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Environmental Photochemistry of Anilines

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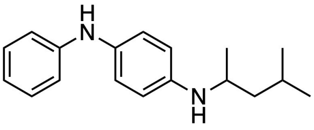
Anilines and aniline derivatives are important synthetic chemicals whose uses are widespread, appearing in almost every consumer sector, from antioxidants in tire rubber to pharmaceuticals. Accordingly, they are found as environmental contaminants. This presentation will focus on one aspect of their environmental fate, which is their photochemistry in natural waters.



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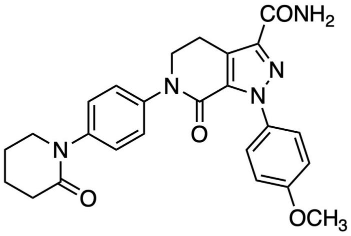

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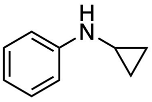

N-cyclopropylaniline
molecular probe

Central to the photochemical fate of anilines in surface waters is their reaction with triplet excited states of natural organic matter.[1] This mixture of excited state oxidants has proven challenging to study, and insight into their behavior has so far only been possible using multiple approaches, including laser spectroscopy, the use of molecular probe compounds, and chemical kinetics. Examples of these various methods will be highlighted in the presentation.

[1] K. McNeill, S. Canonica, *Environ. Sci. Processes Impacts*, **2016**, *16*, 1381.

Mechanistic implications of oxygen uncoupling in two Rieske non-heme iron dioxygenases

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Rieske non-heme iron dioxygenases (RDOs) are the key enzymes responsible for initial steps of aerobic biotransformation of numerous persistent aromatic contaminants in the environment. Knowledge of the catalytic mechanism, substrate specificity, and activity of RDOs enables one to assess which environmental contaminant can be fed into common metabolic pathways through dihydroxylation steps leading to *cis*-dihydrodiols and catechol-type products. However, while the strategies of O_2 activation and control of reactive Fe-oxygen species of many mononuclear non-heme iron oxygenases have been studied in detail, the efficiency of substrate oxygenation is largely unknown. Current hypotheses suggest that RDO substrates other than the native ones are hydroxylated only poorly and thus give rise to so-called O_2 uncoupling and concomitant formation of reactive oxygen species [1]. Given that RDO-expressing microorganisms are exposed to complex mixtures of structurally similar aromatic compounds at contaminated sites, O_2 uncoupling could even be the predominant outcome of enzymatic activity.

In this study, we explored the relevance of O_2 uncoupling pathways of RDOs as well as its implications for the kinetics and mechanisms of O_2 activation and substrate oxygenation. We studied two closely related nitroarene dioxygenases, namely nitrobenzene dioxygenase (NBDO) and 2-nitrotoluene dioxygenase (2NTDO) with a wide range of substrates [2,3]. Substrate-specific uncoupling was observed through measurements of O_2 consumption relative to product formation in purified enzyme assays and revealed an extent of O_2 uncoupling of 30% to 100% of the activated O_2. The efficiency of oxygenation by NDBO showed preference for *meta*-substituted nitroarene substrates as opposed to *ortho*-substituted substrates for 2NTDO. Conversely, ^{18}O kinetic isotope effects (KIEs) used for characterization of reactive Fe-oxygen species were between 1.015 and 1.025 which is indicative of Fe(III)-peroxo species formation and lacked any substrate specificity. ^{13}C KIEs of substrate hydroxylation correlated with the extent of O_2 uncoupling of NBDO whereas these numbers were generally close to unity for 2NDTO. Our observations suggest catalytic mechanisms of RDOs in which the timing of O_2 uncoupling and release of seemingly unreacted substrate are both substrate- and enzyme-specific. The high share of unproductive O_2 activation challenges the widely made assumption of enzyme evolution towards an efficient oxygenation of preferred substrates.

[1] Charlotte E. Bopp, Hans Peter E. Kohler, Thomas B. Hofstetter, *Chimia*, **2020**, 74, 108-114.

[2] Sarah G. Pati, Hans Peter E. Kohler, Anna Pabis, Piotr Paneth, Rebecca E. Parales, Thomas B. Hofstetter, *Environmental Science and Technology*, **2016**, 50, 6708-6716.

[3] Sarah G. Pati, Hans Peter E. Kohler, T.B. Hofstetter *Methods in Enzymology*, **2017**, 596, 291-329.

Reactive Oxygen Species (ROS)-A promising metric linking aerosol toxicity and human health

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It is being speculated that particle-induced reactive oxygen species (ROS), which are indicative of the oxidative potential (OP) of aerosol particles, may be a promising metric to predict particle toxicity. However, accurate ROS quantification remains challenging due to the reactive and short-lived nature of many ROS components and the lack of appropriate analytical methods for a reliable quantification, which makes it difficult to gauge their impact on human health.

In this study, using a novel online particle-bound ROS instrument (OPROSI) [1], we comprehensively characterized and compared the evolution of ROS in secondary organic aerosol (SOA) generated from anthropogenic (naphthalene) and biogenic (β-pinene) precursors coated on soot particles (SP) and aging of these SOA types under varied atmospheric relevant conditions (UV lamp intensity and humidity). We systematically analysed the ability of the two aerosol types to induce the production of ROS, particle OP as measured by both acellular and cellular assays, using lung epithelial cell cultures. We further investigated multiple biological responses caused by the two aerosol types. The links among chemical and biological analyses were compared. The overall results show that compared to β-pinene-derived SOA, naphthalene (i.e., anthropogenic) SOA not only contain a higher ROS content, but also lead to a lower cell viability, higher DNA damage, and a higher oxidative stress potential. These consistent results between chemical-based and biological-based analyses indicate that ROS could be a feasible metric to link aerosol particle composition to toxicity and adverse human effects.

[1] Francis P. H. Wragg, Stephen J. Fuller, Ray Freshwater, David C. Green, Frank J. Kelly, Markus Kalberer, *Atmos. Meas. Tech.*, **2016**, 9, 4891–4900.

NMVOC, CH_4 and NH_3 emissions of different silage-based diets for dairy cows at herd level

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Agricultural activities, such as dairy cattle farming in perticular, make a substantial contribution to the Swiss methane (CH_4) and ammonia (NH_3) emissions [1, 2]. In addition, dairy farming is also a relevant source for non-methane volatile organic compounds (NMVOCs) [3]. Since summer 2015, Agroscope and Empa assess CH_4, NH_3 and CO_2 emissions from dairy cows at the experimental housing for emission measurements, Waldegg, Switzerland [4]. The housing consists of two spatially separated compartments, each for 20 cows, which allows comparative quantification of emissions simultaneously. A dual tracer-ratio method with SF_6 and SF_5CF_3 is applied to determine emissions under natural ventilation and detect cross-contamination [5]. For two years, 2018 and 2020, the focus was additionally on NMVOC emissions under different feeding regimes, silage-based vs. silage-free (2018) and different silage types with and without additives (2020). NMVOC emissions were determined using different analytical techniques, such as gas chromatography with flame ionisation detector (GC-FID) and a total hydrocarbon monitor (THC), while C_4, CO_2 and NH_3 concentrations were quantified using cavity ring down spectroscopy. NMVOC emissions in the compartments with the silage-based diet were generally dominated by ethanol followed by methanol and ethyl acetate. Summer measurements showed around 70% lower ethanol emissions in the compartment with the silage-free diet compared to the silage-based diet. In autumn and winter, ethanol emissions in the silage-free compartment were even lower - in the range or below the detection limit. Based on the collected NMVOC emission data, the statistical model and metrological data from MeteoSchweiz we established a model-based calculation to estimate yearly NMVOC emissions for dairy cattle in mountain and plain regions under different feeding regimes.

[1] Federal Office for the Environment FOEN,*Switzerland's Greenhouse Gas Inventory 1990–2019*, **2011,** 643.
[2] Kupper, T., et al., *Ammoniakemissionen in der Schweiz 1990-2010 und Prognose bis 2020*, **2013**, 110.
[3] Bühler, M., *Agricultural emissions of NMVOC and* PM, **2018**, 51.
[4] Schrade, S., et al., *Versuchsstall zur Entwicklung und Quantifizierung von Massnahmen zur Minderung von Emissionen*, **2015**, 450–455.
[5] Mohn, J., et al., *Atmospheric Environment*, **2018**, 179, 12–22.

Absolute validation of a balloon-borne spectrometer for water vapor measurements in the upper atmosphere

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Water vapor (H_2O) is the strongest greenhouse gas in our atmosphere, and it plays a key role in multiple processes that affect weather and climate. Particularly, H_2O in the upper troposphere - lower stratosphere (UTLS) is of great importance to the Earth's radiative balance, and has a significant impact on the rate of global warming. Currently, the reference method used for in-situ measurements of UTLS H_2O aboard meteorological balloons is cryogenic frostpoint hygrometry (CFH) [1]. However, the cooling agent required for this technique (trifluoromethane) is phasing out as of 2020, due to its strong global warming potential. This represents a major challenge for the continuity of long-term UTLS H_2O monitoring programs worldwide. As an alternative to CFH, we developed a compact instrument based on mid-IR quantum-cascade laser absorption spectroscopy (QCLAS) [2]. The spectrometer incorporates a specifically developed segmented circular multipass cell to extend the laser path length to 6 m [3], while meeting the stringent requirements, in mass, size and temperature resilience, posed by the balloon platform and by the harsh environmental conditions of the UTLS. Two successful test flights performed in December 2019 demonstrate the instrument's outstanding capabilities up to 28 km altitude [2].

The spectrometer relies on a calibration-free retrieval approach, i.e. the H_2O amount fractions are determined from first principles from the acquired spectra, hence it is necessary to validate its absolute accuracy with respect to a high-accuracy reference. To this aim, a dedicated laboratory campaign was conducted at the Swiss Federal Institute of Metrology (METAS) in April-May 2021. Using a dynamic-gravimetric permeation method combined with dynamic dilution [4], we generated SI-traceable reference gas mixtures of H_2O in a synthetic air matrix, with amount fractions between 2.5-35 ppmv and uncertainty < 1.5 %, which were measured by QCLAS at pressures between 30-250 mbar. This dataset provides the basis for the absolute validation in terms of accuracy and linearity of the spectrometer at UTLS-relevant conditions. Furthermore, it allows to investigate secondary effects originating from the assumption of a simplified shape model (the Voigt profile) for the absorption lines in the fitting algorithm. In particular, their contribution to the overall uncertainty of the instrument will be investigated and compared to more sophisticated parameterizations, such as the Hartman-Tran profile (HTP), for a large set of pressure and amount fraction conditions. The ultimate goal is to demonstrate the potential of QCLAS as a highly valuable technique for quantitative balloon-borne measurements of UTLS H_2O, which are directly traceable to the SI units.

[1] Brunamonti et al., *J. Geophys. Res. Atmos.*, **2019**, 124, 13, 7053-7068.
[2] Graf et al., *Atmos. Meas. Tech.*, **2021**, 14, 1365-1378.
[3] Graf, Emmenegger and Tuzson, *Opt. Lett.*, **2018**, 43, 2434-2437.
[4] Guillevic et al., *Atmos. Meas. Tech.,* **2018**, 11, 3351–3372.

Cadmium remobilization during sediment resuspension can lead dissolved concentration exceeding EU water framework maximum

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The EU water Framework (2008/105/EC) delimited total dissolved concentrations thresholds of one or a group of hazardous chemical elements in water, that if exceeded, indicate poor water quality. In parallel, French (JORF n°184 10-08-2000) and Italian (Italian Ministerial Decree 173/2016) authorities have delimited contaminants bulk sediment content thresholds and suspended matter monitoring for the management of dredging operation and the mitigation of their impact on water quality. As a matter of fact, the metals accumulated in sediments can be remobilized by their resuspension [1] through natural and anthropogenic activities (such as dredging), and degrade water quality. Among these metals, Cd is a non-essential, harmful trace metal for biota, causing serious problems towards organisms due to its high toxicity [2,3]. Through this work, we aimed at studying the kinetic and amplitude of Cd remobilization as a function of the origin of the resuspended sediment, its initial Cd content and sediment/water ratio. For that purpose, three Mediterranean coastal sediments were studied, presenting Cd contents considered as not harmful by the guidance of the corresponding country (France or Italy). In lab, controlled continuous resuspension experiments allowed us to demonstrate that the kinetics of the processes were similar in each experiment, but the amplitude of the transfers was specific to each sediment. Indeed, Cd systematically undergone a removal from water by adsorption onto particles in the very first minutes of mixing. Then this element was desorbed from particles after a few hours to reach higher (up to 22.1-fold higher) dissolved Cd concentrations after 2 weeks of mixing than in the initial waters. Finally, with high sediment/water ratio mimicking dredging activities (125 $g_{WW}.L^{-1}$), after 2 weeks of mixing, dissolved Cd concentration was up to 2.4 times higher than the maximum concentration permitted by EU water Framework. Such results point out a risk of water quality degradation that is not considered in sediment management practices (only considering the content metal in the sediment and only regulating / monitoring the resuspended particles concentration.)

[1] Layglon N, Misson B, Gallois N, D'Onofrio S, Lenoble V, Mounier S, et al. Negligible microbial heterotrophic quantitative contribution onto trace metals remobilization during marine sediment resuspension - insights from a Mediterranean urbanized bay. Marine Chemistry 2021:103981. https://doi.org/10.1016/j.marchem.2021.103981.
[2] Miao A, Wang W. Cadmium toxicity to two marine phytoplankton under different nutrient conditions. Aquatic Toxicology 2006;78:114–26. https://doi.org/10.1016/j.aquatox.2006.02.008.
[3] Satarug S, Baker JR, Urbenjapol S, Haswell-Elkins M, Reilly PEB, Williams DJ, et al. A global perspective on cadmium pollution and toxicity in non-occupationally exposed population. Toxicology Letters 2003;137:65–83. https://doi.org/10.1016/S0378-4274(02)00381-8.

Replacing the need for in vivo animal testing - the use of alternative in vitro assays for PBT screening of fragrance chemicals

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PBT screening, i.e. the determination of potential persistence (P), bioaccumulation (B) and toxicity (T), plays a central role in the environmental assessment of chemicals. Persistence is typically screened via standard microbial biodegradation tests. Bioaccumulation refers to the accumulation of chemicals in organisms and is usually assessed in fish exposed to the test chemical determining the bioconcentration factor (BCF). Toxicity is determined at three trophic levels, with fish toxicity as the highest trophic level assessed which involves exposure of fish to different test chemical concentrations. Thus, animal tests are classically needed for both B and T assessment. From an ethical standpoint, the need to move away from animal tests has long been recognised by industry, NGOs, scientists and consumers. Today, this is reflected in many regulatory frameworks, notably the REACH Regulation which promotes and supports the 3Rs principles (reduction, refinement, replacement).

In vitro assays to determine biotransformation rates in hepatocytes or liver S9 fractions from rainbow trout (OECD TG 319 A/B) [1, 2] have been validated to refine BCF predictions using in vitro-in vivo extrapolation (IVIVE) models [3, 4]. For T assessment, in vitro cytotoxicity in the fish gill cell line RTgill-W1 is determined as a surrogate for the LD50 [5] from an acute fish test. The RTgill-WI assay has also recently been adopted as a new OECD test guideline [6].

Here we summarize our findings indicating that these tests are highly predictive for fragrance ingredients, and illustrate with case studies of our latest new registered substances how we apply these tests in particular during development of new ingredients and also for chemical registration. Furthermore potential uncertainties in particular of the in vitro assay and IVIVE models applied for B assessment are discussed. A regression model correlating in vitro S9 biotransformation rates, log Kow and in vivo measured BCFs, which was developed based on our previously published data set [7], is evaluated as a potential additional prediction model.

[1] OECD, Test No. 319A, OECD Guideline for the Testing of Chemicals, OECD Publishing, **2018**.
[2] OECD, Test No. 319B, OECD Guideline for the Testing of Chemicals, OECD Publishing, **2018**.
[3] J. W. Nichols, D. B. Huggett, J. A. Arnot, P. N. Fitzsimmons, C. E. Cowan-Ellsberry, *Environmental Toxicology and Chemistry*. 2013, *32*, 1611-1622.
[4] S. Krause and K. U. Goss. *Chemical Research in Toxicology*, **2018**, *31*, 1195-1202.
[5] M. Fischer et al. *Toxicological Sciences* **2019**, *169*, 353-364.
[6] OECD, Draft Test Guideline, OECD Guideline for the Testing of Chemicals, OECD Publishing, **2021**.
[7] H. Laue, L. Hostettler, R. P. Badertscher, K. J. Jenner, G. Sanders, J. A. Arnot, and A. Natsch. Environmental Science and Technology, 2020, *54*, 9483-9494.

Metabolomic Profiling and Toxicokinetics Modeling to Assess the Effects of the Pharmaceutical Diclofenac in the Aquatic Invertebrate Hyalella azteca

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The exposure of ecologically critical invertebrate species to biologically active pharmaceuticals poses a serious risk to the aquatic ecosystem. Yet, the fate and toxic effects of pharmaceuticals on these non-target aquatic invertebrates and the underlying mechanisms are poorly studied. Herein, we investigated the toxicokinetic (TK) processes (i.e., uptake, biotransformation, and elimination) of the pharmaceutical diclofenac and its biotransformation in the freshwater invertebrate Hyalella azteca. We further employed mass spectrometry-based metabolomics to assess the toxic effects of diclofenac on the metabolic functions of H. azteca exposed to environmentally relevant concentrations (10 and 100 µg/L). The TK results showed a quick uptake of diclofenac by H. azteca (maximum internal concentration of 1.9 µmol/kg) and rapid formation of the conjugate diclofenac taurine (maximum internal concentration of 80.6 µmol/kg), indicating over 40 times higher accumulation of diclofenac taurine than that of diclofenac in H. azteca. Depuration kinetics demonstrated that the elimination of diclofenac taurine was 64 times slower than diclofenac in H. azteca. Metabolomics results suggested that diclofenac inhibited prostaglandin synthesis similar to in humans and other species (e.g., zebrafish, rainbow trout, and marine musse). Furthermore, the carnitine shuttle pathway was affected at environmentally relevant concentrations. These findings shed light on the significance of the TK process of diclofenac, especially the formation of diclofenac taurine, as well as the sub-lethal effects of diclofenac on the bulk metabolome of H. azteca. Combining the TK processes and metabolomics provides complementary insights and, thus a better mechanistic understanding of the effects of diclofenac in aquatic invertebrates.

Assessing biodegradation of commercial plastic mulches in Swiss soils

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Modern agriculture relies heavily on the use of plastic mulch films to increase crop yields while lowering the consumption of water and herbicides. However, repeated application of films composed of non-biodegradable plastics - primarily polyethylene - leads to accumulation of plastic residues in soils, raising concerns on long-term negative effects. A possible strategy to avoid soil plastic pollution is to employ biodegradable mulch films composed of polymers designed to be degraded *in situ* by native soil microorganisms. While such products are already available on the market, the environmental chemistry of these films and our understanding of the factors which drive their biodegradation in soils remains poorly understood. To overcome this knowledge gap we are performing long-term incubations of two selected commercially available mulch films - composed of polybutylene adipate-co-terephthalate (PBAT) and poly lactic acid (PLA) - in three Swiss agricultural soils at three scales – laboratory, greenhouse mesocosm and field. In this contribution, we will discuss the experimental setup and show results of film biodegradation over the first months of the incubation, as determined by quantification of the residual polymer using Soxhlet extraction of the soil followed by quantitative ^{1}H-NMR[1]. We will discuss differences in the biodegradation between soils and scales and assess key soil and polymer factors that control rates and extents of biodegradation of these films.

[1] Taylor Nelson, Michael Sander, *Environmental Science & Technology*, **2019**, 54, 266-275

Antibiotics and hormone steroids in Norwegian biogas digestate

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Anaerobic fermentation is increasingly used in the waste sector to treat biomass and to produce biogas (energy). Nutrients such as nitrogen and phosphorous can be recycled when the residual biomass, i.e. digestate, are used as fertilizer and soil amendment in agriculture. Unfortunately, pollutants present in the waste biomass may also be recycled to the soil, such as persistent organic pollutants (POPs), polycyclic aromatic hydrocarbons (PAHs) [1], trace metals [2], and pharmaceuticals [3,4].

Organic pollutants which are not or only partly degraded through thermal pre-treatment and the subsequent digestion, express a resilience towards high temperatures and (at some production plants) pressure, as well as both aerobic and anaerobic conditions. Spread of chemical pollutants which resist degradation to the environment, by applying digestate from biogas production on farmland, may pose a health risk to wildlife and humans. Hence, we developed a multi-method for the detection of several classes of antibiotics and steroid hormones. The aim of the present study was to determine whether biogas digestates contained pharmaceutical residues.

All over the detection levels and frequencies were low, despite MDLs in the ng – µg kg^{-1} range. However, a few antibiotics and one glucocorticoid were found at concentrations above 400 µg kg^{-1} dw. These elevated levels may promote antibiotic resistance and cause harm towards soil microorganisms when the digestate is applied as fertilizer. Most concerning was the detection of ciprofloxacin at 430 µg kg^{-1} dw, considering the stability of this antibiotic in soil. Further, the penicillin amoxicillin was found at 460 µg kg^{-1} dw in a digestate produced solely from food waste. The levels and implication of our findings are discussed in detail in the planned presentation.

[1] K. Suominen, M. Verta, S. Marttinen, *Science of the Total Environement*, **2014**, 491, 192-199
[2] Ivan Dragicevic, Susanne Eich-Greatorex, Trine A. Sogn, Svein J. Horn, *Journal of Environmental Management*, **2018**, 217, 12-22
[3] Aasim Ali, Astrid S. Nesse, Susanne Eich-Greatorex, Trine A. Sogn, Stine G. Aanrud, John A. Aasen Bunæs, Jan L. Lyche, Roland Kallenborn, *Environmental Science: Processes & Impacts*, **2019**, 9, 1498-1508
[4] Astrid Spielmeyer, Jenny Ahlborn, Gerd Hamscher, *Analytical and Bioanalytical Chemistry*, **2014**, 406, 2513-2524

Development of transient lithium-ion battery with a high-performance Cellulosic Separator

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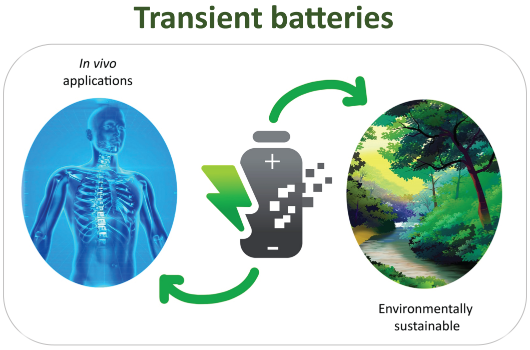
Transient/degradable technology is a flourishing research area aimed at designing materials, devices, or systems that undergo controlled degradation processes after a period of stable and reliable operation. Transient devices work exactly like their conventional analogs but have an extra advantage; these devices can disintegrate into the environment in a controlled fashion without leaving any toxic products behind. Transient technology is rapidly gaining ground for biomedical applications, zero-waste electronics, and data-secure hardware, to name a few. To power such devices, transient batteries are required. To date, there are very few reports on transient batteries in literature, mainly due to the lack of suitable soluble materials, fabrication schemes, and battery designs that must fulfill entirely different requirements than the traditional batteries.[1]

Here, we report the development of a fully transient lithium-ion battery (LIB) with competitive electrochemical performance. At first, we designed a degradable separator based on polyvinyl alcohol and cellulose nanocrystals that offer several unique advantages: electrolyte (organic solvent-based) uptake up to 510%, the ionic conductivity of 3.077 mS·cm^{-1}, electrochemical stability up to 5.5 V *vs.* Li/Li$^+$, and a high transference number of 0.56. As a result, a stable lithium metal deposition and a high specific capacity of 105 mAh·g^{-1} in Li-$LiFePO_4$ cell for over 250 cycles were achieved for the separator soaked in organic electrolyte. The toxic organic electrolyte was replaced with a biodegradable ionic liquid, providing an ionic conductivity of 0.988 mS·cm^{-1} and a specific capacity of 87 mAh·g^{-1}. Finally, the ionic liquid-separator pair was assembled into a fully transient lithium-vanadium(V) oxide (Li-V_2O_5) cell, which can be cycled over 400 times and degraded in 15 minutes once an aqueous trigger was applied.[2] This prototype of a transient LIB represents a proof of concept to develop innovative transient energy storage systems with a long life cycle.



[1] Mittal, N.; Ojanguren, A.; Niederberger, M.; Lizundia, E., *Adv. Sci.*, **2021**, 2004814.
[2] Mittal, N.; Ojanguren, A.; Cavasin, N.; Lizundia, E.; Niederberger, M., *Adv. Funct. Mater.*, *manuscript accepted*.

Diformylxylose as a New Polar Aprotic Solvent Produced from Renewable Biomass

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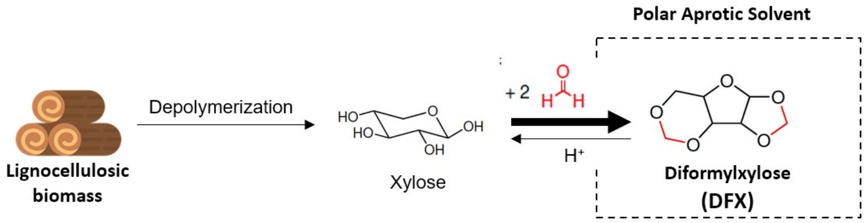
The gradual depletion of fossil resources, increase in global energy consumption, and the environmental issues encourage the development of new chemicals and materials produced from renewable sources. The development of bio-based solvents that could compete with petroleum-derived analogs is an area of high interest to chemical and pharmaceutical industry. Recently, ACS Green Chemistry Institute® Pharmaceutical Roundtable identified the development of viable replacements for polar aprotic solvents (PAS) as a key green chemistry research area.[1] PAS possess unique characteristics such as high polarity and low reactivity, which makes them excellent media for the production of active pharmaceutical ingredients. However, many commonly used PAS are extremely hazardous, mutagenic, and negatively impact the environment, which provokes regulatory response. For example, European Union REACH has restricted the industrial use of N-methylpyrrolidinone (NMP), N,N-dimethylacetamide (DMAc) and N,N-dimethylformamide (DMF) due to their severe reproductive toxicity. Therefore, increasing regulatory and commercial pressure drives switching to greener alternatives such as biomass-derived GVL, 2-Me-THF, Cyrene and other emerging solvents. However, current replacement candidates do not meet all safety requirements, often lack necessary solvation and physical properties, and still considered as “problematic” according to industrial solvent selection guides. Another big challenge is the high production cost of bio-based PAS because aprotic molecules are rarely found in abundance in the natural world and their production from protic ones (e.g., carbohydrates, carboxylic acids, lignin, alcohols, etc.) often requires multi-step processes, sometimes involving metals and high pressure. This factor can be strongly reduced in the case of acetal-stabilized xylose – namely, Diformylxylose (DFX), that can be produced from biomass in almost 100% yield (on xylan basis)[2] or directly from xylose[3] using inexpensive chemicals and common equipment. In this work, we are introducing Diformylxylose in the role of bio-based solvent with polar aprotic nature.



Diformylxylose demonstrated similar performance to conventional PAS such as DMF, NMP, DMSO in alkylation, cross-coupling, and hydrogenation reactions, while having a safer profile. Solvation properties of DFX were fully characterized by two models - Kamlet-Abboud-Taft solvatochromic parameters and Hansen Solubility Parameters. We demonstrated that DFX possesses unique solvation properties — high polarity and high hydrogen-bond accepting ability. Physical properties of DFX such as high boiling (237°C) and melting point (48°C) indicate a lower risk of human exposure and the environmental impact due to low volatility. Finally, toxicological assessment (bacterial Ames test) showed that DFX is a non-mutagenic and non-carcinogenic molecule. Overall, low production cost, high performance, non-mutagenic nature, and renewability make DFX a promising bio-based alternative to traditional polar aprotic solvents.

[1] M. C. Bryan, P. J. Dunn, D. Entwistle, et al, *Green Chem.*, **2018**, 20, 5082–5103.

[2] M. Talebi Amiri, G. R. Dick, Y. M. Questell-Santiago and J. S. Luterbacher. *Nat. Protoc.*, **2019**, 14, 921–954.

[3] Y. M. Questell-Santiago, R. Zambrano-Varela, M. Talebi Amiri and J. S. Luterbacher, *Nat.* Chem., **2018**, 10, 1222–1228.

Seasonal aerosol acidity and liquid water content: impact on aerosol concentration and nitrogen deposition fluxes in Toronto

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Aerosol acidity and liquid water content affect aerosol concentration and composition as well as the fate of the precursor compounds ammonia (NH_3) and nitric acid (HNO_3) [1,2]. Together with temperature, aerosol acidity and liquid water content determine the gas-to-particle partitioning of such precursors. In warm seasons, high aerosol acidity and low water content promote partitioning of ammonia to particulates as ammonium, while at the same time drive aerosol nitrate to the gas phase as HNO_3. In cold seasons, the opposite effect can be observed. Given that the dry deposition rate of gaseous NH_3 and HNO_3 is up to 10 times faster than the particle phase, the conditions that favour partitioning of these species to the gas phase also determine the dry deposition speed of reduced and oxidized nitrogen – with consequences for the accumulation of aerosol in the boundary layer, transport and deposition of nitrogen species over space [2].

In the present work, we explore the seasonal variation of aerosol acidity and liquid water content and their estimated effect on nitrogen dry deposition velocity using data collected over three years in Toronto, Canada, from January 2016 to December 2018. Aerosol H^+ concentrations has an inter- and intra-seasonal variability ranging between 5 and almost 2 orders of magnitude respectively. By applying the framework developed in Nenes et al. 2020, aerosol formation during winter is sensitive to HNO_3 levels, whereas in summer it tends to be insensitive to both NH_3 and HNO_3. The insensitive regime indicates that emissions of other precursors such as SO_x and organic aerosol are major sources of aerosol variability. In terms of N dry deposition, while in winter N dry deposition is dominated by NH_3, during summer deposition of HNO_3 becomes as fast as NH_3 deposition due to the increased aerosol acidity.

In conclusion, the analysis of ambient aerosol data using aerosol pH and liquid water content suggest that in Toronto, that emission controls of NO_x in winter and of SO_x in summer would be most beneficial for air quality.

[1] Nenes A., Pandis S., Weber R.J., Russell A., ACP, 20, 3249–3258, 2020
[2] Nenes A., Pandis S., Kanakidou M., Russell A., Song S., Vasilakos P., Weber R.J., ACPD, 20, 266, 2020

Influence of Transition Metals on Particle-bound Reactive Oxygen Species and the Oxidative Potential of Secondary Organic Aerosol Particles

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Large-scale epidemiological studies have consistently revealed links between airborne particulate matter (PM) exposure and a variety of negative health outcomes [1]. Nonetheless, there is still a lack of comprehension regarding the chemical and physical characteristics of PM, and their influence on toxicity mechanisms upon exposure. This is due in part to the chemical complexity of PM, where chemical interactions may well influence particle reactivity, solubility, bioavailability or redox-activity, and hence alter their potential to induce toxicity upon PM exposure. The oxidative potential (OP), referring to the catalytic production of reactive oxygen species (ROS) by particle components with subsequent depletion of anti-oxidants in the lung, has been widely suggested as a measure of potential PM toxicity. ROS, exogenously delivered by PM or produced by PM components in vivo, can deplete anti-oxidant concentrations to such an extent that anti-oxidant defences are overwhelmed, initiating oxidative stress which can potentially lead to adverse health effects. Recent developments in online methods, such as the Online Particle-bound ROS Instrument (OPROSI) [2], based on the 2,7-dichlorofluorescin (DCFH) assay, and the Online Oxidative Potential Ascorbic Acid Instrument (OOPAI) [3], allow the measurement of particle-bound ROS and OP with a time resolution on the order of 10 minutes, therefore providing rapid *in situ* measurements, compared to traditional offline filter-based measurements which are typically analysed days after collection.

In this study, we applied the OPROSI and OOPAI simultaneously for the first time to elucidate the impact of particle composition on the oxidative potential (OP) of PM. Specifically, we probed particle-bound ROS concentrations and the OP of secondary organic aerosol (SOA) particles derived from the hydroxyl radical (OH) initiated oxidation of β-pinene (from natural, biogenic sources) and naphthalene (from anthropogenic sources). These organic aerosol particles are representative of different SOA sources in the atmosphere. Moreover, we investigated the interaction between a range of transition-metal seed particles, including Fe and Cu, two relatively abundant redox-active transition metals found in ambient aerosol particles, mixed with SOA. We observed that naphthalene-derived SOA is significantly more OP active, compared to β-pinene SOA. Additionally, the OP-activity was non-additive when SOA and metal particles were mixed compared to their individual OP. For example, there was a synergistic enhancement of the OP by approximately 15 % when Fe (III) and naphthalene SOA were mixed, indicating that the interaction of naphthalene SOA with Fe (III) enhances the OP and therefore potential toxicity of the particles. Understanding the role that chemical composition plays on aerosol OP is crucial in order to determine the toxicity mechanisms of ambient aerosol particles.

[1] Lelieveld, J et al., *Cardiovasc. Res.*, **2020**, 116, 1910–1917.

[2] Wragg, F. P. H et al., *Atmos. Meas. Tech.*, **2016**, 9, 4891–4900.

[3] Campbell, S. J et al., *Anal. Chem.*, **2019**, 91, 13088–13095.

One-step extraction of multifunctional lignins from lignocellulosic biomass

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Lignin, one of the main components of biomass, is a promising feedstock to replace those aromatic materials that are currently sourced from non-renewable fossil oil. However, the industrial use of lignin in material application remains limited[1]. This can partially be explained by the uncontrolled side-reactions that happen on the lignin during traditional extraction methods, which despite providing lignin in high yields, irreversibly change its structure. The poor control on the chemical functionalities is what ultimately hinders lignin's further upgrading[2]. We have recently demonstrated that with the Aldehyde Assisted Fractionation (AAF) it is possible to overcome the trade-off between lignin's isolation yields and structure preservation[3]. Moreover, when multifunctional aldehydes are employed, lignin can also be functionalized in a controlled manner[4].

Here, we show how this concept can be expanded to simultaneously extract and introduce two non-native functional groups on the lignin backbone. We functionalized the lignin with aldehydes by using terephthalaldehyde (TALD), and carboxylic acids by using glyoxylic acid (GA). First, we isolated several lignins by performing AAF with increasing ratios of TALD and GA, and then we quantified the introduced functional groups with several spectroscopic techniques. The results clearly showed that the TALD/GA ratio initially used for the AAF linearly correlated with the TALD/GA ratio measured on the isolated lignin.

The different functionalities of TALD/GA lignins were then employed to improve the mechanical properties of gelatin-based hydrogels. We exploited the aldehydic functionalities to perform chemical crosslinking with gelatin, while the carboxylates imparted water solubility properties to the lignin. The rheological, mechanical and structural features of the new hydrogels were then measured and compared to the results obtained for hydrogel obtained in absence of lignin.

Overall, we demonstrated that multifunctional lignins can be designed according to their final application and subsequently extracted in a controlled way and in high yields in one single step from lignocellulosic biomass. Moreover, these lignins can easily be integrated in novel materials for high-end applications.

[1]Vivien Romhányi, David Kun and Béla Pukánszky, *ACS Sust. Chem. Eng.*, **2018**, 6, 14323–14331.
[2]Stefania Bertella and Jeremy Luterbacher, *Trends in Chemistry*, **2020**, 2, 440–453.
[3] Li Shuai, Masoud Talebi Amiri, Ydna Marie Questell-Santiago, Florent Héroguel, Yanding Li, Hoon Kim, Richard Meilan, Clint Chapple, John Ralph and Jeremy Luterbacher, *Science*, **2016**, 354, 329–333.
[4]Stefania Bertella and Jeremy Luterbacher, *Green Chem.*, **2021**, 23, 3459–3467.

Detection and Characterisation of Criegee Intermediates in Secondary Organic Aerosol Particles

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Atmospheric oxidation reactions, such as the ozonolysis of alkenes, contribute substantially to the formation of secondary organic aerosol (SOA) particles, which play a crucial role in air quality and the Earth’s climate. Radical intermediates, for example the Criegee Intermediate (CI), are abundantly formed in the oxidation schemes of organics in the atmosphere. However, their role in gas phase chemistry, particle phase chemistry and aerosol ageing remains uncertain. The detection of CIs in aerosol particles poses an analytical challenge due to their high reactivity, inherently short lifetime and low concentrations.

In this work, developing on the study presented by Giorio et al. [1], we present a novel method that scavenges and stabilises CIs in both the gas phase and particle phase, using the spin trap 5,5-dimethyl-pyrroline-*N*-oxide (DMPO) for gas phase analysis, and *N*-tert-butyl-α-phenylnitrone (PBN) for particle phase analysis. The CI-PBN adduct structures were unambiguously confirmed by nuclear magnetic resonance spectroscopy (NMR). For the first time, multiple particle-bound CIs in SOA particles derived from β-caryophyllene ozonolysis were characterised and quantified using ultra high performance liquid chromatography high resolution mass spectrometry (UHPLC-HRMS). Using synthesised CI-PBN standards, the concentration of two isomeric C_{15} CIs in the particle phase was estimated to constitute approximately 0.1% of the total SOA mass, highlighting the relatively high abundance of these highly reactive species in fresh SOA particles. Furthermore, the lifetime of CIs in highly viscous organic particles was estimated to be in the order of minutes, several orders of magnitude larger than in the gas phase. We determined that the CI-PBN adducts are stable at 5 ^{o}C for days, highlighting the potential to pre-concentrate CI-PBN adducts for ambient measurements at lower CI concentrations. These results demonstrate the potential of this method to both qualitatively and quantitatively study particle-bound radicals and reactive intermediates in situ.

[1] C. Giorio, S. J. Campbell, M. Bruschi, F. Tampieri, A. Barbon, A. Toffoletti, A. Tapparo, C. Paijens, A. J. Wedlake, P. Grice, D. J. Howe and M. Kalberer. *J. Am. Chem. Soc.*, **2017**, 139, 3999–4008.

Catalyst-membrane synergy as a means of improving process intensity and catalyst or metal recovery.

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Homogeneous organometallic catalysis is a technique that has achieved a high level of maturity, and is often an indispensable and reliable method of synthesizing molecular entities produced within several chemical industry sectors [1]. These complexes, however efficient as they are, can be expensive and difficult to remove after reaction. This naturally urged the industry to place emphasis on increasing catalyst turnover numbers (TON) and catalyst recovery [2].

In this context, recent decades have witnessed a significant growth in industrial interest in solvent based separations using membranes stable to organic solvents [3], due in part to the non-thermal, hence mild and energy efficient nature of the technique. The mild nature of membrane separations makes them particularly suited to either downstream processing or integration within reaction systems in which reaction and separation occur simultaneously, a particularly salient example being catalyst recycling [4].

Recent membrane developments include ceramic membranes with modified top-layers designed to effect separation not simply on size exclusion alone, but by also making use of solvent – membrane – solute interactions. These membranes open up the possibility of designing the membrane surface and the catalyst ligands to achieve the desired rejection profile and reaction performance.

This contribution will highlight the ongoing research aimed at catalyst recovery, either internally within a reaction to increase TON or externally i.e. after reaction. To-date the overwhelming majority of examples of metal or catalyst recovery by any technique including membranes, focuses on recovery of the metal, the ligand being typically considered as a single use components. More recently Vito has been researching the possibilities of recovery of catalyst complete with ligands.

[1] J. Magano, J. R. Dunetz, *Chem. Rev.* **2011**, *111*, 2177–2250.

[2] S. Hübner, J. G. de Vries, V. Farina, *Adv. Synth. Catal.* **2015**, 3–25.

[3] P. Marchetti, M. F. J. Solomon, G. Szekely, A. G. Livingston, *Chem. Rev.* **2014**, *114*, 10735–10806.

[4] L. Cseri, T. Fodi, J. Kupai, G. T. Balogh, A. Garforth, G. Szekely, *Adv. Mater. Lett* **2017**, *8*, 1094–1124.

Surface bound molybdenum for the electrochemical detection of phosphate

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Phosphate detection in freshwater is particularly interesting as phosphorus is considered the main responsible for the appearance of eutrophication. Nowadays, two detection methods are mainly employed. The first uses potentiometry and phosphate selective indicators. The second, which is examined in this study, relies on the phosphomolybdenum blue (PMB) reaction. In short, phosphate combines with molybdate under acidic conditions to form a complex that gives an intensely colored species when chemically reduced [1]. The color is detected using spectrophotometry and a calibration procedure enables the direct correlation between phosphate concentration and absorbance, which can then be used for the analysis of phosphate-containing samples of unknown concentration. A similar procedure can take place using voltammetry to electrochemically reduce the complex, thus avoiding the use of chemical reducing reagents. Here, the phosphomolybdenum complex is trapped and directly reduced at the surface of an electrode, at an adequate potential window that enables the reaction to take place. Voltammetric methods that have been examined include amperometry, cyclic voltammetry and square wave voltammetry.

Except for one study [2], the molybdate needed for the PMB reaction is provided in solution form; either it is added through the flow stream in the detection cell, or it is directly produced in situ. With the molybdate ions present in solution, the next step for the formation of the complex is the addition of phosphate. Our goal in this study is to develop a matrix material that can be used both as molybdate source and phosphate accumulator, avoiding thus the addition of molybdate in the sample solution. Molybdate speciation in aqueous solutions changes depending on the pH and different phosphomolybdate species may be formed under different acidic conditions [3].

Taking this into account, we tested different materials incorporating polycationic or polyanionic electrolytes and molybdate in various pH values. Using square wave voltammetry, we examined the performance of glassy carbon electrodes coated with these substrates. A custom-made flow cell was manufactured for the continuous flow of phosphate solutions, simulating the flow of freshwater under realistic conditions. The cell incorporates all electrodes needed for the voltammetric measurements, including an inlet and outlet for the incoming flow. By testing different phosphate concentrations, we observed an increase of peak current at a characteristic potential after various contact times. The onset of this peak current increase (in terms of time) was proportional to the concentration of phosphate solution examined. This indicates an accumulating effect of phosphate in the substrate. This research aims to achieve phosphate detection at sub-micromolar concentrations.

[1] J. Murray, J.P. Riley, Analytical Chemica Acta, 1962, 27, 31-36.

[2] Sheela Berchmans, Rengasamy Karthikeyan, Sandeep Gupta, Gérrard Eddy Jai Poinern, Touma B. Issa, Pritam Singh, Sensors and Actuators B, 2011, 160, 1224-1231.

[3] Edward A. Nagul, Ian D. McKelvie, Paul Worsfold, Spas D. Kolev, Analytica Chimica Acta, 2015, 890, 60-82.

Bimetallic Palladium-Gallium catalysts for the hydrogenation of CO_2 to Methanol

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In combination with the generation of green hydrogen, the thermochemical hydrogenation of CO_2 to methanol represents an appealing reaction for the mitigation of anthropogenic emissions, by re-integrating CO_2 to a closed carbon fuel cycle.[1] Where economically viable, efficient conversion of CO_2 to methanol has the potential to enable the progressive decarbonisation of energy systems, resulting in a so-called 'methanol economy'. However, the development of active, selective and stable catalysts for this transformation remains challenging. For the most part, improvements are made on an empirical basis, through modification of metal, support, promoters and additives, which have been shown to have a profound influence on the observed reactivity, and selectivity for the desired product, methanol.

To confront this observation, and further explore the role of oxide support in driving selectivity for the Pd-catalysed conversion of CO_2 to methanol, we employed a Surface organometallic chemistry (SOMC) approach to generate well-defined supported Pd nanoparticles on doped oxide supports as model materials (Figure 1, left). [2] A major advantage of SOMC, in contrast to classical catalyst preparation methods, is the controlled introduction of well-defined molecular precursors. In this work, we developed a bimetallic Pd-Ga catalyst that is 40 times more active than monometallic Pd@SiO_2, and an order of magnitude more active than benchmark Cu-based systems in the hydrogenation of CO_2 to methanol (Figure 1, centre). Study of the catalyst under reaction conditions by *in situ* X-ray Absorption Spectroscopy (XAS) reveals the presence of an alloyed phase, which undergoes partial (and reversible) oxidation under reaction conditions, while study of the carbon-containing surface species, using *operando* Infrared (IR) spectroscopy shows that the observed surface species are highly dependent on the chemical potential of the gas phase (Figure 1, right). In sum, XAS and IR show that the observed intermediates, and surface Ga species respond to subtle changes composition of the gas phase – highlighting the dynamic nature of these catalytic systems, and informing the design of improved catalysts.

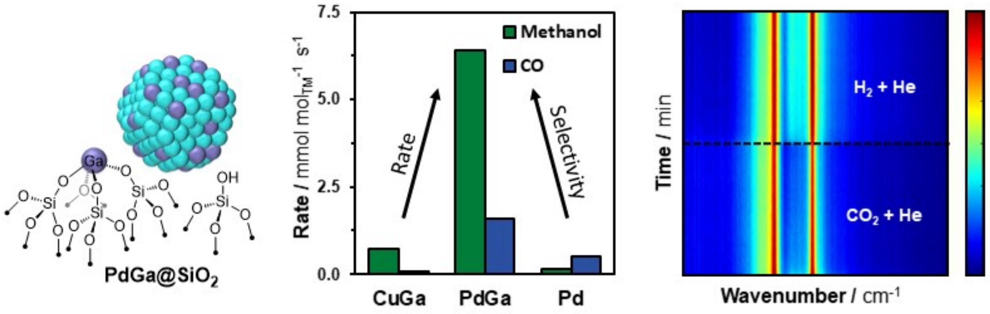

Figure 1. *(left) PdGa@SiO_2, (centre) comparison of rates, and (right) in situ IR for PdGa@SiO_2*

[1] S. R. Docherty, C. Copéret, *J. Am. Chem. Soc.* **2021**, *143*, 6767–6780.

[2] S. R. Docherty, N. Phongprueksathat, E. Lam, G. Noh, O. V. Safonova, A. Urakawa, C. Coperet, *JACS Au* **2021**, *1*, 450–458.

Submersible Probe with In-line Calibration and Symmetrical Reference Element for Long-term Continuous Measurements

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Nitrogen plays an essential role in plant and crop growth, promoting photosynthesis, which is essential for a healthy ecosystem. Although nitrogen is naturally present in the atmosphere, plants mostly absorb it through the soil. To enhance plant growth and therefore productivity, nitrate fertilisers have been used routinely in agriculture all over the world. At the same time, due to leaching in the groundwater or surface runoff, nitrate pollution has become an increasing concern for water pollution. In 1991, the European Commission (EC) established a decree aiming to reduce nitrate pollution and prohibit further pollution [1]. Since this directive, the use of nitrate-based fertilisers has been more adequately regulated and systematic water quality monitoring has been implemented. Although recent trends show a decrease of nitrate levels and an increase of the general water quality, the monitoring process is not uniform and still rather tedious. The current strategy relies on fixed sampling stations and punctual sampling at strategic sites, which both require manpower and expensive measurement techniques making it impossible to ensure a constant monitoring of nitrate levels.

Submersible potentiometric probes have been used previously in environmental studies [2], but they require a pump to drive the sample towards the measuring site. To enable constant monitoring, the pump would have to run continually, which would lead to unreasonable power consumption.

We present here a simple nitrate-selective submersible potentiometric probe, that has the ability to perform constant monitoring for extended periods of time independently. In this new design, the probes are located in a small recess and are in direct contact with the sample allowing constant monitoring without any additional power required. A small peristaltic pump has been programmed to run briefly at a predetermined time interval to perform a one-step calibration that is used to correct underlying drifts that would bias the signal. A new reference element based on the principle of electrochemical symmetry, has also been tested and implemented to reduce temperature influence on the sensor signal. With this low power consumption and signal correction method, it is estimated that this system can run maintenance-free for three months. Finally, to assess the potential of this new probe, we compared it to traditional measurement methods during a field campaign.

[1] EC (1991) Council Directive 91/676/EEC of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources. *European Commission (EC). Official Journal L 375*, **31/12/1991**, 0001–0008.

[2] Nadezda Pankratova, Gaston A. Crespo, Majid Ghahraman Afshar, Miquel Coll Crespi, Stéphane Jeanneret, Thomas Cherubini, Mary-Lou Tercier-Waeber, Francesco Pomati, Eric Bakker, *Environmental Science: Processes & Impacts,* **2015**, 17 (5), 906-914

Tetraaza[14]annulene-Based Covalent Organic Frameworks: An Intriguing Class of Catalytically Active Porous Materials

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CO_2 being the main source of man-made climate change resulted in an increased interest in sophisticated, tunable, and highly porous materials capable to either capture and or directly use CO_2 as a feedstock towards value-added products. Low-density porous materials such as porous organic polymers (POPs)[1] and their crystalline counterparts covalent organic frameworks (COFs), have received considerable attention in this regard due to their chemical tunability and high surface areas. Especially the ordered framework structure of COFs and the abundantly present catalytic sites – given suitable functionalization - make them highly interesting for gas sorption, separation, and conversion applications.[2]

Among COFs, those incorporating metal-containing building blocks such as porphyrins, phthalocyanines or salphenes show exceptional electrical and catalytic properties. Moreover, the chemical tunability of these COFs by the choice of linkers and metal ions, makes them especially promising to tackle the highly specific demands for CO_2 capture and conversion.[3] Recently, a novel group of metal-containing building blocks – tetraaza[14]annulenes – was used in a Ni^{II}-based metal-organic framework and was shown to have semiconductive properties. However, the molecular design of the framework material proved to be detrimental to its porosity and diminished its potential for gas sorption and conversion applications.[4] In this contribution, we present our recent advances in utilizing a rigid and suitably functionalized tetraaza[14]annulene-based precursor to obtain microporous, tunable and catalytically active azaannulene-based COFs. We also present the textural properties of the frameworks along with their affinity towards small gases i.e., CO_2.

[1] K. Kim, S. Kim, S. N. Talapaneni, O. Buyukcakir, A. M. I. Almutawa, K. Polychronopoulou and A. Coskun, *Polymer* **2017**, *126*, 296-302.
[2] O. Buyukcakir, S. H. Je, S. N. Talapaneni, D. Kim and A. Coskun, *ACS Applied Materials & Interfaces* **2017**, *9*, 7209-7216.
[3] M.-D. Zhang, D.-H. Si, J.-D. Yi, S.-S. Zhao, Y.-B. Huang and R. Cao, *Small* **2020**, *16*, 2005254.
[4] Y. Jiang, I. Oh, S. H. Joo, O. Buyukcakir, X. Chen, S. H. Lee, M. Huang, W. K. Seong, S. K. Kwak, J.-W. Yoo and R. S. Ruoff, *Journal of the American Chemical Society* **2019**, *141*, 16884-16893.

Autonomous *in situ* voltammetric monitoring of inorganic arsenic speciation

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Arsenic is a metalloid ubiquitous in aquatic systems of global concern, with its sources being of natural and anthropogenic origins. It is classified as a Group 1 human carcinogenic substance and acts as an endocrine disruptor. The international provisional guidelines for water quality and water quality criteria derived in an attempt to protect a pre-determined percentage of living species are all based on total dissolved As concentration. However, it is well known that the toxicity and bioavailability of As is highly dependent on its chemical form and oxidation state. Arsenic in the water environment is mainly present in the form of inorganic trivalent (As(III) - more toxic) and pentavalent (As(V) - less toxic) oxyanions. Inorganic As speciation is regulated by both biotic and abiotic processes [1]. These processes are function of the bio-physicochemical conditions of the media that may vary continuously in space and time. It is therefore important to closely monitor the concentrations and the speciation of both inorganic As species *in situ* and at an appropriate time scale to correctly assess their behavior and the resulting potential threat to water ecosystems and human health. Voltammetry is an attractive candidate to achieve this goal [2,3].

We report here on the development of an innovative analytical approach enabling in-situ direct quantification of the fractions of As(III) and As(V) available for bio-uptake, the so called dynamic metal fraction. The set-up consists on an antifouling gel-coated nanofilament gold-plated microelectrode array (AuNF-GIME) incorporated in a submersible probe. Optimization of the analytical protocols for the preparation of the AuNF-GIME and the sequential detection of the dynamic As(III) and As(V) at natural pH, results of the *in situ* conducted measurements, and complementary laboratory analyses contributing to a deeper understanding of the behavior and fate of the potentially bioavailable inorganic arsenic species in surface water will be presented.

[1] Laura Barral-Fraga, María Teresa Barral, Keeley L. MacNeill, Diego Martiñá-Prieto,Soizic Morin, María Carolina Rodríguez-Castro , Baigal-Amar Tuulaikhuu and Helena Guasch, *International Journal of Environmental Research and Public Health*, **2020**, 17, 2331-2359.

[2] Mary-Lou Tercier-Waeber, Marianna Fighera, Melina Abdoua, Eric Bakker, Peter van der Wal, *Sensors and Actuators B: Chemical*, **2021**, 328, 128996.

[3] Kristoff Gibbon-Walsh, Pascal Salaün, Constant M.G. van den Berg, *Analytica Chimica Acta*, **2012**, 710, 50-57.

Ensuring healthy babies through non-target screening of disposable baby diapers

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The object of the study is to analyze all disposable baby diapers present on the Belgian market in order to assess their possible content of residues of organic substances. All available baby diapers were collected on the Belgian market and the textile parts of these diapers were extracted and analyzed. The analysis consisted of 2 parts; a non-target screening and a target analysis. The aim of the non-target screening is to assess the possible content of substances in diapers on a large scale and to semi-quantify a list of preselected CMR (carcinogenic, mutagenic or toxic to reproduction) and (possible) EDC (Endocrine Disrupting Chemicals) substances. The target analysis was performed to verify the outcome of the non-target screening and to expand the list of the targeted preselected compounds for a proper quantification of polyaromatic hydrocarbons, biocides, phthalates, phenolic compounds (e.g. nonylphenol), perfluorooctanoic acid (PFOA), BTEX (benzene, toluene, ethylbenzene and xylenes), caprolactam and dioxins using specific analytical techniques.

The extra compounds found with the non-target screening (e.g. nonylphenol, caprolactam,…) were included in the target list and confirmed with the target analysis (highest level of confidence according to the schymanski scale[1]. This makes the non-target screening a powerful tool for the screening of potential harmful, carcinogenic or reprotoxic chemicals .

The target results showed that for most of the selected compounds the concentrations were below the limit of quantification. Other compounds were detected but the concentrations were (very) low (below 1 mg/kg). As a general conclusion, it can be stated that baby diapers present on the Belgian market at the time of the study were free of or only contained negligible amounts of the investigated harmful, carcinogenic or reprotoxic chemicals.

[1] Schymanski, Emma L, Junho Jeon, Rebekka Gulde, Kathrin Fenner, Matthias Ru, Heinz P Singer, and Juliane Hollender, *Environmental Science & Technology* , 2014, 48 (4): 2097–98.

Chemical Mechanism of Microbial Metal Reduction

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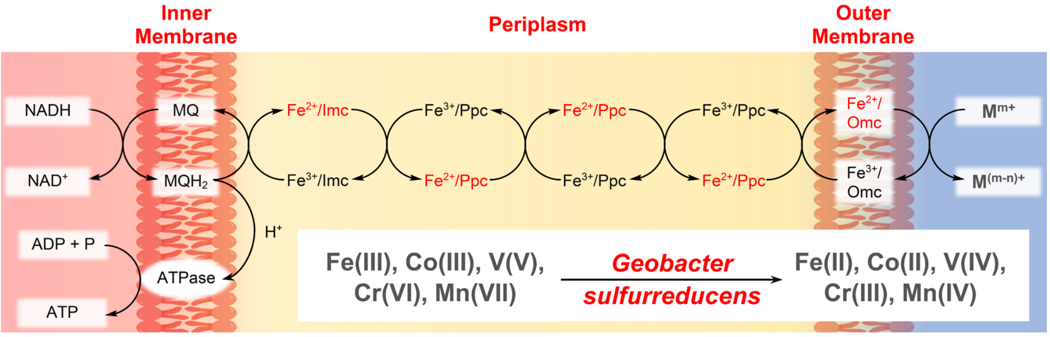
Geobacter sulfurreducens microorganisms are of global ecological significance. They clean polluted water from carcinogenic Cr(VI), antibiotic Ag(I) or radioactive U(VI) salts by reduction into less toxic or easily removable products. These bacteria have learned to survive in the absence of O_2 using Fe-oxide minerals as extracellular oxidants for their respiration.



Respiration occurs by extracellular electron transfer (EET) from NADH in the cytoplasm to the extracellular metal salts. Electron donors and electron acceptors are located in different compartments, which are separated from each other by the inner and the outer cell membranes, and electrons are transported between them by Fe^{2+}/hemes of *c*-cytochromes. Our kinetic experiments demonstrate that respiration is independent of the concentration and the type of the metal salts, which leads to ATP homeostasis. If the workload demands higher ATP production, an increase of the Fe^{2+}/Fe^{3+} ratios in the cytochromes speeds up the EET rates. As a consequence of the different kinetic order of the oxidants and the electron transporting Fe^{2+}/hemes, the bacteria are both highly stable as well as highly flexible, and can do their job under changing environmental conditions.

[1] V. Chabert, L. Babel, M. P. Füeg, M. Karamash, E. S. Madivoli, N. Herault, J. M. Dantas, C. A. Salgueiro, B. Giese, K. M. Fromm, *Angew. Chem.*, **2020**, 59, 12331-12336.

Engineering extracellular electron transfer in *Escherichia coli* for microbial electrochemical systems

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Microbial electrochemical systems (MES) hold great potential for green chemical synthesis, as well as bio-electricity generation from organic waste. The herein used microorganisms are commonly bacteria known as exoelectrogens, which evolved to use extracellular electron transfer (EET) to solid substrates for cellular respiration. While this makes them perfect for electron exchange with electrodes in MES, they often lack in metabolic capabilities necessary for utilization of a broad substrate spectrum or synthesis of specific products. On the contrary, *Escherichia coli* strains lack efficient EET pathways, but are host to rich metabolic reaction networks, which can further be expanded through readily available synthetic biology tools.

In this work, we systematically engineered *E. coli* for enhanced EET. To this end, we expressed proteins from the exoelectrogen *S. oneidensis* MR-1, as well as *E. coli* native proteins involved in electron transfer across the cells insulating envelope. Final engineered strains showed significant improvements in electron transfer rates, as shown through reduction of soluble electron acceptors and electrodes. This paves the way for increased efficiency of existing *E. coli* based MES, and development of new applications.

Predicting pesticide biotransformation products and half-lives in soil and sediment

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Man-made chemicals accumulating in the environment can pose a serious threat to the local ecosystem. Therefore, predicting microbial biotransformation pathways and half-lives of trace contaminants such as pesticides is crucial to understand their fate and to anticipate possible risks. Pesticides, in particular, not only accumulate in agricultural soil, but can also end up in sediments of water bodies through runoff from agricultural areas, making it a priority to study their fate in soil and sediment.

The platform enviPath combines a large collection of biodegradation data, consisting of biodegradation pathways and half-lives of chemicals in the environment including associated metadata on study conditions, with a machine learning-based prediction engine that suggests potential biodegradation products and pathways [1], [2]. Pathway predictions are obtained by applying expert-curated biochemical transformation rules to the chemical of interest, and guided by machine learning algorithms trained on the experimental biodegradation data in enviPath.

Here, we present the latest improvements on the enviPath framework. We complemented its collection of biodegradation data in soil with biodegradation data in sediment, which were obtained from freely accessible regulatory dossiers. In addition, we expanded the set of biotransformation rules toward enzymatic mechanisms that are relevant for the biodegradation of pesticides, thus widening the chemical scope of our prediction platform.

Thanks to the newly integrated data and the extended set of biotransformation rules, we could improve the predictive power of enviPath for the biodegradation of pesticides. We hope that with this contribution we will increase the relevance of enviPath predictions with respect to pesticide degradation and provide a useful tool to the scientific community for a variety of applications.

[1] Jörg Wicker, Tim Lorsbach, Martin Gütlein, Emanuel Schmid, Diogo Latino, Stefan Kramer, Kathrin Fenner, *Nucleic Acids Research*, **2015**, 44 (D1), D502-D508.
[2] Diogo Latino, Jörg Wicker, Martin Gütlein, Emanuel Schmid, Stefan Kramer, Kathrin Fenner, *Environmental Science: Processes & Impacts*, **2017**, 19 (3), 449–64.

Bioengineered photosynthetic bacteria for enhanced electrogenic capabilities.

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Cyanobacteria are the most abundant photosynthetic organisms in the biosphere, residing in almost every aquatic habitat. They are gram-negative photosynthetic organisms, which possess light-active pigments (chlorins, bilins and carotenoids).

Since the discovery of their light-dependent electrogenic capability, their application in biophotovoltaics (BPVs) has grown for the development of cost-effective, renewable energy [1-4]. Moreover, familiarity of the genome of specific strains, such as the *Synechocystis* sp. PCC 6803, has further motivated the use of synthetic biology for genetic engineering purposes.

In this work we investigate how the expression of heme-containing proteins in living *Synechocystis* sp. PCC 6803 affect their light-dependent bioelectricity generation. We found that the these cells show sustained growth, photosynthetic activity and 2-fold increase in light-dependent extracellular electron transfer compared to unmodified wilde-type control cells.

[1] McCormick, A. J., Bombelli, P., Scott, A. M., Philips, A. J., Smith, A. G., Fisher, A. C., & Howe, C. J. (2011). Photosynthetic biofilms in pure culture harness solar energy in a mediatorless bio-photovoltaic cell (BPV) system. Energy & Environmental Science, 4(11), 4699-4709.

[2] Schuergers, N., Werlang, C., Ajo-Franklin, C. M., & Boghossian, A. A. (2017). A synthetic biology approach to engineering living photovoltaics. Energy & environmental science, 10(5), 1102-1115.

[3] Mouhib, M., Antonucci, A., Reggente, M., Amirjani, A., Gillen, A. J., & Boghossian, A. A. (2019). Enhancing bioelectricity generation in microbial fuel cells and biophotovoltaics using nanomaterials. Nano Research, 1-16.

[4] Reggente, M., Politi, S., Antonucci, A., Tamburri, E., & Boghossian, A. A. (2020). Design of Optimized PEDOT-Based Electrodes for Enhancing Performance of Living Photovoltaics Based on Phototropic Bacteria. Advanced Materials Technologies.

Carbon nanotube uptake in photosynthetic bacteria enhanced bioelectricity generation in living photovoltaics

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The distinctive properties of single-walled carbon nanotubes (SWCNTs) have inspired the development of many novel applications in the field of cell nanobiotechnology. However, studies thus far have not yet explored the effect of SWCNT functionalization on transport across the cell walls of prokaryotes.

In this study, we explore the uptake of functionalized SWCNTs (f-SWCNTs) in Gram-negative cyanobacteria. A custom-built, spinning-disc confocal microscope is used to image the distinct near-infrared (NIR) SWCNT fluorescence interacting with the bacterial cells. We demonstrate that f-SWCNTs spontaneously penetrate the cell walls of both unicellular *Synechocystis* sp. PCC 6803 and filamentous *Nostoc* sp. Real-time NIR monitoring of cell growth and division further reveal that the SWCNTs are inherited by daughter cells. Moreover, these nanobionic living cells show retained photosynthetic activity and an improved photo-exoelectrogenicity when incorporated into bioelectrochemical devices.

Fluorescent pH-Sensitive Wood Membranes

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Indoor lighting has a substantial influence on people’s wellbeing but is often non-sustainable, made of glass or plastics. Wood, a renewable and CO_2-storing material with excellent mechanical properties, is a promising substrate for developing sustainable indoor lighting materials [1].

State-of-art reports of wood-based lighting applications make use of potentially toxic quantum dots as fluorophores or impregnate the wood structure with non-biodegradable polymers to improve the matrix transparency, compromising sustainability [2-4].

Our approach makes use of the intrinsically hierarchical wood structure to achieve uniform illumination, maintaining sustainability and aesthetic appearance. We studied how light propagates inside wood as a function of different parameters (wood species, cut direction, lignin composition). We then impregnated wood with environmentally friendly fluorescent metal-organic complexes. In addition to their strong photoluminescence, these metal-organic fluorophores are also responsive to acidic or basic gases, allowing their use as sensors of indoor air quality.

Our concept is applicable even to large-scale applications and, thanks to the preservation of the natural wood structure, could be highly attractive for interior design (such as for lamps or luminescent partition walls).

[1] K. Strobel, A. Q. Nyrud, and K. Bysheim, “Interior wood use: linking user perceptions to physical properties,” *Scand. J. For. Res.*, vol. 32, no. 8, pp. 798–806, 2017, doi: 10.1080/02827581.2017.1287299.

[2] Q. Fu *et al.*, “Luminescent and hydrophobic wood films as optical lighting materials,” *ACS Nano*, vol. 14, no. 10, pp. 13775–13783, 2020, doi: 10.1021/acsnano.0c06110.

[3] K. Yu, T. Fan, S. Lou, and D. Zhang, “Biomimetic optical materials: Integration of nature’s design for manipulation of light,” *Prog. Mater. Sci.*, vol. 58, no. 6, pp. 825–873, 2013, doi: 10.1016/j.pmatsci.2013.03.003.

[4] L. A. Berglund and I. Burgert, “Bioinspired Wood Nanotechnology for Functional Materials,” *Adv. Mater.*, vol. 30, no. 19, pp. 1–15, 2018, doi: 10.1002/adma.201704285.

Estimation of Swiss Halocarbon Emissions Using Regional Atmospheric Measurements

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Man-made halocarbons contribute approximately 11% to the current anthropogenic radiative forcing by long-lived greenhouse gases (GHGs). Moreover, chlorinated or brominated halocarbons cause stratospheric ozone depletion. Therefore, the production and consumption of halocarbons is regulated by international treaties. To derive real-world estimates of halocarbon emissions, so called "top-down" inverse modeling approaches have been developed. These methods rely on atmospheric observations at sites that capture global or continental background concentrations. However, to estimate halocarbon emissions on a country to local level and to validate national emission inventories, additional regional-scale measurements are required.

We present 12 months of continuous halocarbon measurements at the Beromünster tall tower in the center of the Swiss Plateau, and complement these observations with data from the Sottens tall tower in the western part of the Swiss Plateau, which are currently being acquired. Together, the two sites are sensitive to the most densely populated and industrialized region of Switzerland. High-precision, high-frequency atmospheric measurements were obtained directly on-site: Two-Liter air samples were pre-concentrated at low temperatures, before the analytes were separated and detected by gas chromatography and quadrupole mass spectrometry (GC-MS).

Based on the records at Beromünster, we determined emissions of 28 halocarbons regulated by the Montreal and Kyoto Protocols. We quantified the emissions using two independent top-down methods: a tracer ratio method, and a Bayesian inversion based on regional atmospheric transport modeling. We found good agreement between our top-down and the national inventory values for the major hydrofluorcarbons (HFCs), whereas for HFC-134a, our calculated emissions of 300 Mg yr^{-1} hinted at a possible, considerable overestimation of the Swiss GHG inventory as reported to the United Nations Framework Convention on Climate Change (UNFCCC). For the banned chlorofluorocarbons (CFCs) and the regulated hydrochlorofluorocarbons (HCFCs), we observed ongoing outgassing from existing foams and refrigerators. Finally, we report the first Swiss emission estimates of in total 50 Mg yr^{-1} for three recently phased-in, unregulated hydrofluoroolefins (HFOs). The Beromünster-based emission results are currently being complemented with the Sottens records to give an even more substantial and highly resolved picture for Switzerland.

Co/Ni-Polyoxotungstates as photocatalysts and precursors for electrocatalytic water oxidation

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Artificial photosynthesis is an effective and elegant chemical transformation for renewable energy sources via sunlight driven water splitting into hydrogen and oxygen. This complex four electron transfer process needs to be conquered, which renders the development of efficient, cost-effective, stable and noble-metal free water oxidation catalysts crucial for artificial photosynthesis. To this end, polyoxometalates (POMs) are promising water oxidation catalysts due to their combination of robustness and structural as well as redox versatility that enables rapid, reversible and stepwise multi-electron transfer reactions.[1] Due to their low cost, 3d transition metal complexes, especially of cobalt, are widely researched as homogeneous catalyst alternatives to noble metals.[2]

In this study an open-core cobalt POM $[(A\text{-}a\text{-}SiW_9O_{34})Co_4(OH)_3(CH_3COO)_3]^{8-}$ **Co(1)** and its isostructural cobalt/nickel structure $[(A\text{-}a\text{-}SiW_9O_{34})Co_{1.5}Ni_{2.5}(OH)_3(CH_3COO)_3]^{8-}$ **CoNi(2)** were synthesized, analyzed and their photocatalytic activity was investigated. In search of new pathways to electrocatalysts, further annealing of both compounds at various temperatures between 300 and 500 °C led to amorphous and crystalline $CoWO_4$- and $(Co_{1.5}Ni_{2.5})$ WO_4-related nanoparticles. These nanoparticles were further analyzed and their electrocatalytic performances were investigated, with highest activities obtained at the annealing temperature of 300 °C. Comparison of these results with an as-synthesized $CoWO_4$ reference material and its nickel doped analogue revealed that POMs are very promising precursors for electrocatalytic materials.[3]

[1] D.Gao, I. Trentin, L. Schwiedrzik, L. Gonzàlez and C. Streb, *Molecules*, **2019**, 25, 157 – 177
[2] X.-B. Han , D.-X. Wang , E. Gracia-Espino , Y.-H. Luo , Y.-Z. Tan , D.-F. Lu , Y.-G. Li , T. Wågberg , E.-B. Wang and L.-S. Zheng , *Chin. J. Catal.*, **2020**, 41 , 853 —857.
[3] R. Güttinger, G. Wiprächtiger, O. Blacque, and G. R. Patzke, *RSC Adv.* **2021**, 11, 11425 - 11436

Stable Solid Electrolyte Interphase Formation Induced by Monoquat-Based Anchoring in Lithium Metal Batteries

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Lithium (Li) metal anode is considered to be a highly promising candidate for the next generation batteries with high energy density. However, some significant challenges such as uncontrolled Li dendrite growth, unstable solid electrolyte interface (SEI) layer and coulombic efficiency (CE) decay impeded the practical use of Li-metal anodes. Herein, we introduced “anchoring strategy” based on monoquat salts as electrolyte additives.[1] We varied systematically the number and spatial arrangement of anchoring units to reveal the structural effects on Li plating morphology and battery performance. Moreover, the presence of pyridium cations bearing PF_6 counteranions enabled high surface concentration of anions, thus leading to the formation and homogeneous distribution of LiF on the electrode surface. Our results revealed that monoquat dication with two anchoring pyridine sites gives rise to an ionically conductive, dense solid electrolyte interphase and superior cycling performance in both ether-based and carbonate-based electrolytes, thus showing the importance of anchoring strategy as well as the number and spatial arrangement of anchoring units. Our approach can be further extended to other alkali metal batteries that suffer from interfacial instability originating from undesired morphology evolution.

[1] T. Zhou, Y. Zhao, M. El Kazzi, J. W. Choi, A. Coskun, *ACS Energy Letters,* **2021**, *6*, 1711-1718.