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Unravelling the intricate interplay between donor and acceptor materials in bulk heterojunction blends for organic photovoltaics

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Over the last decade, the power conversion efficiencies of bulk heterojunction organic solar cells (OSCs) have increased steadily, demonstrating their great potential for future photovoltaic applications. Through recent advances in the synthesis of small molecule non-fullerene acceptors, the drawbacks of earlier fullerene-based OSCs have been circumvented. With rapid advances in material synthesis and device performance, the long-term stability of the OSCs has become the main remaining challenge towards commercialization. In this talk, it will be shown how a combination of advanced electron paramagnetic resonance (EPR) techniques and optical spectroscopy tools can give unique insight in the degradation mechanisms, involving both radical pathways and triplet exciton formation with the creation of reactive oxygen species. These results provide input for a rational design of new donor and acceptor materials.

A Supramolecular Approach to Hybrid Perovskite Photovoltaics

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Hybrid perovskites have recently emerged as one of the leading materials in thin-film photovoltaics due to their remarkable solar-to-electric power conversion efficiencies.[1-2] However, their limited stability under device operation conditions remains challenging.[1-2] In contrast, low-dimensional perovskite analogs have shown promising operational stabilities.[3-7] We demonstrate a strategy to provide stabilization of hybrid perovskite solar cells without compromising their performance through fine-tuning various noncovalent interactions (i.e. supramolecular engineering),[7-10] such as metal coordination,[10] hydrogen[6,9-10] or halogen bonding,[8] and π-interactions,[7] at the interface with active perovskite materials in a manner uniquely assessed by solid-state NMR spectroscopy.[5-6,8-10] As a result, we obtain perovskite solar cells featuring superior photovoltaic performances, accompanied by enhanced operational stabilities.[6-10] Moreover, the formation of layered perovskite architectures enables further stability enhancements.[3-7] This has been investigated using a combination of techniques complemented by solid-state NMR to unravel the underlying design principles and exemplify the potential of this supramolecular approach in advancing hybrid perovskite photovoltaics.

Schematic representation of low-dimensional perovskites and the corresponding solar cells

[1] J. V. Milić et al. *Chimia* **2019**, *73*, 317; [2] M. Graetzel et al. *Substantia* **2019**, *3*, 27; [3] Y. Li et al. *Nano Lett.* **2019**, *19*, 150; [4] J. V. Milić et al. *Adv. Energy Mater.* **2019**, 1900284;
[5] L. Hong, et al. *Angew. Chem. Int. Ed.* **2020**, doi:10.1002/anie201912051; [6] A. Q. Alanazi, et al. *J. Am. Chem. Soc.* **2019**, *141*, 17659; [7] Y. Liu et al. *Sci. Adv.* **2019**, *5*, eaaw2543;
[8] M. A. Ruiz-Preciado et al. *J. Am. Chem. Soc.* **2020**, doi:10.1021/jacs.9b13701; [9] M. M. Tavakoli et al. *Energy Environ. Sci.* **2018**, *11*, 3310; [10] D. Bi et al. *Nat. Commun.* **2018**, *9*, 4482.

Size-selection: An essential step for understanding lead halide perovskite quantum optics

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Lead halide perovskites are the most promising semiconductor material of modern times. This class of materials is currently investigated for its use in applications from solar-cells and photo-detectors (in particular for hard radiation) to light emitting devices such as LEDs and LCD displays [1]. Nanocrystals of cesium lead bromide ($CsPbBr_3$) have been found to emit single photons with long coherence times [2], that can be optically coupled to give rise to super-fluorescence [3]. This effect was thus far observed in ordered perovskite nanocrystal assemblies. The intrinsic optical characteristics of these nanocrystals and their relation to the nanocrystal habit are, however, not well studied due to a lack of monodisperse ensembles with tunable crystal habit. We present a size selection procedure which enables the isolation of monodisperse ensembles of $CsPbBr_3$ nanocrystals in a size range between 4.1 and 13.3 nm [4]. We analyzed their crystal habit by small angle X-Ray scattering and were able to quantum mechanically model the change of the first and second excitonic transition as well as their radiative lifetime as a function of the nanocrystal size and to predict the effect of the nanocrystal shape. We, additionally, demonstrate the self-assembly of these nanocrystals into super-crystals and their super-fluorescence. Having access to more sizes than previously the effect of the nanocrystal size on the super-fluorescence characteristics could be investigated. This shows that these monodisperse ensembles are a valid reference system for the further investigation of the coupling mechanism giving rise to the super-fluorescence behavior.

[1] Kovalenko, M. V.; Protesescu, L.; Bodnarchuk, M. I., Properties and potential optoelectronic applications of lead halide perovskite nanocrystals. *Science* **2017**, *358*, 745-750.
[2] Utzat, H.; Sun, W.; Kaplan, A. E. K.; Krieg, F.; Ginterseder, M.; Spokoyny, B.; Klein, N. D.; Shulenberger, K. E.; Perkinson, C. F.; Kovalenko, M. V.; Bawendi, M. G., Coherent single-photonemission from colloidal lead halide perovskite quantum dots. *Science* **2019**, *363*, 1068–1072
[3] Raino, G.; Becker, M. A.; Bodnarchuk, M. I.; Mahrt, R. F.; Kovalenko, M. V.; Stoferle, T., Superfluorescence from lead halide perovskite quantum dot superlattices. *Nature* **2018**, *563*, 671-675.
[4] Franziska Krieg *et al*. submitted

Electronegativity and Location of Anionic Ligands Drive Yttrium NMR for Molecular, Surface and Solid-State Structures

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Yttrium containing compounds and materials, that are used in a broad range of applications such as catalysts, lasers and optical devices, can be in principle readily characterized by NMR. Indeed, ^{89}Y, a 100% abundant spin ½ nucleus, is associated with a broad range of NMR chemical shifts.[1] Although the latter greatly depend on the coordination environment at Y, it has so far been difficult to obtain a direct relationship between ^{89}Y chemical shifts and its coordination number. For instance, previous reports in the literature on ^{89}Y NMR showed that the isotropic chemical shifts for oxides tend to decrease for increasing coordination numbers,[2] but a contrary trend was found for silica-supported Y(III) sites.[3] To date, the differences of behaviour between trends found across bulk and surface sites as well as in molecular compounds have remained unclear.

In this contribution, we use computational chemistry along with solution and solid-state NMR data to provide a molecular level understanding of ^{89}Y-chemical shift using a broad range of Y(III) molecular compounds. We show through NCS-analysis that isotropic chemical shifts can easily help to distinguish between different types of ligands solely based on the electronegativity of the atom of the anionic ligands directly bound to Y(III). NCS-analysis further demonstrates that the second most important parameter is location of the three anionic ligands imposed by additional neutral ligands. While isotropic chemical shifts can be similar due to compensating effects, investigation of the chemical shift anisotropy (CSA) enables discriminating between the coordination environment of yttrium. Overall, we show that a molecular level approach to chemical shift is key to understand spectroscopic signatures of molecular compounds and materials, and that Y NMR can thus be used to readily obtain key information about the local environment of Y atoms in a broad range of compounds and materials.

[1] R. E. White, T. P. Hanusa, *Organometallics*, **2006**, 25, 5621–5630.
[2] A. Jaworski, T. Charpentier, B. Stevensson, M. Edén, *J. Phys. Chem. C*, **2017**, 121, 18815–18829.
[3] M. F. Delley, G. Lapadula, F. Núñez-Zarur, A. Comas-Vives, V. Kalendra, G. Jeschke, D. Baabe, M. D. Walter, A. J. Rossini, A. Lesage, L. Emsley, O. Maury, C. Copéret, *J. Am. Chem. Soc.*, **2017**, 139, 8855–8867.

Quantifying interface diffusion in Li ion battery cathode materials

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To be able to reduce internal cell resistances that limit charging rates in a lithium ion battery, a detailed understanding of the underlying charge diffusion processes is crucial. While there are numerous known techniques that can determine the diffusion coefficients in the bulk of a material, measuring diffusion through interfaces is challenging [1]. Nonetheless, as interfaces often are rate-limiting, methods to determine interface diffusion are sought after.

Here, we show an approach to study diffusion at interfaces using muon spin spectroscopy. By performing measurements on $LiFePO_4$ platelets with different sizes, we determine how diffusion through the $LiFePO_4$ (010) interface differs from that in the center of the particle (i.e., bulk diffusion). We perform ab initio calculations to aid the understanding of the results and show the relevance of our interfacial diffusion measurement to electrochemical performance through cyclic voltammetry measurements. These results indicate that surface engineering can be used to improve the performance of lithium-ion batteries [2].

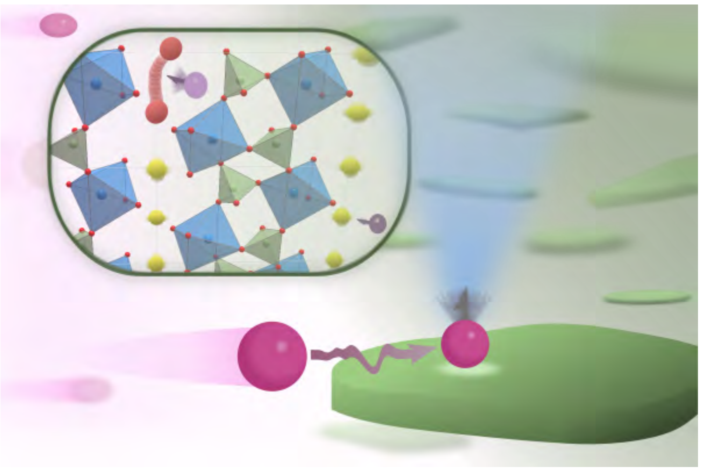

Figure 1. A muon pulse interacts with the $LiFePO_4$ particles leading to a spin rotation of the muon. Inset: Depending on the ion dynamics, the muon spin rotation changes eventually leading to an effective probe of ion dynamics.

[1] Yiyang Li, Hungru Chen, et al., *Nat. Mater.*, **2018**, 17, 915-922.
[2] Peter Benedek, Ola K. Forslund, et al., ACS Appl. Mater. Interfaces, 2020, 12, 16243-16249.

Surface Potential and Interfacial Water Order at the Amorphous TiO_2 Nanoparticle/Aqueous Interface

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Colloidal semiconductor nanoparticles exhibit unique size-dependent properties compared to their bulk counterparts, which can be particularly beneficial for catalytic applications. To develop highly efficient, environmentally-friendly photocatalytic devices it is essential to understand the surface chemical reactivity of nanoscale semiconductor materials and the microscopic structure of the nanoparticle-liquid interface.

Here we use polarimetric angle-resolved second harmonic scattering to determine surface potential values as well as interfacial water orientation of ~100 nm diameter amorphous TiO_2 nanoparticles dispersed in aqueous solutions, without any initial assumption on the distribution of interfacial charges. We find three regions of different behavior with increasing NaCl concentration. At very low ionic strengths (0-10 µM), the Na^+ ions are preferentially adsorbed at the TiO_2 surface as inner sphere complexes. At low ionic strengths (10-100 µM), a distribution of counterions equivalent to a diffuse layer is observed, while at higher ionic strengths (>100 µM), an additional layer of hydrated condensed ions is formed. We find a similar behavior for TiO_2 nanoparticles in solutions of different basic pH. Compared to identically-sized SiO_2 nanoparticles, the TiO_2 interface has a higher affinity for Na^+ ions, which we further confirm with molecular dynamics simulations. With its ability to monitor ion adsorption at the surface with micromolar sensitivity and changes in the surface potential, AR-SHS is a powerful tool to investigate interfacial properties in a variety of (photo)catalytic applications.

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Towards in-cell drug detection and quantification by MAS DNP

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Knowledge of intracellular drug concentration gives information on uptake, trafficking and target engagement, providing a better understanding of function and efficacy. Detection should ideally be performed non-destructively, and without modification of either the drug or the target. It requires the capability to detect low amounts of the molecule of interest, often in the μM – nM range. However, there is currently no experimental technique that can provide direct intracellular drug concentrations satisfying simultaneously all these requirements.

Solution NMR is a well-established technique for the non-destructive, tag free-quantification of analytes, and over the last decade or so has been extensively used for the characterization of molecules (e.g. proteins), in their native cellular environments. However, NMR is hindered by low sensitivity, and biased to the study of molecules in fast motional regime, which is not always the case inside the cell. Magic-angle spinning dynamic nuclear polarization (MAS DNP) can be used to overcome these two drawbacks, providing higher sensitivity and allowing the detection of immobilized species.[1]

Here we present preliminary results demonstrating how MAS DNP can be successfully used for the detection and the quantification of molecules in sub-μM concentration, compatible with intracellular conditions. Our results are a first step towards the use of MAS DNP for the study of intracellular drug trafficking.

[1] J.Schlagnitweit, S. Friebe Sandoz, A. Jaworski, I. Guzzetti, F. Aussenac, R. J. Carbajo, E. Chiarparin, A. J. Pell, K. Petzold, *ChemBioChem,* **2019**, 20, 2474 – 2478

Interchromophore conformation and geometrical flexibility governs the fate of triplet pairs generated by singlet fission

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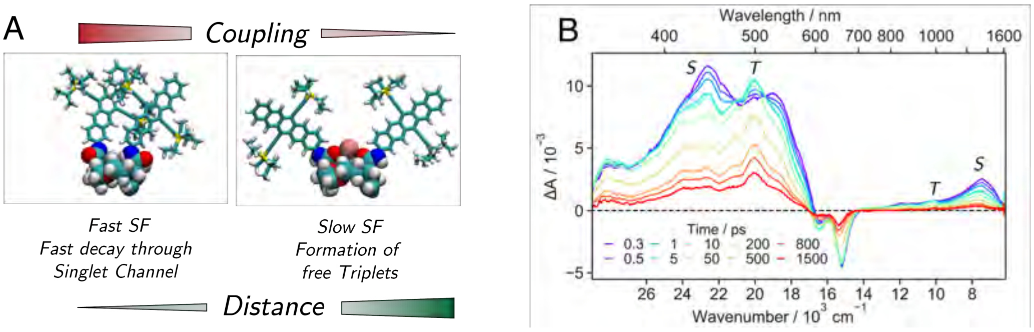
In singlet fission (SF), one high energy singlet (S) exciton is converted to two lower energy triplet (T) excitons which, if separated quantitatively, can lead to a doubling of the photocurrent in a solar cell. The need for efficient solar energy harvesting has boosted the general interest in SF including the impact of intermolecular geometry and coupling of the involved chromophore pair.[1]



In this communication, we will present a bichromophore in which two TIPS-pentacene heads are linked to a crown ether backbone as shown in Figure A. The interchromophore conformation can be controlled by either the solvent-dependent intramolecular aggregation or by a structural change of the crown ether due to cation binding. Transient absorption from femtosecond to microsecond and from UV to NIR (Figure B) is paired with molecular dynamics simulation. This allows the interchromophore geometries to be linked with the rate of singlet fission as well as the fate of the generated triplet pair.

We will show that triplet pairs can be spectrally and kinetically differentiated according to their coupling and that the formation of free, separated triplet pairs depends on geometrical fluctuations of the system.

[1] Millicent B. Smith, Josef Michl, *Chemical Reviews,* **2010**, 110 (11), 6891–6936.

Unravelling the Mechanism of Ultrafast Intrinsic Charge Generation in Cyanine Dyes

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Cyanine dyes have a long history in the field of organic photovoltaics and they have several beneficial properties that contribute to their continued use; for example, the absorption profile of the material can be easily tuned, and they possess high extinction coefficients allowing for the active layer of devices to be very thin (up to 20 nm).[1]

Typically, the cyanine dyes are used alongside a fullerene-based acceptor, such as C60, in a planar heterojunction configuration with efficiencies of up to 3.7% being achieved.[2]

To date, ultrafast studies on these systems have tended to focus on the separation of charge transfer excitons, or the role of blend morphology.[3],[4]

However, recent studies have shown that high bulk photoconductivity can be seen in pristine pentamethine cyanine (Cy5) films, without the presence of a donor-acceptor interface.[5]

Here, we employed ultrafast transient absorption spectroscopy to determine the charge transfer mechanism in Cy5 systems, providing the first direct proof of high efficiency intrinsic charge generation in organic salt semiconductors. Furthermore, the impact of counterion size on charge transfer and transport was studied, again using transient absorption spectroscopy alongside other ultrafast techniques. We found that aggregation played a key role in the efficiency of the intrinsic charge generation and the charge transport processes.

[1] B. Fan, F. Araujo De Castro, B. T. Te Chu, J. Heier, D. Opris, R. Hany and F. Nüesch, *J. Mater. Chem.*, **2010**, 20, 2952–2955.
[2] E. Berner, T. Jäger, T. Lanz, F. Nüesch, J. N. Tisserant, G. Wicht, H. Zhang and R. Hany, *Appl. Phys. Lett.*, **2013**, 102, 98–102.
[3] A. Devižis, J. De Jonghe-Risse, R. Hany, F. Nüesch, S. Jenatsch, V. Gulbinas and J. E. Moser, *J. Am. Chem. Soc.*, **2015**, 137, 8192–8198.
[4] J. De Jonghe-Risse, J. Heier, F. Nüesch and J. E. Moser, *J. Mater. Chem. A*, **2015**, 3, 10935–10941.
[5] L. Wang, S. Jenatsch, B. Ruhstaller, C. Hinderling, D. Gesevičius, R. Hany and F. Nüesch, *Adv. Funct. Mater.*, **2018**, 28, 1–8.

Precision Spectroscopy, Coherent Manipulation and State-to-State Chemistry of Single Molecular Ions

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Recent progress in laser technology, frequency metrology and molecular optics have enabled ultra-precise measurements of molecular frequencies. We present a novel, quantum-logic based, non-destructive state-detection method [1, 2] for single molecular ions trapped in radiofrequency ion traps [3, 4]. Our technique leaves the quantum state of the molecule completely intact, enabling repeated non-invasive measurements on the same molecule and therefore affording an exquisite measurement sensitivity and precision. As an application of our state-detection protocol, we demonstrate a type of “force” spectroscopy [1] on a dipole-allowed transition in N_2^+. We determine transition properties such as the line center and the Einstein-A coefficient which is validated against the results of previous studies using conventional spectroscopic methods. Although we focus on N_2^+ as a prototypical example, our scheme is applicable to a wide range of diatomic and polyatomic molecules.

We have further developed a precise, narrow-linewidth laser which will be used to perform precision spectroscopy on dipole-forbidden ro-vibrational transitions [5, 6] using the state detection scheme. By slaving this laser to the Swiss primary frequency standard at METAS in Bern, we aim, in the first attempt, to push the precision of spectroscopic measurements on molecular ions into the range of 10^{-15}, about four to five orders of magnitudes better than the current state of the art [7].

In addition, the possibility for efficient, non-destructive state readout and precision spectroscopy lays the foundation for studies of cold collisions and chemical reactions between molecular ions and neutrals with state control on the single-molecule level. Additionally, it enables state-selected coherent experiments with single trapped molecules for applications in quantum-information [8] and sensing experiments.

[1] M. Sinhal, Z. Meir, K. Najafian, G. Hegi and S. Willitsch, Science, 367(6483), 1213-1218.
[2] K. Najafian, Z. Meir, M. Sinhal and S. Willitsch, arXiv preprint arXiv: 2004.05306.
[3] S. Willitsch, Int. Rev. Phys. Chem. 31, 175 (2012).
[4] K. Mølhave and M. Drewsen, Phys. Rev. A 62, 011401 (2000).
[5] Z. Meir, G. Hegi, K. Najafian, M. Sinhal, and S. Willitsch, Faraday Discuss. 217, 561 (2019).
[6] M. Kajita, Phys. Rev. A 92, 043423 (2015).
[7] S. Alighanbari, M. G. Hansen, V. I. Korobov, and S. Schiller, Nat. Phys. 14, 555 (2018).
[8] S. Wehner, D. Elkouss, and R. Hanson, Science 362, eaam9288 (2018).

Chiral control of spin-crossover dynamics in Fe(II) complexes

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Fe(II)-based spin-crossover complexes hold tremendous promise as multifunctional switches in molecular devices [1]. However, real-world technological applications are only feasible if the excited spin-states are kinetically stable – a feature that has only been achieved at cryogenic temperatures, most prominently in the light-induced excited spin-state trapping (LIESST) effect. Both the analysis and manipulation of the associated intersystem crossing dynamics are usually based on a single dominant reaction coordinate that preserves the symmetry of the complex: a symmetric stretching mode of the Fe-ligand bonds. We now go beyond this picture and achieve significant kinetic stabilization of a chiral Fe(II)-complex in solution through the control of its symmetry-breaking torsional distortion in the photo-excited quintet state.

The chiral tris-chelate complex $[Fe(4\text{-}4'\text{-}Me_2bpy)_3]^{2+}$ is configurationally labile in solution, with the racemization known to proceed via a trigonal twisting mode. Already 40 years ago, Purcell suggested that this structural distortion must involve a spin-crossover [2]. Here, we reverse this perspective: through supramolecular complex formation with enantiopure counterions [3], we obtain configurationally stable Fe(II) complexes with preferential Λ or Δ configuration and thus effectively block the racemizing trigonal twist. We first demonstrate kinetic stabilization by measuring a four-fold increase in lifetime of the photo-excited quintet state compared to the labile complex. We then employ time-resolved circular dichroism (CD) spectroscopy [4] to extract the CD spectrum of the excited quintet state and track its evolution with sub-picosecond time resolution. This lets us identify a symmetry-breaking torsional distortion as the main reaction coordinate in its relaxation, thus providing direct evidence for the central importance of this mode in the intersystem crossing of Fe(II) complexes. Most importantly, however, we demonstrate that the control of their chirality provides a powerful new strategy for manipulating their spin-crossover dynamics.

[1] A. Bousseksou et al., *Chem. Soc. Rev.* **2011**, 40, 3313
[2] K.F. Purcell, *J. Am. Chem. Soc.* **1979**, 101, 5147
[3] J. Lacour et al., *Angew. Chem. Int. Ed.* **1998**, 37, 2379
[4] M. Oppermann et al., *Optica* **2019**, 6, 56

Synthesis and luminescence properties of strontium aluminate nanospheres as long persistent phosphors

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$SrAl_2O_4:Eu^{2+},Dy^{3+}$ is commonly accepted as the best non-radiative long persistent phosphor in terms of luminescence intensity and afterglow duration, known up to date [1]. However, the big particle sizes raging in between 20-100 µm limits its application mostly to displays and safety signs. Despite many attempts to develop new synthetic method, nanosized particles of strontium aluminate with homogeneous morphology has not been obtained yet. Most of the reports on the strontium aluminate nanoparticles have applied top-down method which results in very bad morphology and wide size distribution. We have developed a new synthesis method for creating strontium aluminate nanospheres with spherical morphology and narrow size distribution, which can be used for different applications including bioimaging. Moreover, investigation of the luminescence properties of these nanoparticles doped with Eu^{3+} lead to very interesting results.

[1] Rocío Estefanía Rojas-Hernandez⁎, Fernando Rubio-Marcos, Miguel Ángel Rodriguez, José Francisco Fernandez, *Renewable and Sustainable Energy Reviews*, **2018**, 81, 2759-2770.

Dynamic Nuclear Polarisation Enhancement of 200 at 21.15 T Enabled by 65 kHz Magic Angle Spinning

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For impact in analytical chemistry, sensitivity and spectral resolution are cornerstone considerations of solid-state NMR experiments. Dynamic Nuclear Polarization (DNP) is a rapidly expanding method that can provide very significant increase in solid-state NMR signal intensity, thereby enabling atomic-level characterization of systems that were previously completely inaccessible. The combination of high magnetic field and fast magic-angle spinning (MAS) is often a prerequisite to allow the study of complex systems and to implement high-level multi-dimensional experiments. Although, state-of-the-art commercial NMR instrumentation uses magnetic fields up to 28 T (1.2 GHz) and MAS probes able to spin samples to 120 kHz at room temperature using 0.7 mm diameter rotors, DNP ssNMR instrumentations have been limited for a long time to a maximum MAS rate of 15 kHz, and only in 2016 first experiment were reported at MAS rate up to 40 kHz.[1]

Here we present the first DNP MAS experiments using a 0.7 mm MAS probe. This allows us to reach spinning frequencies of up to 65 kHz, with µw irradiation, at 100 K, and at a field of 21.15 T. We report the performance, at very fast MAS, of BDPA in 95% deuterated orthoterphenyl and HyTEK2 in 1,1,2,2-tetrachloroethane. In both we find that enhancements continue to increase significantly with increasing spinning rates, and we obtain enhancement factors of up to 200 for HyTEK2. Such regime opens up a new chapter for high-field DNP enhanced NMR.[2]

[1] Chaudhari, S. R.; Berruyer, P.; Gajan, D.; Reiter, C.; Engelke, F.; Silverio, D. L.; Copéret, C.; Lelli, M.; Lesage, A.; Emsley, L. *Phys. Chem. Chem. Phys.***2016**, *18*, 10616–10622.
[2] Berruyer, P.; Björgvinsdóttir, ; Bertarello, A.; Stevanato, G; Rao, Y.; Karthikeyan, G.; Casano, G; Ouari, O.; Lelli, M.; Reiter, C.; Engelke, F.; Emsley,L., *submitted*

Surface and bulk hyperpolarization of lithium titanates

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Solid-state NMR is a method that can be used to investigate structural and electric properties of inorganic materials, for example lithium titanates. Lithium titanates are of interest as anode materials in solid-state batteries, and their atomic-level structure is important for understanding and improving their performance. Solid-state NMR, however, can be limited by low sensitivity. Impregnation dynamic nuclear polarization (DNP) is a method that can be used to improve sensitivity in NMR experiments of powdered materials. This is acheived through impregnation with a radical containing solution, followed by hyperpolarization of nuclei near the surface. This surface hyperpolarization is then relayed towards the bulk of the material by spontaneous spin diffusion. This is well established for proton containing materials[1] (where spin diffusion is fast), but has recently been extended to proton-free inorganic materials.[2]

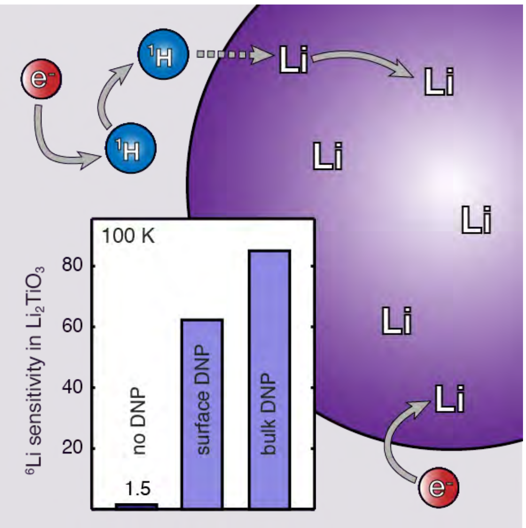

Figure 1. Sensitivity gains in the ^{6}Li NMR spectra of Li_2TiO_3. The lithium titanate was hyperpolarized by impregnation DNP.

We show how two lithium titanates, Li_2TiO_3 and $Li_4Ti_5O_{12}$, can be hyperpolarized using this combination of impregnation DNP and slow spin diffusion between ^{7}Li or ^{6}Li nuclei, resulting in improved sensitivity of both ^{7}Li and ^{6}Li NMR spectra of the compounds. As an example, we show an overall gain in sensitivity of a factor 60 for the ^{6}Li spectrum of the bulk Li_2TiO_3. We also obtain high sensitivity surface spectra of both compounds. The method can in principle be applied to other inorganic lithium contaning materials.

[1] Rossini, Zagdoun, Hegner, Schwarzwalder, Gajan, Copéret, Lesage, Emsley, *J. Am. Chem. Soc.* **2012**, 134 (40), 16899-908
[2] Bjorgvinsdottir, Walder, Pinon, Emsley. *J. Am. Chem. Soc.* **2018,** *140* (25). 7946-7951

Insight into the crystallization of $MgCO_3$ grown by CO_2 capture on (100)-MgO promoted by $NaNO_3$

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Carbon dioxide capture and storage (CCS) offers great promise to contribute to the decarbonization of the chemical and electricity generation industries and avoid a further increase in the atmospheric CO_2 concentration [1]. Among the CO_2 sorbents considered, magnesium oxide is an attractive candidate due to its high theoretical uptake and a comparatively low energy requirement for regeneration. However, MgO requires a promoter, typically a salt (e.g. $NaNO_3$, $LiNO_3$, KNO_3) that is molten at operating conditions to have sufficiently fast kinetics [2]. Significant efforts have been made to understand how the promoters function to enhance further the CO_2 capture characteristics of MgO, but many important questions still remain unsolved [3].

One question that is actively researched is whether magnesium carbonate grows as a uniform product layer or as islands on the MgO surfaces. It is also unknown whether $MgCO_3$ grows most favorably inside the molten salt promoter, the interface of $NaNO_3$|MgO, or at the triple-phase boundary $NaNO_3$|MgO|CO_2.
To shed light on these questions, this work probes the crystallization of $MgCO_3$ on a single crystal (100)-MgO surface coated with a $NaNO_3$ promoter when exposed to CO_2. Employing a well-defined surface and suitable characterization techniques allowed us to describe the $MgCO_3$ product in great detail, *i.e.* from the atomic to the micrometer scale. Using synchrotron based *in situ* grazing incident X-ray diffraction (GIXRD), we show that $MgCO_3$ has grown with preferred orientation on the surface of (100)-MgO and that the thickness of the $MgCO_3$ product layer is less than 5 µm. SEM analysis reveals an island-type $MgCO_3$ growth, *i.e.* heterogeneous nucleation followed by crystal growth in a sectored plate type morphology. Fascinatingly, we also observe that the dissolution of MgO, which is an essential prerequisite for its conversion to $MgCO_3$, occurs in a similar fashion as an acidic etching process, possibly due to the interaction of $NaNO_3$ and CO_2. HRTEM provides insight into the atomic arrangement of the MgO|$MgCO_3$ interface, confirming the epitaxial growth of a carbonate layer. Due to a large lattice mismatch between the carbonate and oxide layers, the carbonate film relaxes through incorporation of lattice misfit dislocations.

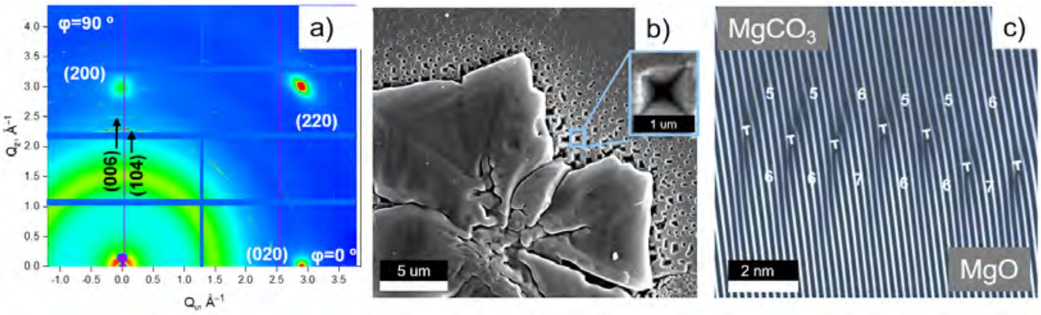

Figure 1. a) 2D GIXRD map of (100)-MgO promoted by $NaNO_3$ at 330 °C after 90 min in CO_2 b) $MgCO_3$ crystal grown on (100)-MgO and inset showing etched pyramid shaped pits near $MgCO_3$. c) Inverse Fourier-filtered STEM image showing misfit dislocations in the (006)-$MgCO_3$ and the (002)-MgO plane system.

[1] Bui et al, *Energy Environ. Sci*. **2018**,11, 1062–1176.
[2] T. Harada, F. Simeon, E.Z. Hamad, T.A. Hatton, *Chem. Mater*. **2015**, 27, 1943–1949.
[3] A. Dal Pozzo, A. Armutlulu, M. Rekhtina, P.M. Abdala, C.R. Müller, *ACS Appl. Energy Mater.* **2019**, 2,1295–1307.

Data mining chemical shifts in the solid state for automated assignment of organic crystals

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Solid-state NMR, in combination with computational methods such as density functional theory chemical shift computation and crystal structure prediction (CSP) procedures, has proven able to determine the crystal structure of organic solids.[1] A key starting point for efficient chemical shift-driven crystal structure determination is the assignment of the experimental NMR spectra. Probabilistic assignments can be obtained without prior knowledge of the three-dimensional structure of molecules through a statistical analysis of large chemical shift databases.[2] However, no such database exists for organic solids. Here, we combine a large database of organic crystals (> 200,000 compounds) with ShiftML, a machine learning model able to predict chemical shifts in molecular solids,[3] in order to construct a statistical basis for the probabilistic assignment of solid-state NMR spectra. Relating molecular fragments to their corresponding chemical shifts, we propose a probabilistic framework to determine the most likely assignment of organic crystals from their topological representation only.

[1] M. Baias, J. N. Dumez, P. H. Svensson, S. Schantz, G. M. Day, L. Emsley, *J Am Chem Soc*, **2013**, 135, 17501-17507.
[2] T. Aeschbacher, E. Schmidt, M. Blatter, C. Maris, O. Duss, F. H. T. Allain, P. Guntert, M. Schubert, *Nucleic Acids Res*, **2013**, 41.
[3] F. M. Paruzzo, A. Hofstetter, F. Musil, S. De, M. Ceriotti, L. Emsley, *Nat Commun*, **2018**, 9.

Analytic calculation and analysis of Atomic Polar Tensors for Molecules and Materials

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Many implementations to simulate vibrational absorption spectra rely on the double harmonic approximation for which the derivative of the electric dipole moment with respect to nuclear coordinates is required. The resulting quantity is called the atomic polar tensor (APT) (or Born effective charge (BEC) in case of periodic systems).

The use of Density Functional Perturbation Theory (DFPT) for the calculation of analytical derivatives offers a number of advantages compared to the numerical differentiation. No trade-off in terms of formula and precision errors has to be made when deciding on a step size. Further, by employing localized molecular orbitals or maximally localized Wannier functions, the APTs/BECs can be decomposed into subset contributions, which allows for a more thorough analysis of the resulting spectra. In this way, the specific influence of functional groups or groups of atoms – both in molecules and condensed systems – can be made apparent. Moreover, BECs can be applied to calculate partial charges in crystal structures.

We implemented the subset analysis of vibrational infrared spectra and partial charges based on BECs in the CP2K code package, which allows for efficient and accurate electronic structure calculations. The calculations rely on Gaussian basis sets centered at the nuclear positions and non-local pseudopotentials for the description of core electrons. We present the implementation and its application to both a molecule and a condensed system.

[1] Joost VandeVondele, Matthias Krack, Fawzi Mohamed, Michele Parrinello, Thomas Chassaing, Jürg Hutter, *Computer Physics Communications*, **2005**, 167, 103-128
[2] E. Bright Wilson, Jr., J. C. Decius, P. C. Cross. Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra. *McGraw-Hill, New York*, **1955**.
[3] Sandra Luber, *Habilitation thesis* **2016**, University of Zürich

Temperature dependence of intermolecular correlations in bulk water and electrolyte solutions

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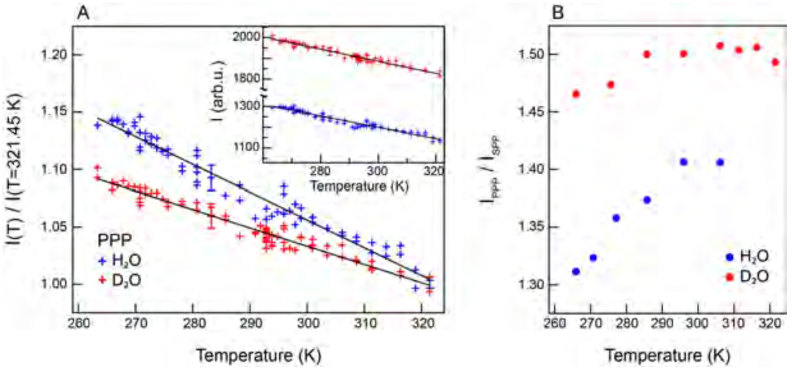
Many physical, chemical, and biological processes depend on water, the “liquid of life”. The critical importance of water and ionic hydration in biology has drawn a lot of interest from scientist. Most studies focused on high concentration range (>0.1M). and it has been proved recently, by using femtosecond elastic second harmonic scattering (fs-ESHS) at lower concentrations, that the influence of ions on water extends to a longer range [1]. This long-range interaction induces a very different response of H_2O and D_2O, indicative of nuclear quantum effects in the hydrogen-bonding (H-bonding) network, and of the importance of collective H-bonding. We investigated recently the temperature dependence on intermolecular correlations by using fs-ESHS [2]. Indeed, fs-ESHS from a material reports on the average structure of the probed material and gives indication on the molecular orientational order, and on the intermolecular correlations.



We measured the SH intensity scattered in PPP polarization at 90° scattering angle from pure H_2O and D_2O. Results are shown in the figure reproduced from Ref. [2] in A, as function of temperature, and normalized by the intensity at the highest temperature (T=321.45K). The intensity drops relatively more for H_2O. This discrepancy between D_2O and H_2O was analyzed in terms of molecular incoherent and intermolecular coherent contributions by comparing the responses in different polarization combinations. The corresponding incoherent SH intensities can be analytically derived [3], and accordingly SPP and PPP incoherent responses at 90° are equal. SPP response is fully incoherent whereas PPP response contains both incoherent and coherent contributions. The measured ratio of these two responses is shown in the figure in B. Here, the excess of ratio value above 1 originates from a reduction in the amount of non-spherical orientational correlations combined with a relative increase in the amount of spherical orientational correlations. We showed that increasing temperature in pure water induces a change in molecular correlations, from correlations with non-spherical symmetry to correlations with spherical symmetry. The larger ratio of D_2O indicates also that it has relatively more spherical correlations than H_2O.

Further measurements in electrolyte solutions in H_2O and D_2O indicated a weakened influence of the electrostatic field emitted by the ions on the water structure. In other terms, the collective influence of ions on the water-water correlations decreases when increasing the temperature. This effect depends on the H-bonding interaction. These findings provide a challenge for future molecular dynamics studies on electrolyte solutions.

[1] Y. Chen et al., Science Advances, 2016, vol. 2, p. e1501891.

[2] Y. Chen, et al., Journal of Chemical Physics, 2018, vol. 148, no 22, p. 222835.
[3] Y. Chen et S. Roke, 2017, ArXiv e-prints, p. arxiv:1705.04231.

Dispersion effects described by the Frozen-Density embedding Theory

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The dispersion part of the Van der Waals interaction energy for a separated system can be described by $-C6*R^{-6}$, where C6 is a constant and R is the intermolecular distance. In computational chemistry people are struggling to reproduce this asymptotic behavior due to the fact that this weak long-range attractive interaction is originated from the self-induced instantaneous dipole moments. Now there are three ways to include the dispersion contribution: a.Within a DFT framework, only a given fully non-local functional is possible to provide a quantitative value. b. Calculate the dispersion contribution separately by a damped multipole expansions and add it in the final energy expression[1].c. Adopting the high-level post-Hartree Fock methods like MP2 etc., which are computational expensive.

In this work we study the accuracy of the description of dispersion effects with the Frozen-Density Embedding Theory (FDET) [2], a formal framework in which the whole system is described by means of two independent quantities: 1.The embedded wavefunction; 2.The density associated with the environment.The key aspect in FDET is the construction of an embedding potential which is added to the isolated Hamiltonian.

The multiscale approach leads us to a computational feasible direction. We also perform symmetry adapted perturbation theory[3] (SAPT0) on the basis of Hartree-Fock level, which decomposes the interaction energy into four contributions: dispersion, induction, electrostatic and exchange. These physically interpretable terms in SAPT0 offer a possibility to compare the FDET-based approach with SAPT0, hence to access both the validity of the embedding potential and the dispersion effect. For ground state calculations the results show that our method is solid and certainly reproduce the dispersion effects at the short-range and middle-range. For excited states, the comparison of preliminary results to the self-consistent reaction field method for dispersion contributions are promising[4].

[1] A. Heßelmann, G. Jansen, *Chemical physical letters,* **2003,** 10, 778-784.
[2] T. Wesolowski, *Phys. Rev. A*, **2008**, 77, 012504.
[3] B. Jeziorski, R. Moszynski, and K. Szalewicz, *Chem. Rev.,* **1994,** 94, 1887.
[4] G.Rauhunt, T. Clark, and T. Steinke, *J.Am.Chem.Soc.,* **1993,** 115, 9174-9181.

Femtosecond broadband fluorescence upconversion spectroscopy to study vibrational energy relaxation dynamics in organic molecules in solution

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Vibrational energy relaxation (VER) is often the first process occurring after photo excitation of a molecule in the condensed phase. This process is usually discussed in terms of two consecutive steps: intramolecular vibrational energy redistribution (IVR) and vibrational cooling (VC).[1] The timescales on which these processes occur, make their detailed investigation challenging, as high resolution in both temporal and spectral domains is required. However, thorough understanding of many ultrafast photochemical processes, such as electron transfer is conditioned by a sufficient comprehension of VER dynamics and on how it is affected by the surrounding environment.

We are applying femtosecond broadband fluorescence up-conversion spectroscopy (FLUPS) with sub 100 fs resolution and tunable excitation to follow the time evolution of the fluorescence spectrum of organic molecules in different solvents after photo-excitation with various amount of excess energy.2 Analysis of the time dependence of the Franck-Condon envelope, based on results obtained from quantum chemical TD-DFT calculations is used to disentangle IVR and VC. We will show the entire broadband time-resolved fluorescence spectra of the model dye, perylene and its derivatives in solution, using multiple solvents as to study the polarity effects on these processes.

[1] Rosspeintner, A.; Lang, B.; Vauthey, E. Ultrafast Photochemistry in Liquids. *Annu. Rev. Phys. Chem.* **2013**, *64* (1), 247–271.
[2] Gerecke, M.; Bierhance, G.; Gutmann, M.; Ernsting, N. P.; Rosspeintner, A. Note on Femtosecond Broadband Fluorescence Upconversion Spectroscopy (FLUPS): Spectral Coverage versus Efficiency. 15.

Cryogenic Ion Vibrational Predissociation (CIVP) Spectroscopy of a Gas-phase Molecular Torsion Balance to probe London dispersion Forces in Large Molecules

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Non-covalent interactions, especially the attractive part of the van der Waals potential – London dispersion forces, had been commonly ignored in organic and organometallic chemistry because individual interactions are small. Nevertheless, the recent recognition that these individually small interactions, whose number rise much faster than does the number of atoms as the molecule gets larger, sum up to "chemically significant" values, i.e. tens of kcal/mol, for organic and organometallic molecules with 50-200 atoms. Molecules in this size-range are typical reagents and substrates for organic synthesis, for which the renewed interest in attractive non-covalent interactions has led to the attribution of reactivity or selectivity to effects of "dispersion energy donors," DEDs, which are then appended as design and control elements, for example, in stereoselective catalysts. Dispersion-corrected quantum chemical computational methods have also proliferated, with DFT-based methods, in particular (but not exclusively), taking a prominent position because of the favorable scaling of performance as the size of the molecule increases.

Despite the applications in design and control of reactions, as well as the widespread use of computational modeling, there have not been comparably extensive experimental determinations of the interaction energies for molecules with 50-200 atoms in the gas phase, which is necessary to avoid accompanying effects of solvation. Quantitative tests by means of gas-phase bond dissociation energies or gas-phase equilibria (second low experiments) are typically restricted to small molecules, for which the desired effects are also correspondingly small. Larger molecules pose technical challenges, whose circumvention has become possible only recently with newly developed experimental methods.

Here we report a third low experiment: a gas-phase molecular torsion balance that uses a conformational equilibrium to “weigh” London dispersion against a competing cation-π interaction, for which the readout is the shift in N-H stretching frequency measured by cryogenic ion vibrational predissociation (CIVP) spectroscopy of electrosprayed pyridinium cations in a FT-ICR trap.

While frequency calculations with DFT, assist in the interpretation of the spectra, the observed complex pattern of N-H in spectra comes from a Fermi resonance of the N-H stretch with overtones of in-plane C-H wagging modes, based on the basis of comparison of the spectrum to those for a range of related cations with systematically varied substitution2. For most of the pyridiniums nondispersion as well as dispersion corrected DFT methods agree to prefer *compact* conformer as the most stable, while for the largest one – possessing highest DED-properties in the series, dispersion corrected methods appear to overestimate the attractive dispersion forces leading to principal improper geometry contrary to the experimental data.

[1] Lukas Fritsche, Andreas Bach, Larisa Miloglyadova, Alexandra Tsybizova, Peter Chen, *Rev. Sci. Instrum.,* **2018**, 89, 063119-1−063119-10.
[2] Alexandra Tsybizova[†], Lukas Fritsche[†], Vladimir Gorbachev[†], Larisa Miloglyadova, Peter Chen, *J Chem Phys*. **2019**, 151, 234304-1-234304-11.

NMR Crystallography Determines the Supramolecular Structure of Layered Hybrid Perovskites

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Solid-state NMR has recently emerged as a powerful technique to study the structure and dynamics of hybrid organic–inorganic perovskites. NMR is exquisitely sensitive to chemical information such as cation incorporation, halide mixing, phase segregation and dynamics [1]. Here, we show how multinuclear (^{1}H, ^{19}F and ^{13}C) solid-state NMR can be employed to reveal the atomic-scale molecular structure of the organic spacer cations in layered hybrid perovskites. 3D hybrid perovskites, consisting of an organic cation—typically methylammonium (MA, CH3NH3$^+$) or formamidinium (FA, CH(NH2)$_2^+$)—in an inorganic lead halide matrix, suffer from poor environmental stability towards moisture, air and heat, hampering the development of devices with sufficiently long lifetimes for commercial application. One strategy to improve the stability is to employ a passivating layer of a 2D perovskite, which comprise slabs of the perovskite structure separated by a hydrophobic organic spacer layer [2], however the structure of this layer must be determined so that it can be optimised, for example by supramolecular engineering. This is a challenge for diffraction-based techniques, whereas NMR, as a local element-specific probe, is the perfect tool to study the supramolecular structure.

The samples investigated in this work are a class of layered perovskites based on the widely studied FAPbI3 perovskite, with the formula A2FAn−1PbnI3n+1, where A$^+$ could be phenylethylammonium (PEA$^+$), pentafluorophenylethylammonium (FEA$^+$), or a 1:1 mixture of the two. These adopt the Ruddlesden–Popper structure with n PbI3$^-$ layers of corner sharing PbI6 octahedra within each perovskite slab, separated by layers of the organic spacers (Figure 1). Double resonance NMR experiments demonstrate the proximity of the two aromatic systems, rather than segregation, and the probable structure for the organic spacer layer is revealed by comparison with the theoretical shifts from DFT calculations, in a novel NMR crystallography approach. The supramolecular structure is compared for samples synthesised with PEA$^+$, FEA$^+$, and a 1:1 mixture, in order to ascertain the effect of π–π templating. This reveals important design principles in 2D/3D hybrid perovskites and paves the way for ever-more efficient optoelectronic devices.

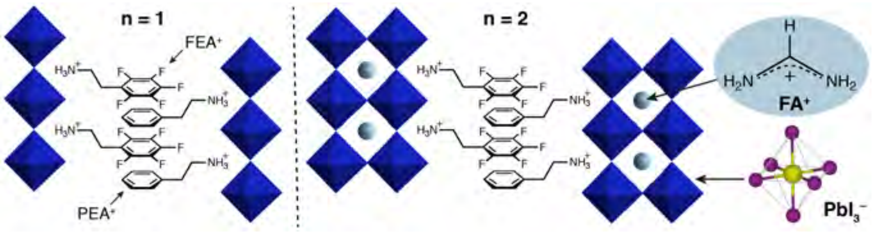

Figure 1: Schematic diagram of the layered 2D perovskites (FEA)(PEA)FA$_{n-1}$Pb$_n$I$_{3n+1}$ with n = 1 and n = 2.

[1] Franssen, W. M. J.; Kentgens, A. P. M. *Solid State Nucl. Magn. Reson.*, **2019**, 100, 36–44.
[2] Chen, Y.; Sun, Y.; Peng, J.; Tang, J.; Kaibo, Z.; Liang, Z., *Adv. Mater.* **2018**, 30, 1703487.

Residual Gas Effects on the Gas Chromatographic Yield of Mercury and Astatine, and Their Impact on the Study of Transactinides Copernicium and Flerovium

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Principal challenges in the discovery and study of transactinide elements (Z ≥ 104) are low production rates requiring the ability to detect single atoms, and generally shortening half-lives as the atomic number Z increases.[1] On-line gas adsorption chromatography setups such as the Cryo-OnLine Detector (COLD)[2] are the primarily employed method of investigation which allows single atom detection with half-lives of ≥ 1 second. Thus, short-lived transactinide elements Cn (Z = 112) and Fl(Z = 114) can be chemically studied. During our experiments, Hg and At are simultaneously produced which allows homolog studies and monitoring experimental conditions. Past results have strongly indicated that minor changes in the experimental conditions can drastically affect yields. Recent upgrades in the setup include mass spectrometry for the gas composition analysis which have shown a strong correlation between the composition of residual gases and transport yields of elements (Fig. 1).

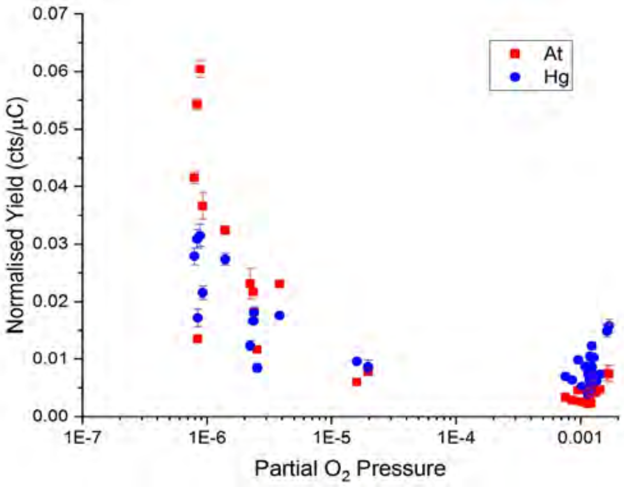

Fig 1: Normalized yield of At and Hg in relation to carrier gas O_2 content; decreasing detection of reaction products as O_2 increases. Partial pressure values are relative, not absolute.

Herein, we present the influence of impurities in the carrier gas on the chromatographic yield and the significance of accurately knowing contaminants in similar experiments. Impure gases may have had an impact on the observed yields during previously conducted experiments with copernicium and flerovium.[3] This knowledge can thus be used to prevent side-reactions and to increase transport yields in the future.[4]

We would like to thank the crew of the U-400 accelerator for their support as well as our futher co-authors Y. V. Albin, V. I. Chepigin, I. Chuprakov^c, R. Dressler, D. Herrmann, K. V. Lebedev, A. Sh. Madumarov, O. N. Malyshev, Y. Melnik, D. Piguet, Y. A. Popov, A. V. Sabel'nikov, A. I. Svirikhin, A. Vögele, A. V. Yeremin

[1] M. Schädel & D. Shaugnessy (editors), 'The Chemistry of Superheavy Elements', 2nd Ed., Springer, **2014**, p. 6
[2] R. Eichler et al, *Nature*, **2007**, 447(7)140, pp. 72-75
[3] N. M. Chiera, 'Towards the Selenides of the Superheavy Elements Copernicium and Flerovium', PhD Thesis, University of Bern, (**2016**)
[4] Y. Byun et al., *Chemosphere*, **2008**, 72, pp. 652-658

High Resolution Infrared Spectroscopy of Cyano-oxirane (c-C_2H_3OCN)

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Oxiranecarbonitrile (cyano-oxirane, c-C_2H_3OCN) is of interest as a possible chiral precursor molecule of evolution [1]. In view of possible experiments and biomolecular homochirality [2], we have previously calculated parity violating energies and the effects resulting from them in this molecule [3]. The spectrum of the molecule has previously been investigated in the microwave, millimeter, submillimeter [4] and terahertz [5] regions. Here we report high resolution (0.0011 cm^{-1}) room temperature measurements of the infrared spectrum of this molecule using the Zurich Prototype ZP 2001 FTIR Spectrometer. We have conducted a rovibrational analysis of two thousand transitions associated with the ν_{12} (915.3 cm^{-1}) and ν_{13} (848.2 cm^{-1}) fundamentals using a Watson Hamiltonian and the WANG program [6]. This analysis includes newly assigned infrared transitions, as well as molecular parameters and ground state energies obtained from our work in the THz region [5]. It has resulted in accurate spectroscopic parameters for c-C_2H_3OCN. Our results will be discussed as they pertain to the evolution of biomolecular homochirality [7] and astrophysical spectroscopic searches, so far unsuccessful [8].

[1] M. Bolli, R. Micura, A. Eschenmoser, *Chem. Biol.*, **1997**, 4, 309 (and refs. cited therein).
[2] M. Quack, *Chem. Phys. Lett.*, **1986**, 132, 147; M. Quack, *Angew. Chem. Intl. Ed.*, **2002**, 41, 4618.
[3] R. Berger, M. Quack, G. Tschumper, *Helv. Chim. Acta.*, **2000**, 83, 1919.
[4] F. Müller, and A. Bauder, *J. Mol. Spectrosc.,* **1996**, 179, 61; M. Behnke, I. Medvedev, M. Winnewisser, F.C. De Lucia, and E. Herbst, *ApJ. Supplement Series,* **2004**, 152, 97.
[5] S. Albert, Ph. Lerch, K. Keppler and M. Quack, Proceedings of the XX. Symposium on Atomic, Cluster and Surface Physics 2016, (SASP 2016), Innsbruck University Press (2016), pp. 165-168 (and cited refs.).
[6] D. Luckhaus and M. Quack, *Mol. Phys.*, **1989**, 68, 745; S. Albert, K. Keppler Albert, H. Hollenstein, C. Manca Tanner, M. Quack in ”Handbook of High Resolution Spectroscopy,” M. Quack and F. Merkt, Eds., 2011, Vol. 1, Chapter 3, pp. 117-173, Wiley, Chichester.
[7] M. Quack, *Adv. Chem. Phys.*, **2014**, 157, 249.
[8] J.E. Dickens, W.M. Irvine , M. Ohishi, G. Arrhenius, S. Pitsch, A. Bauder, F. Müller, A. Eschenmoser, *Origins of Life and Evolution of the Biosphere,* **1996**, 26, 97.

Dynamic second-harmonic imaging of lipid membrane hydration

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Cell membranes are composed of a hydrated lipid bilayer that is molecularly complex and diverse, and the link between molecular hydration structure and membrane macroscopic properties is not well understood. This is mainly due to a lack of technology that can probe hydration on the molecular level and relate this information to micro- and macroscopic properties, such as membrane organization, electrostatics, free energy and curvature. Here, we investigate lipid membrane hydration using high throughput second harmonic imaging, and compare the interaction of different divalent ions such as Ca2+ and Cu2+ with the membrane.

[1] Carlos Macias-Romero, Igor Nahalka, Halil I. Okur, Sylvie Roke, Science, **2017**, 357, 784-788
[2] Orly B. Tarun, Christof Hannesschläger, Peter Pohl, Sylvie Roke, Proceedings of the National Academy of Sciences of the United States of America, **2018**, 115, 4081-4086
[3] Orly B. Tarun, Maksim Yu. Eremchev, Aleksandra Radenovic, Sylvie Roke, Nano Letters, **2019**, 5, 7608-7613

Surface segregation and selective oxidation of CuIn near surface alloys under CO_2 hydrogenation conditions: a near ambient pressure XPS study

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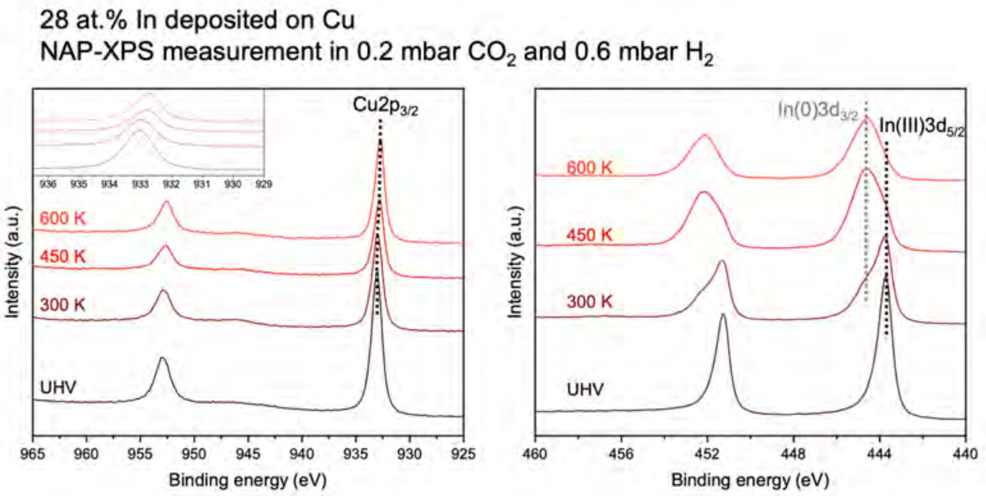
The influence of CO_2 hydrogenation atmosphere on surface segregation, oxidation state, and sintering behavior of CuIn near surface bimetallic phases was systematically studied by near ambient-pressure X-ray photoelectron spectroscopy (NAP-XPS). Deposition of In on the surface of a Cu foil for various durations leads to different degrees of alloying at the Cu-In interface. Upon exposure to 0.3 mbar CO_2 at room temperature, the In phase was partially oxidized and phase separation was observed in the CuIn alloys. As the temperature increase, the In phase was further oxidized and only indium oxide can be observed at 600 K. The oxidation of In and phase separation of CuIn alloy was similar to in the presence of 0.2 mbar CO_2 and 0.6 mbar H_2. In both cases, lattice and defect oxygen species can be observed simultaneously and their ration increase with temperature. C1s spectra revealed that carbonate is the main adsorbate on the surface of CuIn alloys and more CO_2 is chemisorbed on the sample with higher In surface coverage. Scanning electron microscopy (SEM) studies indicated the mobility redispersion of the deposited In nanoparticles on Cu surface under CO2 hydrogenation conditions. These results from *in situ* XPS experiments provide new insights for understanding the active sites of In-based catalysts for CO_2 hydrogenation.



Insights on the formation of nanopores in single-layer graphene

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Graphene nanostructures have attracted increasing attention due to their great potential in various applications such as membranes, batteries, semiconducting devices, etc. Among these, the nanometer-sized pores (vacancy defects in graphene lattice) have emerged as the promising next-generation devices for single-molecule analysis, separation and DNA sequencing. Creating nanoporous single-layer graphene with a resolution in molecular differentiation reaching 0.1 Å with a high degree of tunability, can address a wide range of molecular separation including difficult separations such as carbon capture and O_2/N_2 separation. Till now, plasma treatment,[1] and oxygen-led etching,[2] has led to the incorporation of sub-nanometer-sized nanopores in graphene. Our laboratory has developed ozone-based graphene millisecond gasification chemistry which is highly scalable and easy to control to generate nanometer sized pores in graphene lattice. However, due to the resolution limitation, the direct observation and statistical analysis for the nanopore structure has remained a big problem. Although high-resolution transmission electron microscopy (HRTEM) remains a popular tool to observe the pore structures, the sample preparation for TEM, and exposure to electron beam is known to damage and rearrange the pore structure. Contrary to electron microscope, scanning tunneling microscope (STM), does not damage the sample surface, and is a powerful instrument for imaging surfaces at the atomic-scale. In this talk, I will discuss analyzing the size and density of the nanopores by STM, and shed light on the formation mechanism of nanopores when they are incoporated by gasification of graphene by ozone.

First, I will discuss evolution of pore density as a function of the etching temperature. As shown in Fig. 1, comparing to etching graphene by ozone gas at 250 ℃, decreasing the etching temperature to 200 ℃ and 150 ℃, caused a lower density of nanopores. Based on STM images, the nanopore density ranges from $2.0 \times 10^{11}/cm^2$ to $7.9 \times 10^{11}/cm^2$. Then, I will discuss kinetic modeling of the etching process which explains pore density as a function of temperature. Briefly, upon exposure to O_3, the pore nucleation density is expected to be proportional to the density of the chemisorbed functional group which eventually yields a vacancy defect. Due to different reaction temperature is considered to lead to a different O_3 nucleation density, the nanopore's density will be varied with the temperature changing. The whole process of O_3 etching on graphene membrane can be represented by the following set of reactions.

O_3 (g) + -C ↔ -C-O_3 (Physisorbed), -C-O_3 (Physisorbed) ↔ -C-O (Chemisorbed) + O_2, -C-O (Chemisorbed) → -C-O (Cluster), -C-O (Cluster) → Vacancy + CO (g)

Finally, I will show evidence that these nanopores originate from the epoxy clusters by essentially the unzipping of chains of epoxy-functional groups.

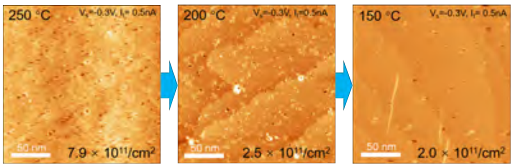

Fig. 1 STM images of graphene membrane after O_3 treatment at 250 ℃, 200 ℃ and 150 ℃.

[1] A. Davydova et al, *J. Appl. Phys.*, **2017**, 121, 133301.
[2] Y. Yamada et al, *J. Am. Chem. Soc.*, **2014**, 136, 2232.

Super-Resolution Microscopy with Mechanosensitive Membrane Tension Probes

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Membrane tension is a key parameter to many different cellular processes (e.g. cell division and intracellular membrane trafficking). However, the imaging of physical forces in living system remains technically challenging[1]. Ground-state planarization of oligothiophenes at room temperature has led to the development of push-pull probes as mechanosensitive molecules, called “flippers”, suited for FLIM (fluorescence lifetime imaging)[2,3]. These probes insert easily into lipid membranes, where they display red-shifted absorption and a much stronger fluorescence emission in the liquid ordered (L_o) lipid phase than in the liquid disordered (L_d) phase due to the forces imposing a planarization of the chromophore already in its ground state. In this contribution, we evaluate different flipper derivatives for single-molecule based super-resolution imaging and demonstrate, to our knowledge for the first time, imaging below the diffraction limit with a mechanosensitive probe (Figure 1), which opens up promising perspectives for imaging local forces with nanometric precision in cell biology.

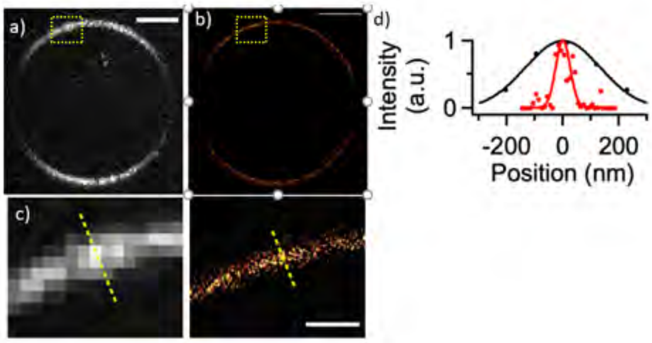

Figure 1. a) Diffraction limited image of a GUV made of lipids in the L_o phase. b) PAINT super-resolution image of the same GUV. c) Magnified view of regions in boxes in b) and c). d) Cross-sections of the GUV membrane indicated by a line in d). Scale bars: a), b), c): 2 µm; d): 500 nm.

[1] Pontes, B.; Monzo, P.; Gauthier, N. C. Membrane Tension: A Challenging but Universal Physical Parameter in Cell Biology. *Semin. Cell Dev. Biol.* **2017**, *71*, 30–41.

[2] Soleimanpour, S.; Colom, A.; Derivery, E.; Gonzalez-Gaitan, M.; Roux, A.; Sakai, N.; Matile, S. Headgroup Engineering in Mechanosensitive Membrane Probes. *Chem. Commun.* **2016**, *52* (100), 14450–14453.

[3] Fin, A.; Vargas Jentzsch, A.; Sakai, N.; Matile, S. Oligothiophene Amphiphiles as Planarizable and Polarizable Fluorescent Membrane Probes. *Angew. Chem. Int. Ed Engl.* **2012**, *51* (51), 12736–12739.

Hybrid Trapping of Stark-Decelerated Polar Molecules and Laser-Cooled Ions in a Cryogenic Trap

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Trapping particles for extended durations is a key factor for collision experiments in the cold regime (translational temperature below 1 K), especially in cases where densities are low. Such experiments allow to study fundamental interactions like reactive and inelastic collisions between particles, which can be highly dependent on their quantum nature. While hybrid systems of trapped cold atoms and ions have been proven to provide a suitable basis for such experiments, the focus is now shifting towards molecular systems due to their increased versatility [1, 2]. In order to trap neutral molecules for these durations, a cryogenic environment is of advantage, as it significantly reduces the surrounding black-body radiation which limits the trapping times.

We present experimental results on the separated trapping of Stark-decelerated OH radicals [3] and Ca^+ ions in a cryogenic hybrid trap, consisting of a magnetic and an RF ion trap. Successful trapping of OH with 1/e trap lifetimes close to half a minute were achieved [3]. Results on the trapping of Ca^+ ions are also shown. These are crucial steps towards the goal of studying cold reactions between neutral and ionic molecules. Results on the connection of both traps via a mechanical shuttling mechanism are pending.

Additionally, we present the design of an improved version of the hybrid trap, with a focus on reliability and increased signal-to-noise ratio. This ratio is improved by a new loading mechanism for the radicals that eliminates the high voltage connections, a clear advantage in a cold and densely packed setup. Additionally, a TOF-MS spectrometer is implemented, which extends the detection possibilities beyond laser-induced fluorescence and allows to study ionic reaction products. The merging of the traps is achieved by shuttling the ions via electric fields and thus removing the shuttle motor used in the current trap design. This results in a hybrid trap without moving parts, which is of advantage not only for cryonic conditions.

[1] S. Willitsch, *Adv. Chem. Phys.*, **2017**, 162, 307.
[2] P. Eberle, A. D. Dörfler, C. von Planta, R. Krishnamurthy, D. Haas, D. Zhang, S. Y. T. van de Meerakker, S. Willitsch, *J. Phys. Conf. Ser.,* **2015**, 635, 012012.
[3] D. Haas, C. von Planta, T. Kierspel, D. Zhang, S. Willitsch, *Commun. Phys.*, **2019**, 2, 101.

Intermediate Phase During Perovskite Crystallization Revealed using solid-state NMR

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All-inorganic halide perovskites have attracted immense interest as long-term stable photovoltaic(PV) materials and in tandem solar cells.[1] However, such solar cells suffer from poor interfacial contact between the inorganic perovskite and themetal oxide charge selective layer, severely limiting the power conversion efficiency and stability of inorganic perovskite solar cells. An effective strategy to improve the interfacial contact is to treat the perovskite with small or large organic molecules such as guanidinium iodide (GUAI), ethyl ammonium iodide (EAI), phenylethyl ammonium iodide (PEAI).[2,3]

Here, we report an intermediate phase engineering strategy by introducing volatile organic salts ($CH(NH_2)_2^+$: FA^+, NH_4^+, $CH_3(CH_2)_3NH_3^+$: BA^+, $CH_3NH_3^+$: MA^+) into the inorganic perovskite ($CsPbX_3$: X=Cl, Br, I) in the intermediate stages of its crystallization. This strategy harnesses the the property of smooth contacts among interlayers in organic perovskite. The atomic-level underlying mechanism is revealed using magic-angle spinning (MAS) solid-state NMR experiments. Our ^{133}Cs experiments unambiguously reveal that existence of formamidinium ion (FA^+) in the $CsPbBr_3$ lattice and formation of mixed $Cs_xFA_{1-x}PbBr_3$ phases following incorporation of FA^+ ions. Further, high temperature annealing process transforms this organic-inorganic phase, $Cs_xFA_{1-x}PbBr_{3,}$ to pure-inorganic phase, $CsPbBr_3$. Moreover, we have shown that other volatile cations (NH_4^+, BA^+, MA^+) segregate and form 2D/3D heterostructures which ultimately not preserve the smooth interfacial contacts, results in very slight improved PV performance. By revealing this atomic-scale mechanism of improved interfacial contact, further strategies can be

[1] National Renewable Energy Laboratory (NREL) https://www.nrel.gov/pv/cell-efficiency.html (accessed in May 2020)
[2] Alharbi, E.A. *et al.* Atomic-level passivation mechanism of ammonium salts enabling highly efficient perovskite solar cells. *Nat Commun* **10,** 3008 (2019)
[3] Hobeom Kim et al. Adv. Funct. Mater. 2020, 30, 1910620

Why is this chiral Europium complex such a good CPL emitter? New insights from time-resolved CD spectroscopy

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Circularly-polarised luminescence (CPL) has promising applications in the fields of optical data storage, biomedical diagnosis, for molecular photoswitches, and also for the creation of more effective OLED displays. [1] Lanthanide-based chiral 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 polarisation. Here, $CsEu((+)\text{-}hfbc)_4$ (hfbc = 3-heptafluoro-butylyrylcamphorate), serves as the prototypical model compound displaying a record CPL emission, with 85% of the photons being left-circularly polarised at 595 nm (g_{lum} = 1.38). [2]

Although the luminescent transition is metal-centred (MC), the chiral ligands play a crucial dual role in the CPL phenomenon. Firstly, they act as photosensitisers providing efficient energy transfer to the dipole-forbidden MC transition. Secondly, it has been proposed that the high degree of luminescence dissymmetry arises from the dynamic coupling of the ligand-centred electronic transition dipoles with the MC transitions of the europium ion. [3] Even though this dual role of the ligand is well-known, neither the energy transfer nor the chiral coupling in the photo-excited state has thus far been characterised with time-resolved spectroscopic methods. As a consequence, the precise reasons for the exceptional excited state chirality of this compound are not yet fully understood.

Here we address this gap by performing time-resolved absorption, emission and circular dichroism spectroscopy on $CsEu((+)\text{-}hfbc)_4$ for the first time. [4] The combination of these methods allows us to obtain a complete picture of the chiral photophysics underlying the exceptionally high CPL activity of $CsEu((+)\text{-}hfbc)_4$. These findings will be crucial for designing improved CPL compounds for future technological applications.

[1] J. R. Brandt, F. Salerno, M. J. Fuchter, *Nat. Rev. Chem.*, **2017**, 1, 0045.
[2] J. L. Lunkley, D. Shirotani, K. Yamanari, S. Kaizaki, G. Muller, *J. Am. Chem. Soc.*, **2008**, 130, 13814-13815.
[3] S. Di Pietro, L. Di Bari, *Inorg. Chem.*, **2012**, 51, 12007-12014.
[4] M. Oppermann, B. Bauer, T. Rossi, F. Zinna, J. Helbing, J. Lacour, M. Chergui, *Optica*, **2019**, 6, 56-60.

Investigating State-Specific and Conformational Effects in Penning Ionisation Reactions

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The three-dimensional structure of molecules has a profound impact on their chemical reactivity [1]. Among the dominant form of structural isomers are molecular conformers, which influence on the mechanism of reactions is still not sufficiently understood.

The major experimental obstacle for investigating conformer specific effects was till recently the isolation and control of individual conformers due to their strong tendency to thermal interconversion. This challenge was recently overcome by the successful spatial separation of conformers in cold, supersonic molecular beams, where the interconversion between conformers is effectively suppressed. Separation was achieved by exploiting the interaction of the strong, inhomogeneous field of an electrostatic deflector with the dipole moment of different conformational isomers [2,3]. Separation and selection of different rotational states depending on their effective dipole moment is also possible with this method [4]. The resulting molecular beams of state- or conformationally selected species provide an ideal starting point for controlled, state- and conformer-selective reaction experiments. This experimental technique has already been successfully applied for the in-depth study of conformational effects in neutral-ionic reaction collisions of 3-aminophenol with a Coulomb crystal of Ca^+ ions and more recently, for the reaction of nuclear-spin isomers of water with sympathetically cooled N_2H^+ ions [5,6,7].

Here, we present a novel crossed-molecular beam setup, featuring an electrostatic deflector for the investigation of state-selective or conformational effects of neutral reactions. Product detection is performed by a combination of TOF-MS and velocity-map imaging [8] allowing us to obtain angle-, energy- and mass-resolved distributions of the reaction products.

First target systems include the Penning ionization reaction of rotational state-selected polar molecules, like OCS, or conformational prepared rotamers, like 3-aminophenol, with metastable rare gas atoms. Perspectively, also the investigation of a wide range of complex, strong-field seeking stereoisomers and radical reactions will be possible with the new crossed molecular beam setup.

[1] E. L. Eliel and S. H. Wilen, Stereochemistry of organic compounds, New York, 1994.
[2] F. Filsinger, et. al., Phys. Rev. Lett. 100, 133003 (2008).
[3] F. Filsinger, et. al., Angew. Chem. Int. Ed. 48, 6900 (2009).
[4] Y. P. Chang, et. al., Int. Rev. in Phys. Chem. 34, 557-590 (2015).
[5] S. Willitsch, Adv. Chem. Phys. 162, 307 (2017).
[6] Y. P. Chang, et. al., Science 342 (6154), 98-101 (2013).
[7] A. Kilaj et. al., Nat. Commun. 9, 2096 (2018).
[8] A. T. J. B. Eppink et. al., Rev. Sci. Instrum. 68, 3477 (1997)

Exciton and multi-excitons recombination dynamics in perovskite $CsPbBr_3$ QDs unveiled by single QD optical spectroscopy

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Lead-halide perovskite $APbX_3$ (A=Cs or organic cation; X=Cl, Br, I) quantum dots (QDs) are subject of intense research due to their exceptional properties as both classical[1] and quantum light sources.[2-4] Many challenges often faced with this material class concern the long-term optical stability, a serious intrinsic issue connected with the labile and polar crystal structure of $APbX_3$ compounds. When conducting spectroscopy at a single particle level, due to the highly enhanced contaminants (e.g., water molecules, oxygen) over NC ratio, deterioration of NC optical properties occurs within tens of seconds, with typically used excitation power densities (1-100 W/cm^2), and in ambient conditions. By using a suitable polymer matrix, these detrimental effects can be suppressed, and intrinsic exciton and multi-exciton dynamics can be explored at the single-particle level.

Here, we report a comprehensive investigation of the room temperature single QD optical properties. The results reveal the origin of the QD homogeneous PL linewidths, and the peculiar size-dependent exciton and multi-excitons recombination dynamics.

Such findings guide the further design of robust single-photon sources operating at room temperature.

[1] Akkerman *et al., Genesis, challenges and opportunities for colloidal lead halide perovskite nanocrystals.* Nat. Mater. **17**, 394–405 (2018).
[2] Becker *et al., Bright triplet excitons in caesium lead halide perovskites.* Nature **553**, 189–193 (2018).
[3] Rainò *et al., Superfluorescence from lead halide perovskite quantum dot superlattices. Nature* **563**, 671–675 (2018).
[4] Utzat *et al., Coherent single-photon emission from colloidal lead halide perovskite quantum dots.* Science **363**, 1068–1072 (2019).
[5] Rainò *et al., Underestimated Effect of a Polymer Matrix on the Light Emission of Single* $CsPbBr_3$ *Nanocrystals.* Nano Lett. **19**, 3648-3653, (2019).

In situ pair distribution function analysis of the decomposition pathways of hydrated magnesium hydroxycarbonate in the presence of sodium nitrate

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The development of efficient solid sorbents for CO_2 capture is vital for the deployment of carbon capture storage and utilization technologies, which are strategic to mitigate climate change.[1] MgO is a promising CO_2-sorbent due to its high theoretical capture capacity, comparatively low energy penalty for sorbent regeneration and its natural abundance.[2, 3] The presence of a promoter, typically alkali nitrates that are molten at the operating conditions, is a pre-requisite for MgO to capture CO_2 with industrially relevant rates and quantities; yet the exact mechanism through which the promoter functions remains unresolved. Thus, elucidating the functioning of the promoter in the magnesium oxide carbonation and magnesium carbonate decomposition reactions is a first step for the manufacturing of more effective sorbents. In this work, we decipher the physical state of $NaNO_3$ and its effect on the decomposition pathways of hydrated magnesium hydroxycarbonate ($Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$, HM) to magnesium oxide. We use *in situ* pair distribution function (PDF) analysis assisted by a multivariate curve resolution (MCR-ALS) approach to probe the structural evolution of pristine and $NaNO_3$-promoted HM (HM and HM-20$NaNO_3$). We found that HM decomposes via an amorphous magnesium carbonate (AMC) intermediate, formed during the gradual release of water of crystallization from the HM structure. The release of carbon dioxide from AMC, led to the formation of nanocrystalline (4 nm) MgO, with a plate-like particle morphology. The presence of $NaNO_3$ in its molten state modifies drastically the decomposition pathway of HM (HM-20$NaNO_3$) by accelerating the crystallization of $MgCO_3$ and MgO, proceeding in this case through AMC and crystalline $MgCO_3$, and yielding highly crystalline MgO (10 nm) with irregular polyhedron particle morphology.

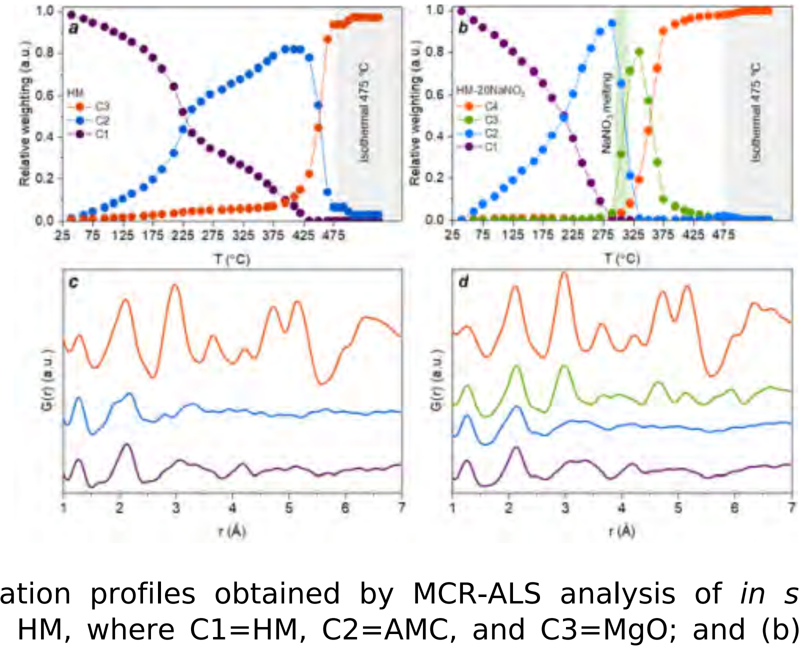

Figure 1. Concentration profiles obtained by MCR-ALS analysis of *in situ* PDF data for the decomposition of (a) HM, where C1=HM, C2=AMC, and C3=MgO; and (b) HM-20$NaNO_3$, where C1=HM-20$NaNO_3$, C2=AMC-20$NaNO_3$, C3=crystalline-$MgCO_3$-20$NaNO_3$ and C4=MgO-20$NaNO_3$. The PDFs of components extracted for (c) HM and (d) HM-20$NaNO_3$.

[1] B. D. Santer *et al.*, *Nature*, **1996**, 382, 39-46.
[2] Y. Hu *et al.*, *J. Mater. Chem. A.*, **2019**, 7, 20103-20120.
[3] A. Dal Pozzo *et al.*, *ACS Appl. Energy Mater.*, **2019**, 2, 1295–1307.

Label-free and charge-sensitive second-harmonic imaging of giant vesicle hydration

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A biological membrane forms a dynamic and complex barrier between compartments of the living cell and its environment. However, its in vivo studies are difficult because it consists of a high variety of lipids and proteins and is continuously reorganized by the cell. Therefore, membrane model systems with precisely controlled composition are used to investigate fundamental interactions of membrane components under well-defined conditions. Giant unilamellar vesicles (GUVs) are a powerful model system of the cell membrane due to their comparable size and membrane curvature. The majority of studies carried out on GUVs utilize fluorescence microscopy in combination with fluorescent markers. However, these methods of membrane imaging typically neglect molecular level details. As a consequence, there is virtually no knowledge on the role of membrane hydration, even though it is clear that without water lipid bilayer membranes cannot exist. A recent improvement in imaging throughput has resulted in the construction of a second harmonic imaging device that can non-resonantly and dynamically image interfacial water molecules [1,2]. This microscope was subsequently used to image the hydration of macroscopic free-floating membranes in aqueous solutions [3] and membrane curvature fluctuations by means of tracking transient domains of ordered water [4]. Here, we envision to extend our approach to SH image the interfacial hydration of GUVs. By varying the ionic strength of the adjacent solutions and lipid composition of the vesicles, we show that the nonresonant SH response of water molecules aligned by charge−dipole interactions with charged lipids can also be used as a label-free probe of membrane structure of GUVs.

[1] Carlos Macias-Romero et al., Optics express, **2014**, 22 (25), 31102–31112.
[2] Carlos Macias-Romero et al., Science, **2017**, 357 (6353), 784–88.
[3] Orly B. Tarun et al., PNAS, **2018**, 115 (16), 4081–4086.
[4] Orly B. Tarun et al., Nature Communications Chemistry, **2020**, 3 (1), 1–8.

Lipid membrane phase transitions involve structural redistribution of interfacial water

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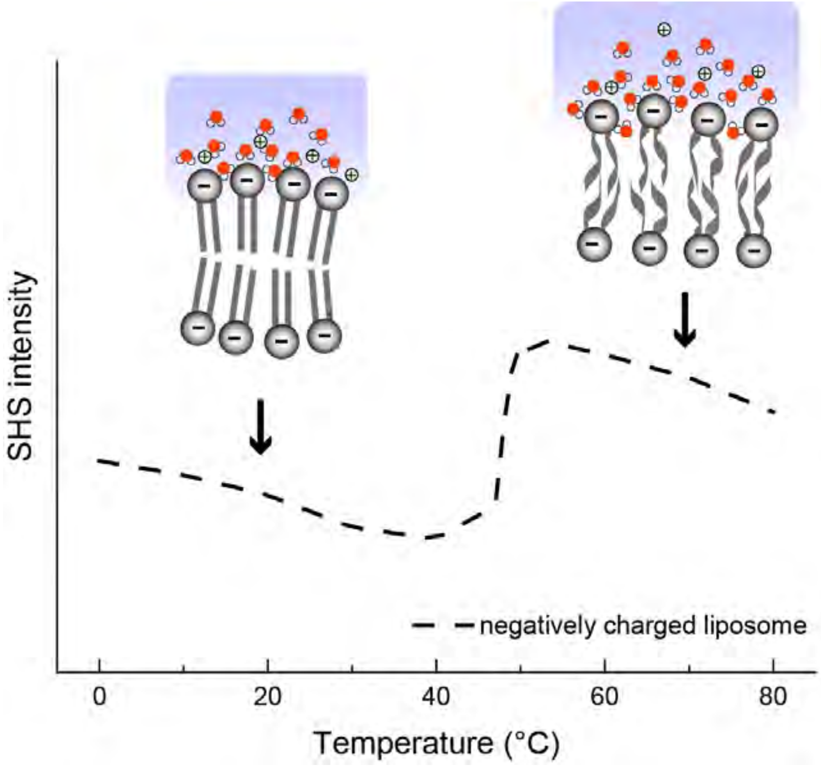
Morphological transitions of lipid membranes are thought to depend primarily on the chain length diversity of its components. However, the role of different lipid head groups, their counter ions and hydrating water molecules in the close proximity of the membrane on the gel-to-liquid phase transition of lipid is mostly unknown. We employed second harmonic (SH) scattering measurements to probe asymmetric distribution of water molecules between the lipid leaflets. Measurements on the same acyl chain length and single lipid component liposomes consisting of 1,2-dimyristoyl-*sn*-glycero-3-phosphate (sodium salt) (DMPA), 1,2-dimyristoyl-*sn*-glycero-3-phospho-L-serine (sodium salt) (DMPS), 1,2-dimyristoyl-*sn*-glycero-3-phospho-(1'-rac-glycerol) (sodium salt) (DMPG), 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine (DMPC) and 1,2-dimyristoyl-3-trimethylammonium-propane (chloride salt) (DMTAP) showed a significant lipid hydration alteration as a function of temperature. More specifically, we observed a > 20% increase in the second harmonic intensity at the phase transition temperature for liposomes made of charged lipids. Zwitterionic DMPC lipids on the other hand, display only smaller (~ 8%) changes. This data implied that an increasing number of water molecules anisotropically oriented towards surface normal above the phase transition and the charge state of the lipids play key role on the gel-to-liquid phase transition. Our data demonstrate that lipid phase transitions not only lead to structural changes in the bilayer itself but also in the adjacent aqueous phase.



Self-assembled peptide-based nanoparticles for the delivery of nucleic acids

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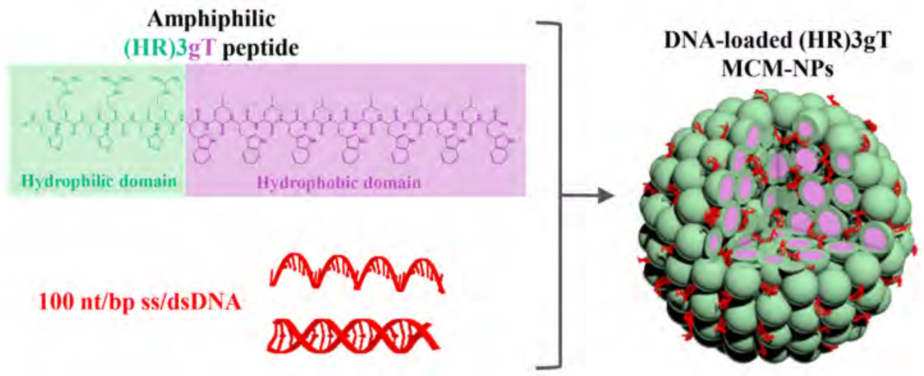
The delivery of nucleic acids as therapeutic agents to the site of pathogenesis has considerable potential in the treatment of many diseases. While viral delivery systems dominate in clinical applications, safety concerns led to the emergence of non-viral vectors. However, non-viral methods generally suffer from a low delivery efficiency. To sidestep this limitation and bridge the gap between non-viral delivery systems that exist for antisense oligonucleotides (AOS) and those that transfer entire genes, we developed a purely peptidic delivery system that is able to entrap DNA larger than the average ASO. For this purpose, we designed an amphiphilic peptide (HR)3gT comprising a hydrophilic domain prone to undergo electrostatic interactions with DNA cargo, and a hydrophobic domain at a ratio that promotes the self-assembly into micellar nanostructures [1]. Purified (HR)3gT peptide was tested for its ability to self-assemble into nanoparticles and entrap single- and double-stranded DNA (ssDNA/dsDNA) of 22 and 100 nucleotide length.The (HR)3gT peptide vector offers several advantages over other non-viral delivery systems including the precursor peptide H3gT [2]. A particle size between 100 to 180 nm supporting a rapid and efficient cellular uptake, no adverse effects on HeLa cell viability, and long-term structural stability at 4°C distinguish the (HR)3gT peptide delivery system. Furthermore, at 37°C the multicompartmental organization of the (HR)3gT disassembles which should facilitate DNA release. Our data unravel a unique non-viral strategy for DNA delivery that sets the stage for developing amphiphilic peptide nanoparticles as candidates for future systemic gene delivery.



[1] Shabnam Tarvirdipour, Cora-Ann Schoenenberger, Yaakov Benenson, Cornelia G. Palivan, *Soft Matter,* **2020**, *16*, 1678–1691.
[2] Severin J. Sigg, Viktoriia Postupalenko, Jason T. Duskey, Cornelia G. Palivan, and Wolfgang Meier, *Biomacromolecules*, **2016,** 17(3), 935-945.

Quantum-non-demolition state detection and spectroscopy of single trapped molecules

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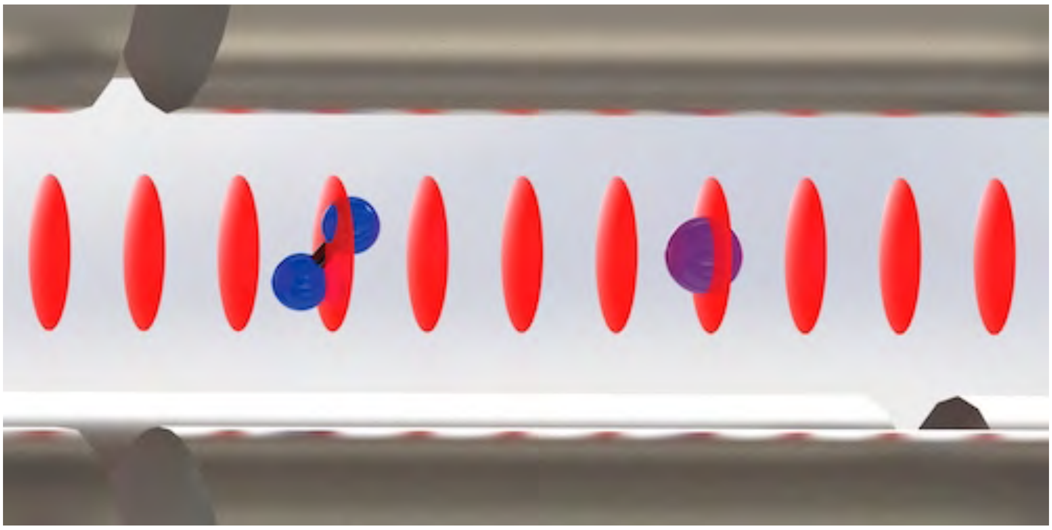
Trapped atoms and ions are among the best controlled quantum systems which find widespread applications in quantum science. For molecules, a similar degree of control is currently lacking owing to their complex energy-level structure. Quantum-logic protocols in which atomic ions serve as probes for molecular ions are a promising route for achieving this aim, especially with homonuclear species that decouple from black-body radiation. Here, a quantum-non-demolition protocol on single trapped N_2^+ molecules is demonstrated. The spin-rovibronic state of the molecule is detected with more than 99% fidelity and a spectroscopic transition is measured without destroying the quantum state. The present method lays the foundations for new approaches to molecular spectroscopy, state-to-state chemistry and probing molecular energy transfer.



3rd order Average Hamiltonian Theory analytical expression for 2 and 3 spins systems in solid-state NMR

B. Simões de Almeida[1], P. Moutzouri[1], G. Stevanato[1], L. Emsley[1]*

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In solid-state NMR, homonuclear dipolar couplings contribute greatly to the broadening of ^{1}H spectral line shapes. Even at the fastest magic-angle spinning rates (MAS) available today [100-150kHz], the linewidths still extend over several hundred Hertz, limiting the ^{1}H resolution. Reducing this contribution could provide rich structural information for organic solids.

Theoretical studies help understand the behavior of the ^{1}H spins under MAS in order to design new approaches to reduce the homonuclear broadening. In the past, the case of two equivalent spins was studied using Average Hamiltonian Theory (AHT)[1], and two inequivalent spins were studied with Floquet theory[2-3].Here we use AHT to study 2 and 3 spin system in the fast MAS regime. Specifically, we develop the analytical expressions to 3rd order[4] for the AHT analysis in the case of two and three inequivalent spins (I= ½).

The expressions we obtain show, for the case of two spins, a 3rd order residual shift term. This term depends on the isotropic chemical shift difference between the two spins, on the square of the dipolar coupling, and on the inverse square of the MAS rate.It also has an intricate dependence on the Euler angles describing the dipolar coupling tensor.

In the three spins case, in addition to the residual shift term, there is a residual coupling term at 3rd order. In the NMR spectrum, this results in a splitting of the resonances into doublets of doublets. The residual coupling has the same dependence on MAS rate as the residual shift term.Both of these residual terms contribute to the broadening of the spectra, so one should aim to reduce their influence, in order to improve the spectral resolution.

We show how the residual splitting can be successfully removed with the anti-z-COSY experiment[5].

In conclusion, we develop a fully analytical AHT expression describing both the cases of two and three spins, under fast MAS. We detect, at 3rd order, the presence of residual shift and a coupling terms (the latter only in the case of three spins), which contribute to the broadening of the signal.

[1] M. M. Maricq, J. S. Waugh**,** *J. Chem. Phys.,***1979**, *70 ,3300-3316*
[2]M. H. Levitt, D. P. Raleigh, F. Creuzet, R. G. Griffin, *J Chem Phys*,**1990,** 92, 6347-6364.
[3] Nakai, C. A. McDowell, *J Chem Phys,* **1992**, 96, 3452-3466.
[4] Brinkmann, A.,Concepts Magn Reson *Part A*, **2016**; 45A:e21414.
[5] P. Moutzouri, F.M. Paruzzo, B. S. de Almeida, G. Stevanato, L. Emsley, Angewandte Chemie, **2020,** Vol. 59, 15, 6235-6238

Probing liquid interfaces with room-temperature ionic liquids using the excited-state dynamics of a cationic dye

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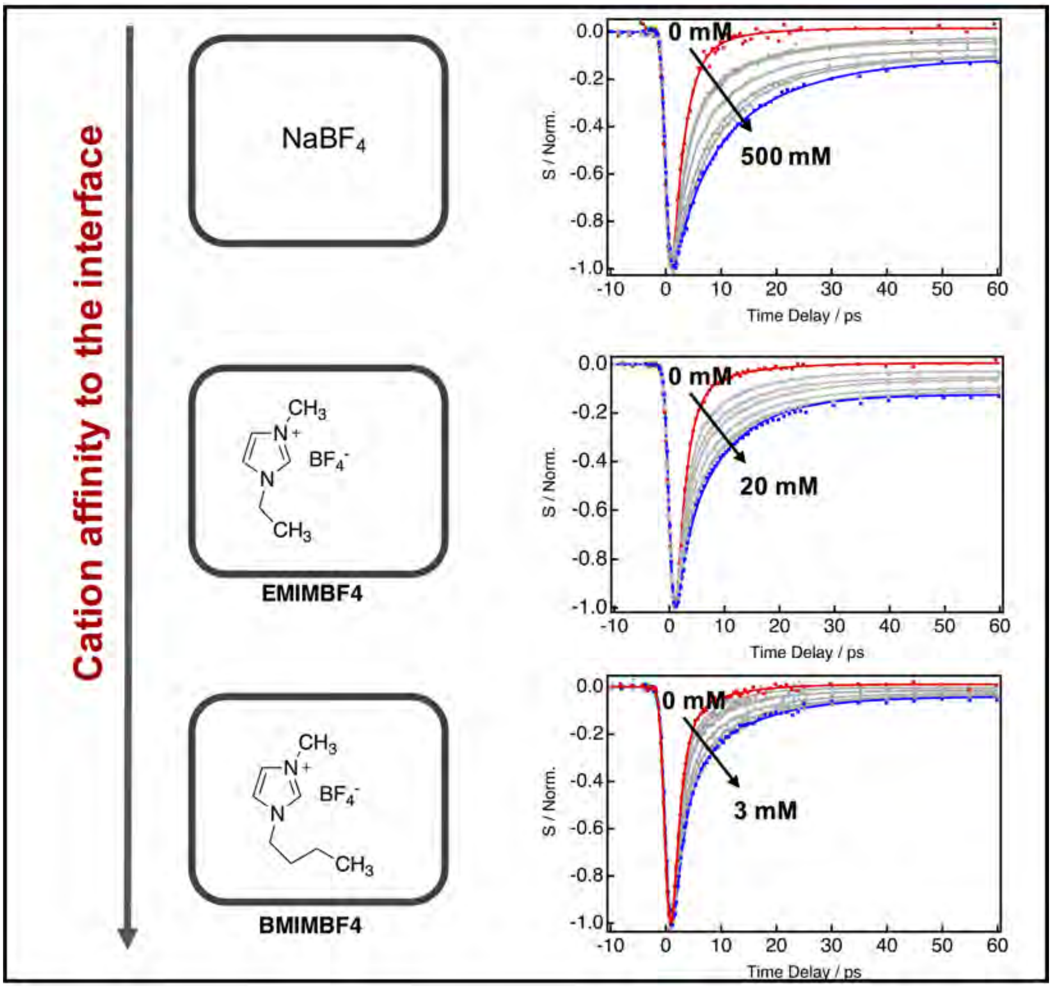
Interfaces play crucial roles in many applications of room-temperature ionic liquids (RTILs). However, our understanding of their properties is still limited. We investigated interfaces between dodecane and water/RTILs mixtures using various surface second harmonic generation techniques. As interfacial probe, we selected the cationic dye malachite green (MG) whose excited-state dynamics is sensitive to aggregation effects. We found that the interfacial concentration of MG depends crucially on both the anionic and cationic constituents of the RTIL. Depending on the relative affinity of the anions and cations, the overall charge of the interface is either negative or positive and, thus, either repels or attracts MG molecules. This approach offers totally new insight into the nature and properties of liquid interfaces with RTILs.



Towards high precision half-life measurements of exotic radio-lanthanides

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Long-lived radio-lanthanides are of great interest in a wide range of research domains [1-4]. In particular, ^{146}Sm, ^{148,150}Gd, ^{154}Dy, and ^{157,158}Tb play a fundamental role in astrophysics and nuclear physics applications. For many of these studies, an accurate knowledge on the nuclear properties of the above-mentioned radionuclides is required. However, the currently available data for the half-life ($T_{1/2}$) of ^{146}Sm, ^{148,150}Gd, ^{154}Dy, and ^{157,158}Tb are inconsistent, or affected by high uncertainty [5-7]. Reasons for these shortcomings in the nuclear databases are in many cases the limited availability of the isotopes of interest, often accompanied by difficulties in the preparation of samples with a high chemical purity. To overcome these limitations, the initiative "Exotic Radionuclides from Accelerator Waste for Science and Technology – ERAWAST", was launched in 2006 by Paul Scherrer Institute (PSI) [8, 9]. This long-term project aims to reprocess irradiated materials from the PSI accelerator-facilities, in order to obtain exotic radionuclides for scientific purposes. Detailed information can be found at the website: *psi.ch/en/lrc/erawast*. Among the several applications of ERAWAST, special focus is given to the improvement of the existent nuclear databases by re-determining the half-life of exotic radionuclides.

In this work, we use irradiated Ta samples from the second SINQ Target Irradiation Program [10] carried out at Paul Scherrer Institute in 2000-2001, with the main goal of retrieving the exotic ^{146}Sm, ^{148,150}Gd, ^{154}Dy, and ^{157,158}Tb radio-lanthanides in sufficient amounts and purity for high precision $T_{1/2}$ determination studies. Although several methods for the extraction and separation of lanthanides are known [11-13], none of them provides a sufficient accuracy to obtain pure material at the ppb level from a Ta matrix. Thus, we developed a liquid-phase stepwise procedure for the sequential separation of lanthanides from the Ta irradiated samples. The separation profile was monitored via γ-spectrometry using suitable tracers. Both the purity of each obtained lanthanide fraction and the quantification of the desired isotopes were assessed by inductively coupled plasma mass spectrometry (ICP-MS). After the obtainment of the purified lanthanide fractions, suitable radioactive sources for $T_{1/2}$ measurements were prepared. For isotopes with $T_{1/2}$ of considerably more than 100 years, the so-called direct method is applied. This consists of the determination of the number of atoms of interest (N) using ICP-MS or Multicollector-ICP-MS, followed by the measurement of its activity (A). From $T_{1/2} = N*\ln2/A$, a reliable half-life value, with an uncertainty below 5%, can be obtained. For radionuclides with $T_{1/2} \leq 100$ years, decay measurements can be performed. In this case, a source with the radionuclide of interest is prepared (e.g., *via* molecular plating), and its decay is monitored with periodic measurements over a time span of at least a year. Also with this method, uncertainties below 5% can be reached. Here, the separation method, together with preliminary results on the measured half-life of ^{148}Gd (decay method) and ^{154}Dy (direct method), will be presented.

[1] Giora Shaviv, *Springer Science & Business Media*, **2012**, 387, 1-684. [2] Yuki Tanoue, Tsugio Yokoyama, Masaki Ozawa, *Journal of Energy and Power Engineering*, **2016**, 10, 237-241. [3] PE Filianin et al., *Journal of Physics G: Nuclear Physics,* **2014**, 41, 095004-095021. [4] S. Möller, T. Wegener, *arXiv:1608.05199 [physics.ins-det],* **2016**, 1-9. [5] Georges Audi, et al., *Chinese Physics C,* **2017**, 41, 030001-030138. [6] David Brown, et al. *Nuclear Data Sheets,* **2018***,* 148, 1-142. [7] Zsolt Sóti, Joseph Magill, Raymond Dreher, *EPJ Nuclear Sciences & Technologies,* **2019**, 5, 6-17. [8] Dorothea Schumann, Jörg Neuhausen. *Journal of Physics G: Nuclear and Particle Physics,* **2007**, 35, 014046-014052. [9] Dorothea Schumann, et al. *Radiochimca Acta,* **2013**, 101, 501-508. [10] Yong Dai, et al., *Journal of Nuclear Materials,* **2005**, 343, 33-44. [11] Kenneth L. Nash, Mark P. Jensen, *Separation Science and Technology*, **2001**, 36, 1257-1282. [12] KE Thomas, *Radiochimica Acta*, **1983**, 34, 135-137. [13] Jacob Kleinberg. *Los Alamos National Lab. Technical Report (LA—1721-5th-Ed.)*, **1990**, Section II, 19-20.

Excited-state symmetry breaking in multibranched donor-acceptor dyes - The effect of quadrupole moment

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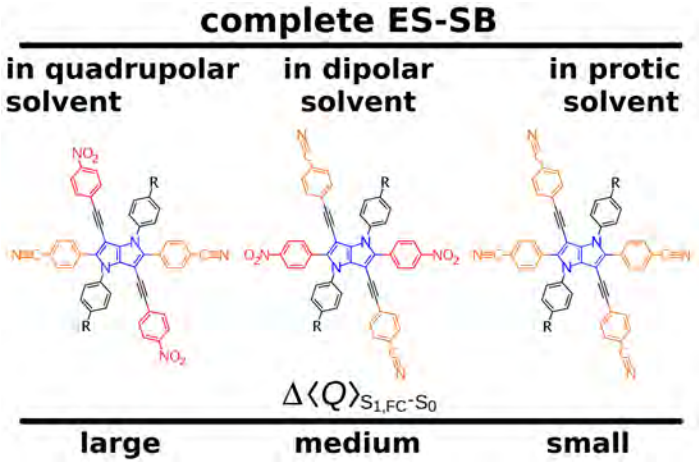
Excited-state symmetry breaking (ES-SB), i.e. the transition from a quadrupolar to a dipolar excited state, was observed with many centrosymmetric dyes developed for large two-photon absorption. Whereas, until now most of the studies have investigated the role of the environment on ES-SB, the influence of molecular properties is less documented. In the present study, we will show how the ES-SB depends on the change of quadrupole moment upon excitation (ΔQ) using four recently synthesized multibranched pyrrolo[3,2-b]pyrrole derivatives with **A**-π-**D**-π-**A** motifs appended by secondary acceptor groups, **A'**. Tuning of ΔQ was achieved by varying the acceptor groups, and the ES-SB was followed using ultrafast time-resolved infrared spectroscopy (TRIR) and broadband fluorescence upconversion spectroscopy (FLUPS). Our results reveal how the excited-state properties of such dyes, here the quadrupole moment, can be tuned to enable or disable ESSB.



Acknowledgement: The authors are grateful to Prof. D. T. Gryko for providing the investigated compounds. Financial support from the SNF (nr.200020-184607) is acknowledged.

Infrared Spectroscopy of Chemisorbed Methylidyne coadsorbed with Hydrogen on Pt(211)

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The dissociation of methane on the surface of a transition metal catalyst (Ni, Pt) is the rate limiting step in the steam reforming process used for the production of large scale hydrogen. In our lab, we perform highly controlled experiments to better understand this reaction at the microscopic scale.

Recently, we have demonstrated the capabilities of Reflection Absorption Infrared Spectroscopy (RAIRS) to perform surface site-specific studies of methane dissociation on stepped Pt surfaces[1]. RAIRS can be used to distinguish the nascent methyl product of the methane dissociation on the steps and terraces of Pt(211)[2], enabling the measurement of surface site specific sticking coefficients which yield information on the difference in dissociation barrier heights for different surface sites. These studies help closing the so-called “structure gap”, which refers to the structural difference between the single crystal flat surfaces commonly used in surface science and the real catalysts used in industry.

In my poster presentation, I will present a RAIRS study of the thermal dehydrogenation of the nascent methyl species on the Pt(211) surface yielding chemisorbed methylidyne CH(ads). Remarkably, the infrared spectrum of CH(ads) on a Pt(211) surface differs significantly from that of CH(ads) adsorbed on a flat Pt(111) surface reported in the literature[3]. While the C-H stretch frequency for methylene adsorbed on Pt(111) was found to shift continuously from 2956 cm^{-1} to 2974 cm^{-1} with increasing coverage of coadsorbed H atoms[3], we observe three distinct vibrational frequencies at 2950, 2960 and 2970 cm^{-1} for CH(ads) on Pt(211) when the coverage of coadsorbed hydrogen is increased. If you want to know more about why there are ‘quantized’ C-H stretch vibrations on Pt(211), I welcome you to see my presentation!

[1] Ana Gutiérrez-González, Maria Eugenia Torio, Heriberto Fabio Busnengo, Rainer Beck, *Topics in Catalysis*, **2019**, 62, 859-873.
[2] Helen Chadwick, Han Guo, Ana Gutiérrez-González, Jan Paul Menzel, Bret Jackson and Rainer Beck, *The Journal of Chemical Physics*, **2018**, 148, 014701.
[3] Rongping Deng, Eldad Herceg and Michael Trenary, *Surface Science*, **2004**, 573, 310-319.

Proton Transfer in a Propyl Acetate/Butyronitrile Mixture

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Solvation dynamics play an important role in many ultrafast photochemical reactions in solutions.[1] In particular, dielectric stabilization can significantly influence the driving force of chemical reactions involving charged intermediates or products, such as electron and proton transfer reactions. A binary mixture between propyl acetate and butyronitrile is ideally suited for investigating the effect of dielectric stabilization. The dielectric constant (ε_r) of the mixture increases from 6 to 24.8 upon increasing fraction of butyronitrile from 0 to 1 whereas the viscosity and refractive index remain constant. The static and dynamic dielectric stabilization in the mixtures has been investigated in detail in our group using several push-pull dyes.

Here, we present the effect of dielectric stabilization on the ground- and excited-state bimolecular proton transfer reactions from a naphthalimide-based photoacid (C_4-dHONI) to organic bases in the mixtures. The photoacid, C_4-dHONI, is a weak acid in the ground state but becomes extremely acidic in the excited state (pK_a = 8.8, $pK_a^* \approx -1$).[2] Therefore, the proton transfer can be initiated by excitation with a laser pulse in the presence of proton acceptor. The reaction kinetics are subsequently monitored using a broadband femtosecond (fs) fluorescence up-conversion technique, which provides the entire fluorescence spectrum as a function of time.[3] Our results indicate the bimolecular ESPT is ultrafast and occurs on the same time scale as solvation, reaching the so-called "solvent controlled" limit. Moreover, broad spectral coverage allows us to resolve contact ion pairs as a reaction intermediate as suggested by the Eigen-Weller model.[4,5]

[1] T. Kumpulainen, B. Lang, A. Rosspeintner, and E. Vauthey, *Chem. Rev.,* **2017**, *117* (16), 10826-10939.
[2] T. Kumpulainen, B.H. Bakker, and A.M. Brouwer, *Phys. Chem. Chem. Phys.,* **2015**, *17* (32), 20715-20724.
[3] X.-X. Zhang, C. Würth, L. Zhao, U. Resch-Genger, N. P. Ernsting, *Rev. Sci. Instrum. 82*, 063108 (**2011**).
[4] A. Weller *Prog. React. Kinet.*, **1961**, *1*, 187-214.
[5] M. Eigen, W. Kruse , G. Maass and L. De Maeyer , *Prog. React. Kinet.*, **1964**, *2*, 285-318.

Conformationally and state-controlled ion-molecule reactions

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Studies of the dynamics of chemical reactions have made impressive advances in recent years owing to the development of techniques for the cooling and manipulation of the motion of molecules in the gas phase. These methods have enabled new insights into the microscopic mechanisms, the quantum nature and the detailed dynamics of chemical processes which were not accessible before. Our new approach will be applied to study conformationally and state-specific dynamics in a range of pertinent model systems including the reactions of rotationally state-selected water molecules[1] and of conformationally selected methyl vinyl ketone molecules with conformationally selected dichloroethylene[2] and m-methoxystyrene ions[3]. These advancements will take the study of ion-molecule chemistry of polyatomic systems to a new level and enable insights into their state- and geometry-specific reaction dynamics, kinetics and mechanisms in unprecedented detail.

[1] A. Kilaj, H. Gao, D. Rösch, U. Rivero, J. Küpper, and S. Willitsch, *Nat. Commun.* **2018**, *9* (1), 1–7.
[2] A. Bodi, W. R. Stevens, and T. Baer, *J. Phys. Chem. A* **2011**, *115* (5), 726–734.
[3] Y. Xu, S. Y. Tzeng, V. Shivatare, K. Takahashi, B. Zhang, and W. B. Tzeng, *J. Chem. Phys.* **2015**, *142* (12).

A Formulation Protocol with Pyridine to Enable DNP-SENS on Reactive Surface Sites: Case Study with Olefin Polymerization and Metathesis Catalysts

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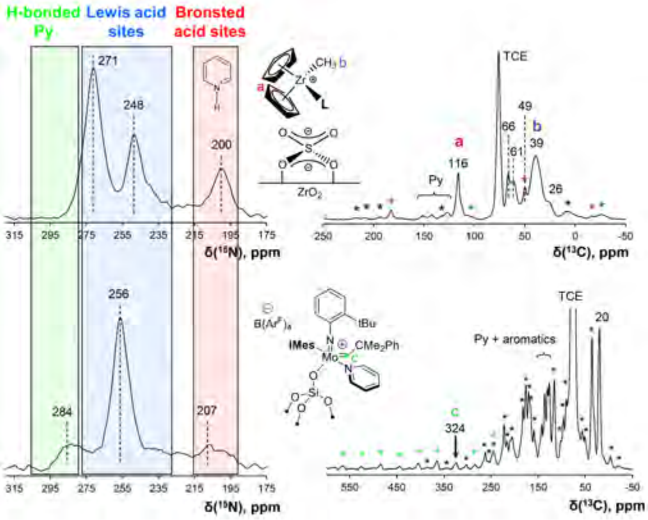
Dynamic nuclear polarization surface-enhanced NMR spectroscopy (DNP-SENS) has emerged as a powerful characterization tool in material chemistry and heterogeneous catalysis by dramatically increasing, by up to 2 orders of magnitude, the NMR signals associated with surface sites.[1] DNP-SENS mostly relies on using exogenous polarizing agents (PAs), typically dinitroxyl radicals, to boost the NMR signals. However, the PAs may interact with the surface or even react with surface sites, thus leading to loss or quenching of DNP enhancements.[2]

Herein, we describe the development of a DNP-SENS formulation that allows broadening the application of DNP-SENS to samples containing highly reactive surface sites, namely a Ziegler−Natta propylene polymerization catalyst, a sulfated zirconia-supported metallocene (Figure - top), and a silica-supported cationic Mo-alkylidene (Figure - bottom). The protocol consists of adsorbing pyridine prior to the DNP formulation (impregnation with TEKPol radical in TCE solution). The addition of pyridine allows for preservation of the PAs at the surface and thereby restoring the DNP enhancements, thus enabling high-quality NMR measurements for the studied catalysts.

We show the application of this protocol, here on prototypical highly sensitive catalysts. With surface DNP enhancements up to 24, this approach enables simultaneous NMR characterization of Lewis/Brønsted surface acid sites as well as the observation of “passivated” active sites coordinated by the adsorbed pyridine.[3] The protocol developed is likely applicable to a variety of materials containing reactive surface sites.



[1] Aaron Rossini, Alexandre Zagdoun, Moreno Lelli, Anne Lesage, Christophe Copéret, Lyndon Emsley, *Accounts of Chemical Research*, **2012**, 46, 1942-1951.
[2] Wei-Chih Liao, Ta-Chung Ong, David Gajan, Florian Bernada, Claire Sauvee, Maxim Yulikov, Margherita Pucino, Roman Schowner, Martin Schwarzwalder, Michael Buchmeiser, Gunnar Jeschke, Paul Tordo, Olivier Ouari, Anne Lesage, Lyndon Emsley, Christophe Copéret, *Chemical Science*, **2017**, 8, 416-422.
[3] Alexander Yakimov, Deni Mance, Keith Searles, Christophe Copéret, *Journal of Physical Chemistry Letters*, **2020**, 11, 3401-3407.

Transfer of Nanoscale Objects into Giant Plasma Membrane Vesicles (GPMVs) serving as cellular model systems

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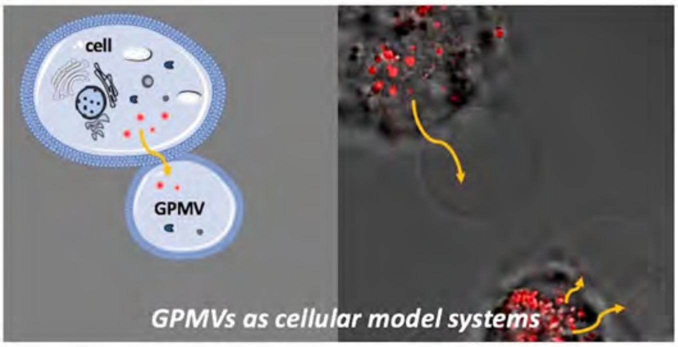
Cellular model systems play an important role in exploring the fundaments of biology and biochemistry and allow to break down the complex nature of living organisms into individual parts in order to studying various interactions on their membrane interfaces and within them. Here, we present Giant Plasma Membrane Vesicles (GPMVs) including diverse cell components, such as cell membrane and cytoplasm, as a biomimicking platform for investigating the behavior of solid polystyrene (PS) nanoparticles (NPs) within a biorelevant environment and promote their further development. We studied the impact of different particle and cell line depending factors on the transfer of cellularly uptaken NPs into formed GPMVs.

We investigated NP parameters playing a role in GPMV transfer (size, concentration and surface charge) along with 3 different cell lines: HepG2, HeLa, and Caco-2. We observed that PS NPs with a carboxylate-modified surface and a size of 40 nm and 100 nm were successfully and efficiently transferred to GPMVs derived from all cell lines. We investigated the distribution of these NPs inside formed GPMVs, established the average number of NPs/GPMVs and the percentage of all GPMVs with NPs in their cavity. Compared to synthetic and lipidic GUVs, also used as cell-mimicking platforms, the GPMV platform allows us to prescreen all non-biorelevant nanostructures prior to loading thus giving this system a strong advantage towards the application as an essential platform for nanotechnology and the medical domain.



A donor-acceptor ensemble: merging of TTF and dipyrrolylquinoxaline difluoroborate chemistry

P. Zhou[1], U. Aschauer[1], T. Feurer [2], R. Häner[1], S. Liu[1]

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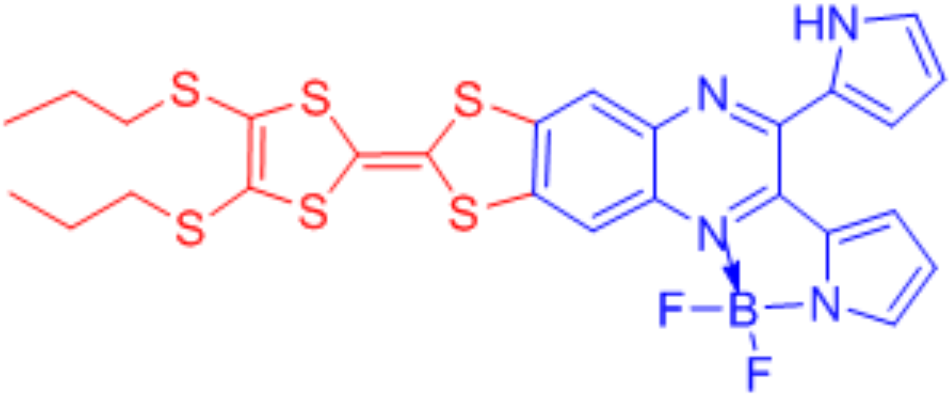
Tetrathiafulvalene(TTF)-fused donor-acceptor (D–A) ensembles are of high interest due to their unique (opto)electronic properties and potential applications in organic conductors, photovoltaics, sensors, switches and molecular electronics.[1, 2] A direct annulation of a TTF with a variety of electron-acceptors has been achieved for studying photo-induced intramolecular charge transfer (ICT) as well as the photogeneration of long-lived charge separated states in resultant D-A systems.[3] Herein, we describe redox and optical properties of a new D–A ensemble (Chart 1) which was prepared by complexation of BF_2 with a TTF-fused 2,3-di(1*H*-2-pyrrolyl)quinoxaline ligand. A detailed experimental and theoretical study of an ICT process in TTF-QB is presented.



[1] Bergkamp, J. J.; Decurtins, S.; Liu, S. X., Current advances in fused tetrathiafulvalene donor-acceptor systems. *Chem. Soc. Rev.* **2015,** *44* (4), 863-74.
[2] Jana, A.; Ishida, M.; Park, J. S.; Bahring, S.; Jeppesen, J. O.; Sessler, J. L., Tetrathiafulvalene-(TTF-) Derived Oligopyrrolic Macrocycles. *Chem. Rev.* **2017,** *117* (4), 2641-2710.
[3] Pfattner, R.; Pavlica, E.; Jaggi, M.; Liu, S.-X.; Decurtins, S.; Bratina, G.; Veciana, J.; Mas-Torrent, M.; Rovira, C., Photo-induced intramolecular charge transfer in an ambipolar field-effect transistor based on a π-conjugated donor–acceptor dyad. *J. Mater. Chem. C* **2013,** *1* (25).