hard" Janus nanoparticles (JNPs) and "soft" polymersomes [6]. These polymer-based JNPs provide an asymmetric platform suited for directional interaction with soft polymersomes [7]. The clusters are modularly assembled through programmed DNA hybridization. Furthermore, the vesicular architecture of the polymersomes after assembly into JNP-polymersome clusters allows the encapsulation of various kinds of catalytic compounds. The asymmetry of the JNPs has unique advantages by allowing a precise arrangement of the polymersomes and enabling, in a modular manner, various reaction configurations, including single, parallel and cascade enzymatic reactions. Additionally, these clusters, which integrate imaging and therapeutic nanocompartments, support nanotheranostic applications by enabling precise in vitro detection and simultaneously producing reactive oxygen species (ROS) to induce apoptosis.

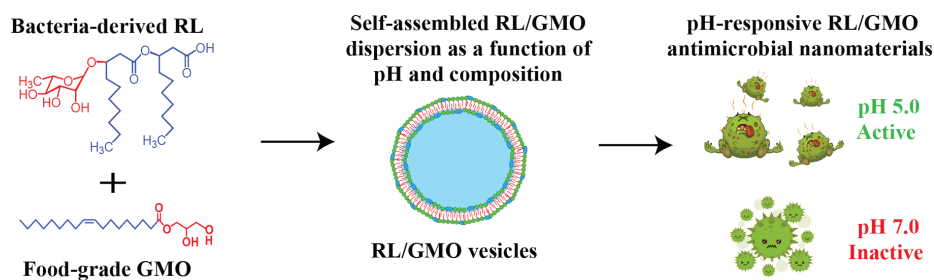
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## Innovative pH-Responsive Rhamnolipid Nanomaterials: Advanced Antimicrobial Solutions

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Bacterial resistance to conventional antibiotics in acidic environments is a concerning and persistent issue since a long time.<sup>[1]</sup> Hence, development of an alternative, biocompatible, sustainable, and pH-responsive antimicrobial biomaterials is urgently needed.<sup>[2]</sup> This study demonstrates the rational design and characterization of a novel biocompatible pH-responsive antimicrobial material developed by combining microbial-derived rhamnolipids (RL) and food-grade glyceryl monooleate (GMO).<sup>[3]</sup> The resulting supramolecular materials are tailored for their antimicrobial and biofilm inhibition activities in the acidic pH conditions often found in acute wounds (Figure 1). A key finding is that while RL alone tends to phase separate at pH levels below 6.0, its incorporation into dispersed GMO particles creates a colloiddally stable dispersion crucial for practical applications. Structural changes influenced by composition and pH variations are examined using small-angle X-ray scattering, cryogenic transmission electron microscopy, and dynamic light scattering. These characterization techniques revealed that the structures transition from an Im3m type cubic phase to vesicles in these nanomaterials. Biological assays conducted *in-vitro* show that RL/GMO dispersions effectively target Gram-positive bacteria such as *Staphylococcus aureus* (*S. aureus*) and methicillin-resistant *S. aureus* (MRSA), preventing their biofilm formation at pH 5.0. Notably, these materials are inactive at pH 7.0, indicating a high degree of pH specificity. Additionally, the materials do not exhibit antimicrobial activity against various Gram-negative bacteria at either pH levels, suggesting targeted efficacy. The cytocompatibility of these nanomaterials with human dermal fibroblasts suggests their safety for potential medical use. Overall, these findings enhance our understanding of lipid self-assembly and demonstrate the potential of lipid-based biomaterials as effective bio-based antibacterial solutions. Furthermore, the study identifies promising interactions between RL and mucin, paving the way for the development of innovative nutrient and drug delivery systems to address unmet clinical needs.



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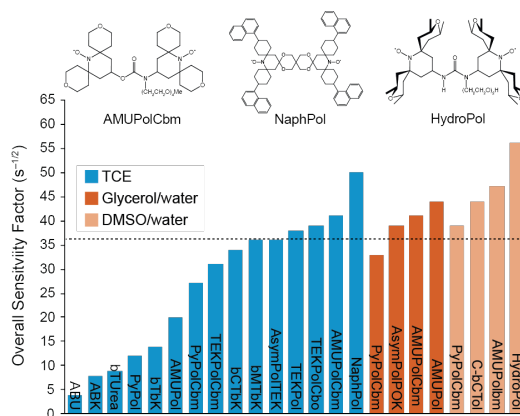
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## Rational Design of Dinitroxide Polarizing Agents for Dynamic Nuclear Polarization to Enhance Overall NMR Sensitivity

R. Wei<sup>1</sup>, A. Venkatesh<sup>1</sup>, G. Casano<sup>2</sup>, Y. Rao<sup>1</sup>, H. Lingua<sup>2</sup>, H. Karoui<sup>2</sup>, M. Yulikov<sup>3</sup>, O. Ouari<sup>2\*</sup>, L. Emsley<sup>1\*</sup>

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NMR suffers from a long-standing limitation of its intrinsically low sensitivity, primarily due to the small population difference between nuclear spin states. Today Dynamic nuclear polarisation (DNP) under magic angle spinning (MAS) performed at high magnetic fields provides sensitivity enhancement by up to 2 orders of magnitude, typically via the currently most efficient cross-effect (CE) process. This sensitivity gain has led to the development of a variety of nitroxide-based biradicals, with tailored properties such as electron-electron dipolar couplings, g-tensor orientation, electron relaxation times, and solubility for better performance.<sup>[1]</sup>



To evaluate the overall DNP performance of different radical/solvent formulations, a series of 18 biradicals (including 8 newly-synthesized biradicals) were prepared.<sup>[2]</sup> We systematically compared the overall sensitivity gains provided by these formulations at 9.4 T and 100 K, taking into account the DNP enhancement factor  $\epsilon$ , the DNP build-up times  $T_B$ , and the depolarization and quenching effects. Overall, NaphPol and HydroPol were identified to be the best performing biradicals in organic and water-based solutions, respectively. A new biradical, C-bcTol, which has a closed conformation and is more resistant to reducing conditions, yields the highest enhancement seen so far in the closed class of radicals. We also introduce a newly-developed biradical, AMUPolCbm, which provides high efficiency in all three solvent formulations considered here, making it the most versatile polarizing agent.

In addition, we pinpointed that although biradicals can significantly differ in the obtained enhancements and build-up times, these factors often compete, and consequently many radicals yield similar overall NMR sensitivity gains. Therefore it appears that the current design strategies of new dinitroxide biradicals has reached a glass ceiling in CE DNP performance at 9.4 T and 100 K, and new considerations need to be introduced to make further progress in the future.

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**Improved super-resolution imaging with cucurbituril-encapsulated fluorophores**L. Briant<sup>1,2</sup>, A. Fürstenberg<sup>1,2\*</sup><sup>1</sup>Department of Physical Chemistry, University of Geneva, <sup>2</sup>Department of Inorganic and Analytical Chemistry, University of Geneva

The development of super-resolution microscopy has been one of the most important advances in order to image tissue structure or cellular dynamics below the diffraction limit. Because of the biological targets, super-resolution experiments are typically performed in aqueous solution. However, water is known to be a fluorescence quencher of organic dyes and the replacement of H<sub>2</sub>O by D<sub>2</sub>O can drastically increase the fluorescence quantum yield and the localization precision[1,2]. Recently, the quenching of 40 dyes was investigated leading to the conclusion of a FRET mechanism between red-emitting fluorophores and vibrational overtones and combination bands of OH groups of the solvent in direct contact with the dyes[3]. Since fluorophores in biological samples are mostly surrounded by water, one way to prevent quenching from occurring would be to isolate them from the solvent using macrocyclic cavities such as cyclodextrins[4] and cucurbiturils. The aim of this study was to investigate a possible isolation of common red-emitting dyes from water by cucurbiturils. After a successful synthesis of the macrocyclic hosts, the photophysics of host-guest complexes between cucurbiturils and red-emitting fluorophores was investigated and their binding affinities determined. Furthermore, the suitability of encapsulated fluorophores for single-molecule and super-resolution experiments was evaluated and super-resolution imaging on cells in the absence and in the presence of cucurbiturils was successfully achieved with cucurbiturils significantly increasing the brightness and the localization precision in single-molecule-based super-resolution imaging.

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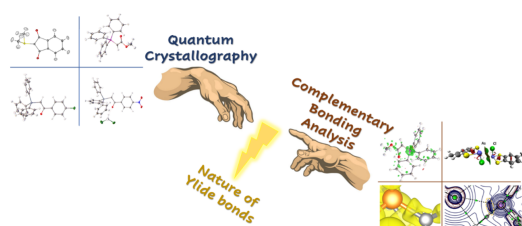
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## Insights into the Bonding Nature of Arsenic, Phosphorus, and Sulphur Ylides: an answer from quantum crystallography

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Ylides are a class of chemical compounds classified as zwitterion by having a positively charged atom directly attached to a negatively charged atom. The most common types of ylides involve a positively charged heteroatom like nitrogen, phosphorus, sulphur, or arsenic attached to a negatively charged carbon atom. <sup>[1,2]</sup> Ylides are textbook examples of the interplay between Lewis resonance forms and molecular reactivity/function. Phosphorus ylides or phosphonium ylides have been widely used in organometallic and organic synthesis, most famously as Wittig reagents in the Wittig reaction. Sulphur ylides (sulfonium ylides and sulfoxonium ylides) are also employed in organic synthesis, e.g. in the Johnson–Corey–Chaykovsky reaction. Another class of ylide compounds is arsenic ylides which are less commonly encountered compared to phosphorus and sulphur ylides despite being discovered more than a century ago. However, arsenic ylides have been explored for their synthetic utility and attracted chemist's attention especially as a representative of a different synthesis mechanism compared to phosphorus ylides like Cyclopropanation reaction. The ylide bond plays a key role in all these applications. Despite all these applications, the nature of the ylide bond is still unclear and under debate. <sup>[3,4]</sup>



**Figure 1.** Schematic representation of the study

In this regard, a combination of quantum crystallography (Hirshfeld atom refinement + x-ray constrained wave function fitting) and complementary bonding analysis [5] (QTAIM, ELI-D, EDA, NBO, VBT) reveals the nature and character of the P-C, S-C, and As-C bonds in ylides in detail. It is of practical importance and will also clarify concepts such as the hypervalency of P, S, and As atoms as well as the interplay between covalency and ionicity of heteroatom bonds. To the best of our knowledge, there are four experimental charge density studies about these bonds using multipole refinement, and there is no Hirshfeld atom refinement (HAR) and X-ray wavefunction (XCW) fitting study about these bonds. <sup>[6]</sup> Here, high-resolution XRD data is collected for one sulphur ylide, two phosphorus ylides, and two arsenic ylides. Then, X-ray wavefunction refinements (HAR + XCW fitting) plus complementary bonding analyses are performed to evaluate the ylide bonds. Our results demonstrate that the ylide bond is a charge-separated bond with a localized lone pair on the ylide carbon. This bond is an intermediate between covalent and ionic bond and the concept of double bond should be ruled out. Also, the theory of the hypervalent hetero atom (P, S, As) in ylides can be ruled out due to the minor contribution of d orbitals in the bonding and the low energy of this specific orbital interactions. From the energy perspective, the electrostatic term plays a significant role in stabilizing the bond and it influence the bonding more than orbital interactions.

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**Surface Immobilization of Magnetic Polymeric Giant Unilamellar Vesicles**

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Synthetic vesicles have garnered significant interest in bioengineering due to their resemblance to biological membranes. Giant unilamellar vesicles (GUVs) are micron-sized compartments that can be categorized into lipid-based and polymer-based GUVs based on the membrane-forming substances. Surface immobilization of GUVs has been previously explored using various methods, including DNA hybridization and avidin-biotin interactions. In our study, we utilize magnetic force to manipulate, direct, and immobilize temporarily and reversibly polymeric GUVs. The vesicles were prepared via a double-emulsion templated microfluidics using the amphiphilic diblock copolymer of poly(dimethylsiloxane)<sub>25</sub>-*b*-poly(2-methyl-2-oxazoline)<sub>10</sub> (PDMS<sub>25</sub>-*b*-PMOXA<sub>10</sub>) as the polymeric phase. Hydrophilic magnetic particles were introduced into the lumen of the GUVs during fabrication. These particles, with an approximate size of 1 μm, are suspended within the GUVs and can be externally manipulated using a magnetic field. The GUV membranes showed no signs of change or permanent deformation during manipulation. We studied the stability of these magnetic GUVs over time and confirmed the effect of polymeric phase concentration on their stability. Surface immobilization was investigated using an in-house-built substrate composed of permanent magnets. Results demonstrated the successful immobilization of GUVs on the substrate and their mechanical stability under an external magnetic field. This system has potential applications in surface treatments, and wastewater purification.

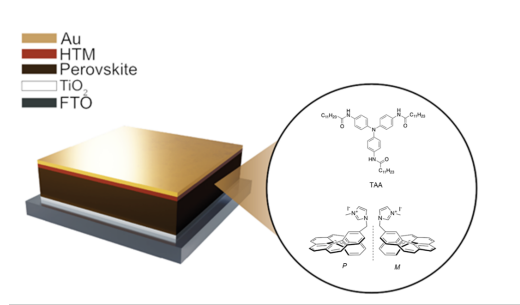
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### Supramolecular Modulation for Hybrid Perovskite Photovoltaics

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Hybrid perovskites are emerging as top contenders in the next generation of photovoltaics, yet their stability under operational conditions remains a significant challenge. Specifically, degradation occurs at the interface with charge transport layers in perovskite solar cells during operation.<sup>[1]</sup> To address this, we explore using supramolecular interfacial modulators at the interface of charge-transport layers with the purpose of suppressing degradation without interfering with the photovoltaic performance.<sup>[2,3]</sup> This included functionalized triarylamine-based modulators, which are known to form hole-transporting supramolecular stacks,<sup>[2]</sup> as well as chiral P,M-(1-methylene-3-methyl-imidazolium)[6]helicene iodides, which could contribute to the charge transport through chiral-induced spin-selectivity (CISS) effects. These modulators were applied at the interface between the perovskite active layer and the hole-transporting material in conventional perovskite solar cells (Figure 1). We have investigated their impact on the structural characteristics and optoelectronic properties via a combination of techniques, including X-ray diffraction, UV-vis and both steady-state and time-resolved photoluminescence spectroscopy, complemented with the further analysis of photovoltaic devices. Our investigation challenges the role of chirality in perovskite photovoltaics and reveals the contribution to the improvement of operational stabilities without compromising device performance, offering promising new strategies for advancing perovskite photovoltaics.<sup>[3]</sup>



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## Understanding the activation mechanism of Ru-based catalyst for CO<sub>2</sub> reduction via Ultrafast Transient-IR

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<sup>1</sup>University of Zurich

CO<sub>2</sub> reaction has been studied extensively over the last few decades due to environmental concerns [1]. Various possible solutions to reduce it have been put into practice, ranging from atmospheric CO<sub>2</sub> capture to heterogeneous and homogeneous catalysis to produce value-added chemicals. The latter approach has been widely tested, but unfortunately, there is not a clear understanding of the mechanism to choose a route to reach hydrogen-rich compounds such as MeOH or HCOOH, and CO. The scientific community aims to continue developing existing catalysts to improve the performance/cost ratio, as well as investing in green alternatives for the materials used. Despite the vast information available in literature, the lack of a solid and accepted mechanism motivates us research such systems. Ruthenium-based catalysts have been explored since the 80s, appearing to be a good model system. My current research focuses on Ru(x,x'-dimethylbipyridyl)(CO)<sub>2</sub>Cl<sub>2</sub> to study a catalytic cycle proposed by Ishida [2]. The experimental setup to “interrogate” the chemical system is a visible pump – IR probe type experiment, where we can observe in operando (Fig 1 and Fig 2) the catalysis to reveal transient chemical species in contrast to the classical steady-state experiments.

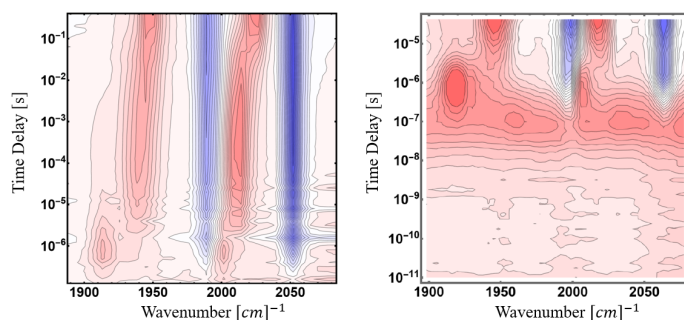


Fig 1: Transient-IR data for Ru(6,6' - dmbpy)(CO)<sub>2</sub>Cl<sub>2</sub> catalyst in presence of Ru(bpy)<sub>3</sub> as a photosensitizer and BNAH as an electron donor in DMF.

Fig 2: Transient-IR data for Ru(5,5' - dmbpy)(CO)<sub>2</sub>Cl<sub>2</sub> catalyst in presence of Ru(bpy)<sub>3</sub> as a photosensitizer and BNAH as an electron donor in DMSO.

The screening of different solvents, isomers of the catalyst, DFT calculations and synthetic proofs led us to conclude a feasible mechanism, furthering the understanding of the stepwise reaction. In this study, we have fully resolved the labyrinthine mechanism leading to the catalyst's activation:

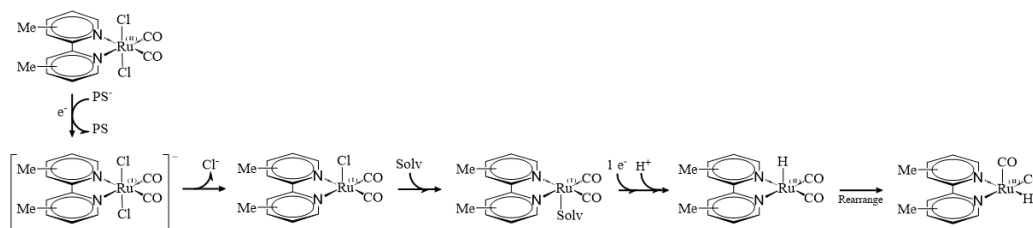


Fig 3: Proposed reaction mechanism focused on Ru(6,6' - dmbpy)(CO)<sub>2</sub>Cl<sub>2</sub>

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**Polymer assembly as artificial cell for compartmentalizing lactate enzymatic reaction**A. Balestri<sup>1</sup>, C. Palivan<sup>1\*</sup><sup>1</sup>Department of Chemistry, University of Basel, Mattenstrasse 24a, Basel CH-4058, Switzerland

Advanced synthetic formulations resembling structures and functions of cells represent an innovative approach to biomedical applications. Once internalized, they mimic their vital functions or influence their activities, providing an advanced approach to various biological applications, such as replacing diseased cells or influencing their metabolic activities. These systems can act as compartments in which enzymatic reactions can take place in a safe environment to produce bio-relevant species ensuring close communication with cells <sup>[1]</sup>. In particular, polymer assemblies, like liquid-liquid phase separated systems, called coacervates, are emerging as one of the most promising synthetic assemblies for artificial cell design. Coacervates, by mimicking membrane organelles and confining increased localized proteins, ensure increased production of active molecules at the cell target site. In this view, complex segregated coacervates, consisting of the polymers polyethylene glycol (PEG) and dextran (DEX), have been developed as efficient catalytic reactors for the production of lactate from pyruvate using the enzyme lactic dehydrogenase (LDH). Combining advanced techniques, such as microfluidics and confocal laser scanning microscopy (CLSM), artificial cells were constructed by encapsulating the coacervates in giant unilamellar vesicles (GUVs) made of the polymer poly(dimethylsiloxane)-poly-b-(methyloxazoline) (PDMS-b-PMOXA), demonstrating an environment effect on the enzymatic reaction development and suggesting these new polymeric formulations as promising artificial cells for the production of bio-relevant signaling molecules.

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**Charge-carrier dynamics in chiral gold nanoclusters**T. Blandenier<sup>1</sup>, T. Bürgi<sup>2</sup>, M. Oppermann<sup>1\*</sup><sup>1</sup>Department of Chemistry, University of Basel, Switzerland, <sup>2</sup>Department of Physical Chemistry, University of Geneva, Switzerland

Thiolate-protected gold nanoclusters (Au-NCs), i.e. gold nanoparticles of a few tens of gold atoms, exhibit single-electron transitions upon photoexcitation, which resemble electronic transitions in molecules, instead of a plasmonic response [1]. Moreover, their chiral analogues promise to add enantioselectivity to various applications, such as photocatalysis, biosensing or bioimaging [2]. In this context, understanding the chiral properties of Au-NCs in the relevant excited states is key. Despite prominent breakthroughs in the synthesis, characterization, and computations of monolayer-protected metal clusters, ultrafast spectroscopy studies of chiral Au-NCs are still scarce.

To address this challenge, we investigate the excited state dynamics of chiral Au-NCs of different sizes. Here we present a comprehensive study of their population kinetics via femtosecond transient absorption. Future studies will then employ time-resolved circular dichroism to study the chiral features of the associated photoexcited states and their coupling to the NC's structural properties [1,2,3]. Since the photo-induced charge-carrier dynamics of Au-NCs are known to show a strong structural dependence [4], this approach promises novel insights into the underlying interaction between the metal core, its interface and the ligand layer. On this basis, we aim to achieve a detailed understanding of the interplay between the Au-NC's chiral structure and the resulting stereo-control of their charge-carrier dynamics.

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**Extending ultrafast spectroscopy to the deep ultraviolet with stretched hollow core fiber technology**

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Ultrafast spectroscopy in the ultraviolet (UV) is an attractive tool to probe the dynamics of (bio)molecules via important UV-chromophores, such as peptide bonds, amino acids, nucleotides, and many organic ligands [1]. However, despite recent progress in photonic technology [2], the region below 300 nm, known as the deep-UV, has remained underexplored, with only few reports of broadband ultrafast spectroscopy setups and studies in the deep-UV region [3].

To extend the spectral range of ultrafast spectroscopy, we now employ a novel source of intense, broadband deep-UV pulses: soliton dynamics in gas-filled hollow capillary fibers (HCF) [4,5]. Here we present a full characterization of our laser pulse source, compare it to numerical simulations, and apply it to transient absorption spectroscopy.

The results demonstrate of the unique potential of HCF technology to extend ultrafast molecular spectroscopy to the deep-UV, where it opens new opportunities to study (bio)molecular dynamics in solution.

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## Use of NMR to study cubic phases for drug delivery in topical photodynamic therapy

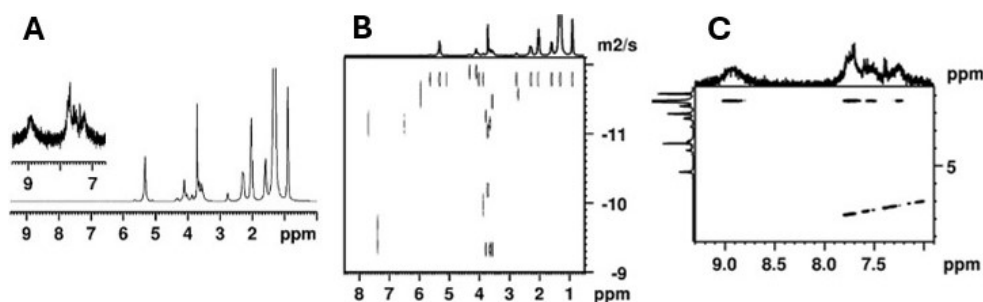
J. Bruegger<sup>1</sup>, I. Gjurroski<sup>1</sup>, P. Vermathen<sup>2</sup>, J. Furrer<sup>1</sup>, M. Vermathen<sup>1\*</sup>

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For the efficient application of promising photosensitizers (PS) like phthalocyanines (Pcs) and porphyrins in topical photodynamic therapy, drug delivery systems are required and here, lipid cubic phases have great potential. [1][2] NMR is a powerful tool to investigate the interaction of the carrier system and the drug as well as for characterisation of the system. [3] The aim of this project is to prepare cubic phase formulations followed by NMR characterisation and investigation of PS-cubic phase interactions.

Empty and PS loaded Monoolein hydrogels and cubic phase nanoparticles, called cubosomes, were prepared. As PSs, 5,10,15,20-tetrakis(*m*-hydroxyphenyl)-porphyrin (mTHPP) and ZnPc were used. The systems were characterised by liquid and High-Resolution Magic Angle Spinning (HR-MAS) NMR spectroscopy. Lipid-lipid as well as lipid-PS interactions were investigated by 2D-<sup>1</sup>H<sup>1</sup>H NOESY and spectral perturbation in 1D <sup>1</sup>H NMR spectra. In addition, UV-Vis spectroscopy was used to study the encapsulation of the PSs. The diffusion of the components, the fraction of different compartments as well as the size of the cubosomes were analysed by diffusion ordered spectroscopy (DOSY). The sizes of the cubosomes were determined by dynamic light scattering.

As of now, results indicate that the prepared cubosomes are smaller than 250 nm with a narrow size distribution and the size can be tuned by the preparation method. <sup>1</sup>H NMR and UV-Vis analysis indicate that mTHPP was successfully encapsulated into cubosomes, whereas the highly aggregating ZnPc turns out more challenging for detectable encapsulation. Multi-exponential fitting of DOSY data showed pools of free and bound water and surfactant, which was used as stabilizer for cubosomes.



Cubosomes-mTHPP in D<sub>2</sub>O: A, 1D <sup>1</sup>H NMR, B, <sup>1</sup>H DOSY, and C, <sup>1</sup>H<sup>1</sup>H-NOESY spectrum

Further optimisations of sample preparation are ongoing. Moreover, scanning electron microscopy (SEM) and cryo transmission electron microscopy (cryo-TEM) of the cubosomes are planned to study their morphology. Additionally, encapsulation efficiency, release studies and skin penetration tests are anticipated for the prepared systems.

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## Deciphering the oxygen evolution reaction mechanism on 3d transition metal oxides by using pump-probe X-ray absorption spectroscopy

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Electrochemical water splitting is one of the ways of using renewable energies to produce H<sub>2</sub>. The anodic oxygen evolution reaction (OER) is the rate-limiting step in water splitting, being a multistep oxidation reaction, needing high overpotentials and having sluggish reaction kinetics.[1],[2]

In this project, we use the pump-probe X-ray absorption spectroscopy (XAS) where UV- vis source serves as the pump and X-rays as the probe. XAS offers the distinct advantage of being element-specific, enabling the precise probing of changes in the oxidation state as well as local changes around the atom, including coordination number and bond lengths.[3] We aim to gain a deeper understanding of the OER process by using time-resolved X-ray absorption spectroscopy (XAS) to identify the intermediates formed at the solid-liquid interface. Processes like charge carrier recombination that occur in the bulk of the semiconductor and charge transfer to the surface are expected to be in the ultrafast fs-ps time domain. While the processes at the interface, including the oxygen generation and formation of different long-lived as well as short-lived intermediates during the water oxidation cycle, lie in the time range of  $\mu$ s-ms. Time-resolved XAS is crucial as it provides information about short-lived intermediates. This data can be supplemented by time-resolved optical spectroscopy, which will provide insights into photogenerated charge carrier dynamics.

Photochemically stable  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (hematite) photoanodes in combination with 3d metal-based co-catalysts (like CoPi (cobalt-phosphate) were excited with a modulated 447nm light source and probed at Co-K edge. When the light source was kept at a repetition rate of 100 Hz, we obtained a time resolution of 100  $\mu$ s. The difference light ON-OFF XAS spectra obtained pointed towards changes in the structure of our catalyst.

Further, the goal is to observe changes in the XAS spectra at Co and Fe K edges with simultaneous excitation with modulated light. These time-resolved studies will help us to look into the specific mechanistic insights based on the hypothesis provided in the literature. Questions such as the formation of oxo intermediates by Co, the accumulation of holes at the interface to drive the reaction, and the role of photochemistry in OER catalysis will be addressed. [4],[5]. These mechanistic insights will help us develop catalysts with improved performance.

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**Precision spectroscopy of Rydberg states in  $^4\text{He}$  and  $^3\text{He}$** G. Clausen<sup>1</sup>, F. Merkt<sup>1\*</sup><sup>1</sup>Institute of Molecular Physical Science, ETH Zurich

The metastable He ((1s)<sup>1</sup>(2s)<sup>1</sup>) atom in its singlet (<sup>1</sup>S<sub>0</sub>) or triplet (<sup>3</sup>S<sub>1</sub>) states is an ideal system to perform tests of ab-initio calculations of two-electron systems that include quantum-electrodynamics and nuclear finite-size effects. The recent determination of the ionization energy of the metastable 2 <sup>1</sup>S<sub>0</sub> state of <sup>4</sup>He [1] confirmed a discrepancy between the latest theoretical values of the Lamb shifts in low-lying electronic states of triplet helium [2] and the measured 3 <sup>3</sup>D ← 2 <sup>3</sup>S [3] and 3 <sup>3</sup>D ← 2 <sup>3</sup>P [4] transition frequencies. This discrepancy could not be resolved in the latest calculations [5,6].

Recently, we developed a new experimental method for the determination of the ionization energy of the 2 <sup>3</sup>S<sub>1</sub> state of <sup>4</sup>He via the measurement of transitions from the 2 <sup>3</sup>S<sub>1</sub> state to np Rydberg states.

In this poster, we present the the first results on the ionization energy of metastable helium obtained with improved experimental setup and methods, which include (i) the preparation of a cold, supersonic expansion of helium atoms in the 2 <sup>3</sup>S<sub>1</sub> state, (ii) the development and characterization of a laser system for driving the transitions to np Rydberg states, (iii) the implementation of a new sub-Doppler, background-free detection method, and (iv) the integration of an interferometer-based retro-reflector canceling the 1<sup>st</sup>-order Doppler shift to enable Doppler-free spectroscopy. We illustrate its power with a new determination of the ionization energy of 2 <sup>3</sup>S<sub>1</sub> metastable He with a fractional uncertainty in the 10<sup>-12</sup> range using extrapolation of the np series.

The first results of similar experiments carried out on the <sup>3</sup>He isotope are also presented as part of an effort to determine the difference between the charge radii of the <sup>3</sup>He<sup>+2</sup> and <sup>4</sup>He<sup>+2</sup> nuclei.

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## pH-Responsive Nanocarriers Formed via an Improved Synthesis of PMOXa-b-PDPA Amphiphilic Block Copolymers

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Amphiphilic block-copolymers (BCPs) are a well-established building block in the bottom-up synthesis of biocompatible nanocarriers intended for applications such as drug delivery, nanoreactors and cell-mimics.<sup>[1]</sup> BCPs are capable of assembling into a variety of larger morphologies such as micelles, cylindrical worms, vesicles, multi compartment vesicles and giant unilamellar vesicles (GUVs); all of which have their own unique properties and functions.<sup>[2]</sup> This versatility is accessible to many BCP systems by simply tuning the hydrophilic weight percentage of the self-assembling polymer to create the ideal 3D structure for the intended applications.

pH-responsive polymers are regularly used for targeting acidic cancerous tissue to increase therapeutic delivery and diagnostic imaging.<sup>[3]</sup> Poly(2-(diisopropylamino)ethyl methacrylate) (PDPA) was selected for this BCP system due to its  $pK_a$  of 6.7 which causes the polymer to undergo significant structural changes and hydrophilic/hydrophobic transitions when moving from neutral blood pH into the acidic cancerous microenvironment. To ensure biocompatibility of our system, poly(2-methyl-2-oxazoline) (PMOXa) was utilized as the second block because it resembles a pseudo polypeptoid structure which affords stealth properties to the nanocarrier thus maximizing its retention time in the body.<sup>[4]</sup> These nanocarriers were loaded with various fluorescent molecules to investigate differences in the nanocarrier membrane properties between neutral and acidic environments and to demonstrate anti-cancer applications *via* triggered and extended release of DOX.HCl.

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**Second harmonic imaging of osmotic gradients**

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Cells experiencing a hypertonic (hypotonic) gradient will release (uptake) water reducing (increasing) their volume, a process called osmosis. Osmotic pressure regulation is a common feature of all living organisms and can become the dominant energy cost. Yet, its nanoscale dynamics are not well understood as it requires following lipid-water interactions during osmosis. Recently, high-throughput wide-field second harmonic imaging was invented, which opened up the possibility to selectively image in real-time interfacial water. The water response allows the retrieval of surface potentials and electric double layer dynamics. Here, we use this method to investigate osmotic shocks induced on cell membrane-mimicking model systems. The retrieved transmembrane potential maps of the hydrated membranes allow us to construct a molecular level coupling between osmotic pressure and dynamic interfacial structuring. Our findings open up new pathways for the regulation of osmotic gradients.

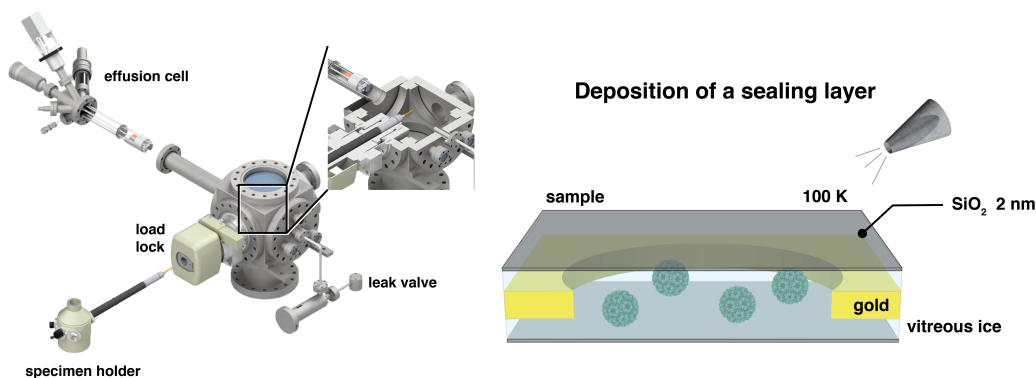


## High-resolution liquid cell architecture for microsecond time-resolved cryo-EM

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Microsecond melting and revitrification of cryo-electron microscopy specimens has been used to study several biological systems and recover the time evolution and structural dynamics of proteins.<sup>[1-4]</sup> However, due to the vacuum environment within the microscope, sample evaporation limits the maximum achievable observational time windows and reachable temperatures during an experiment to tens of microseconds and temperatures near 300 K.<sup>[5]</sup> As a result of this limitation, there exists a large gap in achievable time windows accessible with microsecond melting and revitrification ( $\sim 10^2$   $\mu$ s) and more traditional time-resolved cryo-electron microscopy experiments ( $\sim 10^3$   $\mu$ s), in which many protein-associated large-domain motions occur.<sup>[6,7]</sup> In this work we demonstrate a method for overcoming the limitations imposed by sample evaporation during the melting and revitrification process, where the specimen is sealed prior to laser melting with a layer of thin, amorphous silicon dioxide. Specimen sealing is performed in a custom evaporation chamber where silicon dioxide is deposited directly on the top and bottom of a holder-loaded cryogenic specimen to prevent evaporation, as depicted in the figure below. Using this technique, we observe that a test specimen of mApoF retains visible proteins after illumination with ten 30  $\mu$ s pulses resulting in a total observational time-window of 300  $\mu$ s. We also show the ability to retain sub-2 Å resolution of mApoF after deposition, melting, and revitrification with a loss in resolution of only 0.13 Å as compared to a control specimen. These results directly demonstrate that by using this technique, high spatial resolution may be retained while expanding the maximum achievable observation window by an order of magnitude in melting and revitrification experiments, further bridging the gap to conventional time-resolved cryo-electron microscopy methods.



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**High-field optically induced NMR hyperpolarization in solids**

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Low sensitivity is among the major limitations to cutting edge applications of nuclear magnetic resonance (NMR) spectroscopy. Nuclear spin hyperpolarization provides a solution to this issue by enhancing the population imbalance between the nuclear spin states, and thus the NMR signal. For solid-state NMR spectroscopy, optical hyperpolarization methods are of particular interest. In the specific, they exploit transient electronic excited states as the spin polarization source, allowing very large nuclear spin polarization to be generated.

One such optical technique is solid-state photochemically induced dynamic nuclear polarization (photo-CIDNP), where light is used to irradiate a donor–acceptor system that, upon charge separation, forms a spin-correlated radical pair whose evolution and decay can accumulate nuclear hyperpolarization. We recently showed that bulk optical <sup>1</sup>H hyperpolarization can be observed at low magnetic field (0.3 T) by polarization relay from synthetic donor–acceptor molecules.[1] Here, we extend the concept of photo-CIDNP from synthetic donor–acceptor systems to the high magnetic fields required for high-resolution NMR spectroscopy, demonstrating optically enhanced <sup>1</sup>H and <sup>13</sup>C NMR at 9.4 T and 21.1 T.

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**Advancing polymer-based catalytic nanocompartments in localized drug production and delivery**I. A. Dinu<sup>1,2</sup>, M. Korphidou<sup>1</sup>, C. G. Palivan<sup>1,3</sup>

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The current advances in nanomedicine are focusing on the development of stimuli-responsive delivery systems to address the limitations, side effects or the unsolved needs of traditional drug delivery [1]. Here, we present several polymer-based innovative nanosystems specifically tailored to produce and/or deliver drugs locally [2-4]. Our research focuses on polymersomes made from amphiphilic PDMS-*b*-PMOXA diblock copolymers, which are being developed as catalytic nanocompartments that encapsulate therapeutically relevant enzymes [2,4] or as stimuli-responsive drug delivery systems [3]. Thus, we have developed a nanosystem capable of either locally reactivating hymecromone, a therapeutic compound, [2] or simultaneously producing the drug and an increase of reactive oxygen species through parallel enzymatic reactions [4]. The insertion of the pore-forming peptide, melittin, facilitates the diffusion of substrates and products through the synthetic membranes. To address the significant shortcomings associated with the application of enzymes in drug synergism, we have also introduced catalytic nanocompartments decorated with glycoligomeric binders comprising eight mannose-containing repeating units for selective cell targeting [4]. Our results highlight the potential of these advanced nanosystems in improving the accuracy and efficacy of drug delivery. In addition, we have achieved a spatiotemporally controlled delivery system with a tunable release profile by incorporating a synthetic rotary molecular motor into the hydrophobic domain of the polymer membrane [3]. This nanosystem presents a stimuli-responsive behavior due to its ability to turn “on” and “off” on demand over sequential cycles of activation by irradiation with visible light. Furthermore, even low concentrations of molecular motors are shown to effectively promote the release. The development of such smart nanosystems is an important step in the field of next generation nanomedicine, where there is a growing interest in the controlled, local and on demand production and delivery of drugs.

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**Colloidal-ALD for hybrid QD@oxide core@shell structures to photocatalyze organic reactions**

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Colloidal quantum dots (QDs) have been used in applications spanning from medicine to catalysis and optoelectronics. Yet, their stability under ambient and processing conditions remains a challenge. We have proposed the growth of inert and stable metal-oxide shells to overcome this issue. To this aim, we have adapted the gas-phase method of atomic layer deposition (ALD) for thin films to grow metal-oxide shells on nanocrystals while preserving their colloidal stability, known as colloidal-ALD (c-ALD).<sup>1</sup> Organic chromophores are often combined with QDs as photoactive ligands to expand the functionality of QDs. Recently, polyaromatic hydrocarbons (PAHs) have been used as shuttles to transfer the QD exciton energy to organic molecules in order to achieve triplet energy transfer (TEnT)-based photocatalysis of organic transformations.<sup>2,3</sup> The most common methodology to introduce these chromophores involves ligand exchange procedures. However, ligand exchanges suffer from a few limitations, which include reversible binding, restricted access to binding sites, and the need for purification of the samples, which can result in loss of colloidal stability. Herein, we demonstrate that c-ALD of a thin layer of oxide around the QDs and subsequent binding of photoactive molecules is a valid method to create hybrid QD@oxide core@shell structures and to overcome the challenges of traditional ligand exchange cited above.<sup>4</sup> We also report on the photophysical properties of these materials. Specifically, we prove that the energy transfer from the CdSe to PAH can occur through the shell. Furthermore, we show that the CdSe@MOx/PAH hybrid assemblies can be used to deliberately tune the QD-PAH distance and the PAH loading in order to understand the impact of these parameters on the photophysical and photocatalytic properties, using the [2+2] cycloadditions as test reactions.

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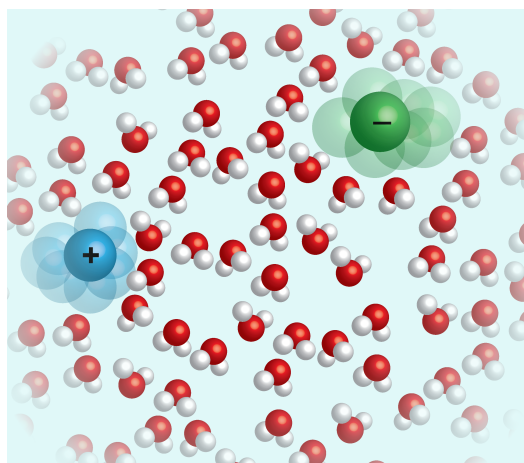
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**Multiscale probing of interactions in aqueous ionic solutions**M. Flór<sup>1</sup>, A. Bouchez<sup>1</sup>, V. Vorobev<sup>1</sup>, S. Roke<sup>1\*</sup><sup>1</sup>Laboratory for fundamental BioPhotonics (LBP), Institute of Bio-engineering (IBI), School of Engineering (STI), École Polytechnique Fédérale de Lausanne (EPFL), CH-1015, Lausanne, Switzerland

Solutions of charged atoms/molecules in water are an essential ingredient of many diverse aspects of life and relevant to technology: The bodily fluids (blood and cellular fluid are prime examples), but also are the key contents of batteries. Ionic solutions are commonly described as homogeneous mixtures in which ions are statistically distributed. However, Kirkwood showed nearly a century ago that this simple description is incomplete for the relevant concentration range and that the structure of electrolyte solutions is far more complex. Disentangling the structural complexity of water, ions and (macro)molecules and their respective interactions requires structural information on multiple length scales, from the single water molecule to the nano- and microscale. Here, we present a combination of linear and nonlinear light scattering approaches combined with vibrational spectroscopy that can be used to map both short – and long-range interactions as well as collective effects pertaining to all molecular actors. Our findings can shed new light on a variety of biological and technological processes.



**The effect of pH on enzyme catalyzed lipolysis at the oil/water interface**

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Triglycerides play a crucial role as a primary source of nutrients and energy, although they are not absorbed in their original form within the digestive system. Through the action of lipases and pH at the oil-water interface, triglycerides are broken down into more hydrophilic and amphiphilic substances such as fatty acids and monoglycerides. The impact of this breakdown on the structure of the oil-water interface, which is essential for digestion and nutrient absorption, remains not fully comprehended. This process may create new interfaces between oil and water that facilitate effective digestion.

This study investigates the changes occurring at the interface during the hydrolysis of triolein triggered by pH and enzymes in the presence of water. By employing spinning drop tensiometry, imaging ellipsometry, and microfocus small angle X-ray scattering (SAXS), the research reveals the development of nanostructured interfacial layers between oil and water. Furthermore, the simultaneous examination of colloidal structure formation in the oil and water phases using SAXS and dynamic light scattering demonstrates the spontaneous generation of highly uniform water-in-oil emulsions within the triolein phase containing lipase. Techniques like Karl Fischer titration and Bradford's assay validate the transfer of water into the triolein. Notably, acid-base titration confirms that the lipase retains its efficacy in breaking down lipids once within the oil phase.

These findings provide valuable insights into the hydrolysis of triglycerides catalyzed by pH and lipase. Various pH levels and ionic strength conditions were explored to enhance our understanding of this process. The study reveals that the duration of hydrolysis and pH levels have a synergistic impact, gradually transforming the oil-based environment into more hydrophilic structures with increased internal surface area. This knowledge contributes to a foundational understanding of the colloidal aspects of lipid digestion, which are vital for sustaining life and nutrient provision. The formation of colloidal structures is intricately linked to their function as carriers for lipases and nutrients.

## Photoinduced Charge Transfer and Symmetry Breaking in Pyrrolopyrrole Based Quadrupolar Molecules

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There has been growing interest in symmetry-breaking (SB) charge transfer processes occurring in multibranch electron donor-acceptor (D-A) systems, driven by their promising applications in two-photon initiated polymerization and organic photovoltaics. Excited-state symmetry breaking (ES-SB) results either partial or complete localization of electronic excitation on one of the D-A branches in a multipolar D-A system. In this work, the excited state charge transfer and symmetry breaking in a series of quadrupolar pyrrolopyrrole-based molecules [1] with various electron donating and accepting groups in the core and the periphery were investigated by using a combination of transient electronic and vibrational absorption spectroscopies. With a neutral group in the periphery (methylphenyl) and a strong accepting group in the core (cyanophenyl), electronic excitation remains on the pyrrolopyrrole core and decays on the 1.5 ns time (Fig. 1a). Additionally, TRIR measurements confirmed an asymmetric distribution of the excitation within the core (Fig. 1d). By contrast, a faster intramolecular charge transfer (ICT) followed by 610 ps intersystem crossing (ISC) is observed with a stronger electron accepting cyanophenyl in the periphery (Fig. 1b). Appearance of both  $-C\equiv C-$  and  $-C\equiv N$  stretching in the TRIR spectra reveals that ICT results in full symmetry breaking with the transferred electron solely on a single branch (Fig. 1e). Furthermore, an ultrafast CT to a symmetry-broken state followed by recombination to the ground state is observed when neutral functional groups are attached to the pyrrolopyrrole core (Figure 1c and f). The dynamics of this process and of the ensuing recombination depend significantly on the driving force. Our results reveal that electron donating and accepting strength of substituents not only affects the nature of the excited state (local excited ((LE) or CT) but also influences the decay pathway of the ICT state.

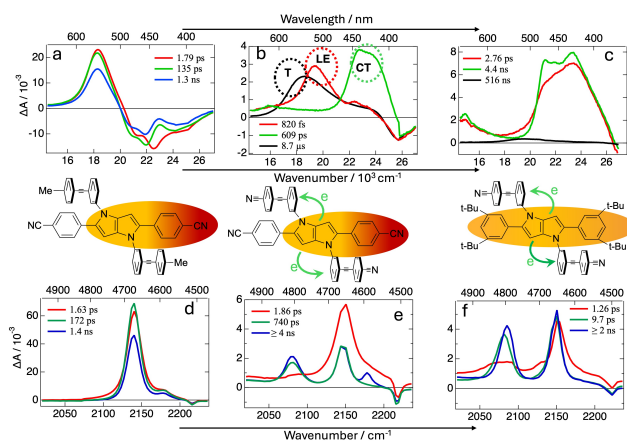


Figure 1. Evolution-associated difference absorption spectra (EAS) obtained from a global analysis of the transient electronic (top) and vibrational (bottom) absorption data in THF.

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**Using Gas-Phase FRET to Study the Structure of Diabetes-Related Polypeptides**

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Determining the structure of biomolecules is challenging as it normally requires large amounts of sample and high purity. These limitations can be overcome by using mass spectrometry (MS)-based techniques. Electrospray ionization allows the gentle ionization of biomolecules and their assemblies so that they retain their native structure. However, MS commonly only yields mass-to-charge ratios, which do not bear direct structural information. MS has been hyphenated to Förster resonance energy transfer (FRET), a technique that allows one to measure the distance between a fluorescence donor and acceptor in biomolecular ions. By combining distances from FRET with ion mobility spectrometry and computational modeling, unprecedented insight into the three-dimensional structure of biomolecular ions can be gained.

In this work, we use this technique to study the secondary structure of the diabetes-related polypeptides. These polypeptides are known as islet amyloid polypeptides (IAPP) and can undergo self-aggregation, which ultimately leads to type II diabetes. However, only the human IAPP leads to the disease, whereas rat IAPP is considered non-toxic. These peptides only differ in six amino acids. Based on ion mobility-mass spectrometry and computational data, it was proposed that hIAPP forms two different conformations, a compact helix and an extended  $\beta$ -hairpin structure, whereas rIAPP only forms compact helices. It was suggested that the  $\beta$ -hairpin structure of hIAPP is an amyloidogenic precursor for the formation of  $\beta$ -sheet rich dimers. Although these studies provided valuable data, they lack direct structural information of the IAPPs. Direct structural data on the secondary structure of IAPPs can be obtained by using FRET in combination with ion mobility.

Therefore, we designed a workflow to label the peptides at the N-terminus with a fluorescent dye. To avoid labeling with a second dye, the transition metal ion  $\text{Cu}^{2+}$  was used as a quencher, which is binding to the histidine moiety at the 18-position. Finally, we can extract the distance between the quencher and the dye from the FRET experiments and together with computational and ion mobility data assign a structure to the peptides with high fidelity. This workflow allows getting in-depth insight into the aggregation mechanism



**Gas-phase study of rotational-state and conformational effects in chemi-ionization reactions under single-collision conditions**C. He<sup>1</sup>, A. Mishra<sup>1</sup>, L. Ploenes<sup>1</sup>, P. Stranak<sup>1</sup>, J. Kim<sup>2</sup>, S. K. Kim<sup>2</sup>, S. Willitsch<sup>1\*</sup><sup>1</sup>Department of Chemistry, University of Basel, Klingelbergstrasse 80, 4056 Basel, Switzerland, <sup>2</sup>Department of Chemistry, KAIST, Daejeon 34141, Republic of Korea

Characterizing the role of the molecular geometry and of specific quantum states is essential for understanding the dynamics of chemical reactions. However, due to the challenges of isolating and controlling individual rotational states and conformers in experimental studies, only a limited number of investigations has been conducted to reveal the impact of rotational-state and conformational effects on chemical reactivity [1]. Over the past years, our group has implemented novel experimental approaches to study conformational effects in ion-molecule reactions [2, 3]. Here, we summarise recent results from a new crossed-molecular-beam experiment which extends our methodology to neutral-neutral gas-phase reactions [4, 5, 6]. This setup is equipped with an electrostatic deflector which enables the spatial separation of different conformers and individual rotational states of molecules according to their different effective dipole moments.

We studied rotational-state-dependent chemi-ionization reactions of carbonyl sulfide (OCS) with metastable neon atoms (Ne\*) in which a pronounced state-specificity of the product branching ratio was observed [4]. Further, studies on the chemi-ionization reactions of 1,4-dihydroxybenzene (hydroquinone, HYQ) with Ne\* were performed [5]. Combining the experimental results with quantum chemistry calculations, it was demonstrated that for the cis-HYQ conformer, the relative reactivities towards PI and DI, and thus the product-branching ratios, depend on the rotational state. We also studied the chemi-ionization reaction of 1,2-dibromoethylene [6] for which cis- and trans-isomers can also be chemically separated [7]. Also in this system, different product branching ratios for PI and DI were observed for the two isomers. The DI products appear to be formed with a higher efficiency in low rotational states of cis-DBE which was tentatively discussed within the framework of a stereodynamic effect [8].

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**Two-dimensional organic frameworks investigated by *in-situ* time-resolved spectroscopy**L. Holzer<sup>1</sup>, R. Guntermann<sup>2</sup>, K. Muggli<sup>2</sup>, T. Bein<sup>2</sup>, N. Banerji<sup>1\*</sup>

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Organic mixed ionic-electronic conductors (OMIECs) are materials that enable both ionic and electronic transport and have other advantages, such as versatile processing conditions, synthetic tuneability and flexible nature. These properties make it possible for OMIECs to perform in a wide range of applications such as bioelectronics, supercapacitors, electrochromic displays and batteries. So far, a lot of focus was laid on conjugated polymers and organic small molecules. However, the field is evolving towards more complex structures and recently a new class of materials was proposed for OMIECs, the two-dimensional organic frameworks (2D COFs).<sup>1</sup> 2D COFs are systems with well-defined porosity, high surface area, high crystallinity and good chemical stability.<sup>2</sup> Until now only a limited amount of work and knowledge is available for these materials and the performance of devices and the fundamental processes happening during the device operation still needs to be understood.<sup>3</sup>

The material investigated in this study is Cz-ttTII, a tetragonal COF with a high vertical conductivity ( $7.60 \times 10^{-4}$  S/cm), intriguing optical properties and fast switching speeds during the redox reaction during operation.<sup>4</sup>

We study electrochemical doping in Cz-ttTII COF with spectroscopic techniques such as *in-situ* time-resolved Vis-NIR spectroscopy and Raman spectroscopy to explore the oxidation and reduction behavior and measure the transistor characteristics based on the aforementioned material. Furthermore, with Multivariate Curve Resolution (MCR) analysis the evolution of neutral segments and charged species as a function of gate bias are determined. Further, time-domain terahertz (THz) spectroscopy is planned to access the intrinsic nanoscale conductivity which is not affected by any grain boundaries or electrodes. This will enhance the understanding on the mobility and density of charges altogether. This study aims to shed light on the understanding of the potentials of COFs in the field of OMIECs.

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**The influence of the bipolaron formation rate on the charge transport properties of chemically doped oligoetherized polythiophene**

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In the last decades, organic semiconductors have attracted significant attention due to their mechanical flexibility, solution processability, and lightweight nature. A recent achievement brought the engineering of side chains in polymer films to enhance ion intercalation, as demonstrated by the newly developed polymer P(g<sub>3</sub>2T-T). This derivative of P3HT, featuring oligoether instead of aliphatic side chains, emerges as a promising candidate for chemical doping because of the affinity of its side chains to dopant anions. Chemical doping of the P(g<sub>3</sub>2T-T) has been found to achieve an up to fourfold increase in macroscopic conductivity compared to P3HT. However, this enhanced conductivity is highly dependent on specific doping conditions. While general principles of doping are now well-understood, the precise effects of various doping parameters on the charge transport properties of doped thin films still need to be investigated.

Our study employs *in-situ* absorbance spectroscopy as well as THz spectroscopy to investigate the effects of differing dopant and electrolyte concentrations on the conductivity of chemically doped P(g<sub>3</sub>2T-T) films. We reveal that the early kinetics of the doping process have a significant influence on the final thin film conductivity. The results demonstrate that the bipolaron-to-polaron ratio is a rather weak indicator of favorable charge transport properties and that instead the bipolaron formation rate is a superior predictor. We presume that the bipolaron formation rate is entangled with the swelling of the polymer film, the intercalation of the dopant anions, and thus the packing of the polymer film as well as its charge transport properties. We explore two distinct doping methods—immersed doping and anion exchange doping—and use two different dopants, F<sub>4</sub>TCNQ and Magic Blue, to rule out the impacts of specific doping techniques. Especially for the anion exchange doping method, our results offer for the first time an explanation for the dependence of the electrolyte concentration on the film conductivity. Moreover, we report an excellent restoration of long-range charge transport in chemically doped P(g<sub>3</sub>2T-T), compared to the short range (100 nm) derived from THz spectroscopy. Overall, our results shed light on the underlying principles of chemical doping and the revealed dependencies on specific doping conditions can help facilitate the development of the next generation of organic semiconducting polymers.

**Doping of Polythiophenes and Polythienothiophenes with Alkyl or Glycol Sidechains****B. Hunger<sup>1</sup>, D. Tsokkou<sup>1</sup>, M. Horn<sup>1</sup>, E. Röck<sup>1</sup>, N. Banerji<sup>1\*</sup>**<sup>1</sup>Department of Chemistry, Biochemistry and Pharmacy, University of Bern, Freiestrasse 3, 3012 Bern, Switzerland

Organic semiconductors have a wide range of near future applications, such as: bioelectronics, thermoelectronics and optoelectronics<sup>1,2</sup> where their low production cost and chemical tunability make them very attractive candidates for the aforementioned fields. Current challenges include the low conductivity which can be addressed *via* doping. In particular for conjugated polymers doping increases the conductivity by several orders of magnitude.<sup>2-4</sup> Recently, sidechain engineering has been shown to be a useful tool for the modification and improvement of conjugated polymers.<sup>5</sup> By exchanging the commonly used alkyl sidechains with glycol sidechains the dopant-polymer miscibility and the ionic uptake is improved.<sup>6</sup> Herein we investigate how these improvements affect chemical and anion exchange doping of thiophene and thienothiophene type polymers in respect to their conductivity. To characterize these changes, we use steady state absorbance spectroscopy, four-point probe, time domain THz spectroscopy, *in situ* absorbance measurements and chronoamperometry. For P(g<sub>3</sub>BTTT), we find extraordinarily high conductivities of over 2 000 S/cm combined with a high charge carrier mobility. We show that such high conductivities are achieved in the presence of a high bipolaron density, and this is observed for all the polymers with thienothiophene backbones we studied. In contrast, for thiophene based backbones there is an optimal bipolaron to polaron ratio (0.8) where the maximum conductivity is achieved. In addition, for the high conductive polymers studied we show that the DC conductivity is similar in amplitude to the THz conductivity, which means that the factors that limit the transport over few nanometers are also the limiting factors over longer distances. We demonstrate the benefit of glycol side chains for the conductivity in thiophene and thienothiophene type polymers especially when combined with anion exchange doping.

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## Structural Dynamics of SARS-CoV-2 Spike Proteins Revealed by Microsecond TimeResolved Cryo-EM

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The SARS-CoV-2 spike protein promotes viral entry into cells by engaging its receptor binding domains (RBDs) to the human angiotensin-converting enzyme 2 (ACE2) receptors on cellular membranes<sup>1,2</sup>. Studies revealed that the specific RBD positioning is crucial for the cellular recognition of the virus and evasion against the body's immune system, thus a detailed understanding of the mechanism of RBD movement is pivotal for developing vaccines<sup>1,3</sup>. Reports suggest that surrounding pH plays a key role in determining the RBD positioning, thus depicting distinct structural conformations of the spike proteins, however real-time information about the intermediate states that connect these stable structures is lacking<sup>1,2,4</sup>. To enable such observations, we have recently proposed a novel technique that improves the time resolution of cryo-electron microscopy (cryo-EM) to microseconds<sup>5-9</sup>. Here we demonstrate that microsecond time-resolved cryo-EM enables observations of fast conformational dynamics. We have used our approach to elucidate the mechanism of RBD movement in SARS-CoV-2 spike proteins. In our experiment, we observed the structural transition of one RBD up conformation to all-RBD down state in response to an in situ pH change in microsecond timescale. While this is a concerted process, the motions of the spike RBDs involve different timescales, leading to a curved reaction path.

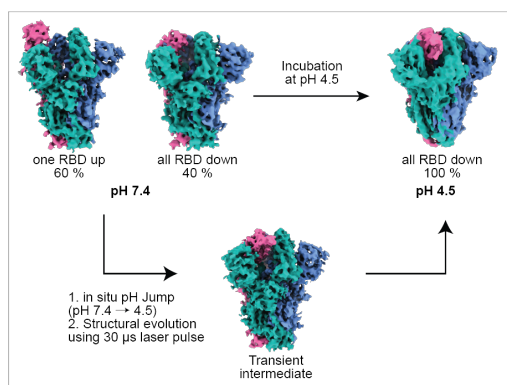


Figure 1. Microsecond time-resolved cryo-EM of the SARS-CoV-2 RBD movement

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**Precision Spectroscopy and Coherent Manipulation of a Single Molecular Nitrogen Ion**

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Within the rich energy level structure of molecules, transitions with advantageous properties for precision studies and molecular quantum technologies can be found [1]. However, without closed cycling transitions and frequencies ranging from MHz for hyperfine transitions to GHz in rotational transitions and THz in ro-vibrational transitions [2], efficient cooling of translational degrees of freedom as well as coherent state preparation, manipulation, and readout becomes challenging.

We produce a single  $N_2^+$  ion in its internal ground state using threshold photoionisation [3] and use Doppler, Sideband, and EIT laser cooling on a co-trapped calcium ion to reach the motional ground state. With a quantum-logic protocol that uses the calcium ion as a probe for the molecular state, we achieve quantum non-demolition state detection with fidelities over 99% [4].

Our current efforts are towards precision-spectroscopy on non-dipole-allowed rotational and ro-vibrational transitions using frequency sources that are referenced to the Swiss primary frequency standard at METAS [5]. Beyond precision-spectroscopy, the methodologies that we develop pave the way for the implementation of molecular qubits and frequency standards in the mid-IR regime, as well as for tests of theories about physics beyond the standard model and for high-resolution studies of state-to-state dynamics in chemical reactions.

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**Detecting metal hyperfine couplings with chirped radiofrequency pulses in Electron Nuclear Double Resonance**

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Electron Nuclear Double Resonance (ENDOR) spectroscopy is an EPR technique to study the hyperfine coupled nuclei close to paramagnetic centres, including interactions that are not resolved in continuous wave EPR spectra. Since relevant samples of interest are non-crystalline solids, i.e. catalysts as powders or frozen solutions, the anisotropy of the hyperfine and nuclear quadrupole interactions renders NMR/ENDOR lines often several MHz broad, thus diminishing intensity. In commonly used pulsed ENDOR experiments, only a small fraction of the NMR line is excited even with high power radiofrequency pulses and this limits the sensitivity in conventional ENDOR experiments, and regularly precludes the direct observation of metal hyperfine couplings by ENDOR.

In this work, we show improved sensitivity in frequency domain ENDOR by chirped RF excitation, introduced previously for sharp lines of crystals in time domain ENDOR [1]. The frequency-swept RF pulses are generated by a dedicated arbitrary waveform generator (AWG) on a home-built X-band EPR spectrometer. We demonstrate on a frozen solution of Cu(II) tetraphenylporphyrin that the broad copper and nitrogen ENDOR lines increase at least 5-fold compared to single frequency RF excitation, with further achievable increase for the broad metal resonances. The sensitivity increase is also observed for nuclei with small hyperfine couplings, although a smaller RF chirp bandwidth is required to maintain the resolution compared to single frequency ENDOR.

In conclusion, we show that chirped RF pulses significantly enhance the signal intensity, and thus sensitivity, especially of broad lines in frequency domain ENDOR experiments, thus allowing for enhanced selective probing and identification of overlapping species often encountered in heterogeneous catalysts.

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**A soft X-ray absorption spectroscopy setup for liquid samples at SwissFEL**

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Performing spectroscopy on liquids and solutes is essential for advancing our understanding of various chemical and biological processes. Liquids, due to their fluid nature, provide a unique environment, facilitating the studies of dynamic interactions, reaction kinetics, and solute-solvent relationships. This is particularly important for biological systems and chemical reactions that occur naturally in aqueous environments.

I present a novel experimental setup for time-resolved soft X-ray absorption spectroscopy on liquid samples at SwissFEL. The setup allows the investigation of important absorption edges, such as the nitrogen K-edge, the oxygen K-edge and transition metal L-edges, for site-selective studies of a sample in a single experiment. A key feature of the setup is a novel catcher design in combination with a gas-squeezing liquid jet. This allows the reliable use of liquid sheets of adjustable thickness in a high vacuum environment adhering to the requirements of experiments at free-electron laser sources. The setup can be operated with small sample volumes of 50µL, and recirculation of the sample is possible. At the X-ray free-electron laser, proof-of-concept experiments yielded absorption spectra of water around the oxygen K-edge and the transient absorption of a 30mM aqueous iron(II)-trisbipyridine solution around the nitrogen K-edge and the iron L3-edge after an optical excitation at a wavelength of 266 nm.



## Beyond Excited-State Symmetry Breaking in Donor–Acceptor–Donor Systems: Torsional Disorder, Redox Dependence and Synthetic Modifications

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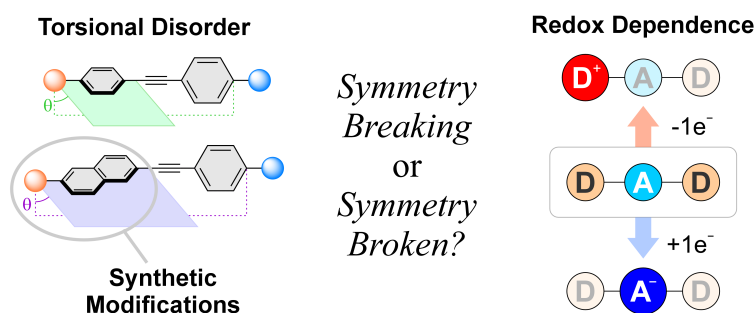
We are investigating the ground- and excited-state symmetry breaking properties of a series of Donor–Acceptor–Donor (D–A–D) systems based on a fluorenone acceptor, linked via acetylene bridges to a series of donors.[1]

Using time-resolved infrared spectroscopy (TRIR), we explore the dependence of both the extent and the dynamics of charge localisation in the excited state as a function of both solvent polarity and the identity of the donor—the latter directly impacting the energetics of the involved forward/backward electron transfers. To gain deeper insights, we compare these D–A–D systems with corresponding single-branched Donor–Acceptor (D–A) molecules. This comparison helps us understand the role of the donor groups and serves as a model for fully localized dipolar states.

The presence of the acetylene bridges leads to a wide distribution of dihedral angles between the donor and acceptor planes in the ground state. In the excited state, however, the rotational barrier is significantly increased.[2] In the phenyl-substituted molecules, rotation around the C–C bond produces a symmetric modulation of the conjugation of the system, whilst in the naphthyl-substituted molecules this modulation is asymmetric. This in turn gives rise to increased differences in both the electronic absorption spectra and the observed dynamics as a function of the D–A torsion angle ( $\vartheta$ ). Transient two-dimensional infrared (t2DIR) spectroscopy is uniquely suited to study this phenomenon, in combination with excitation wavelength dependence studies.

Furthermore, we explore the effects of electrochemically reducing or oxidizing the D–A–D molecules. This allows us to determine whether single-electron transfer can induce or inhibit symmetry breaking in both ground and excited states, drawing parallels with inorganic mixed-valence complexes.

Altogether, our research aims to develop and design functional photoresponsive materials by leveraging excited-state symmetry breaking charge transfer.[3] This approach has the potential to enhance solar-to-energy conversion and advance the field of asymmetric photochemistry.[4]



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**Investigations on Fission Product Release Behavior for GEN-IV Nuclear Reactor Designs**

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<sup>1</sup>Paul Scherrer Institute

Analyzing the potential dispersion of radioactive material into the environment is essential for nuclear reactor licensing. This project examines the release behavior of fission product radionuclides (FPs) in the cooling systems of two GEN-IV reactor types: lead-cooled fast reactors and molten salt reactors. To achieve this, a wide spectrum of FPs is extracted from a U-235 fission chamber located at the PSI-SINQ Gasjet facility and subsequently incorporated into reference liquid lead or molten salt matrices [1].

Among the various FPs, Cs has been selected here for a detailed study due to its high radiological risk and volatility. Electrochemical methods are proposed for the preparation of homogeneous Pb-Cs samples (electrolysis) and the precise determination of the thermodynamic properties of Cs in lead (electromotive force measurement). These electrochemical approaches are also expected to be applicable to other liquid lead-FP systems [2] in this starting PhD project.

Gas phase chemical release experiments will be developed to reveal the vapor pressure and chemical speciation of the released Cs using the transpiration method, thermochromatography (carrier-free amounts of Cs) and thermosublimatography (macroscopic amounts of Cs). These methods will quantify critical volatilization data of Cs under reactor-relevant conditions.

We will compare the outcome to existing reference data [3, 4]. Benchmarking and validating the data for Cs this research intends to develop suitable methods to address the behavior of various FPs in GEN-IV reactors, aiding the development of robust safety protocols and improving the reactor designs.

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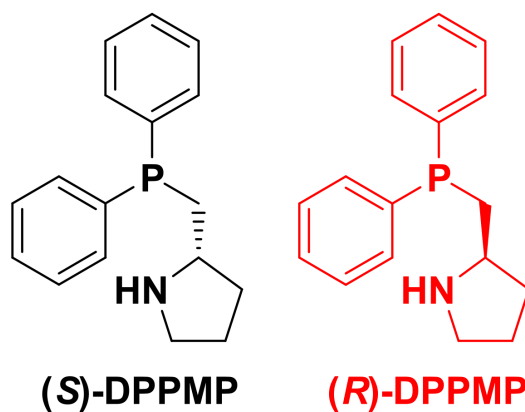
### Synthesis and Properties of Ag<sub>29</sub> Nanocluster

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Atomically precise silver nanoclusters (Ag NCs) demonstrated wide ranges of applications for example as sensors<sup>[1]</sup> and catalysts<sup>[2]</sup>, for surface enhanced Raman scattering (SERS)<sup>[3]</sup> and in biology<sup>[4]</sup>. They also show very interesting properties like two photon induced luminescence<sup>[5]</sup> and therefore this class of clusters found high interest in the community over the last two decades.<sup>[6]</sup>

In this poster presentation, I will present the bulk-scale synthesis of Ag<sub>29</sub>(BDT)<sub>12</sub>(TPP)<sub>4</sub> NCs<sup>[7]</sup> and discuss its structure and properties. Particularly I will focus on the dynamic properties of the metal core and the ligand shell studied by NMR spectroscopy (<sup>1</sup>H, <sup>31</sup>P and <sup>109</sup>Ag). Furthermore I will discuss chiral properties of the cluster studied by circular dichroism (CD) and ligand exchange reactions (LER)<sup>[8]</sup> with chiral phosphines (DPPMP).



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**Understanding the mechanism of voltage-sensitive SH fluorescent probes**

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Voltage-sensitive probes are frequently used to measure electrostatic potentials on and inside cells. This use is mainly based on the observation that the fluorescent or second harmonic (SH) emission correlates linearly with the readout of electrodes. However, the SH emission is also strongly dependent on the orientational distribution and number density which are implicitly assumed to be constant in the intensity to potential conversion. Here, we investigate in more detail the SH response of the voltage-sensitive probe and its response in diverse lipid membrane environments.

**Resolving the intrinsic heterogeneity of the splicing process of a group II intron through multiple pairwise labelling**

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Non-coding RNA was first considered to be useless until the discovery of its ability to catalyse chemical reactions. Most of the so-called ribozymes undergo self-cleavage reactions mediated through large ion strength dependent conformational rearrangements. Group IIB introns are large ribozymes found in prokaryotes and organelles of eukaryotic cells, of which ai5  $\gamma$  from *Saccharomyces cerevisiae* is one of the most studied system. <sup>[1]</sup> To infer the folding pathway of the splicing mechanism, a minimal construct was considered retaining the crucial domains for folding and subsequent splicing. The splicing reaction is a stepwise process that faces conformational dynamics in each step introduced by magnesium ions. The best method to resolve this is single-molecule Förster resonance energy transfer (smFRET), not only because the minimal construct possesses appropriate labelling platforms, but also because it further enables to go beyond the ensemble properties providing information on even transient intermediates. <sup>[2]</sup> Nevertheless, most FRET studies of macromolecules concentrate on only one FRET pair to which the whole dynamic is summarised, ignoring the conformational changes at other parts of the structure. Therefore, to obtain a comprehensive picture of the folding pathway of the highly dynamic minimal construct we introduced multiple pairwise labelling positions to shed light on the intrinsic heterogeneity of this macromolecule.

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## One Ring to Rule Them All: Ultrafast Spectroscopy Study of Chiral Platina[n]helicenes with Circularly Polarized Emission

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Circularly polarized luminescence (CPL) from chiral luminescent materials has promising applications such as high-efficiency displays, security inks, telecommunications and cryptography.<sup>[1]</sup> In particular, chiral d-block complexes have emerged as attractive CPL systems due to their high luminescence quantum yield, kinetic inertness and tunable emission wavelength covering the visible part of the electromagnetic spectrum.<sup>[2]</sup> Among this group of compounds, platina[n]helicenes have attracted much attention owing to their relatively high dissymmetry factor  $g_{CPL}$  compared to other d-block complexes, resulting from the chirality of the helicene ligand along its helical axis. Despite great progress in optimizing their CPL properties, a clear understanding of the excited state molecular properties, that give rise to the observed strong CPL, has not been achieved yet.

To address this gap, we now investigate a series of three platina[n]helicenes (n=6,7,8) (Figure 1), which differ only in the number of benzene rings constituting the helicene ligand. Quite remarkably, this structural variation significantly influences their CPL dissymmetry factors, with the Pt[8]helicene  $g_{CPL}$  value being three times higher than that of the Pt[6]helicene ( $g_{CPL} = +4.0 \times 10^{-3}$  for (S)-Pt[8]helicene,  $g_{CPL} = +1.3 \times 10^{-2}$  for (S)-Pt[6]helicene).<sup>[3]</sup> However, there is still no clear understanding of how the CPL mechanism proceeds and how it is affected by the number of benzene rings in the helicene ligands.

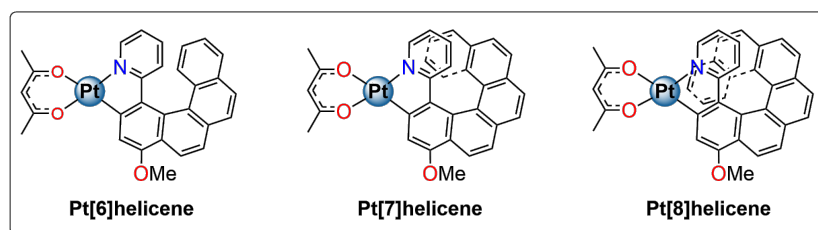


Figure 1: Structure of the platina 6,7 and 8 helicene complexes investigated in this study.

To determine the underlying CPL mechanism and its structural dependence, we have carried out a systematic study of the three platina[n]helicenes (n=6,7,8) using ultrafast time-resolved absorption (TA) and absorption anisotropy (TAA), covering the spectral range from the deep UV to the near IR. With this methodology in hand, we are able to follow the formation and evolution of the emissive excited states after photoexcitation. In future studies we intend to employ time-resolved circular dichroism spectroscopy<sup>[4]</sup> to identify their chiral features as part of the CPL mechanism.

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**Real-time tracking of the ultrafast chirality and energy transfer in a chiral OLED complex with circularly-polarized luminescence**L. Müller<sup>1</sup>, F. Zinna<sup>2</sup>, G. Pescitelli<sup>2</sup>, M. Puppini<sup>3</sup>, M. Oppermann<sup>1\*</sup><sup>1</sup>Department of Chemistry, University of Basel, Switzerland, <sup>2</sup>Department of Chemistry and Industrial Chemistry, University of Pisa, Italy, <sup>3</sup>Lausanne Centre for Ultrafast Science, EPFL, Switzerland

Circularly-polarized luminescence (CPL) has promising applications in the fields of optical data storage, biomedical diagnosis and for the creation of more efficient OLED displays.<sup>1</sup> In this respect, chiral lanthanide complexes have gained a lot of attention as CPL emitters due to their sharp and intense emission lines, long emission lifetimes and above all, due to their high degree of circular polarization. However, despite the impressive progress in the synthesis of metallo-organic CPL complexes, the underlying excited state dynamics of their chiral luminescent states have thus far remained inaccessible due to a lack of ultrafast spectroscopic techniques with sufficient chiral sensitivity.

To address this gap, we have developed a novel ultrafast circular dichroism (CD) instrument that combines ultra-sensitive broadband detection with sub-picosecond time resolution.<sup>2</sup> We now apply this technique to resolve the CPL mechanism of the prototypical CsEu((+)-hfbc)4 (hfbc = 3-heptafluoro-butylyrylcamphorate), which displays a record CPL emission with 85% of the photons being left-circularly polarized at 595 nm.<sup>3</sup> Although its luminescent transitions are metal-centered (MC), the chiral ligands play a crucial role in the CPL mechanism. First, they act as photosensitizers providing efficient energy transfer to the dipole-forbidden MC transition. Second, the CPL emission requires the coupling of the chiral ligands' electric transition dipoles to the MC magnetic transition dipoles, known as the dynamic coupling mechanism.<sup>4,5</sup>

Combining ultrafast CD with transient absorption and anisotropy measurements from the visible to the deep ultraviolet, we now present the first ultrafast spectroscopy study of a CPL complex. We found that the energy transfer proceeds via a chiral ligand-centered triplet state in 150 ps. Quite remarkably, we observe a change in optical activity of the ligand system upon energy transfer, which we attribute to an electronic coupling with the excited emissive MC states.

More generally, our results highlight that with ultrafast circular dichroism it is now possible to capture the evolution of chiral excited states in real-time, opening a new path to the direct investigation and optimization of CPL compounds.

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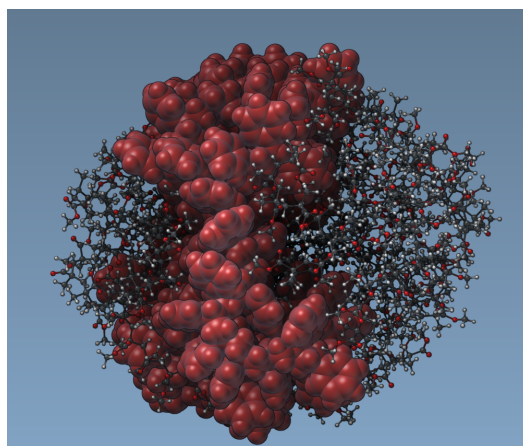
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**How we can tackle the dielectric response around spherical polymer surface**

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Hydrophobic and hydrophilic surfaces exhibit especially large qualitative differences in interfacial water structure depending on the surface chemistry. The water phase is almost seamlessly connected to hydrophilic interfaces, whereas water density at hydrophobic interfaces shows a gap between the water and the surface. The standard continuum theory does not predict several key experimental results from electrostatic and electrokinetic measurements at aqueous electrolyte interfaces. The dynamic dielectric profile for such systems has been extracted from long (1.5s) atomistic molecular dynamics (MD) simulations to overcome continuum theory limitations and to take into account the effects of curvature and surface chemistry. The MD simulations provided basic insight into liquid water bond structure, and the molecule response function for the spherical profiles presented in Fig. 1. This contribution presents a framework for extracting the dielectric response tensor from MD simulations of water at hydrophilic and hydrophobic polymeric surfaces. Based on the results of MD dipole moment, the static dielectric response tensor at an interface can be calculated. The static regime could be captured properly only when we are calculating the higher-order multipole moments with MD only. For that the presented framework for the dynamic dielectric response tensor should be applied.





**Controlled laboratory astrochemistry: Rotational-state-selected carbon reactions in space**A. Ravindran<sup>1</sup>, L. Xu<sup>1</sup>, T. Lejeune<sup>2</sup>, S. Willitsch<sup>1</sup>, J. Toscano<sup>1\*</sup><sup>1</sup>Department of Chemistry, University of Basel, Klingelbergstrasse 80, Basel 4056, Switzerland, <sup>2</sup>Chemistry department, ENS Paris Saclay, 91190 Gif-sur-Yvette, France

HOC<sup>+</sup> ions are far more abundant in the X-ray-dominated regions (XDRs) than in the Photon-dominated regions (PDRs) of space, which makes them useful molecular tracers for distinguishing between these entangled regions of ionized gases in interstellar molecular clouds [1]. Unlike its more stable and more abundant isomer HCO<sup>+</sup>, which is primarily formed by the protonation of CO by H<sub>3</sub><sup>+</sup> and of CO<sup>+</sup> by H<sub>2</sub>, HOC<sup>+</sup> is mainly formed by the reaction:



However, water has two nuclear spin isomers, *para*- and *ortho*- H<sub>2</sub>O, with  $j=0$  and  $j=1$  as their lowest rotational states, respectively. Their reactivity towards diazenylium (N<sub>2</sub>H<sup>+</sup>) ions was recently shown to be significantly different [2] and the relative abundance of *para*- and *ortho*- H<sub>2</sub>O is shown to vary in different regions of the interstellar medium [3]. We aim to find out whether the two spin isomers of water react differently towards C<sup>+</sup> ions and, consequently, whether they should be treated as different chemical entities in astrochemical models in order to improve the predictive power of the latter [4].

We can separate *para* and *ortho* water in a molecular beam using an electrostatic deflector due to their different effective dipole moment and therefore Stark energy shifts. We plan to collide the individual spin isomers of water from this deflected beam with C<sup>+</sup> ions trapped and sympathetically cooled within a Ca<sup>+</sup> Coulomb crystal in a linear radiofrequency Paul trap. Finally, we aim to measure the rotational-state-dependent reaction rate coefficients and branching ratios by analyzing the ion peak signals following ejection of the ion crystals into a time-of-flight mass spectrometer.

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**New apparatus for single-photon Doppler-free VUV/XUV spectroscopy**

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The ionisation energies of many atoms and molecules lie in the vacuum ultraviolet (VUV) and extreme ultraviolet (XUV) regions of the electromagnetic spectrum, which correspond to wavelengths (frequencies) of light of  $\lambda < 200$  nm ( $> 1.5 \times 10^{15}$  Hz) and  $< 105$  nm ( $> 2.9 \times 10^{15}$  Hz), respectively. Laser radiation generated at these wavelengths can therefore be utilised to perform single-photon ionisation from the ground electronic state of an atom or molecule, or single-photon excitation to highly excited electronic states, including Rydberg states with a large value of the principal quantum number,  $n$  [1]. Although VUV/XUV laser sources with  $< 250$  MHz bandwidths have been achieved [2-6], large Doppler broadening of transitions at VUV/XUV frequencies (with Doppler widths typically  $> 100$  MHz) often limit the resolution of single-photon VUV/XUV spectroscopy, even when collimated molecular beams are used. Additionally, the Doppler effect can result in  $> 100$  MHz systematic shifts of transition frequencies in the VUV/XUV.

We present the development of a new experimental method and apparatus for performing Doppler-free spectroscopy at VUV/XUV frequencies. This method is based on combining an imaging-assisted single-photon Doppler-free spectroscopy technique, recently developed for precision spectroscopy of Rydberg states of He atoms [7], with a long-pulse-length ( $\sim 100$  ns -  $1.0$   $\mu$ s) narrow-bandwidth VUV/XUV laser. The initial aim of such an experiment is to generate laser radiation with a wavelength of  $\sim 80$  nm, for use in precision single-photon XUV spectroscopy of high- $n$  ( $n > 30$ ) Rydberg states  $H_2$  from the ground  $X^1\Sigma_g^+$  state. The method can also be applied to perform precision spectroscopy of high- $n$  Rydberg states of noble gases such as Ar, and for studying highly excited electronic states of other molecules, such as  $O_2$ , in which the rapid predissociation of low-lying electronic states prevents access to high Rydberg states in resonant multi-photon excitation schemes.

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## Conservation of wavefunction reflection parity in methane-surface scattering

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The close-packed gold surface is so inert to methane activation that a molecule impinging on the surface is turned around before it can resolve atomic corrugation. As a result, the scattering potential presented by the surface to the molecule is essentially flat in that it is invariant under arbitrary rotations and roto-reflections about the surface normal. Rotational invariance implies in a classical context conservation of the projection  $J \cdot \hat{n}$  of the molecule's angular momentum about the surface normal, and quantum mechanically this invariance implies the scattering selection rule  $\Delta M_J = 0$  where  $M_J$  is the eigenvalue of the corresponding operator. The conserved property associated with invariance under reflection (Fig. 1a) is however uniquely quantum mechanical: the parity of the molecular wavefunction under reflection.

Using laser-based quantum state preparation and detection[1], we are able to detect, for the first time to our knowledge, conservation of wavefunction reflection parity in molecule-surface scattering. By preparing molecules in a  $J = 0$  rotational state we prepare a state of pure (odd) reflection parity, and when probing the scattering molecules we find an almost total absence of population in rovibrational states of the opposite parity (Fig 1b). Preparing states of nonzero  $J$  results in an incident population of mixed reflection parity, in which case no such absence is observed. Conservation of wavefunction reflection parity is observed in vibrationally elastic collisions of molecules prepared in both the ground and  $\nu_3$  excited state, where in the latter we observe “parity purity ratios” approaching 100:1. Remarkably, we also observe strong conservation of reflection parity in the relatively rare  $\nu_3 \rightarrow \nu_1$  vibrational relaxation events. Finally, the alignment of molecular rotation produced on  $J_0 = 0 \rightarrow J' \neq 0$  rotational excitation is probed by measuring the polarization sensitive optical response of the scattered molecules. We observe an optical response which systematically tracks changes in the surface normal (Fig. 1c), consistent with the expected  $M_J = 0 \rightarrow 0$  selection rule.

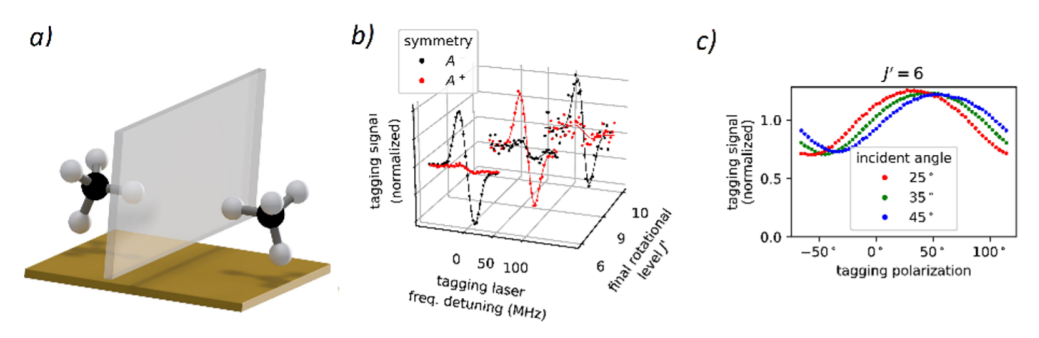


Figure 1. **a)** Illustration of reflection symmetry operation. **b)** FM line scans showing alternation of preferred inversion ( $x \rightarrow -x$ ) parity channel with parity of rotational state  $J$ . **c)** Optical response of scattered molecules vs. laser polarization for different incident scattering angles.

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**Production of holmium radioisotopes for Targeted Radionuclide Therapy**

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Targeted Radionuclide Therapy (TRT) offers significant advantages in cancer treatment, minimizing collateral damage to healthy tissues by selectively delivering radionuclides to tumor sites[1]. Its success lies in personalized treatment tailored to cancer features, utilizing precise targeting molecules and novel radionuclides. Radiolanthanides have gained attention in nuclear medicine due to their promising nuclear properties and chelation chemistry. Notably, <sup>161</sup>Ho ( $t_{1/2} = 2.48$  h) emits conversion and Auger electrons after electron-capture (EC 100 %) decay, potentially effective for the killing of micro metastases [2]. Conversely,  $\beta^-$ -particles ( $E_{\beta,ave} = 665$  keV) emitted by <sup>166</sup>Ho ( $t_{1/2} = 26.8$  h) travel much longer distances, which is useful for treating clusters of malignant cells[3]. To the best of our knowledge, no method has been developed to produce no-carrier-added (n.c.a.) <sup>161</sup>Ho and <sup>166</sup>Ho for TRT. Our goal is to produce these radiolanthanides in high specific activity and radionuclidic purity for systematic preclinical studies.

Cross-section measurements of relevant holmium radioisotopes were initially conducted using natural and enriched dysprosium targets (enr. <sup>161</sup>Dy 91.1%, <sup>162</sup>Dy 94.5%), irradiated with protons at the Bern medical cyclotron laboratory. Production yield measurements were performed by employing a 50- $\mu$ A proton beam from Paul Scherrer Institute's Injector II cyclotron, using natural and enriched dysprosium for <sup>161</sup>Ho production. Indirect production of <sup>166</sup>Ho can be achieved using natural and enriched (enr. <sup>164</sup>Dy 96.8 %) dysprosium targets utilizing high neutron fluxes available at the Institut Laue-Langevin (ILL) research reactor (Grenoble, FR) to produce its parent radionuclide <sup>166</sup>Dy ( $t_{1/2} = 81.6$  h). This production route should also enable the implementation of a generator to obtain radionuclidically pure <sup>166</sup>Ho in n.c.a. form. In this context, subsequent radiochemical separation experiments were also conducted to investigate the potential of extraction resins (LN, TK211).

The cross sections of <sup>156,159,160g,160m,161,162g,162m</sup>Ho and <sup>157</sup>Dy were measured using the aforementioned target materials up to 18.2 MeV. Currently, production yield measurements using <sup>162</sup>Dy targets exhibited the highest end-of-bombardment (EoB) activity and radionuclidic purity using 24-MeV proton beams. Additional irradiations are planned to assess whether both radionuclidic purity and <sup>161</sup>Ho activity can be increased using natural holmium as target material. Microgram quantities of <sup>164</sup>Dy were irradiated at ILL using a neutron flux of  $1.2 \times 10^{15}$  cm<sup>-2</sup>s<sup>-1</sup>, yielding approximately 120 GBq/mg of <sup>166</sup>Dy at the end of irradiation. Based on these findings, preliminary separation experiments have been conducted using LN and TK211 resins. Separation profile of Dy and Ho were plotted utilizing 1 M HNO<sub>3</sub> as the eluent for both resins to collect <sup>166</sup>Dy, yielding promising results for the subsequent separation step. This step involves using of cation exchange resins (Sykam, AG MP-50) to collect <sup>166</sup>Ho.

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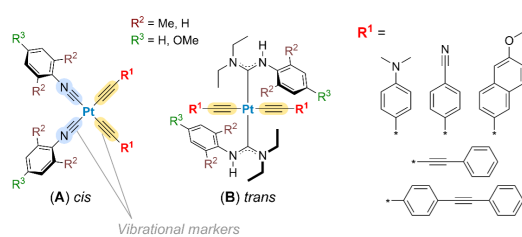
## Photoinduced Dynamics of Symmetric $\pi$ -Extended Aryl Acetylide Platinum Complexes with Isocyanides or Acyclic Diaminocarbenes: Symmetric or not?

A. Ruiz-Lera<sup>1</sup>, J. López-López<sup>2</sup>, Y. Nguyen<sup>2</sup>, T. Teets<sup>2</sup>, R. Fernández-Terán<sup>1\*</sup>

<sup>1</sup>Department of Physical Chemistry, University of Geneva. CH-1205, Geneva. Switzerland., <sup>2</sup>Department of Chemistry, University of Houston. 77204-5003, Houston, Texas. United States

We are investigating the excited-state dynamics of two families of luminescent Pt(II) complexes with  $\pi$ -extended aryl acetylide ligands, supported by isocyanides (*cis*-acetylides, **Fig. 1a**) or acyclic diaminocarbenes (*trans*-acetylides, **Fig. 1b**).<sup>[1]</sup> In both families, we explore the role of the substituent on the aryl acetylide moieties in determining the character and lifetimes of the excited states. Furthermore, the role of solvation, the solvent and the side group identities in determining whether the excited state undergoes spontaneous symmetry breaking are investigated.

Both acetylide and isocyanide ligands provide excellent vibrational markers to track and identify the charge distribution in the excited state(s) of interest. Taking advantage of this, we combine transient electronic absorption (TA), transient infrared (TRIR) and transient two-dimensional infrared (tr2D-IR) to obtain a broad picture of the excited-state photophysics and photochemistry of these and related complexes. In addition, these ligands provide potential spectroscopic handles to control the directionality of electron/charge transfer by mode-selective vibrational excitation of the bridge, akin to studies of similar Pt(II) complexes previously reported by the Weinstein group.<sup>[2,3]</sup>



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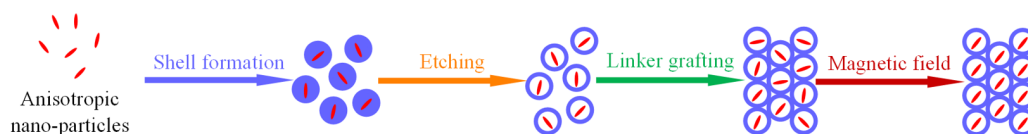
## Two level ordering in nano-rattles for optical properties

A. Scalabre<sup>1</sup>, K. M. Fromm<sup>1\*</sup>

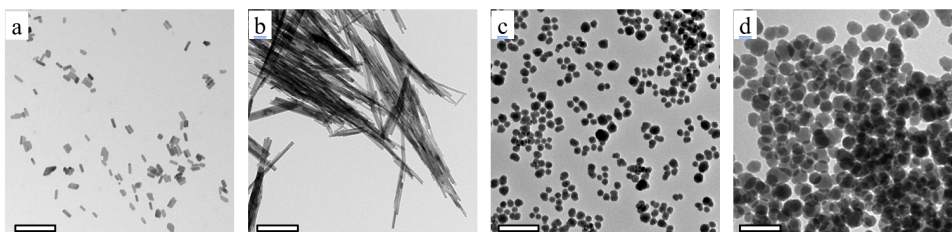
<sup>1</sup>University of Fribourg, Chemistry Department, Chemin du Musée 9, CH-1700 Fribourg

Nano-rattles are in the center of many studies thanks to their interesting properties. These come from their non-homogeneous composition, and from the particular environment around the core. Synthesizing such objects is challenging, but we decided to go further by organizing them in different ways and levels for optical effects.

First we focused on obtaining a controllable and reversible way of aggregating particles, using silica spheres as model. Secondly, we developed anisotropic and magnetic particles based on gadolinium. Finally, the most recent research focus on the synthesis of capsules able to contain the rods. Having such high control over the organization of materials might allow to control opalescent properties of the aggregates.



**Figure 1.** Schematic representation of the different synthesis and organization steps



**Figure 2.** TEM pictures of synthesized NaGdF<sub>4</sub> (a) and GdPO<sub>4</sub> (b) nanorods and of functionalized silica beads before (c) and after (d) irradiation at 380nm (scales: 200nm)

A. M. El-Toni, M. A. Habila, J. P. Labis, Z. A. ALOthman, M. Alhoshan, A. A. Elzatahry and F. Zhang, *Nanoscale*, 2016, **8**, 2510–2531

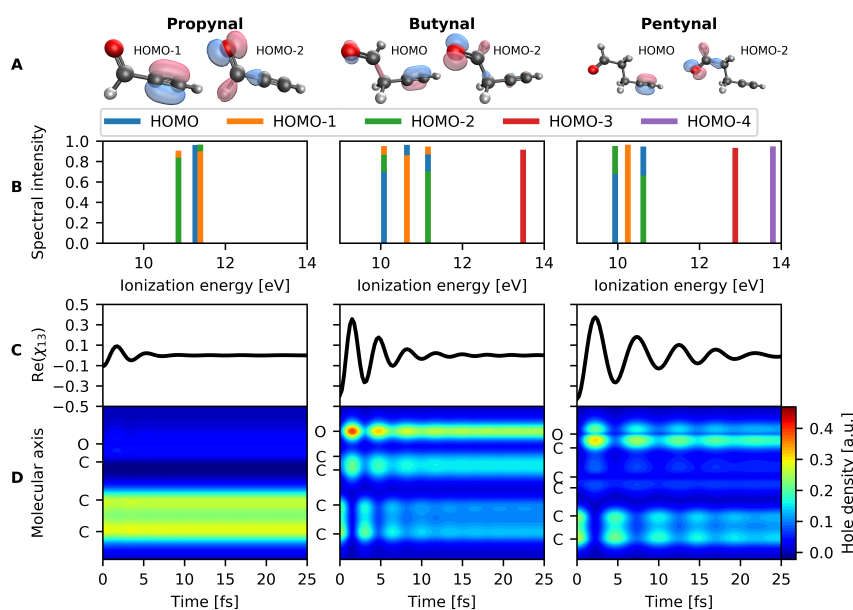
L.-S. Lin, J. Song, H.-H. Yang and X. Chen, *Adv. Mater.*, 2018, **30**, 1704639

## Can increasing the size and flexibility of a molecule reduce decoherence?

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Coherent superposition of electronic states, created by ionizing a molecule, can initiate ultrafast dynamics of the electron density. Correlation between nuclear and electron motions, however, typically dissipates the electronic coherence in only a few femtoseconds, especially in larger and more flexible molecules. We, therefore, use ab initio semiclassical dynamics to study decoherence in a sequence of analogous organic molecules of increasing size and find, surprisingly, that extending the carbon skeleton in propynal analogs slows down decoherence and extends the duration of charge migration. To elucidate this observation, we decompose the overall decoherence into contributions from individual vibrational modes and show that: (1) The initial decay of electronic coherence is caused by *high- and intermediate-frequency* vibrations via *momentum* separation of nuclear wavepackets evolving on different electronic surfaces. (2) At later times, the coherence disappears completely due to the increasing *position* separation in the *low-frequency* modes. (3) In agreement with another study, we observe that only normal modes preserving the molecule's symmetry induce decoherence. All together, we justify the enhanced charge migration by a combination of increased hole-mixing and the disappearance of decoherence contributions from specific vibrational modes—CO stretching in butynal and various H rockings in pentynal.



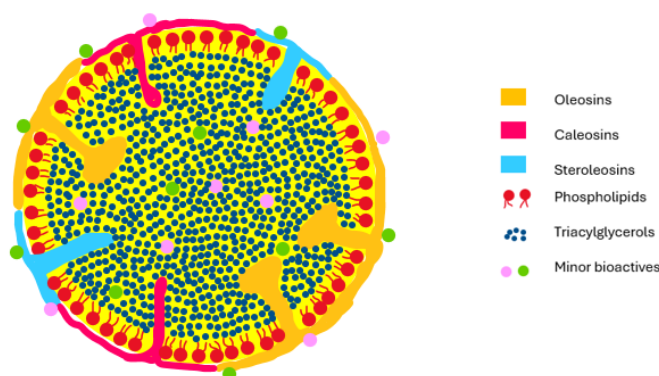
**Fig.1** Ionization spectrum and charge migration triggered by ionizing the propynal (left), butynal (middle), and pentynal (right) molecules. (A) Hartree-Fock molecular orbitals involved in the hole-mixing. (B) First cationic states in the energy range of 9 to 14 eV. (C) Time evolution of the electronic coherence between the first and third cationic states created by the ionization. (D) Charge migration projected along the molecular axis passing through the carbon triple bond.

**Extraction and characterization of oleosomes from wheat germ.**

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Oleosomes<sup>1</sup> are natural oil droplets found in plant seeds and other plant tissues. They are sub-micron sized particles with a triacylglycerol core surrounded by phospholipids and proteins and represent a promising system for the development of low-processed plant-based food emulsions. The objective of this project is the extraction and purification of oleosomes from locally sourced wheat germ to create stable food emulsions. Oleosomes have been found to be difficult to extract, but it is easier to extract them as an intact emulsion<sup>2</sup>. Their composition is analysed using mass spectrometry for fatty acid profiling and SDS-PAGE for protein analysis. Their structural characterization with the impact of environmental variables such as pH, temperature and ionic strength are studied using dynamic light scattering, zeta potential measurements, small angle X-ray scattering, and confocal laser scanning and Raman microscopy. These findings will guide the optimization of oleosomes for their application in various food formulations such as plant-based milk, butter and creams.



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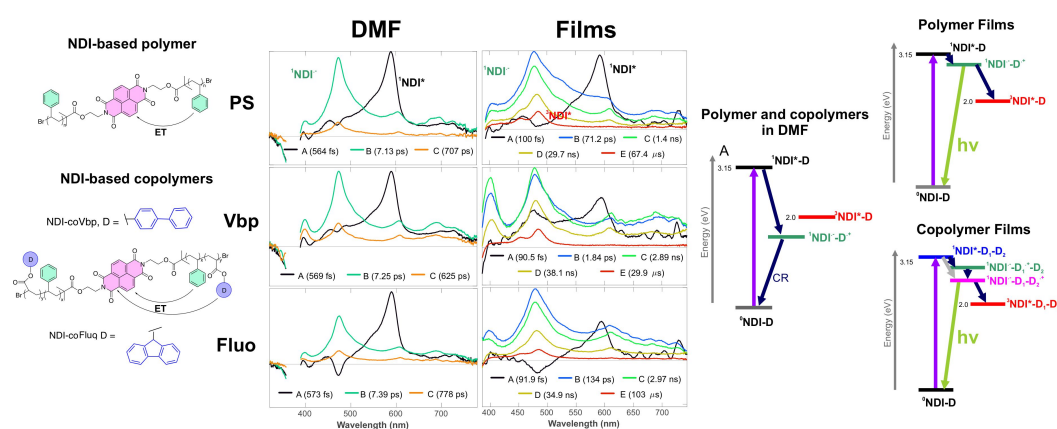


## Understanding the ultrafast charge transfer process in naphthalene diimide (NDI) based polymers and copolymers

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A new strategy to synthesize polymeric materials with tunable emission through a controlled polymerization-mediated through-space charge transfer was recently reported [1]. These polymers consist of a single naphthalene diimide (NDI) unit as an acceptor group, and a chain of donor groups. Theoretical studies suggest that emission color tunability originates from structurally dependent through-space charge transfer, but experimental evidence of this process was still missing. Herein, we provide a thorough spectroscopic investigation of the charge transfer process occurring in these systems.



**Figure:** Left: NDI-based polymer and copolymers. Center: global analysis assuming three (solutions in DMF) and four (spin-coated films) successive exponential steps. Right: Energy level diagrams

Using transient absorption spectroscopy, we successfully demonstrated the occurrence of a subpicosecond photoinduced electron transfer between the NDI chromophore and the primary donor in solution, and both donors in the solid via the direct observation of the transient bands of the NDI radical anion and the biphenyl and fluorene radical cations. In DMF solution, intrachain charge transfer (CT) is dominant, and the high stabilization of the charge-separated state (CSS) results in its faster recombination when compared with the solid. In this last case, the CT process occurs mostly interchain; and the CSS state recombines to the neutral ground state through fluorescence or by the triplet state of the NDI through spin-orbit-charge-transfer intersystem crossing. We hypothesize that a better secondary donor group could deactivate the triplet population channel by lowering the energy of the CSS, thus enhancing the fluorescence quantum yield

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**State-preparation and quantum control of polyatomic molecular ions**

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Trapped molecular systems are excellent tools for precise quantum control, offering a wide range of applications in quantum computing, precision spectroscopy, tests of fundamental physics and state-to-state chemistry [1,2]. However, these systems have complex internal energy-level structures and in addition, they lack readily accessible closed cycling transitions which makes their state preparation, laser cooling, quantum control and coherent manipulation difficult.

Currently, in our lab, we utilize quantum logic spectroscopy to co-trap molecular ions such as  $\text{N}_2^+$  with atomic ions such as  $\text{Ca}^+$  ions in an RF ion trap [1,2].  $\text{N}_2^+$  is prepared in its ground rovibrational state, sympathetically cooled using Doppler cooled  $\text{Ca}^+$  atomic ions and non-destructively state detected using quantum logic spectroscopy [3].

Quantum-logic schemes have proved to be useful for the cooling, for the non-destructive detection of the quantum states and for the coherent manipulation of diatomic molecular ions which was otherwise challenging [1,4,5]. Our goal is to work towards the quantum control of complex polyatomic molecular systems and further understand their chemistry, spectroscopy and collision dynamics.

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**Comparing membrane potential imaging using water and FM4-64 dye as a probe**

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The electrostatic potential of membrane interfaces is an important metric to gain insight into the physiological state of cells. Second harmonic imaging is a powerful tool to perform in-situ and in-vivo electrostatic potential measurements, either with targeted probes as contrast agents or label-free with water [1, 2]. Here, we compare the two methods by measuring membrane potential distributions on free standing and giant unilamellar vesicle membranes. Correlating the SH intensity to an applied external potential bias [3], the resonant voltage probe and the water response display distinctly different responses, which can be traced back to the susceptibility element that dominates the light-matter interactions. The extracted potential distributions vary significantly, which is due to the fact that the voltage probe responds to both the external field as well as the local chemical environment. Combining both methods can be proven a useful strategy, since the water response is accurate yet limited by a temporal resolution of  $\sim 100$  ms, whereas the resonant probe is less accurate and invasive, but allows a temporal resolution of  $\sim 10$   $\mu$ s.

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**Testing the ion funnel-to-IVAC system for fast chemistry experiments with superheavy elements**

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The limited production rates and short half-lives of isotopes of late superheavy elements (SHEs) have primarily confined their chemical characterization to gas adsorption chromatography experiments within the continuum flow regime [1]. This method has been successfully used for chemical studies of SHEs [2] with isotopes possessing half-lives of at least 1 s. However, for the chemical characterization of SHEs beyond flerovium (Fl, Z = 114), new experimental approaches are necessary, as the radioisotopes of these elements have half-lives solely in the millisecond range ( $t_{1/2} \leq 650$  ms). Transitioning from continuum flow conditions to the molecular flow regime offers a promising strategy to address this challenge, potentially enabling experiments with radionuclides having half-lives as short as 50 ms or even less.

A buffer gas cell [3,4], interfacing the gas-filled recoil separator AGGIE (Al Ghiorso's Gas-filled Ion Equipment) with isothermal vacuum adsorption chromatography (IVAC) [5], was developed to thermalize, focus, and transfer nuclear reaction products into a vacuum chromatography setup. Within this system, produced short-lived radionuclides undergo multiple adsorption-desorption interactions with a specific stationary phase at different isothermal temperatures. Subsequently, atoms or chemical compounds of these radionuclides escape the chromatography column and are detected using wide bandgap semiconductors such as 4H-SiC.  $\alpha$ -detectors based on said materials allow continued operation at high temperatures [6].

Here, we present initial experiments conducted at the Cyclotron Institute of Texas A&M University. These focus on the adsorption behavior of short-lived radionuclides of the lighter homologs of SHEs, such as mercury or polonium, on fused silica surfaces. These experiments aim to demonstrate the potential of an IVAC experiment to study even the heaviest SHEs.

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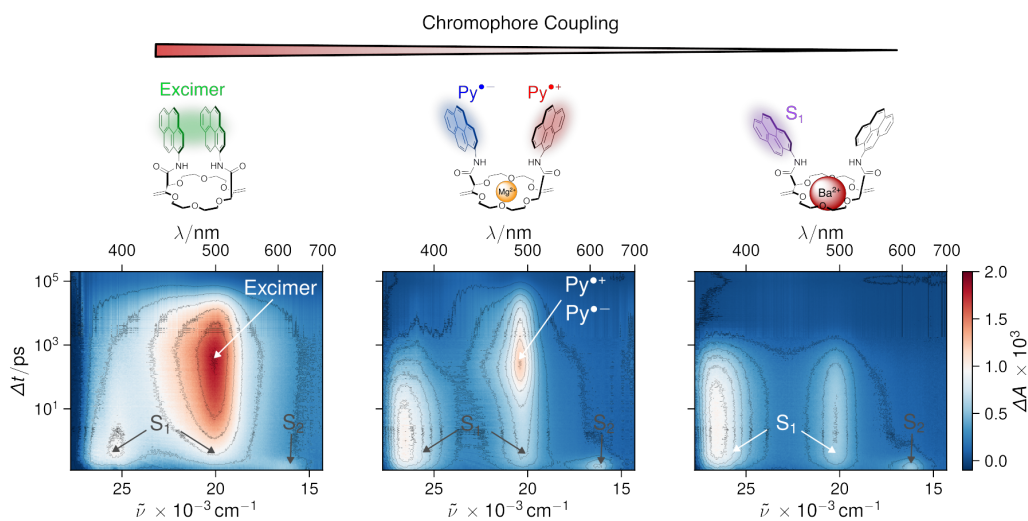
## Controlling Symmetry-Breaking Charge Separation in Pyrene Bichromophores

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The photophysics of multichromophoric systems are generally distinct from those of the monomeric subunits on which they are built.<sup>1-3</sup> Depending on the molecular orientations/coupling of the chromophores, the system can show vastly different responses such as excimer<sup>1,2</sup>, triplet formation<sup>1,3</sup> or even charge transfer<sup>1,2</sup>, upon photoexcitation.

Here<sup>4</sup> we report on the photophysics of a bichromophoric system based on two pyrene (Py) moieties connected through an 18-crown-6 backbone (Py<sub>2</sub>, Fig. below). By binding cations of different sizes into the crown ether macromolecule we can effectively control the average distance between the two Py-units.

We show using steady-state and time-resolved spectroscopic experiments that depending on the interchromophore distance the photophysics are differing substantially. Transient absorption spectroscopy from the femto-microsecond timescale (Fig. below) reveals the underlying dynamics and shows that Py<sub>2</sub> rapidly forms an excimer. Upon binding of Ba<sup>2+</sup> the excitonic coupling is essentially totally lost and the dynamics are dominated by the excitation localized on a single Py. We show that symmetry-breaking charge separation (SB-CS), *i.e.* electron transfer  $\text{Py}^* + \text{Py} \rightarrow \text{Py}^+ + \text{Py}^-$ , is operative in the intermediate coupling regime achieved upon binding of Mg<sup>2+</sup>, where excimer formation is restricted.



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**Isotopic chirality and high resolution infrared spectroscopy of  $\text{PFCl}_2$** 

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The concept of isotopic chirality is of fundamental interest because it introduces a completely new isotope effect arising from the parity violating weak nuclear force [1–3]. In this context we have previously presented the first quantitative theoretical calculations of this effect for the isotopically chiral molecule  $\text{PF}^{35}\text{Cl}^{37}\text{Cl}$  [4]. Because of the different weak nuclear charge of the isotopes with different numbers of neutrons, the enantiomers of molecules which become chiral by isotopic substitution are predicted to have different ground state energies separated by a parity violating energy difference  $\Delta_{\text{pv}}E$  in the aeV range, which can, in principle, be measured by special experiments [5], although no successful experiment has been reported to date in spite of ongoing efforts reviewed in [2,6].  $\Delta_{\text{pv}}E$  is exactly zero by symmetry for the  $C_s$  symmetric achiral isotopomers of  $\text{PFCl}_2$ . The analysis of rovibrationally resolved and assigned infrared spectra provides a first step towards experiments on parity violation in chiral molecules. We present here the initial results of our experimental study and the analysis of the high resolution infrared spectra of  $\text{PFCl}_2$ . The infrared spectrum of  $\text{PFCl}_2$  has been measured with our Bruker IFS 125 HR(ZP 2001) Zürich Prototype Fourier Transform spectrometer (room temperature, 650–1000  $\text{cm}^{-1}$ , resolution: 0.0015  $\text{cm}^{-1}$ ) and in a supersonic jet expansion ( $T = 15\text{--}20$  K) with our diode laser spectrometer between 830–834  $\text{cm}^{-1}$  and 838–841  $\text{cm}^{-1}$ . We were able to analyze the  $\nu_1$  PF-stretching fundamental of  $\text{PF}^{35}\text{Cl}_2$  ( $\nu_0 = 836.6$   $\text{cm}^{-1}$ ), and of  $\text{PF}^{35}\text{Cl}^{37}\text{Cl}$  ( $\nu_0 = 835.5$   $\text{cm}^{-1}$ ) strongly perturbed in both isotopomers by a Coriolis-type resonance with the  $\nu_3 + \nu_5$  level. The cold diode laser spectra at 15 K simplified the spectra considerably, making it possible to analyze the  $\nu_1$  absorption lines of  $\text{PF}^{35}\text{Cl}^{37}\text{Cl}$ . The  $\nu_5$  fundamental was analyzed as well for  $\text{PF}^{35}\text{Cl}_2$  ( $\nu_0 = 517.8$   $\text{cm}^{-1}$ ). We present also results on the first ground state rotational parameters obtained from combination differences, and on the structure of  $\text{PFCl}_2$ . The results will be discussed in relation to our ab-initio calculations and as they pertain to isotopic chirality, molecular parity violation, biomolecular homochirality, and the fundamental symmetries of physics and chemistry.

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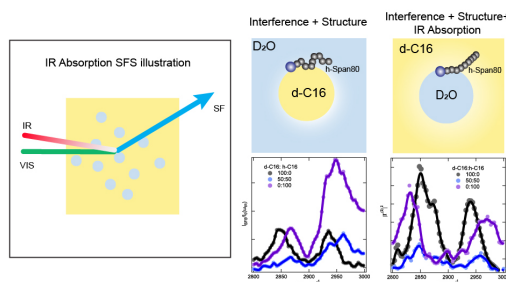
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## Interfacial Inversion, Interference, and IR Absorption in Vibrational Sum Frequency Scattering Experiments

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Molecular interfacial structure greatly determines the properties of nano- and microscale systems. Vibrational sum frequency scattering (SFS) spectroscopy is a unique interface selective tool to measure the interfacial vibrational spectrum of submicron to micron-scale objects dispersed in liquid and solid media. The interfacial structure is extracted from the interfacial susceptibility, a physical property derived from the intensity. Here, we describe the effect of infrared absorption that occurs in a bulk medium that is spectroscopically complex and use the results to investigate the effects of interfacial inversion, interfacial interference, and interfacial interference combined with absorption. We use the same three chemicals to do so, hexadecane oil, water, and a neutral Span80 surfactant. For all cases, the effective surface susceptibility can be retrieved from the intensity. We further find that inverting the phases results in different interfacial structures, even though they are composed of the same three chemicals, and explain this in terms of the different interactions that are necessary to stabilize the drops: steric stabilization for water drops in oil vs. charge stabilization for oil drops in water. Interfacial interference can be used to estimate the surface density of different compounds.



## In vivo <sup>1</sup>H MR Spectroscopy of bile acids from human gallbladder—Detection and quantification of metabolites after a lipid load

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### Introduction

Bile is fluid secreted by liver, stored and concentrated in the gallbladder until needed, and closely reflects the available bile acid pool. It exerts multiple functions in several physiological processes and is involved in various hepatopancreatobiliary (HPB) diseases.<sup>1,2</sup> Bile acids, one of the main components of bile, are synthesized by the liver from cholesterol through a series of enzymatic reactions. They play an important role in human fat metabolism, especially emulsification, digestion, and absorption of lipids.<sup>3</sup> Previously we have shown that bile acids can be assessed non-invasively by <sup>1</sup>H-MRS.<sup>1</sup> In the current study we aimed at determining the sensitivity of the method to detect changes and at determining how lipids and bile acids change in vivo after fat ingestion.

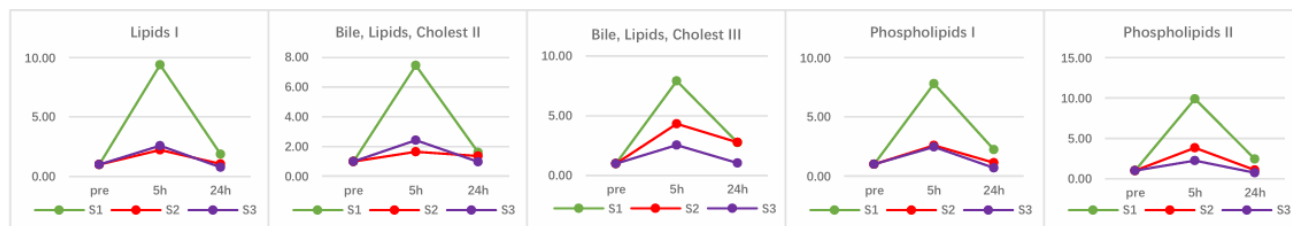
### Aim

The study focuses on detecting and analyzing the changes of metabolites of bile acids in human gallbladder before and after fat suspension ingestion using in vivo <sup>1</sup>H-MRS at a 3T MR scanner.

### Method

Three healthy slim male volunteers participated in this pilot study. The subjects underwent MRI examinations at three time points: at baseline after an overnight fast and 5h and 24h after fat ingestion (180ml fat ingestion, ~ 800 kcal). All measurements were performed on a 3T-MR Scanner (Verio, Siemens) with the subjects in back position. A single-voxel PRESS sequence with PACE-triggering was acquired with the voxel placed in the center of the gallbladder. MRS measurement duration was ~5min, depending on breathing cycle. The spectra were analyzed using jMRUI.

### Results



S1, S2, and S3 represent the bile metabolism of three volunteers. The "5h" and "24h" values are normalized to the "pre" value, i.e., the values at 5h and 24h indicate fold-changes of bile acid metabolite concentrations compared to initial. Example results from five analyzes of bile metabolites are shown here. Lipid concentrations in bile metabolites increased significantly within 5 h after drinking lipids and recovered after 24 h. Furthermore, S1 metabolites showed much stronger increases and decreases compared to the other two subjects, possibly indicating individually different responses to fat ingestion.

### Discussion

In vivo bile <sup>1</sup>H MR spectra enabled the detection of a variety of bile metabolites before and after drinking lipids. The method proved valuable for detecting changes in bile acid composition.

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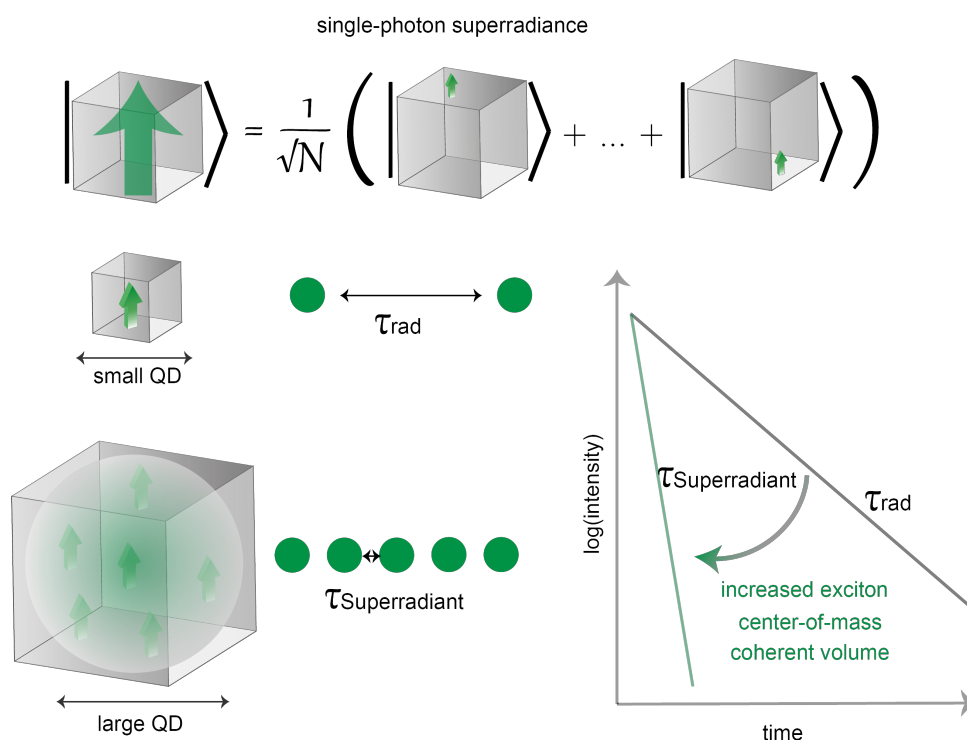


### Single-photon superradiance in individual cesium lead halide quantum dots

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The brightness of an emitter is ultimately described by Fermi's golden rule, with a radiative rate proportional to its oscillator strength times the local density of photonic states (LDOS). Since the oscillator strength is an intrinsic material property, the quest for ever brighter emission has relied on LDOS engineering, via dielectric or plasmonic resonators<sup>1,2</sup>. In contrast, a much less explored avenue is to boost the oscillator strength, and hence the emission rate, via a collective behavior termed superradiance. Recently, it had been proposed<sup>3</sup> that the latter can be realized via the giant oscillator-strength transitions of a weakly confined exciton in a quantum well when its coherent motion extends over many unit cells. Here, we demonstrate single-photon superradiance in perovskite quantum dots (QDs) with a sub-100 ps radiative decay time, almost as short as the reported exciton coherence time<sup>4</sup>. The characteristic dependence of radiative rates on QD size, composition, and temperature suggests the formation of giant transition dipoles, as confirmed by effective-mass calculations. The results aid the development of ultrabright, coherent quantum-light sources and attest that quantum effects, e.g., single-photon emission, persist in nanoparticles ten times larger than the exciton Bohr radius.



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**Evaporation of Po from LBE-cooled reactors**

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Utilizing liquid metals like lead-bismuth eutectic (LBE) as a coolant presents a promising direction for the advancement of generation IV nuclear power reactors. These reactors are primarily designed for the application as breeder reactors or for nuclear waste transmutation, consequently closing the nuclear fuel cycle.

LBE displays a range of remarkable properties, including superior thermal characteristics, low vapor pressure, high boiling point, and the capacity to shield  $\gamma$ -radiation. For its application as a coolant, understanding the distribution and behavior of produced or introduced radionuclides within LBE is crucial for assessing the safety aspects of such systems. Accurate predictions necessitate a thorough comprehension of radionuclide release from the coolant, particularly in potential accident scenarios.

The HORIZON2020 project PATRICIA extends prior research on the radionuclide volatilization from LBE, which is relevant to the safety of future accelerator-driven systems. The study specifically focuses on the volatility of Po, as it is one of the most radiotoxic and volatile elements produced during the operation of these reactors.

Here, we present the most recent findings on the volatilization investigations of Po from MEGAPIE, utilizing the transpiration technique.

### Tellurium speciation in vapors over Lead-Bismuth eutectic melts

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This study focuses on the behavior of tellurium evaporation in Lead-Alloy-Cooled Fast Reactors (LFRs). Tellurium isotopes appear in heavy metal coolant via the activation of impurities, a spallation reaction on a high-energy proton beam in Accelerator Driven Systems (ADS), or as a fission product from fuel pellets in the event of their failure. Given its volatility, understanding the speciation of tellurium in the gas phase and its vapor pressure is crucial for assessing its dose rate impact and behavior during accidental scenarios. A thermosublimatographic method was employed in our research to examine the gas phase speciation of tellurium over a Lead-Bismuth Eutectic (LBE) melt. Experiments were conducted using Lead-Bismuth Eutectic (LBE) supplied by SCK CEN, which was doped with elemental tellurium activated at the neutron irradiation facility at PSI. Pure helium was used as a carrier gas. By adding oxygen, hydrogen, and water vapors to the helium, oxidizing and reducing conditions were examined. Two different surface materials, quartz and stainless steel, were used. Under inert conditions, a substantial fraction of tellurium evaporation was lead telluride (PbTe) in both types of columns. SEM/EDX scans of depositions on column's surface confirmed those results. In quartz columns, another deposition was noticed at around 300 °C, which revealed as a crystalline tellurium in SEM scans. It was shown that the formation of this additional deposition is associated with the presence of water vapors in the gas phase. In high humidity conditions, only a lower temperature deposition was observed in quartz columns. This effect of water vapors was not observed in steel columns and only PbTe was confirmed under all conditions.

The results provide insights, especially concerning humidity's influence, for designing future experiments to determine tellurium vapor pressure over LBE and for the general safety assessment of LBE-cooled reactors.

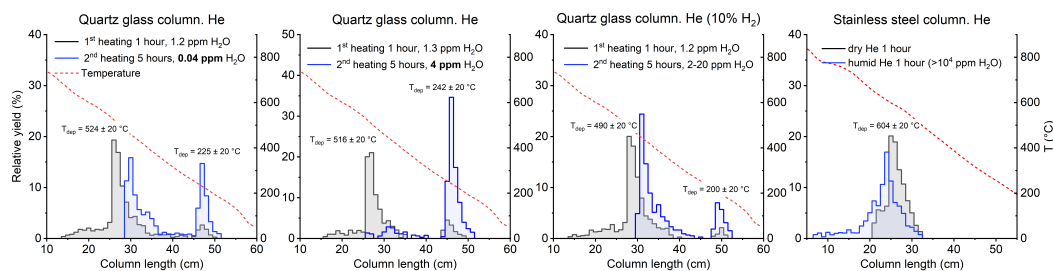


Figure 1. Distribution of Tellurium along quartz glass and stainless steel columns in thermosublimatographic experiments.