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Materials Chemistry and the Future of Human Civilization

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From the Stone Age to the Bronze Age to the Iron Age, every major advance in human civilization has been driven by a development in Materials. The forthcoming end of today's Silicon Age, in which aspects of society as diverse as commerce, transportation and communication are underpinned by silicon-based microelectronic devices, offers a unique opportunity -- defining the future of civilization -- and challenge -- how to maintain and improve our modern way of life -- to Materials Chemists. I will discuss how developments in Materials Chemistry are essential for addressing many of the world's most urgent problems, and present one of my favourite emerging material classes, the multiferroics, which could help facilitate the transition to a new energy-efficient, climate friendly Age.

End-functionalized high dielectric permittivity polysiloxanes for solvent-free processing

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High dielectric permittivity polysiloxanes have interesting properties for applications in batteries and dielectric elastomer transducers.[1,2] A major challenge is to synthesize materials combining high dielectric permittivity with good elastic properties. Such materials can be achieved with polar polysiloxanes with defined end groups. However, their synthesis is challenging because anionic ring-opening polymerization (AROP) in the presence of an end blocker gives a low degree of end functionalization. Additionally, certain end groups prove difficult to introduce when polar groups are grafted through post-polymerization reactions. Controlled and defined end groups are highly desirable as they allow better control of the cross-linking and fine-tuning of the mechanical properties. Here, we present a synthetic route to a polar polysiloxane with defined and reactive end groups. The synthesis is based on the hydrolysis condensation of polar dichlorosilanes to give polar polysiloxanes with silanol end groups. The subsequent condensation of the silanol end groups with vinylchlorosilane allows the formation of a polar polysiloxane with vinyl end groups. The degree of polymerization, the amount of low molecular cyclic siloxanes, and the efficiency of the end-functionalization were investigated by 29Si NMR. Additionally, polar polysiloxanes with other end groups are accessible using other chlorosilanes for the end-group functionalization. The synthesized low-viscosity polar polysiloxanes allow solvent-free processing by blade or slot-die coating to give defect-free thin films with improved performance.

[1] Dorina M. Opris, *Advanced Materials*, **2018**, 30, 1703678.
[2] Hualan Wang, Shuangxi Chen, Yan Li, Yongfeng Liu, Qiuju Jing, Xue Liu, Zhaoping Liu, Xiaogang Zhang, *Advanced Energy Materials*, **2021**, 11, 2101057.

A Dye-Sensitized Sensor for Oxygen Detection under Visible Light

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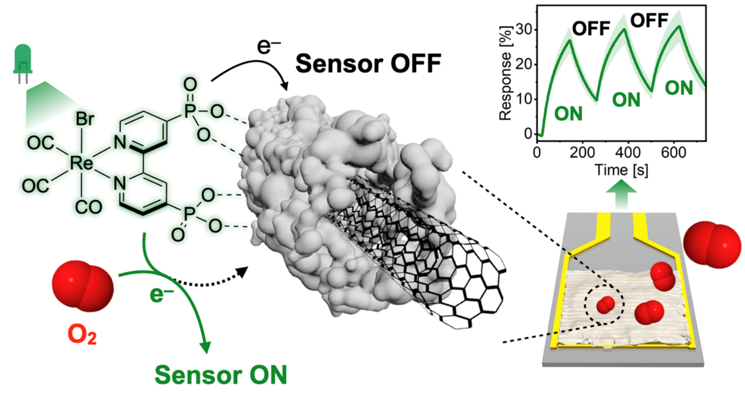
As humanity strives to improve environmental stewardship in the 21st century, sensors that provide real-time information about their chemical surroundings will play an essential role. In particular, the accurate assessment of oxygen (O_2) levels is crucial for a range of applications including personal health protection, water quality monitoring, and automobile exhaust analysis.[1,2] For this purpose, lightweight chemiresistive sensors based on carbon nanomaterials represent an attractive chemical detection platform owing to room-temperature operation and the possibility of incorporation into low-cost microelectronic devices with minimal power requirements.[3]

Herein, we present a chemiresistive sensor that allows for the rapid detection of O_2 at room temperature under visible light illumination.[4] Inspired by the operating principles of dye-sensitized solar cells,[5] the chemiresistor is based on a single-walled carbon nanotube-titania hybrid (SWCNT-TiO_2) bearing a molecular Re photosensitizer $[(^{P}bpy)(CO)_3ReBr]$ (^{P}bpy = 4,4'-$[P(O)(OH)_2]_2$-2,2'-bipyridine). Under green light illumination, the resulting **SWCNT-TiO_2-Re** composite undergoes photoinduced charge transfer that is sensitive to parts-per-billion levels of O_2, resulting in a rapid and reversible chemiresistive response. Due to its mode of operation and robust components, the sensor shows a high degree of selectivity to O_2 over a wide range of interferants, humidity tolerance, and multi-month benchtop stability. The approach presented herein demonstrates the translatability of concepts in light harvesting to the development of high-performance sensing technologies.



[1] I. Bergman, *Nature* **1968**, 218, 396–396.
[2] S. Jouanneau, L. Recoules, M. J. Durand, A. Boukabache, V. Picot, Y. Primault, A. Lakel, M. Sengelin, B. Barillon, G. Thouand, *Water Res*. **2014**, 49, 62–82.
[3] D. R. Kauffman, A. Star, *Angew. Chem. Int. Ed*. **2008**, 47, 6550−6570.
[4] L. Wettstein, J. Specht, V. Kesselring, L. Sieben, Y. Pan, D. Käch, F. Krumeich, D. Baster, M. El Kazzi, M. J. Bezdek, *Manuscript submitted.*
[5] Y. Ren, D. Zhang, J. Suo, Y. Cao, F. T. Eickemeyer, N. Vlachopoulos, S. M. Zakeeruddin, A. Hagfeldt, M. Grätzel, *Nature* **2023**, 613, 60–65.

Supramolecular Modulation for Hybrid Perovskite Photovoltaics

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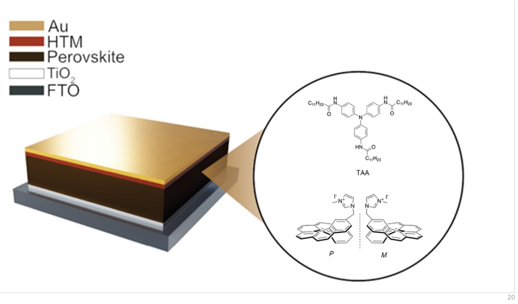
Hybrid perovskites are emerging as top contenders in the next generation of photovoltaics, yet their stability under operational conditions remains a significant challenge. Specifically, degradation occurs at the interface with charge transport layers in perovskite solar cells during operation.[1] To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



[1] Luo, W.; AlSabeh, G.; Milić, *Photochemistry* **2022**, *50*, 342−366.

[2] M. Almalki, G. AlSabeh, M. A. Ruiz-Preciado, H. Zhang, M. Galerne, E. Moulin, F. T. Eickemeyer, S. M. Zakeeruddin, J. V. Milić, N. Giuseppone, M. Grätzel, *Adv. Mater. Interfaces* **2024**, doi: 10.101002/admi.202301053.

[3] G. AlSabeh, M. Almalki, S. Kasemthaveechok, M. A. Ruiz-Preciado, H. Zhang, N. Vanthuyne, P. Zimmermann, D. Dekker, F. T. Eickemeyer, A. Hinderhofer, F. Schreiber, S. M. Zakeeruddin, B. Ehrler, J. Crassous, J. V. Milić, and M. Grätzel, *Nanoscale Adv.* **2024**, doi: 10.1039/d4na0002g.

All-Perovskite Multicomponent Nanocrystal Superlattices

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Self-assembly of colloidal nanocrystals (NCs) into highly ordered structures – superlattices (SLs) – became feasible a few decades ago with the first successful syntheses of monodisperse and shape-uniform colloidal NCs [1]. The close proximity of NCs with long-range positional and orientational ordering facilitates the emergence of diverse synergistic and collective effects, significantly different from ensemble-average properties. In this regard, monodisperse and size-tunable lead halide perovskite NCs have drawn much attention owing to their spectrally tunable and narrow, fast and optically coherent fluorescence. In particular, $CsPbBr_3$ NCs assembled into the single-component SLs were shown to exhibit superfluorescence – collective light emission [2]. This stimulated the research into their multicomponent SLs, where lead halide perovskite NCs are co-assembled with dielectric NCs acting as spacers between fluorescent NCs. Consequently, a plethora of novel SL types has become accessible, displaying the superfluorescence phenomena as well [3]. An interesting avenue, therefore, is to devise SLs comprising several distinct kinds of light emitters. To this end, we succeeded to co-assemble differently sized $CsPbBr_3$ NCs into various binary SLs (ABO_6-, ABO_3- and NaCl-types) with a high degree of ordering and a large domain area. For ABO_6-type SL, a model system containing two types of luminescent NCs in different confinement regimes, we explored NC coupling within the SL and revealed, for the first time, a highly efficient Förster-like energy transfer from strongly confined NCs to weakly confined NCs. In a strong excitation regime, the ABO_6-type SL exhibits key signatures of SF, corroborating the occurrence of collective emission behavior. Spatiotemporal exciton dynamics measurements reveal enhanced exciton diffusivity in binary SL compared to single-component SL [4].

[1] M. A. Boles et al. Chem Rev. 2016, 116, 11220-11289.

[2] G. Rainò et al. Nature, 2018, 563, 671-675.

[3] I. Cherniukh et al. Nature, 2021, 593, 535-542.

[4] T. V. Sekh et al. ACS Nano, 2024, 18, 8423-8436.

hybrid hole-selective protection layer towards long-term stability of low-cost metal oxide in solar water oxidation

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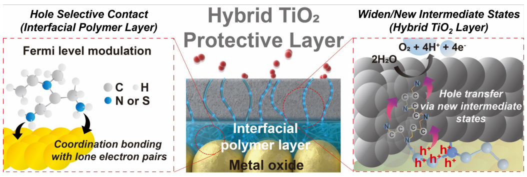
The (photo)corrosion of earth-abundant metal oxide photoanodes remains a significant challenge for widespread appilication of photoelectrochemical water splitting, and the use of corrosion resistant protective has been considered a key strategy for improving the photostability of the metal oxide. Amorphous TiO_2 (a-TiO_2), depoisted by atomic layer deposition, is often used as a protective layer for photoanodes such as silicon, GaAs, and GaP. In this application, photogenerated holes are transmiitted to the electrolyte interface via a defect band in the a-TiO_2, thereby driving solar water oxidation. However, despite several studies proposing a-TiO_2 protective coatings for the low-cost metal oxides, their practical utilization is highly challenging due to the inevitable presence of pinholes in ultrathin films and sluggish hole transfer through the protective layer so far. In this study, we introduce a hybrid polyethyleneimine (PEI)/TiO_2 layer to address these issues. The abundant amine groups in PEI promote the formation of highly defective a-TiO_2 during atomic layer deposition, enhancing hole-selective contact and preventing the undesired photodegradtion of metal oxide photoanodes. Based on these results, we propose a design principle for developing stable TiO_2 protective layers for metal oxide photoanodes.



Award Ceremony of the MatChem PhD Student Award 2024

D. Opris[1,2], M. Kovalenko[3,4]

[1]Empa Dübendorf , [2]Chair of the MatChem PhD Student Award Committee, [3]ETH Zurich, [4]President of the MatChem Division

The SCS Division of Materials Chemistry awards the MatChem PhD Student Award 2024 to

Dr. Pardis Adams, University of Zurich
for her outstanding PhD thesis "Enhancing the Efficiency of Antimony Selenide Photocathodes Towards Solar Hydrogen Production",

Dr. Mikalai Artsiusheuski, ETH Zurich
for his outstanding PhD thesis focusing on copper-containing zeolites – materials with unique combination of redox, sorption and catalytic properties, and

Dr. Hyun Suk Wang, ETH Zurich
for his outstanding work during his PhD focusing on Controlled Radical Depolymerization: Structural Differentiation and Molecular Weight Control

The MatChem PhD Student Award is given to researchers that defended a PhD in the area of materials chemistry within Switzerland between January 2023 and May 2024. The prize includes a certificate and a prize money of CHF 1'000 and the winner is invited to give an elevator talk in the MatChem Session of the SCS Fall Meeting 2024.

The prize is sponsored by Vigor, Sika and ETH Zurich.

Gloveboxes – Operation, Maintenance, and Common Misunderstandings

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In the last 60 years, gloveboxes with integrated gas purifiers have become more and more important worldwide in applications (R&D and manufacturing) of synthetic chemistry, in the pharmaceutical industry, welding processes, OLED technology, perovskite solar cells, battery technology, and 3D printing, as convenient devices to handle air sensitive compounds (e.g. hydrides, borohydrides, phosphorus halides, and metal-organic compounds), processes, and reactions.[1-4]

It is very important to refine the specifications of the gloveboxes carefully regarding the requirements of the processes being carried out inside and the demands of the users. Often, misunderstandings in choosing the right specifications, or while operating the standard gloveboxes, can result in significant consequences for the equipment itself, as well as anything which is stored or handled inside the glovebox.

While 15 to 20 years ago, the use of volatile chemicals (e.g. organic solvents) inside the glovebox (with gas purifier) was rare and very limited, or done in bare bones “purge boxes”,[5, 6] today, many processes which are being carried out inside gloveboxes (with gas purifiers) can require large amounts of organic solvents. Because of this, a well-considered maintenance schedule is required to extend the lifetime of the equipment and to protect the processes and items stored in the gloveboxes.

In this talk, we highlight different examples of common issues our service team has experienced recently and in the past, independent of the glovebox brand, and caused by misunderstandings, inefficient maintenance schedules, or an unsuitable specification of the chosen glovebox for a specific process.

Furthermore, we will propose solutions to avoid these kinds of issues and to extend the lifetime of the equipment.

[1] G. R. Thomas and N. N. Lichtin, Apparatus for Controlled Atmosphere Research, *Rev. Sci. Instrum.* **1952**,*23*, 738–740.
[2] J. M. Sherfey, Inert Atmosphere Dry Box for Chemical Operations, Ind. Eng. Chem.. **1954**, *46*, 3, 435–440
[3] T. R. P. Gibb, Inert-Atmosphere Dry Box, *Anal. Chem.* **1957**, *29 (4)*, 584-587.
[4] R. E. Johnson, Dry Box Construction, *J. Chem. Ed.* **1957**, *34*, 2, 80
[5] T. B. Marder, Continuous Inert Gas Purge Glovebox for Organometallic Synthesis, *ACS Symp. Ser.* **1987**, *Vol. 357, Experimental Organometallic Chemistry*, Chapter 6, 153-155.
[6] S. Penn, Proper Glove Box Etiquette, *J. Chem. Ed.* **1993**, *70*, 519-520.

Epitaxial Core/Shell Nanocrystals of (Europium-Doped) zirconia and hafnia

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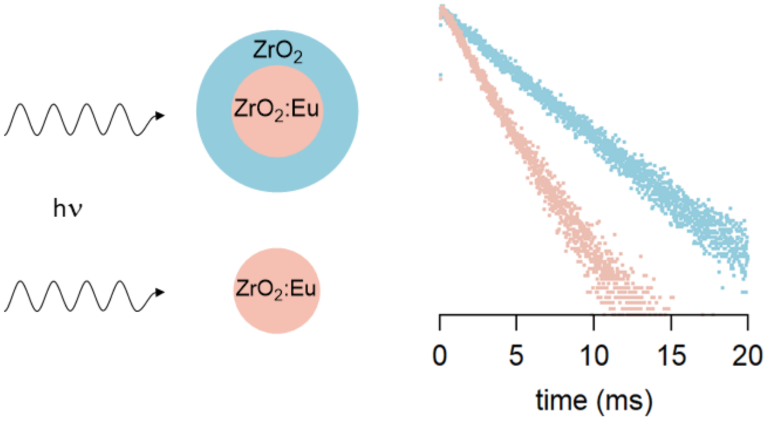
Metal oxides, like ZrO_2 and HfO_2, and fluorides (e.g. $NaYF_4$ and $NaGdF_4$), are two classes of nanocrystals that serve as hosts for optically active lanthanides ions (e.g. europium).[1-5] While doped fluorides are widely studied and their syntheses are well developed, the oxide hosts struggle with the synthetic challenge of producing colloidally stable nanocrystals with a complex architecture (as for example core/shells). In this work, we pioneer the synthesis of metal oxide core/shell nanocrystals where HfO_2 epitaxially grows onto ZrO_2, confirmed by high resolution transmission electron microscopy images and energy-dispersive Xray spectroscopy compositional maps. Furthermore, the beneficial effect of the shell on the optical properties is established by investigating the photoluminescence of ZrO_2:Eu and of ZrO_2:Eu/ZrO_2 after growing a protective zirconia shell on it. After shelling, the lifetime of the europium-doped zirconia nanocrystals increases to 5.3 ± 0.1 ms, showing that we successfully shut down non-radiative pathways. The long lifetime is unprecedented for the high doping percentage (9% Eu). The method has been demonstrated to improve the local environment of europium dopants in zirconia nanocrystals, giving access to novel heterostructures with improved optical properties. This opens up possibilities for their application in different areas, from microelectronics to scintillators.



[1] T. Ninjbadgar, G. Garnweitner, A. Börger, L. M. Goldenberg, O. V. Sakhno, J. Stumpe, Adv. Funct. Mater. 2009, 19 (11), 1819-1825.

[2] Y. Liu, S. Zhou, D. Tu, Z. Chen, M. Huang, H. Zhu, E. Ma, X. Chen, Journal of the American Chemical Society, 2012, 134 (36), 15083-15090.

[3] A. Lauria, I. Villa, M. Fasoli, M. Niederberger, A. Vedda, ACS Nano 2013, 7 (8), 7041-7052

[4] B. Zheng, J. Fan, B. Chen, X. Qin, J. Wang, F. Wang, R. Deng, X. Liu, Chem. Rev. 2022, 122 (6), 5519-5603

[5] S. Gai, C. Li, P. Yang, J. Lin, Chem. Rev. 2014, 114 (4), 2343-2389

Tetraoxa[8]circulenes - A Platform for Polymers and Frameworks

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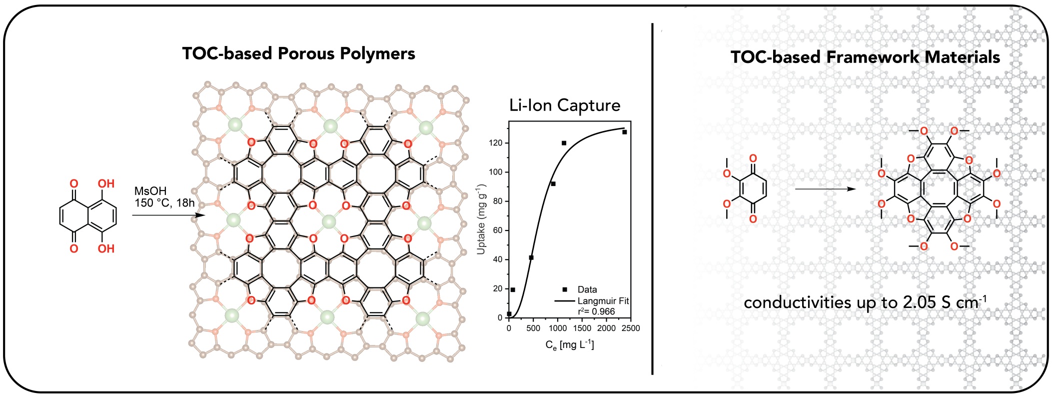
Tetraoxa[8]circulenes (TOCs) are a subclass of hetero[X]circulenes that have seen considerable interest from the computational community due to their aromatic motifs and from experimentalists due to their electronic properties. [1, 2] Despite that, only a few small-molecule TOCs have been reported in the literature, while extended structures such as polymers or framework materials were missing completely.

In 2022, we reported the first extended polymeric TOC (pTOCs) based on a Lewis acid-mediated cyclization procedure.[3] The obtained polymers featured tunable porosity and could be post-synthetically doped to tune their semiconducting properties. Based on these findings, we developed new protocols for synthesizing pTOCs. We obtained a system with crown ether-like pores capable of selectively capturing Li-ions from complex mixtures (Na^+, Ca^{2+}, Mg^{2+}, …) and were able to leverage it for the recycling of used energy storage devices of various electrode chemistries (LiS, Li-ion, and Li-metal).[4]



The biggest drawback of pTOCs are their anisotropic properties. Framework-type materials could solve these problems, however, the preparation of functionalized TOC precursors beyond alkylation or π-extension had not been realized. To that end, we have developed a synthetic protocol toward an hydroxy-functionalized TOC precursor and have used it for the synthesis of metal-organic frameworks (MOFs) and covalent organic frameworks (COFs). While the framework chemistry of the fully organic systems resulted in poor semiconductors, the TOC-based MOFs showed exceptional conductivities of up to 2.05 S cm^{-1} enabling their use as chemical sensors or as active materials in energy storage devices.

[1] T. Hensel, N. Andersen, M. Plesner, M. Pittelkow, *Synlett*, **2015**, 27, 498-525.
[2] S. Radenkovic, I. Gutman, P. Bultinck, *J Phys Chem A*, **2012**, 116, 9421-9430.
[3] P. W. Fritz, T. Chen, T. Ashirov, A-D Nguyen, M. Dinca, A. Coskun, *Angew. Chem. Int. Ed.*, **2022**, e202116527.
[4] P. W. Fritz, T. Ashirov, A. Coskun, *Chem*, **2024**.

Soft actuators based on stimuli-responsive composite hydrogels.

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The ability of living organisms to convert energy into motion has inspired the development of advanced materials capable of actuation. However, creating materials that faithfully mimic the function of mammalian muscles remains a challenge. Powerful artificial muscle technologies are often limited by the rigidity of their materials, hindering compatibility with soft tissues, while softer counterparts lack strong actuation or rely on bulky external devices. Therefore, composite materials that combine the two features have gained attention as a basis for artificial muscles.[1,2]

We here report a design concept for artificial muscle architectures that combines bioderived colloidal nanoparticles and stimuli-responsive polymers in hydrogels.[3] The mechanical strength of such actuators is provided by colloidal nanoparticles with a high aspect ratio, while the actuation capability relies on the collapse and elongation of stimuli-responsive polymer chains having lower critical solution temperatures (LCST).[4,5] The integration is achieved through grafting thermoresponsive polymer chains onto colloidal nanoparticles using controlled radical polymerization. Subsequently, we employ light-triggered click chemistry to cross-link the composite building blocks, resulting in thermoresponsive composite hydrogels.

This presentation will include discussions of the design rationale, the synthetic approaches, and the thermoresponsive behavior and mechanical properties of these composite hydrogels.

[1] Mahdi Ilami, Hosain Bagheri, Reza Ahmed, Olga E. Skowronek, Hamid Marvi, Advanced Materials, 2020, 33, 2003139.

[2] Matteo Cianchetti, Cecilia Laschi, Arianna Menciassi, Paolo Dario, Nature Reviews Materials, 2018, 3, 143–153.

[3] Alessandro Ianiro, José A. Berrocal, Remco Tuinier, Michael Mayer, Christoph Weder, Journal of Chemical Physics, 2023, 158, 014901.

[4] Menglian Wei, Yongfeng Gao, Xue Lia, Michael J. Serpe, Polymer Chemistry, 2017, 8, 127.

[5] Pedro Lavrador, Marco R. Esteves, Vítor M. Gaspar, João F. Mano, Advanced Functional Materials 2021, 31, 2005941

Constructing Diverse Colloidal Suprastructures for Biomedical Advancements

M. Hu[1,2], S. Pané[1], B. Nelson[1], H. Thérien-Aubin[3], H. J. Butt[3], A. deMello[4], L. Isa[2]

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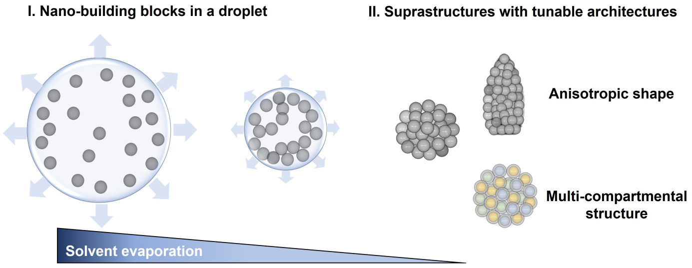
The self-assembly of nanomaterials into complex suprastructures holds substantial promise for biomedical applications, including drug delivery, diagnostics, and therapeutic interventions.[1] By precisely tuning the architecture of these assemblies, we can significantly enhance their collective properties and unlock new functionalities. In this study, we demonstrate the construction of suprastructures with precisely controlled architectures via evaporation-driven self-assembly of various colloidal building blocks.

Initially, we employed superparamagnetic nanoparticles as the foundational building blocks to create suprastructures. By adjusting parameters such as nanoparticle concentration and external magnetic fields, we achieved a range of anisotropic shapes. These assemblies exhibited superparamagnetic properties and anisotropic characteristics, which were harnessed to develop magnetically driven microswimmers. These microswimmers have potential applications in targeted drug delivery, where precise control over movement and positioning is crucial.[2] Building upon this approach, we transitioned from nanoparticles to nanocapsules as the building blocks, resulting in the formation of multi-compartmental suprastructures. This multi-compartmental design allowed each spatially distinct nanocapsule unit to retain its cargo and functionalities independently. Notably, the multi-compartment suprastructures demonstrated programmable release kinetics, highlighting their potential for controlled and sustained drug delivery applications.[3]

Our findings suggest that these advanced assembled suprastructures could revolutionize various biomedical applications by providing new tools for precision medicine, enhanced diagnostic capabilities, and innovative therapeutic strategies. The enhanced functional capabilities and programmable behaviors of these colloidal machines position them as promising candidates for future research and development in the biomedical field.



Acknowledgements
M. Hu thanks Swiss National Science Foundation (Ambizione Grant, No. 216253) for their financial support.

[1] S. Wintzheimer, T. Granath, M. Oppmann, T. Kister, T. Thai, T. Kraus, N. Vogel and K. Mandel, *ACS Nano*, **2018**, 12, 5093.

[2] M. Hu, H. J. Butt, K. Landfester, M. B. Bannwarth, S. Wooh, and H. Thérien-Aubin, *ACS Nano*, **2019**, 13, 3015.

[3] M. Hu, N. Reichholf, Y. Xia, L. Alvarez, X. Cao, S. Ma, A. J. deMello, and L. Isa, *Materials Horizons*, **2022**, 9, 1641.

Crystal growth and anisotropic magnetic properties of incommensurately modulated $K_{0.87}CrSe_2$

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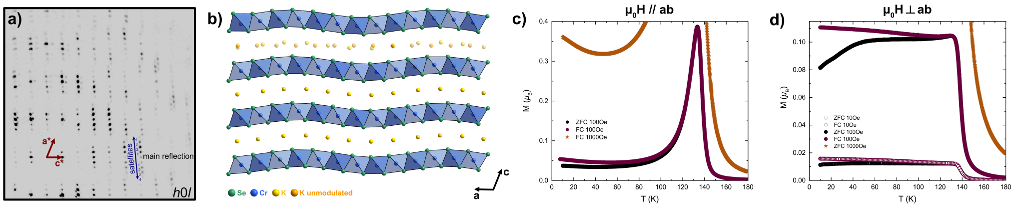
Magnetic van der Waals materials currently receive booming interest, since their exfoliability down to the atomic limit allows for the exploration of 2D magnetism[1]. One prominent member of this family, $CrSe_2$, is commonly synthesized by oxidative deintercalation of $KCrSe_2$[2]. $KCrSe_2$ itself is an *A*-type antiferromagnet (AFM), similar to $NaCrSe_2$ and $KCrS_2$[3]. However, literature reports on the Neel temperature (T_N) of $KCrSe_2$ vary from 40 to 85 K[4],[5]. Besides that, understoichiometric $K_{0.6–0.8}CrSe_2$ (AFM with a T_N of 40 K[3]) and a $K_{0.9}CrSe_2$ phase obtained by quenching a stoichiometric synthesis of $KCrSe_2$[4] with unknown crystal structure have been reported.

Using a mixed K-Se flux method, we were able to grow large single crystals of a $K_{1–x}CrSe_2$ ($x \approx 0.13$), which likely correspond to the latter compound. Our single crystal X-ray diffraction measurements revealed intense satellite reflections (Fig. 1a), which originate from a 3+1 dimensional incommensurately modulated structure, which has not been observed in this family of compounds. The under-occupation of the K cations is the driving force of the modulation, and the K content can be determined from the size of the modulation vector **q**. Different crystals of $K_{1–x}CrSe_2$ have varying modulation vectors, the hereby determined K contents of 0.866–0.871 are in line with the elemental compositions determined by elemental dispersive spectrometry ($K_{0.83–0.87(2)}CrSe_2$). The modulation results in an undulation of the $[CrSe_2]$ layers (Fig. 1b) and consequently in a variation of the Cr—Se and K—Se bond lengths as well as the coordination geometry of the K cations.



Anisotropic magnetization measurements in direct current mode on oriented single crystals reveal a transition, which appears AFM for a field parallel to the layers (Fig. 1c) and ferromagnetic (FM) for a field perpendicular to them (Fig. 1d). Our results, including a Curie-Weiss temperature of about 180 K, are consistent with FM coupled spins oriented in-plane, which are arranged AFM to those of neighboring layers – like it was reported for $KCrSe_2$, $NaCrSe_2$ and $KCrS_2$ as well[3]. Remarkably, our transition temperature ($T_N = 133$ K) is significantly higher than that of stoichiometric $KCrSe_2$. Anisotropic magnetization measurements in alternating current mode suggest a second transition around 40 K and complicated spin-dynamics in the temperature range in-between, which is also indicated by the splitting between field cooled (FC) and zero field cooled (ZFC) responses in Fig. 1d.

[1] J.-G. Park, *J. Phys.: Condens. Matter* 2016, **28**, 301001.

[2] C. van Bruggen, R. Haange, G. Wiegers, D. de Boer, *Physica B+C* 1980, **99**, 166.
[3] G. Wiegers, *Physica B+C* 1980, **99**, 151.
[4] C. M. Fang, P. R. Tolsma, C. F. van Bruggen, R. A. de Groot, G. A. Wiegers, C. Haas, *J. Phys.: Condens. Matter* 1996, **8**, 4381.
[5] X. Song, S. N. Schneider, G. Cheng, J. F. Khoury, M. Jovanovic, N. Yao, L. M. Schoop, *Chem Mater.* 2021, **33**, 8070.

Multicolor Emission with Photo-Switchable Cationic Pyridine-Pyrene (PyPy) for OLED

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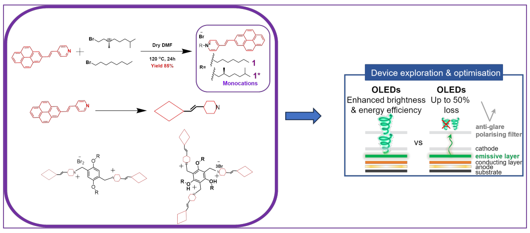
Abstract

Constructing multicolor photoluminescent materials is attractive research due to their intense applications in materials science and biomedical engineering. By comparison with covalent synthesis, supramolecular chemistry has provided a more inexpensive and promising approach to producing organic materials and the control of their photophysical properties. By taking advantage of dynamic and reversible noncovalent bonding interactions, supramolecular strategies can, not only simplify the design and fabrication of organic materials but also give them active reversibility and stimuli responsiveness, making it much easier to adjust the superstructures and properties of the materials.[1] In this work we design an organic dyes pyridine-pyrene (PyPy) to explore the photoswitches topologies. Herein, we present the photochemistry of PyPy, which can be controlled by a macromolecular environment. Through the decoration of a pyridine moiety with a conjugated aromatic pyrene containing a double bond accessible to [2 +2] photocycloaddition. Their inherent helical supramolecular polymerization (HSP) makes them especially attractive as functional materials with the capability of manipulating and responding to multicolor emissions. We approached by developing mono, di- and trication PyPy (quaternization with chiral and achiral aliphatic chains), as a result of which comparative HSP interactions study in different polar and non-polar solvents and in host-guest self-assembly (HGS) studies with cyclodextrin. In addition to establishing fundamental structure, light-induced photochemistry, optoelectronic properties,[2] and supramolecular chemistry under aggregation for optimizing the OLEDs.

Keywords: light-induced photochemistry, organic light emitting devices (OLEDs), and helical supramolecular polymers.



1. M. Xu, G. Li, W. Li, B. An, J. Sun, Z. Chen, H. Yu, J. Li, G. Yang and S. Liu, *Angew. Chem., Int. Ed.*, 2022, **61**, e202117042.

2. G. Zhang, X. Cheng, Y. Wang and W. J. A. Zhang, 2023, **4**, e262.

Electroactive napthalimide and napthalenediimide interlayers for inverted perovskite solar cells

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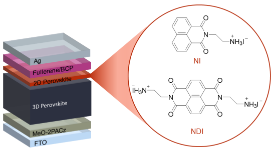
Perovskite solar cells (PSCs) based on hybrid organic-inorganic lead halide perovskites have attracted attention over the past decade as third-generation solar cells. An important factor for fabricating highly efficient and stable PSCs is the suitability of charge transport layers, employed to extract charge carriers from the perovskite absorber. In the case of inverted PSCs with p-i-n architecture, the most widely employed electron transport layer (ETL) material is the fullerene-based [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) and the C_{60} buckminsterfullerene (C_{60}) deposited on top of the perovskite absorber. However, fullerene-based materials exhibit stability issues due to their photodegradation and thermal decomposition.[1] At the same time, a wide variety of small molecules, mostly ammonium salts, have been employed as stabilizing interlayers or additives, with passivating properties on top of or in the bulk of the perovskite absorber. These molecules often form more stable low-dimensional or layered (2D) structures, yet exhibit performance limitations due to their electronically insulating properties.[2] Herein, we report the employment of two tailored electroactive small molecules based on a 1,8-naphthalimide (NI) and naphthalenediimide (NDI) core, with electron-accepting properties, as n-type interlayers in p-i-n PSCs.[3,4] The materials have been deposited on top of the perovskite absorber layer. The ability of these spacers to form a 3D/2D interface with the perovskite while simultaneously acting as electron-accepting and hole-blocking layers with interface passivating properties were examined. Furthermore, their suitability as interlayers in fullerene-based p-i-n PSCs was assessed in terms of performance and stability to demonstrate a versatile new strategy for advancing inverted perovskite solar cell architectures.



[1] J.-P. Correa-Baena, A. Abate, M. Saliba, W. Tress, T. J. Jacobsson, M. Grätzel, A. Hagfeldt, *Energy Environ. Sci.*, **2017**, 10, 710. [2] J. V. Milić, *Mater. Chem. C*, **2021**, 9, 11428. [3] S. Nussbaum, E. Socie, L. Yao, J.-H. Yum, J.-E. Moser, K. Sivula, *Chem. Mater.*, **2022**, 34, 8, 3798–3805. [4] K.-K. Armadorou et al. **2024**, *manuscript in preparation*.

Diels-Alder Cycloaddition Polymerization for Porous Poly-phenylenes with Exceptional Gas Uptake Properties

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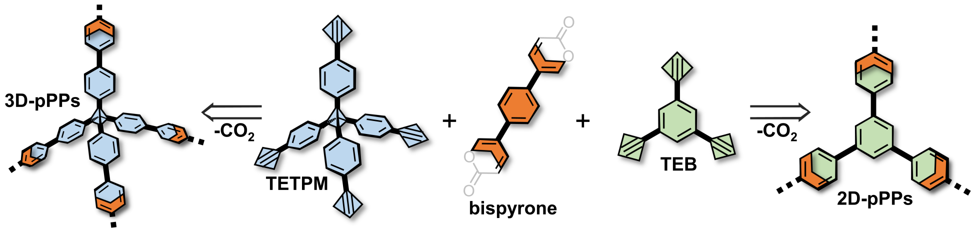
Diamond, known for its unrivaled hardness and physiochemical stability, inspires the synthesis of materials with similar properties. Porous aromatic frameworks (PAFs), a subclass of porous organic polymers (POPs), mimic diamond's structure and exhibit exceptional porosity, high thermal stabilities over 400 °C, chemical robustness, and extensive surface areas, with PAF-1 displaying 5600 $m^2\ g^{-1}$ and maintaining stability up to 450 °C. Traditionally reliant on metal-catalyzed cross-coupling reactions requiring costly or environmentally impactful catalysts, the synthesis of PAFs has explored alternative methods using less expensive catalysts like $AlCl_3$ and $FeCl_3$, though these have led to reduced stability and complex structures due to side reactions. In a novel approach, we employ Diels–Alder cycloaddition polymerization using 5,5′-(1,4-phenylene)bis(2H-pyran-2-one) (Bispyrone) as the diene and 1,3,5-triethynylbenzene (TEB) and tetrakis(4-ethynylphenyl)methane (TETPM) as dienophiles, producing 2D and 3D porous polyphenylenes (pPPs) that achieve surface areas up to 1553 $m^2\ g^{-1}$, a pore volume of 1.45 $cm^3\ g^{-1}$, and remarkable high-pressure hydrogen uptake capacities of 7.4 and 7.1 wt% at 77 K. This synthesis strategy not only avoids the use of metal catalysts but also reduces environmental impact, marking a significant advance in the development of environmentally friendly and efficient porous materials.



[1] T. Ben, H. Ren, S. Ma, D. Cao, J. Lan, X. Jing, W. Wang, J. Xu, F. Deng, J. M. Simmons, S. Qiu and G. Zhu, *Angew. Chem., Int. Ed.*, 2009, 48, 9457–9460

[2] T. Ashirov, P. W. Fritz, T. Yildirim, A. Coskun, *Chem. Commun.*, 2024, **60**, 2657-2660

From Chicken Feathers to Antimicrobial Peptides for Smart, Self-Disinfecting Nanocoating

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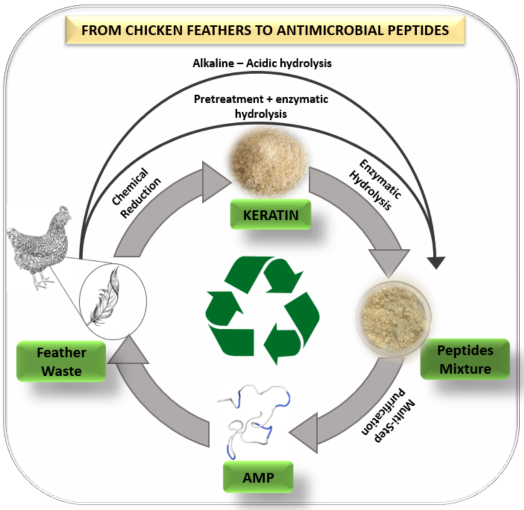
Microbial colonization of high traffic surfaces burdens our society by causing significant cost to human lives and economy [1]. The prevention of microbes' transmission remains a global challenge [2]. Efficient self-disinfecting nanocoating that rapidly act by contact killing can help reduce the spread of infections. However, ensuring the sustainability, safety and durability of such a coating is challenging.

The Horizon Europe Reliance project aims to develop an innovative, smart response antimicrobial coating that incorporates unique antimicrobial peptides (AMPs) sourced from chicken feathers, a keratin-rich waste source [3]. Herein, we report the extraction, isolation and purification of AMPs from chicken feathers with optimal bioactivity. Various promising hydrolysis methods, such as chemical, enzymatic and using pretreatment of feathers are investigated on gram scale and a spectrum of analytical methods are used for the purification and characterization of the extracted peptides. Several AMP fractions have revealed various antimicrobial activities allowing the selection of a sustainable scalable process, that is currently under optimization. These bioactive keratin-based peptides are further explored for their anchoring on the surface of mesoporous copper-silica nanoparticles, aiming to enhance contact killing action of the coating. This work drives advancements in sustainable coating applications, while valorizing the use of a protein-rich waste source, promoting therefore circular economy and innovative resource utilization.



[1] Murray, CJ., et al., Global burden of bacterial antimicrobial resistance in 2019: a systematic analysis. *Lancet*, **2022**. 399(10325): p. 629-655.
[2] Yılmaz, G.E., et al., Antimicrobial Nanomaterials: A Review. *Hygiene*, **2023**. 3(3): p. 269-290.
[3] Shavandi, A., et al., Keratin: dissolution, extraction and biomedical application. *Biomater Sci*, **2017**. 5(9): p. 1699-1735.

Dynamically-bound Guanidinium-based Ligands for Lead Halide Perovskite Nanocrystals

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Lead halide perovskite (LHP) nanocrystals (NCs) recently gained significant attention as a promising class of materials for optoelectronic applications. Their ionic lattice and labile surface chemistry call for new strategies in designing ligands. A range of ligands that significantly improve the colloidal stability of LHP NCs has been developed recently, which was primarily achieved through employing zwitterionic ligands. To advance further development of ligands for LHP NCs, we sought to rationalize the binding behavior of the most commonly used ones. Our study identifies that phosphocholine- and phosphoethanolamine-based zwitterionic ligands bind statically to the LHP NC surface, providing the highest stability. Sulfobetaine-based ligands offer a balance between stability and binding dynamicity. Various ammonium-based ligands exhibit high dynamicity but often result in insufficient stability due to pH sensitivity or suboptimal binding to the A-site pockets.[1]

In this work, we propose a new family of guanidinium-based long-chain ligands that, without compromising stability, offer dynamic binding to the surface of NCs and therefore highly accessible active sites on the surface. A library of guanidinium-based ligands was synthesized and applied to LHP NCs of various sizes and compositions, such as $CsPbBr_3$, $FAPbBr_3$, and $CsPbI_3$. The new synthetic approach allows obtaining LHP NCs with quantum yields as high as 95% in colloidal solutions and up to 80% in compact films. This combination of properties makes LHP NCs capped with guanidinium-based ligands highly promising for photocatalytic applications in which.

[1] Berezovska et al., In preparation

Optically actuated metallosupramolecular systems comprising opto-chemical transducers

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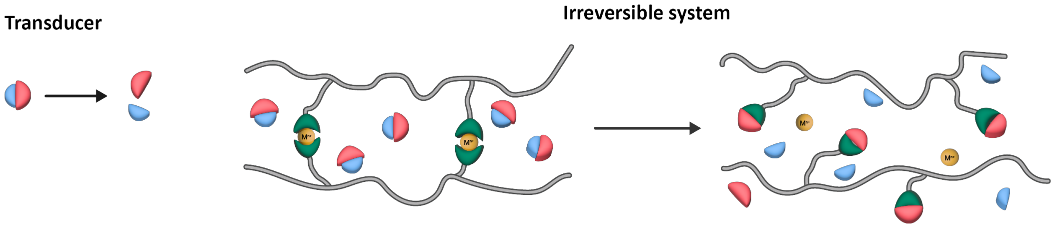
Stimuli-responsive materials have garnered much interest as functional materials that are multi-purposed and, therefore, efficient. Dynamic, adaptive materials that can react to stimuli on demand but are otherwise operationally robust are appealing for the design of biodegradable, reusable, self-healable, and smart materials.[1, 2] Light, heat, chemicals, and electrical fields are illustrative examples of stimuli that can be used to elicit specific responses in such materials. More recently, an interest in developing material *systems* has emerged for which responsive materials are the building blocks.[3] Such systems combine supramolecular polymers with specific switch molecules, whose activation causes a reversible or irreversible change of the systems' properties. Metallosupramolecular polymers (MSPs) are interesting candidates for the development of responsive materials due to the dynamic, secondary, and non-covalent nature of the interactions involved.[1, 4] The metal-ligand interactions can be readily tuned by the choice of the metal salt (and/or ligand) to provide an attractive framework for the design of adaptive supramolecular polymer *systems*.



Here, we report materials that combine an MSP and an opto-chemical transducer that can elicit significant changes in the materials' properties. We combined a photoacid generator 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine (MBTT) with poly(acrylates) that comprise a few mol % of the 2,6-bis(1′-methyl-benzimidazolyl)pyridine (Mebip) ligand. The latter forms supramolecular cross-links upon the addition of metal salts, such as Zn^{2+}, Eu^{3+} and Cu^{2+}. We utilized titration experiments, optical spectroscopy, and rheology to demonstrate that the MSP network can be rapidly disassembled upon optical activation of the photoacid generator, on account of protonation of the ligand.

[1] L. Brunsveld, B. J. B. Folmer, E. W. Meijer and R. P. Sijbesma, *Chem. Rev.*, **2001**, 101, 4071-4098.
[2] C. J. Kloxin and C. N. Bowman, *Chem. Soc. Rev.*, **2013**, 42, 7161-7173.
[3] N. Giuseppone, *Acc. Chem. Res.*, **2012**, 45, 2178-2188.
[4] M. Burnworth, L. Tang, J. R. Kumpfer, A. J. Duncan, F. L. Beyer, G. L. Fiore, S. J. Rowan and C. Weder, *Nature*, **2011**, 472, 334-337.

A Colloidal Nanofoundry for Solid-Liquid-Solid Nanoparticles

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Liquid metal (LM) nanoparticles (NPs) represent a highly attractive class of materials for various applications, including catalysis, electronics and sensing. Especially, Ga-based NPs have recently emerged as promising candidates in the electrochemical CO_2 reduction reaction (CO2RR) [1,2]. However, knowledge on the chemistry of LM NPs and their reactivity with other metals is still in its infancy [3,4]. Thus, the design of novel LM structures with desired properties is currently inaccessible.

In this contribution, we propose a colloidal approach for synthesizing tunable and monodispersed solid-liquid-solid Ga-based nanoparticles wherein a solid metal is embedded into a liquid Ga nanoparticles confined by its oxide native skin. We combine state-of-the-art in-situ techniques, including electron microscopy and X-Ray absorption spectroscopy, to elucidate the formation mechanism of these unique nanostructures. We demonstrate that Ga NPs act as nanoreactors for the crystallization of the solid core. This unique liquid metal environment enables the synthesis of multimetallic NPs which would be challenging to obtain otherwise. Finally, we demonstrate the functionality of these novel NPs as CO2RR electrocatalysts.

[1] Okatenko, V.; Castilla-Amorós, L.; Stoian, D. C.; Vávra, J.; Loiudice, A.; Buonsanti, R. J. Am. Chem. Soc. 2022, 144, 10053–10063

[2] Okatenko, V.; Loiudice, A.; Newton, M. A.; Stoian, D. C.; Blokhina, A.; Chen A. N.; Rossi, K.; Buonsanti, R. J. Am. Chem. Soc. 2023, 125, 9, 5370-5383

[3] Castilla-Amorós, L.; Stoian, D. C.; Pankhurst, J. R.; Varandili, S. B.; Buonsanti, R. J. Am. Chem. Soc. 2020, 142, 45, 19283-19290

[4] Okatenko, V.; Boulanger, C.; Chen, A. N. ; Kumar, K. ; Schouwink, P.; Loiudice, A.; Buonsanti, R. J. Am. Chem. Soc. 2023, 145, 46, 25401-25410

Organic Additive Approach for the Interfacial Stabilization in Sulfide-based All-Solid-State Batteries

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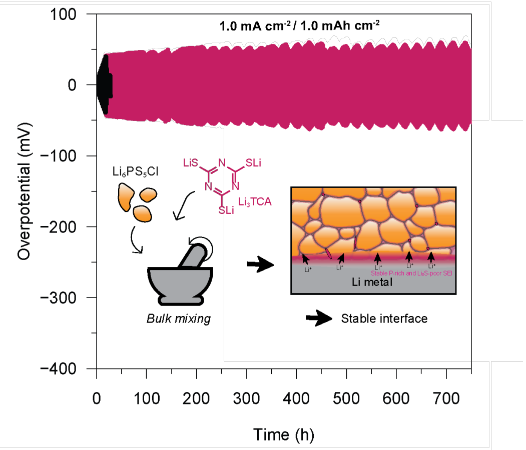
Sulfide-based all-solid-state battery (ASSB) with a lithium metal anode (LMA) is a promising candidate to surpass conventional Li-ion batteries owing to their inherent safety against fire hazards and potential to achieve a higher energy density. However, the narrow electrochemical stability window and chemical reactivity of the sulfide solid electrolyte towards the LMA results in interfacial degradation and poor electrochemical performance. Many strategies have been introduced to stabilize the lithium metal, including protection of the lithium metal with an artificial solid electrolyte interphase (SEI), substitution of the lithium metal anode or modification of the solid electrolyte using inorganic additives.[1] However, organic additives, that can promote interfacial stability and form a more favorable SEI in-situ, have yet to be explored. In this direction, we introduce an organic additive approach, that is the mixing of prelithiated trithiocyanuric acid, Li_3TCA, with Li_6PS_5Cl, to establish a stable interface while preserving high ionic conductivity. Including 2.5 wt% Li_3TCA alleviates the decomposition of the electrolyte on the lithium metal interface, decreasing the Li_2S content in the solid-electrolyte interface (SEI) thus forming a more stable interface. In Li|Li symmetric cells this enables a rise in the critical current density from 1.0 to 1.9 mA cm^{-2} and stable cycling for over 750 hours at a high current density of 1.0 mA cm^{-2}. This approach also enables Li|NbO-NCM811 full cell to operate more than 500 cycles at 0.3C.



[1] J. Li, J. Luo, X. Li, Y. Fu, J. Zhu, X. Zhuang, Ecomaterals, 2023, 5(8):e12383

Novel synthesis and ligand design for lead-free halide perovskites.

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Exploration of metal halide perovskite nanocrystals (MHP NCs) has thus far focused on lead-based materials[1,2]; however, lower toxicity alternatives are of immense interest as well, including their potentially broader range of functionalities. Tin is a primary candidate to replace lead, owing to its similar electronic structure and ionic radius.[3,4] Synthetic procedures to prepare tin halide perovskite (THP) NCs are scarce.[3,4] We report a room-temperature synthesis yielding THP NCs, wherein precursor solutions of metal-halide tri-octyl phosphine oxide (TOPO) complexes and A-site cations dissolved in organic acids are combined to yield perovskite NCs. Judicious choice of A-site cations and halides gives access to various compositions exceeding the existing reports on THP NCs. The equilibrium between the metal-halide TOPO complex and the free ionic species allows for controlled nucleation and growth of these nanoparticles. The sizes of the obtained NCs can be controlled via the amount of TOPO. The exchange of TOPO and organic acids with strongly binding zwitterionic ligands yields stable colloids. The ligand binding group is adapted to the composition and surface structure by a library of specifically designed ligands making the nanoparticles colloidally stable for months.

[1] Kovalenko, M.V., Protesescu, L., Bodnarchuk, M., Science, 2017, 358 (6364), 745-750

[2] Dey, A. et al., ACS Nano, 2021, 15 (7), 10775-10981

[3] Chen, J.K. et al., ACS Mat. Lett., 2021, 3 (11), 1541-1557

[4] Lopez-Fernandez, I. et al., Adv. Fun. Mat., 2024, 34 (6), 2307896

Phonon-driven wavefunction localization promotes room-temperature, pure single-photon emission in large organic-inorganic lead-halide quantum dots

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In lead halide perovskites ($APbX_3$), the effect of the A-site cation on optical and electronic properties has initially been thought to be marginal because band edge states are formed by lead halide orbitals. Yet, evidence of beneficial effects on solar cell performance and light emission is accumulating. We report that the A-cation in soft $APbBr_3$ colloidal quantum dots (QDs) controls the phonon-induced localization of the exciton wavefunction. Insights from ab initio molecular dynamics and single-particle fluorescence spectroscopy demonstrate that anharmonic lattice vibrations and the resulting polymorphism act as an additional confinement potential. Avoiding the trade-off between single-photon purity and optical stability faced by downsizing conventional QDs into the strong confinement regime, dynamical phonon-induced confinement in large organic-inorganic perovskite QDs enables bright (10^6 photons/s), stable (> 1h), and pure (> 95%) single-photon emission in a widely tuneable spectral range (495-745 nm).[1] Strong electron-phonon interaction in soft perovskite QDs provides an unconventional route toward the development of scalable room-temperature quantum light sources.

[1] Leon G. Feld, Simon C. Boehme, Sebastian Sabisch, Nadav Frenkel, et al., *Preprint at* https://doi.org/10.48550/arXiv.2404.15920, **2024**

Designing inherently degradable epoxy resins around a carbohydrate core

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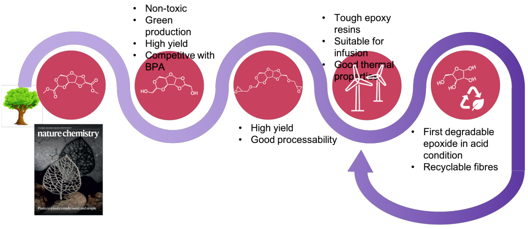
The development of high-performance bio-based epoxy resins has been limited by the lack of competitivity with the harmful bisphenol-A precursor (DGEBA). Here, we detail the synthesis of a bio-based epoxy building block from a novel tricyclic diester (DMGX) that can be produced directly from the hemicellulosic fraction of non-edible biomass1,2. DMGX was reduced at high yield to a diol (XGDO) which was further reacted with epichlorohydrin to a resin precursor. Epoxy resins were made with commercial diamines and the properties of the resulting bio-based resins were compared to their DGEBA counterparts. All cured DGEXGDO epoxy resins had degradation temperatures above 300°C, high glass transition temperature (>120°C), and higher glassy storage moduli than DGEBA-cured epoxy resins. Furthermore, the unique acetal chemistry of the carbohydrate building blocks led to improved end-of-life as DGEXGDO-cured epoxy resins are more easily degradable compared to classical DGEBA-based epoxy resins.



[1]: Manker, L. P.; **Hedou, M. A**.; Broggi, C.; Jones, M. J.; Kortsen, K.; Puvanenthiran, K.; Kupper, Y.; Frauenrath, H.; Marechal, F.; Michaud, V.; Marti, R.; Shaver, M. P.; Luterbacher, J. S. Performance Polyamides Built on a Sustainable Carbohydrate Core. Nat Sustain 2024, 1–12. https://doi.org/10.1038/s41893-024-01298-7.

[2]: Manker, L. P.; Dick, G. R.; Demongeot, A.; **Hedou, M. A.**; Rayroud, C.; Rambert, T.; Jones, M. J.; Sulaeva, I.; Vieli, M.; Leterrier, Y.; Potthast, A.; Maréchal, F.; Michaud, V.; Klok, H.-A.; Luterbacher, J. S. Sustainable Polyesters via Direct Functionalization of Lignocellulosic Sugars. Nat. Chem. 2022, 1–9. https://doi.org/10.1038/s41557-022-00974-5.

Sensitized triplet-triplet annihilation in nanostructured polymeric scintillators allows for pulse shape discrimination

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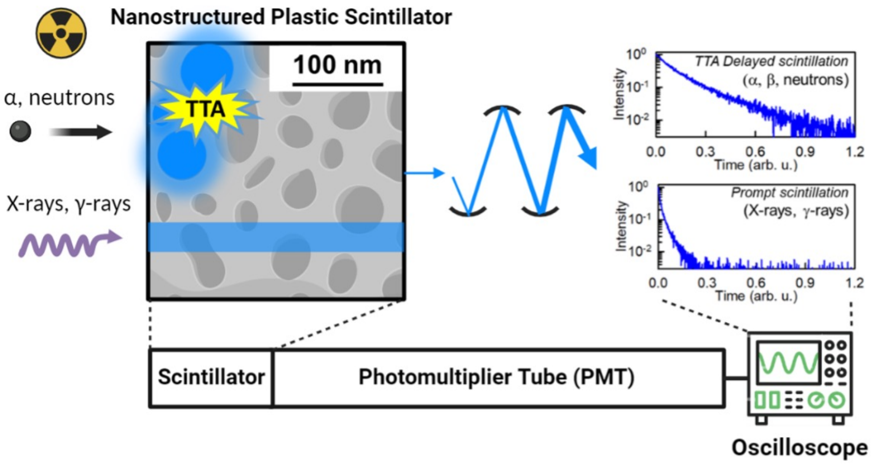
Scintillation counters are widely employed to detect and measure ionizing radiation, including X-rays, γ-rays, α and β particles, as well as neutrons, by recording the emission of a scintillating material exposed to the radiation. These radiation detectors are crucial in various applications, such as nuclear threat detection, gas exploration, medical dosimetry, and high-energy physics experiments. For some applications, it is important to differentiate between charged particles, high-energy neutrons, and γ-ray background. This can be achieved by pulse shape discrimination (PSD), i.e., a time-gated analysis of the voltage pulses generated by the scintillation counter's photodetector. The scintillation signal is thus deconvoluted into components associated with fast and slow emission processes, whose lifetimes are characteristic of the type of incident radiation. While plastic scintillators are attractive on account of their shapeability, mechanical robustness, low cost, and fast response, achieving efficient PSD with these materials remains a significant challenge. We recently demonstrated that nanostructured polymer systems consisting of a cross-linked solid polymer matrix and non-polar liquid nanodroplets represent an attractive platform for the design of sensitive and fast PSD-capable polymer scintillators.[1,2] Scintillating dyes capable of triplet-triplet annihilation (TTA) are dissolved in the nanodroplets, whose liquid nature facilitates bimolecular energy transfer processes. Consequently, the TTA-generated delayed emission fraction of the scintillation signals is enhanced. Moreover, incorporating a triplet sensitizer enhances the sensitivity and PSD performance of the scintillator compared to its non-sensitized counterparts. The nanostructured plastic scintillators allow the discrimination of α particles, γ-rays, and neutrons with a time response that is better than that of commercially available systems. The scintillators also exhibit excellent stability upon high X-ray radiation doses and high dose rates.



[1] X. Hu, C. Weder, A. Monguzzi, et al, *Adv. Mater*. 2400443, **2024**
[2] C. Weder, X. Hu, A. Monguzzi, L. Pollice, *US patent 63/568,479 (filed)*. **2024**

Supramolecular assembly induced fluorescence based on acridone oligomers

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Dicyanomethylenated acridone trimers have been synthesized and characterized. In aqueous conditions the oligomers self-assemble into 50-150 nm large spherical aggregates, which was observed by AFM and DLS measurements. UV-vis and fluorescence spectroscopy revealed, that the supramolecular polymers are luminescent at 20°C, whereas at 75°C the oligomers are disassembled and show no luminescence due to the aggregation-induced emission (AIE) behaviour.[1]This phenomenon is attributed to the restricted torsional vibration of molecules in an aggregate.[2][3]The molecular packing of the supramolecular aggregates can be changed by varying the length of the N-substituent from a methyl to a butyl group. These different arrangements have an influence on the emission properties of the supramolecular aggregates. The sterically more demanding butyl group probably prevents close-packing and leads to a significantly lower fluorescence of the supramolecular spheres in contrast to the methyl group.

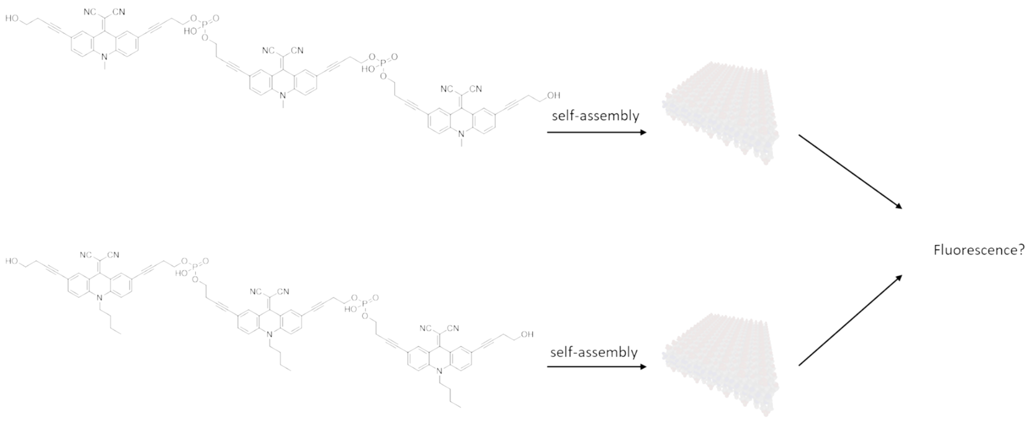

Figure 1: Dicyanomethylenated acridone trimers self-assemble into fluorescent aggregates

[1] T. Takeda, T. Akutagawa, *Chemistry – A European Journal* **2016**, *22*, 7763.
[2] W. Chen, S. Wang, G. Yang, S. Chen, K. Ye, Z. Hu, Z. Zhang, Y. Wang, *J. Phys. Chem. C* **2016**, *120*, 587.
[3] T. Takeda, H. Sugihara, Y. Suzuki, J. Kawamata, T. Akutagawa, *J. Org. Chem.* **2014**, *79*, 9669.

Bronze-type niobium tungsten oxides: intricate structures for battery research

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Currently, the potential of Nb-W oxides for battery applications is intensively explored as their structure allows a reversible high-rate Li-ion exchange [1]. Multiple phases occur in the system Nb_2O_5/WO_3 with odd but well-defined stoichiometry [2]. Their structures contain frameworks of corner-sharing octahedra MO_6 (M=Nb,W) that are related to the ReO_3 and the tetragonal tungsten bronze (TTB) type (Figure 1) [3]. The structure of $Nb_8W_9O_{47}$ with a ratio O/M = 47:17 represents a threefold TTB superstructure with 1/3 of pentagonal channels filled by M-O strings. Deviating O/M ratios lead to structural adaptions. On the oxygen-rich side, structures with less occupied pentagonal channels and incorporated single units of the neighboring phase $Nb_4W_7O_{31}$ appear (Figure 1) [4]. On the metal-rich side of $Nb_8W_9O_{47}$, a denser occupation of the pentagonal channels accomodates the decreased O/M ratio. The close structural relationship of all these phases enables their intimate intergrowth as schematically shown in Figure 1. For evaluating the details of such complex real structures, the characterization by high-resolution transmission electron microscopy was already established in 1974 [5]. Today, high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) that provides not only the positions of the metal atoms but also some information about their occupancy is the preferred method (Figure 1).

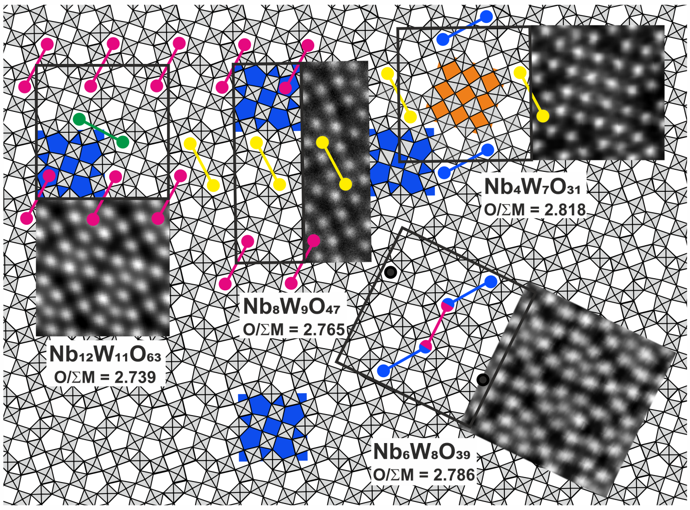

Figure 1: Schemes and HAADF-STEM images of Nb-W oxides with superstructures of the TTB type (blue squares) caused by varying occuption of pentagonal channels. $Nb_4W_7O_{31}$ is an intergrowth of the TTB and the ReO_3 type (orange square).

[1] K. J. Griffith, K. M. Wiaderek, G. Cibin, L. E. Marbella, C. P. Grey, *Nature* **2018**, *559*, 556-563.

[2] R. S. Roth, J. L. Waring, *J. Res. Natl. Bur. Stand.* **1966**, *70A*, 281-303.

[3] F. Krumeich, *Chemistry of Materials* **2022**, *34*, 911-934.

[4] M. Wörle, F. Krumeich, *Z. Anorg. Allg. Chem.* **2021**, *647*, 98-106.

[5] S. Iijima, J. G. Allpress, *Acta Crystallographica A* **1974**, *30*, 22-29.

Iron-carbohydrate complexes treating anaemia: understanding the dynamic Interactions with human blood serum

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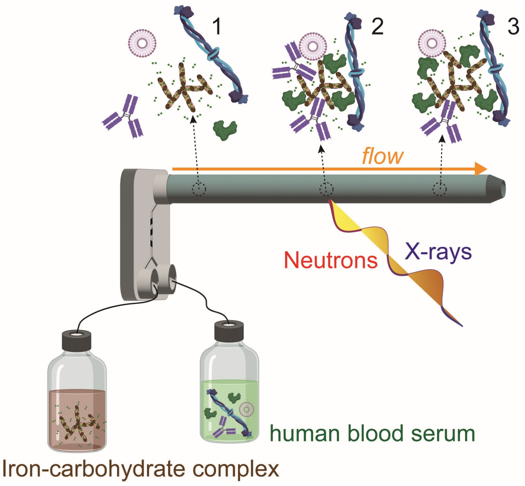
Intravenous (IV) iron-carbohydrate complexes (ICCs) are widely used nanoparticles (NPs) to treat iron deficiency anaemia, associated with chronic kidney disease, cancer and other etiologies[1]. However, despite the abundance of physicochemical characterisation data and clinical studies for these formulations, clear evidence-based understanding between physicochemical properties of ICCs and clinical outcome remains elusive[2]. Studies suggest that early interactions between NPs and blood upon IV injection are key to understanding how differences in physicochemical characteristics of ICCs cause variance in clinical outcomes[1,3].

We therefore investigated the nano-structure of two clinically applied ICCs, iron sucrose (IS) and ferric carboxymaltose (FCM), and their dynamic interactions with serum proteins[4]. We revealed differences in the surface morphology of these two ICCs. FCM showed a localised carbohydrate shell around its core, in contrast to IS, which was characterised by a diffuse layer of carbohydrate ligand. We hypothesised that such differences in carbohydrate morphology determine interactions between ICCs and serum proteins and therefore investigated the NPs in presence of human serum albumin (HSA). Intriguingly, IS showed significant interaction with HSA, while FCM did not. These insights motivated us to study dynamic interactions between ICCs and human blood serum under flow conditions, a system more closely resembling the human bloodstream. Experiments revealed that interaction between FCM and HSA is affected by flow as well as the NP concentration. Our approach sets a path for the detailed correlation between physicochemical properties of iron-carbohydrate complexes, their intracellular responses and biodistribution profiles.



[1] N. Nikravesh, et. al., *Nanomedicine: Nanotechnology, Biology and Medicine*, **2020**, 26, 102178.

[2] L. Krupnik, et. al., *European Journal of Pharmaceutical Sciences*, **2023**, 188, 106521.

[3] N. Anaraki, et. al., *Advanced Functional Materials*, **2022**, 23.9, 2110253.

[4] L. Krupnik, et. al., *Journal of Controlled Release*, **2024**, 368, 566-579.

Tuning crystal growth of 2D Covalent Organic Frameworks with acid catalysts

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Covalent organic frameworks (COFs) are porous and tunable materials which are attractive for multiple applications, such as molecular separations, energy/gas storage, chemical sensing, catalysis, and organic electronics. To reach full potential for most of these applications, materials quality must improve from low to high crystallinity, and a better understanding of the crystallization process is required. Our lab recently reported single crystalline 2D imine-linked COFs via a colloidal synthesis method.[1] The single crystalline material outperformed the lower quality polycrystalline material, by separating benzene from cyclohexane by gas chromatography with greater efficiency. The colloidal synthesis is performed under mild conditions and short reaction times, from 5 min up to 48 h. When optimizing the materials quality, it was shown that the main parameters to tune the single crystals are monomer loading, aniline loading, and temperature. In this work, we investigated the roles of the acid as an imine-bond formation catalyst and colloidal stabilizer.[2] Based on SEM, FTIR, PXRD, an optimal acidity range was found for single crystal formation, which is controlled by acid identity and concentration. In addition, by changing the sterics on the acid catalyst, the morphology can be changed. Further kinetic studies indicated fusion of small particles into single crystals, and the rate of the single crystal formation was catalyst dependent. In addition to identifying key reaction parameters, we aim to get a detailed insights on the nucleation and crystallization processes, by using our new developed technique in situ Ultra Small and Wide Angle and X-ray Scattering (USAXS/WAXS) for colloidal 2D COFs.[3] The in situ USAXS/WAXS method was applicable to the acid scope and similar trends were observed. Altogether, identifying key parameters and gaining mechanistic insights provides valuable information into single crystal COF growth. Similar strategies will be applied to other COF systems to improve their quality so they can also reach their full potential as porous and tunable materials.

[1] A. Natraj; W. Ji; J. Xin; I. Castano; D. W. Burke; A. M. Evans; M. J. Strauss; M. Ateia; L. S. Hamachi; N. C. Gianneschi; Z. A. ALOthman; J. Sun; K. Yusuf; W. R. Dichtel. Single-Crystalline Imine-Linked Two-Dimensional Covalent Organic Frameworks Separate Benzene and Cyclohexane Efficiently. *J Am Chem Soc*, **2022**, 144 (43), 19813-19824.

[2] I. R. Landman; W. R. Dichtel. *Manuscript in preparation*, **2024**.

[3] A. Natraj; I. R. Landman; C. E. Pelkowski; D. W. Burke; S. Kewalramani; W. R. Dichtel. Nonclassical crystallization processes of single-crystalline two-dimensional covalent organic frameworks. *Accepted*, **2024**.

Triplet-Triplet Annihilation Upconversion with a New Class of UV Emitters

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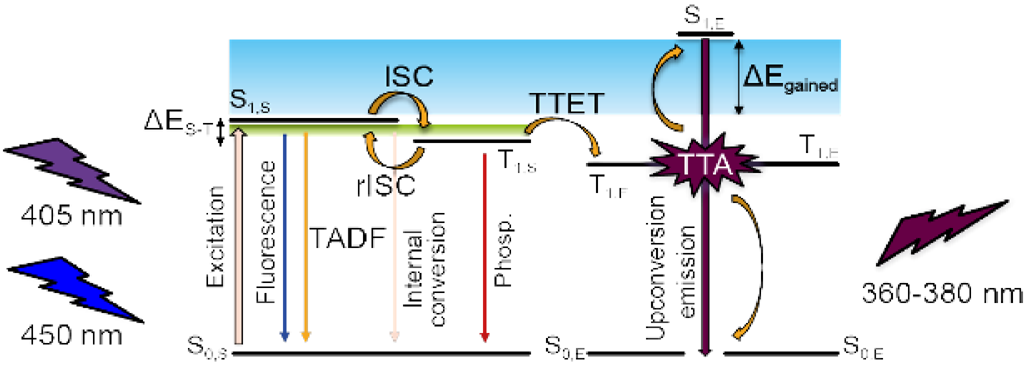
Ultraviolet (UV) light plays a crucial role in various industrial applications, including photochemical reactions and water purification, but it makes up only 10% of the solar spectrum, which necessitates the development of efficient collection or conversion methods if sunlight should be used for such processes. One promising approach is triplet-triplet annihilation upconversion (TTA-UC), discovered in the early 1960s.[1] TTA-UC allows the conversion of low-frequency to high-frequency photons and is applicable to non-coherent, low-power-density radiation, making it particularly suitable for solar applications.[2] The process involves a sensitizer that absorbs low-frequency photons and is excited from its ground state (S0,S) to its first singlet excited state (S1,S), before inter-system crossing (ISC) leads to the population of the first triplet excited state (T1,S) of the sensitizer. In a subsequent triplet-triplet energy transfer (TTET) process, the energy is transferred to an emitter molecule. In the final step, two emitter triplets (2xT1,E) annihilate under the formation of an emitter singlet (S1,E), which radiatively relaxes to the ground state and causes delayed fluorescence. Here, we summarize our efforts to identify dye systems that allow for efficient Vis-to-UV TTA-UC. We have discovered 1,4-bis(2-phenylethynyl)benzene (BPEB) as a suitable, hitherto unexplored UV emitter. BPEB, which exhibits an emission maximum of 360 nm, is combined with several organic sensitizers that exhibit thermally activated delayed fluorescence (TADF). This class of sensitizers offers good photostability, reduced toxicity and cost in comparison to traditionally employed metal-based sensitizers. We characterized the photophysical properties of BPEB-based emitters with different TADF sensitizers in deaerated toluene solutions under excitation wavelengths of 405 and 450 nm. We demonstrate robust Vis-to-UV TTA-UC with anti-Stokes shift of up to ca. 100 nm. Additionally, we incorporated these dye pairs into nanophase-separated polymer hosts with the goal of creating mechanically robust and efficient upconversion systems for practical application.[3]



[1] Parker, C. A.; Hatchard, C. G., *The Journal of Physical Chemistry*, **1962**, 66, 12, 2506-2511.
[2] Uji, M.; Zähringer, T. J. B.; Kerzig, C.; Yanai, N., *Angewandte Chemie*, **2023**, 62, e202301506.
[3] Vadrucci, R.; Monguzzi, A.; Saenz, F.; Wilts, B.D.; Simon, Y.C.; Weder, C., *Advanced Materials*, **2017**, 29, 1702992.

Chemical stability of gold-silica core-shell nanoparticles in biological media

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Core-shell nanoparticles (CSNPs)-based multimodal imaging is promising for understanding the intracellular fate of NPs at the single-cell level. A core-shell structure, such as an electro-dense gold coated by a fluorescent silica shell, allows fluorescence and electron microscopy imaging. However, silica shells are dissolvable in biological media, leading to possible unexpected effects such as leaching of the fluorophore. Therefore, the chemical stability of CSNPs in biological media needs to be investigated and improved. Herein, the chemical stability of gold-silica CSNPs (Au@SiO_2-Cy5) in biological media was investigated. The results showed that the gold core was marginally involved in the dissolution of silica shells. In contrast, the degree of dissolution highly depended on the particle concentration and properties of the biological media, such as pH and composition. In particular, it was observed that the presence of proteins in the media could accelerate the dissolution. Additionally, we confirmed that the chemical stability of Au@SiO_2-Cy5 could be improved by calcination, which can change the ratio of silica chemical structures between silanol and siloxane groups. Based on these results, we demonstrated that understanding and improving the chemical stability of CSNPs in biological media is necessary for a safe and long-term investigation of intracellular NPs.

Accelerated Reversible Conversion of Li_2S_2 to Li_2S by Spidroin Regulated Li^+ Flux for High-performance Li-Sulfur Batteries

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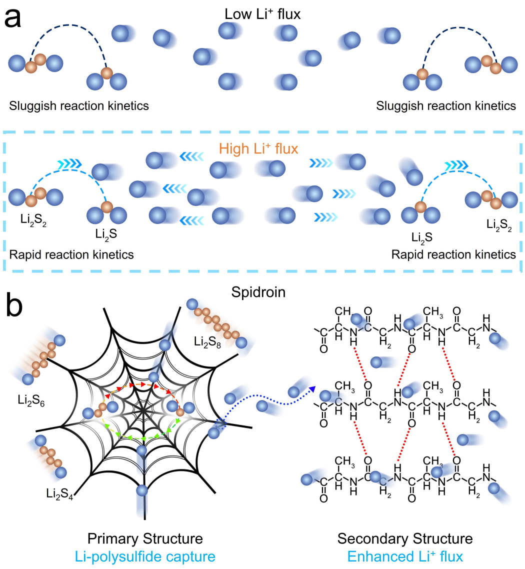
Regulating the transformation of sulfur species is the key to improving the electrochemical performance of lithium-sulfur (Li-S) batteries, in particular, to accelerate the reversible conversion between solid phase Li_2S_2 and Li_2S[1], which requires a strong affinity for polysulfides and simultaneous regulation of Li□ flux. However, materials that can simultaneously exhibit both lithophilicity and thiophilicity have rarely been reported. Herein, we introduced Spidroin, which is a main protein in spider silk, as a dual functional separator coating in Li-S batteries to effectively adsorb polysulfides via the sequence of amino acids[2] in its primary structure and regulate Li^+ flux through the β-sheet of its secondary structure[3], thus accelerating the reversible transformation between Li_2S_2 and Li_2S. Spidroin-based Li-S cells exhibited an exceptional electrochemical performance with a high specific capacity of 823.3 mAh g^{-1} at 6C and a high areal capacity of 6.1 mAh cm^{-2} at a low electrolyte-to-sulfur (E/S) ratio of 6 μL mg_s^{-1} and a sulfur loading of 6.7 mg_s cm^{-2}.



[1] S. Zhou, J. Shi, S. Liu, G. Li, F. Pei, Y. Chen, J. Deng, Q. Zheng, J. Li, C. Zhao, I. Hwang, C. J. Sun, Y. Liu, Y. Deng, L. Huang, Y. Qiao, G. Xu, J. Chen, K. Amine, S. Sun, H. Liao, Nature, 2023, 621, 75-81.

[2] M. Liu, P. Chen, X. Pan, S. Pan, X. Zhang, Y. Zhou, M. Bi, J. Sun, S. Yang, A. L. Vasiliev, P. J. Kulesza, X. Ouyang, J. Xu, X. Wang, J. Zhu, Y. Fu, Advanced Functional Materials, 2022, 32, 2205031.

[3] X. Li, L. Yuan, D. Liu, M. Liao, J. Chen, K. Yuan, J. Xiang, Z. Li, Y. Huang, Advanced Functional Materials, 2021, 31, 2100537.

Controlling the Magnetic Properties of the van der Waals Multiferroic Crystals $Co_{1-x}Ni_xI_2$

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In the growing family of magnetic van der Waals materials multiferroic compounds CoI and NiI_2have drawn significant attention lately due to the multiferroicity down to the monolayer and frustrated cycloid ground state caused by Kitaev interactions, respectively.[1,2] Despite prior investigations of these materials, the evolution of magnetic ground states within the solid solution between them remains unresolved. We have successfully grown crystals of the whole solid solution $Co_{1-x}Ni_xI_2$by employing the self-selecting vapor growth (SSVG) technique and carefully tuning the synthesis conditions according to the composition. Both the lattice parameters and magnetic properties evolve continuously and smoothly from one end member to the other, showing that they can be finely chemically tuned. We also observe that the Ni substitution for Co affects the metamagnetic transition typical for CoI_2. In particular, we find the existence of the metamagnetic transition similar to that for CoI_2in the NiI_2structure. Based on magnetic and structural measurements we construct the phase diagram of the $Co_{1-x}Ni_xI_2$system, which shows that physical properties can be finely chemically tuned by composition. Bulk crystals of the solid solution $Co_{1-x}Ni_xI_2$hold a possibility to be exfoliated into two-dimensional (2D) thin flakes and are expected to have thickness-dependent magnetic behavior down to a monolayer. This may open a pathway for fabricating 2D magnetic devices with new magnetic properties.

[1] C.Kim, *et al.*, *Nature Physics*, **2023**, 19, 1624–1629.

[2] Q.Song *et al.*, *Nature*, **2022**, 602, 601–605.

S–Mediated Interactions in Hybrid Perovskite Photovoltaics

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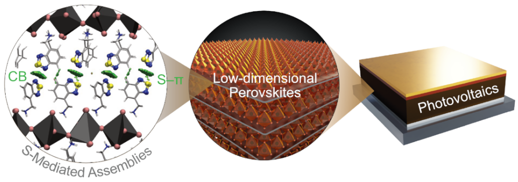
The stability of hybrid halide perovskite materials, one of the most prominent semiconductors in photovoltaics, remains a significant challenge to their application.[1] The use of low-dimensional (LD) perovskites, which incorporate hydrophobic organic moieties, provides an effective strategy to improve their stability, yet often at the expense of their device performance.[2] To address this, supramolecular engineering of non-covalent interactions between organic and inorganic components has shown potential.[3] We explore the capacity to access novel LD perovskite structures that uniquely assemble through unorthodox S-mediated interactions, such as σ-hole interactions in the form of chalcogen bonding,[3] by incorporating benzothiadiazole-based organic spacers.[4] We evidence the formation of S-mediated LD structures, including 1D and 2D perovskite phases, assembled via chalcogen bonding and S–π interactions through a combination of techniques, including X-ray diffraction, as well as solid-state NMR spectroscopy, complemented by molecular dynamics simulations, density functional theory calculations, and optoelectronic characterization, revealing superior conductivities of S-mediated LD perovskites.[4] The LD materials were applied in n-i-p and p-i-n perovskite solar cells, demonstrating enhancements in performance and stability that reveal a versatile supramolecular strategy for advancing photovoltaics.



[1] Jena, A. K., Kulkarni, A. & Miyasaka, T. Halide Perovskite Photovoltaics: Background, Status, and Future Prospects. *Chem Rev* **119**, 3036–3103 (2019).
[2] Milić, J. V. Multifunctional layered hybrid perovskites. *J Mater Chem C Mater* **9**, 11428–11443 (2021).
[3] W. Luo, G. AlSabeh, J. V Milić, in Photochem. Vol. 50 (Eds.: S. Crespi, S. Protti), The Royal Society Of Chemistry, 2022, p. 346–370.
[4] W. Luo, J. V. Milić, et al. *manuscript submitted* (2024)

Shape-controlled synthesis of cubic hematite (α-Fe_2O_3) particles

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Many recent research studies have focused on the fabrication of nanostructured iron oxides. Iron oxide materials have received considerable attention for their unique size- and shape-dependent properties (magnetic, catalytic, chemical properties, etc.). Since many efforts have been made to control their morphology, studying how shape-controlled nanomaterials are synthesized is interesting. Hematite (a-Fe_2O_3) is, in this respect, particularly promising. Its distinct red color, high refractive index, strong UV-blue absorption, and high visible-NIR reflectance are characteristic properties of hematite that arise from its crystal structure and electronic transitions involving Fe^{3+} ions. These properties make it useful in various applications like pigments, UV protection, and optical coatings. Almost all of the properties of a-Fe_2O_3 particles depend on their size and shape. Hydrothermal synthesis can be utilized to effectively control the shape of nano- and micro-sized hematite particles to obtain well-defined spheres, double spheres, ellipsoids, cubes, peanuts, disks or platelets, and bipyramids.

Our study details the formation of shape-controlled cubic - Fe_2O_3 particles, achieved through an ionic liquid-mediated hydrothermal reaction environment. This method was chosen for its ability to use iron chloride precursors and decyl and dodecyl-trimethylammonium chloride additives, leading to particles with excellent geometrical features.

Introducing oxygen vacancies into cubic nanoparticles enhanced their electronic, optical, and catalytic properties. This opens up a range of potential applications for our particles, including environmental remediation, sensing, and antimicrobial activity, demonstrating the practical relevance of our research.

Photoacid-induced supramolecular network disassembly

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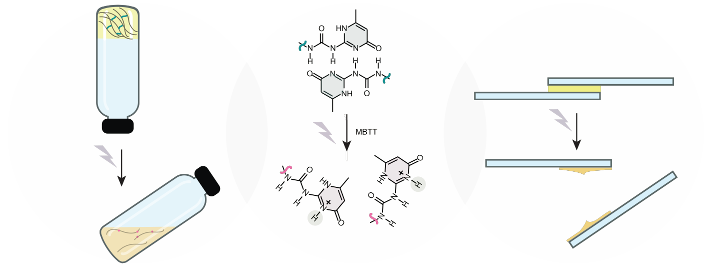
Supramolecular networks (SNs), as opposed to their covalently bound counterparts, offer dynamic properties such as self-healing and stimuli-responsiveness. This is due to the reversibility of the underlying intermolecular interactions that bind the monomers in a supramolecular manner. [1] In the late 1990s, the ureido-pyrimidinone (UPy) motif, a binding motif that exhibits a strong tendency to self-dimerize via the formation of four complementary hydrogen bonds, was discovered. [2] Since its conception, UPy has continued to be among the most researched supramolecular motifs and has enabled the fabrication of linear, chain-extended supramolecular polymers as well as supramolecular networks with useful functions and mechanical properties. [3] One such function exhibited by UPy-bearing SNs is the ability to change their mechanical properties in response to chemical, optical, or thermal stimuli. [4] Here, we report new supramolecular polymer systems that combine supramolecular polymers and an opto-chemical switch molecule, whose activation causes a rapid, on-demand change of the materials' mechanical properties. In our first embodiments of this approach, we incorporate a photoacid generator (PAG) into solutions, organogels, and solid films that contain polyacrylates carrying UPy pendant groups, which form supramolecular cross-links. We first use a pyrene-tagged UPy motif to demonstrate via fluorescence spectroscopy that the optical activation of the PAG 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine causes the protonation and, hence, dissociation of UPy dimers in response to irradiation with UV light. Moving to polymer systems, we use oscillatory rheology to demonstrate that organogels and solid films made from UPy-modified polyacrylates and the PAG can be uncross-linked and liquified via UV irradiation. These results represent the first steps towards a new family of robust SNs whose stimuli-responsive behaviour is imparted by a molecular switch, which renders the SNs dynamic only in response to a specific stimulus. Such materials may be useful as reversible adhesives, recyclable plastics, or healable glasses.



[1] R. F. M. Lange, M. Van Gurp, E. W. Meijer, Journal of Polymer Science: Part A: Polymer Chemistry, 1999, 37, 3657-3670.

[2] R. P. Sijbesma, F. H. Beijer, L. Brunsveld, B. J. B. Folmer, J. H. K. K. Hirschberg, R. F. M. Lange, J. K. L. Lowe, E. W. Meijer, Science, 1997, 278, 1601-1604.

[3] D. W.R. Balkenende , C. A. Monnier, G. L. Fiore, C. Weder, Nature Communications, 2016, 7, 10995.

[4] I. Onori, J. A. Berrocal, C. Weder, Polymer, 2024, 298, 126886.

Templated Synthesis of Atomically Precise Silver Nanoclusters in Programmable Three-Dimensional DNA Materials

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Noble metal nanoclusters bridge the gap between molecular materials and plasmonic nanoparticles, their size of > 2nm induces strong quantum confinement, discrete energy levels, a size and surface-dependent tunable band gap, and interesting optical and electronic properties.[1] DNA stabilized silver nanoclusters stand out through their bright and tunable fluorescence across the visible and NIR [2] at higher quantum yields than other surface ligands [3] and the specificity and selectivity of cluster size via DNA sequence.[4] Particular interest lies in developing a method to periodically arrange silver nanoclusters, for applications in functional sensors and photonic metamaterials, which had remained elusive till now.[5]

Implementing a mismatch of pyrimidines in the double-stranded DNA creates a binding site for Ag^+ within a three-dimensional DNA construct. [6] We investigated the function of these programmable metal-mediated DNA (mmDNA) sites as nucleation sites for silver nanoclusters.

By developing a compatible redox reaction of Ag^+ within self-assembled crystals we achieved the formation of silver nanocluster Ag_4-DNA constructs, in which the clusters solely formed at the previously programmed mmDNA sites and showed an even distribution throughout the material. We then characterized crystals of the Ag_4-DNA constructs by XRD and confocal microscopy, which was further utilized to investigate growth kinetics limited by the adsorption of Ag^+, cluster stability over time, pH and buffer exchange, and the site-specificity of Ag_4 synthesis. Increasing the silver-to-nucleation-site ratio enabled us to shift the dominant species from four- to six-atom silver nanoclusters.

Ultimately, we show in this work that we synthesized atomically precise four- and six-atom silver nanoclusters nucleated on native DNA base-pair mismatches, enabling templated monodisperse silver nanocluster synthesis directly into a 3D DNA nanostructure. We envision this work as a first step towards visible wavelength photonic metamaterials.

[1] A. Desireddy, B. E. Conn, J. Guo, B. Yoon, R. N. Barnett, B. M. Monahan, K. Kirschbaum, W. P. Griffith, R. L. Whetten, U. Landman, T. P. Bigioni, Nature, 2013, 501, 399–402.

[2] J. Sharma, H.-C. Yeh, H. Yoo, J. H. Werner, J. S. Martinez, Chemical Communications 2010, 46, 3280–3282.

[3] I. Díez, R. H. A. Ras, Nanoscale 2011, 3, 1963–1970.

[4] E. G. Gwinn, P. O'Neill, A. J. Guerrero, D. Bouwmeester, D. K. Fygenson, Advanced Materials 2008, 20, 279–28

[5] A. Gonzàlez-Rosell, C. Cerretani, P. Mastracco, T. Vosch, S. M. Copp, Nanoscale Advances 2021, 3, 1230–1260

[6] S. Vecchioni, B. Lu, W. Livernois, Y. P. Ohayon, J. B. Yoder, C.-F. Yang, K. Woloszyn, W. Bernfeld, M. P. Anantram, J. W. Canary, W. A. Hendrickson, L. J. Rothschild, C. Mao, S. J. Wind, N. C. Seeman, R. Sha, Advanced Materials 2023, 35, 2210938.

Synthesis and cytotoxicity of mesoporous bioactive glass nanoparticles

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Mesoporous silica particles (MSP) are gaining interest as drug delivery systems due to their tunable pore size and large specific surface area, enabling efficient loading of active pharmaceutical ingredients. To enhance the biocompatibility of MSP, we set out to synthesize mesoporous bioactive glass nanoparticles (MBGN) using a modified Stöber-type method to obtain spherical nanoparticles, pseudomorphic transformation to introduce the defined mesopores and subsequent removal of the structure-directing agent (SDA) to render the mesopores accessible. The size, morphology, and pore size of the MBGN were characterized and their cytotoxicity and uptake by phagocytic cells (RAW 264.7) was investigated. A lactate dehydrogenase assay was employed for the investigation of the cytotoxicity. To facilitate the study of MBGN uptake by RAW 264.7 cells using fluorescence microscopy, the MBGN surface was functionalized with fluorescent labels. The spherical MBGN exhibited a particle diameter ranging from 170 to 240 nm and a well-defined pore diameter of 3.5 to 4.1 nm. The investigation of the cytotoxicity confirmed that only MBGN containing SDA exhibited cytotoxicity. Our results demonstrate a rapid uptake of MBGN by phagocytic cells and stress the importance of complete removal of the SDA if MBGN are to be used as carriers in drug delivery systems.

In situ light-responsive hydrogels to study cell behavior

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The pressing need for innovative biomaterials that can effectively regulate cellular responses in tissue engineering and other biomedical applications is a challenge that continues to grow. The potential of cells' mechanosensitive behaviour represents a crucial area that demands immediate and thorough investigation.

In this context, we have created *in situ* light-responsive substrates that integrate isotropic and anisotropic plasmonic nanoparticles into a thermoresponsive polymeric matrix to assess cellular behaviour upon irradiation. Before cell exposure, we optimized the thermal and mechanical properties of the polymeric hydrogels by exploring different nanoparticle shapes, matrix thicknesses, and cross-linking densities.

Combining Solar Hydrogen Production and value-added Oxidations: Reforming of HMF on unbiased Photoelectrochemical Devices

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The global transition from fossil fuels to renewable energy sources represents one of the world’s most critical challenges. Photoelectrochemical water splitting offers a sustainable method for producing hydrogen fuel from solar energy. In this study, Sb_2Se_3 was utilized as photocathode for the hydrogen evolution reaction, while concurrently driving the oxidation of HMF to HMFCA using abundant copper catalysts, all without external bias. The approach holds promise for a sustainable and cost-effective way towards the generation of FDCA, which is a key building block of bio-based plastics.

Improving local antibiotic therapy through the study of interactions and release mechanisms between $CaSO_4$ carriers and antibiotics

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The treatment of infections in orthopaedic and trauma surgery remains a significant challenge in modern medicine. Local antibiotic treatment plays a pivotal role in the treatment of bone and joint infections. It offers the advantage of increased drug availability at the site of infection while minimizing systemic toxicity.[1]

This study investigates the structural and morphological aspects of local drug delivery systems using calcium-containing carrier materials such as $CaSO_4$. It also studies the interaction of prominent antibiotics, including vancomycin, tobramycin, and ceftriaxone, within the crystalline matrix of $CaSO_4$. At the core of our approach are advanced density functional theory (DFT) computational techniques that provide insights into surface adsorption energies and investigate forces such as chemical bonds, van der Waals interactions, and hydrogen bonding. These computational findings are complemented by experimental X-ray diffraction (XRD) data for comprehensive analysis.[2] Thus the research extends its focus to multiple dimensions of local drug delivery.[3,4] It explores the kinetics of drug release and cellular uptake, evaluates antimicrobial effectiveness, and employs simulation tools to elucidate underlying mechanisms governing the drug-carrier interactions and release profiles. The ultimate objective of this study is to provide a comprehensive understanding of the binding mechanisms of antibiotics within the $CaSO_4$ crystal structure, improving the treatment outcomes in orthopedic infections.[1,4]

[1] Wahl, P., M. Guidi, E. Benninger, K. Ronn, E. Gautier, T. Buclin, J. L. Magnin and F. Livio, *Bone Joint J.* **2017,** 99-B(11), 1537-1544.

[2] Yakutovich A. V., K. Eimre, O. Schütt, L. Talirz, C. S. Adorf, C. W. Andersen, E. Ditler, D. Passerone, *Comput. Mater. Sci.* **2021,** 188, 110165.

[3] Gramlich, Y., T. Johnson, M. Kemmerer, G. Walter, R. Hoffmann and A. Klug, *Knee Surg. Sports Traumatol. Arthrosc.* **2020**, 28(9), 2823-2834.

[4] Reinisch, K., M. Schlappi, C. Meier and P. Wahl, *J. Bone Jt. Infect* **2022,** 7(1) 11-21.

Controlled microstructure of cellulose nanofiber sponges through simultaneous stirring and freezing

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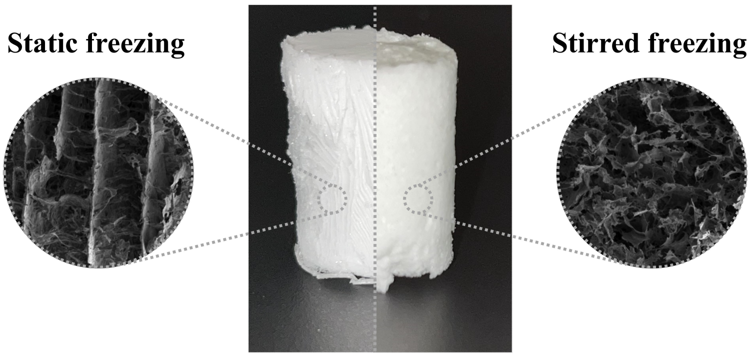
Nanofiber sponges are highly porous materials with low densities and a broad application potential from biomedicine and filtration technologies to thermal insulation [1]. Typically, nanofiber sponges are produced from electrospun nanofibers, which are then dispersed, frozen and freeze-dried, followed by cross-linking. The freezing step is particularly critical as it determines the porous architecture of the nanofiber sponges. By selecting appropriate freezing conditions, crystal growth of the dispersing agent and thus pore size and pore structure can be tailored. Common static freezing techniques lead to anisotropic pores, e.g. lamellar channels in case of water [2, 3].The focus of this work was on the precise control of the freezing step and to obtain homogeneous and isotropic nanofiber sponges. Therefore, freezing conditions were adopted from ice cream manufacturing, where simultaneous freezing and mechanical stirring led to an ice mass with a predefined structure and texture. Our cellulose nanofiber sponges were synthesized from nanofibrillated cellulose or electrospun regenerated cellulose nanofibers with special attention to the freezing conditions. The materials were characterized with infrared spectroscopy (IR) and scanning electron microscopy (SEM) and their physical properties such as air permeability, compression modulus or water stability were investigated. The obtained nanofiber sponges displayed densities between 14 and 61 mg cm^{-3} with up to 99 % porosity. Variation of the freezing conditions led to either lamellar channels (static, - 20 °C), very small lamellar channels (shock freezing) or globular and isotropic pores (stirred freezing). The flexible nanofiber sponges were stable in water and displayed favorable air permeability properties.



[1] Mandana Dilamian, Majid Joghataei, Zahra Ashrafi, Christoph Bohr, Sanjay Mathur, Hajar Maleki, *Applied Materials Today*, **2021,** 22, 100964.

[2] Fabian Deuber, Christian Adlhart, *CHIMIA*, **2017**, 71, 236-240.

[3] Shubham Gupta, Florian Martoïa, Laurent Orgéas, Pierre J. J. Dumont, *Appl. Sci.*, **2018**, 8, 2463.

Functionalization within a supramolecular triaxially woven framework

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Self-assembly can yield large and complicated architectures from simple molecules but their formation is a delicate process. Even slight alteration of conditions or seemingly simple modifications to a molecular building block can lead to drastically different results.[1] One major challenge is to create robust and reliable frameworks that can be functionalized to serve a specific purpose yet still retain the same internal structure such that one may have control over the application.

Our group reported the formation of a triaxially woven supramolecular weave, self-assembled from oligoprolines bearing perylene monoimide moieties (Figure).[2] The framework is stabilized through ?–? and CH–? interactions and features a regular distribution of pores within the structure. Functionalization at specific positions of the proline backbone allows for the same triaxial weave formation and inclusion of functional moieties within the pore. The functional group may be altered to change the purpose of the weave and the chemistry that may occur within its pores.

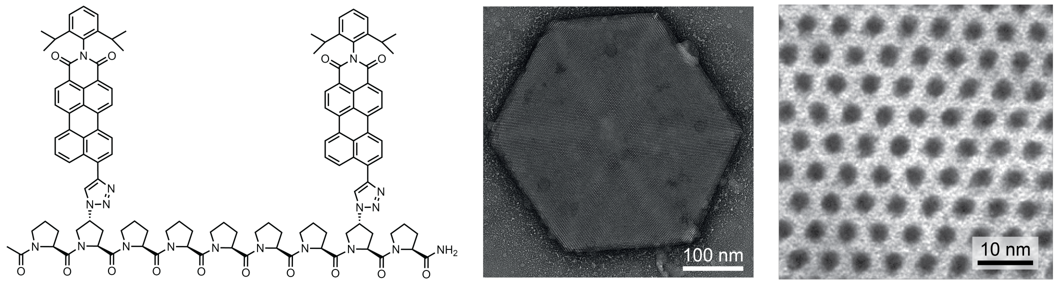

Figure. Chemical structure of an oligoproline functionalized with perylene monoimides, left, that self-assembles into a triaxial supramolecular weave as observed from TEM, middle, and its porous structure at higher magnification, right.

[1] T. Fukui, S. Kawai, S. Fujinuma, Y. Matsushita, T. Yasuda, T. Sakurai, S. Seki, M. Takeuchi, K. Sugiyasu, *Nat. Chem.* **2017**, *9*, 493–499.

[2] U. Lewandowska, *et. al. Nat. Chem.*, **2017**, *9*, 1068–1072.

Reprocessability and flame-retardancy epoxy vitrimers via phosphonated approach and their application in FRPCs

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[1]Laboratory for Advanced Fibers, Empa Swiss Federal Laboratories for Materials Science and Technology

One of the most urgent challenges of the future decades will be the rising volume of fossil-based plastic waste that ends up in our environment. Thus, the discovery of re-usable polymers with extended useful lifetimes marks the beginning of a shift toward a more circular economy. 1 Several recyclable materials have been created by including a wide range of covalent exchangeable bonds. Some of these materials, if they include enough carboxylic ester, disulfide, siloxane, imine, diketoenamine, Diels-Alder adduct, dioxaborolane links, and so on, can "flow" like thermoplastics again via network topological rearrangement through thermally driven catalytic bond exchanges. 2 When the exchange reaction kinetics are frozen, such network architectures are locked at product operating temperatures. Among the different dynamic covalent bonds, the transesterification process based on phosphorous esters may give an elaborate answer. 3 Phosphorous ester can also offer excellent fire protection,4 and broad industrial relevance due to ready availability of monomers and straightforward synthesis procedure. Phosphate triester-based thermosets sparked fresh ideas for multifunctional vitrimer materials. Because it is a chemically and thermally stable homologue of a P-O link, replacing the phosphate with phosphonate should improve material stability and flame retardancy.

In our recent work, we developed and synthesized a novel dynamic phosphonate ester bonds rich thermoset using a simple one-pot, two-step synthetic approach that displayed remarkable reparability, recyclability, and flame retardancy, with FR as part of the network as presented in Fig. 1 upleft. 5 Another polyester thermoset system using FR as a pedant group was also developed, as presented in Fig. 1 upright. As shown in the work one, the covalent incorporation of phosphonate moieties in the thermoset matrix introduced sufficient dynamic P-O ester bonds, and promoted the exchange of network strands under moderate heating condition, resulting in scratch reparability and recyclability, as demonstrated in Fig. 1 downleft. Coatings on wood and fiber reinforced polymer composites were utilized to demonstrate the potential applications for such materials in contributing to a circular economy.

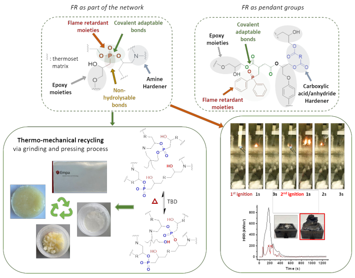

Fig. 1 The phosphonate dynamic cross-link approach for obtaining recyclable and flame-retardant epoxy thermosets.

(1) Häußler, M.; Eck, M.; Rothauer, D.; Mecking, S. Closed-loop recycling of polyethylene-like materials. Nature 2021, 590 (7846), 423-427. DOI: 10.1038/s41586-020-03149-9.

(2) Krishnakumar, B.; Sanka, R. V. S. P.; Binder, W. H.; Parthasarthy, V.; Rana, S.; Karak, N. Vitrimers: Associative dynamic covalent adaptive networks in thermoset polymers. Chemical Engineering Journal 2020, 385, 123820. DOI: https://doi.org/10.1016/j.cej.2019.123820.

(3) Wu Klingler, W.; Bifulco, A.; Polisi, C.; Huang, Z.; Gaan, S. Recyclable inherently flame-retardant thermosets: Chemistry, properties and applications. Composites Part B: Engineering 2023, 110667. DOI: https://doi.org/10.1016/j.compositesb.2023.110667.

(4) Bifulco, A.; Varganici, C. D.; Rosu, L.; Mustata, F.; Rosu, D.; Gaan, S. Recent advances in flame retardant epoxy systems containing non-reactive DOPO based phosphorus additives. Polymer Degradation and Stability 2022, 200, 109962. DOI: https://doi.org/10.1016/j.polymdegradstab.2022.109962.

(5) Wu Klingler, W.; Rougier, V.; Huang, Z.; Parida, D.; Lehner, S.; Casutt, A.; Rentsch, D.; Hedlund, K. B.; Barandun, G. A.; Michaud, V.; et al. Recyclable flame retardant phosphonated epoxy based thermosets enabled via a reactive approach. Chemical Engineering Journal 2023, 466, 143051. DOI: https://doi.org/10.1016/j.cej.2023.143051.

Sb_2S_3 Particle Based Photoanodes for Oxygen Evolution Reaction

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The main challenge of overall water splitting is the anodic part as it demands high energy to be carried out. Sb_2S_3 is a n-type semiconductor with a band gap of 1.7-1.6 eV which hold promise for solar water splitting applications in Z-scheme arquitectures. Here, particulate Sb_2S_3 has been synthesized by a simple solvothermal route and optimized to deliver a higher current density when processed into powder-based electrodes by the particle transfer method. The electrodes showed high photocurrent density compared to their respective thin films electrodes. The photoelectrochemical performance in terms of photocurrent density demonstrate the potential of Sb_2S_3 as an alternative photoanode material to $BiVO_4$ which has the record in efficiency on similar systems.

[1] Qian Wang, et al., *Nature Materials, 2016, 15, 611-615*

Enhanced Photoelectrochemical Performance of Sb_2Se_3 via Solvent-Based Hole Transport Layer Incorporation for Improved Crystalline Growth and Interface Charge Carrier Transport

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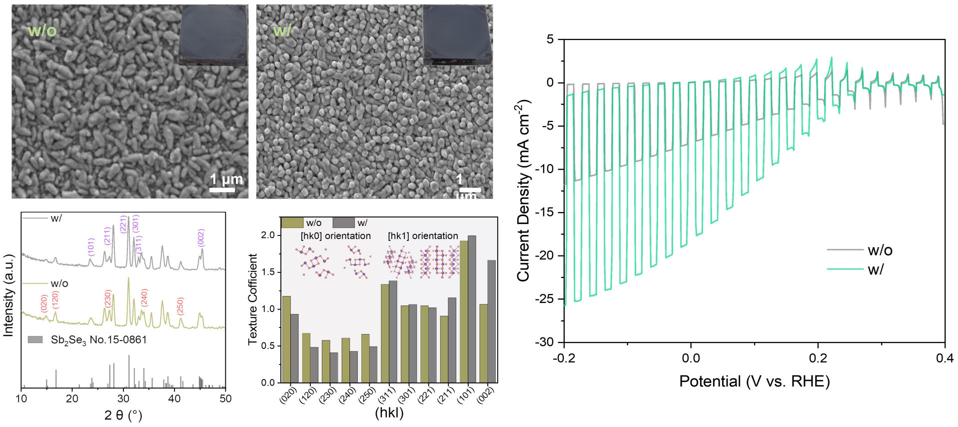
With the continuous development of renewable energy sources, photoelectrochemical energy conversion has attracted much attention as a green and sustainable energy conversion technology. Antimony selenide (Sb_2Se_3) is a highly investigated material due to its excellent photovoltaic properties; however, its application in photoelectrochemistry is still limited by charge separation and transport efficiency. In order to overcome this challenge, this study introduces a new strategy to improve the photoelectrochemical properties of antimony selenide by introducing a hole-transporting layer (HTL) via a solution method. Our study first investigated in detail the effect of HTL prepared by different solution methods on the light-absorbing layer material of antimony selenide. The experimental results show that the introduction of HTL not only significantly promotes the crystal growth of the antimony selenide light-absorbing layer material, but also optimizes the carrier transport at the interface between them. Through photoelectrochemical performance tests, we observed that the introduction of HTL significantly enhanced the photocurrent response and photoabsorption properties of antimony selenide, thus improving the photoelectrochemical efficiency. In addition, we thoroughly investigated the mechanisms of interfacial electron transport and charge separation by characterization techniques such as electrochemical impedance spectroscopy (EIS), revealing the key role of HTL introduction on the improvement of photoelectrochemical performance. Finally, our study provides a new understanding for utilizing the potential of antimony selenide in the field of photoelectrochemistry, which offers a promising path for the development and application of renewable energy. In conclusion, this study successfully enhanced the photoelectrochemical performance of antimony selenide-based photoelectrochemistry by introducing a hole transport layer through a solution method, a strategy that opens up new possibilities for further research and applications in the field of photoelectrochemical energy conversion.



[1] Lee, H.; Yang, W.; Tan, J.; Oh, Y.; Park, J.; Moon, ACS Energy Lett. 2019, 4 (5), 995–1003.

[2] Li, P.; Yuan, X.; Feng, M.; Ran, F.; Zhang, D.; Chen, S, Appl. Phys. Lett. 2021, 119 (10), 102101.

Perfluoroarene-based layered tin halide perovskites in hybrid photovoltaics

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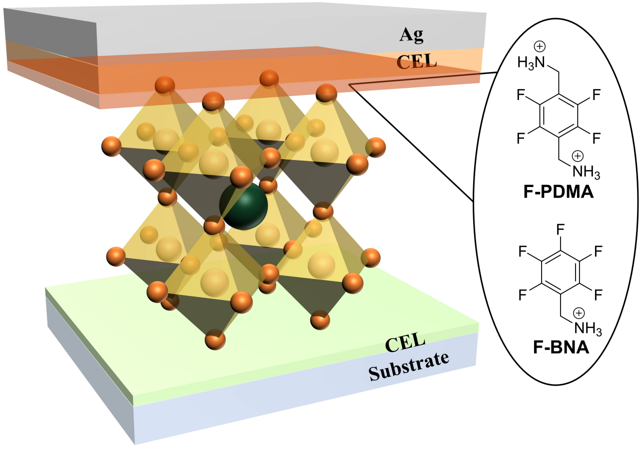
Hybrid halide perovskites are the most promising candidate for next-generation photovoltaics due to their outstanding optoelectronic properties. However, the most investigated lead-based perovskite solar cells are toxic and environmentally harmful, and finding sustainable alternatives is a pressing issue.[1] Tin-based (Sn) perovskites are attracting interest owing to their lower toxicity, similar chemical properties, and favorable characteristics in functional devices.[1,2] However, the development of Sn-based photovoltaics is hindered by the high concentration of defects in the bulk and surface due to the fast crystallization process and easy oxidation of Sn(II) to Sn(IV).[2,3] Efforts to overcome this challenge include compositional, interface, and device engineering.[2–5] One of the most effective strategies relies on interfacial molecular assemblies and layered hybrid perovskites based on hydrophobic moieties.[4–5] We have thereby investigated tin-based hybrid perovskites based on perfluoroarene organic cations, namely 2-(perfluorophenyl)methylammonium (F-BNA) and 1,4-(perfluorophenyl)dimethylammonium (F-PDMA),[6] which form Ruddlesden-Popper and Dion-Jacobson layered (2D) perovskites, respectively. We have analyzed their structural and optoelectronic characteristics by a combination of techniques to demonstrate the formation of 2D perovskite phases, which are thereafter applied to 2D/3D perovskite solar cells to demonstrate a versatile strategy in the advancement of tin-based perovskite photovoltaics.[7]



[1] A. Abate, *ACS Energy Lett.*, **2023**, 8, 1896-1899.

[2] E. Aktas, N. Rajamanickam, J. Pascual, S. Hu, M. H. Aldamasy, D. Di Girolamo, W. Li, G. Nasti, E. Martínez-Ferrero, A. Wakamiya, E. Palomares and A. Abate, *Commun. Mater.*, **2022**, 3, 1-14.

[3] M. Aldamasy, Z. Iqbal, G. Li, J. Pascual, F. Alharthi, A. Abate and M. Li, *Phys. Chem. Chem. Phys.*, **2021**, 23, 23413-23427.

[4] J. Zhao, Z. Zhang, G. Li, M. H. Aldamasy, M. Li and A. Abate, *Adv. Energy Mater.*, **2023**, 13, 2204233.

[5] F. Yang, R. Zhu, Z. Zhang, Z. Su, W. Zuo, B. He, M. H. Aldamasy, Y. Jia, G. Li, X. Gao, Z. Li, M. Saliba, A. Abate and M. Li, *Advanced Materials*, **2024**, 36, 2308655.

[6] J. V. Milić, *J. Phys. Chem. Lett.*, **2022**, 13, 9869-9874.

[7] M. Zhu, J. V. Milić et al. manuscript in preparation.

Triphenylphosphine Oxide: A Versatile Covalent Functionality for Carbon Nanotubes

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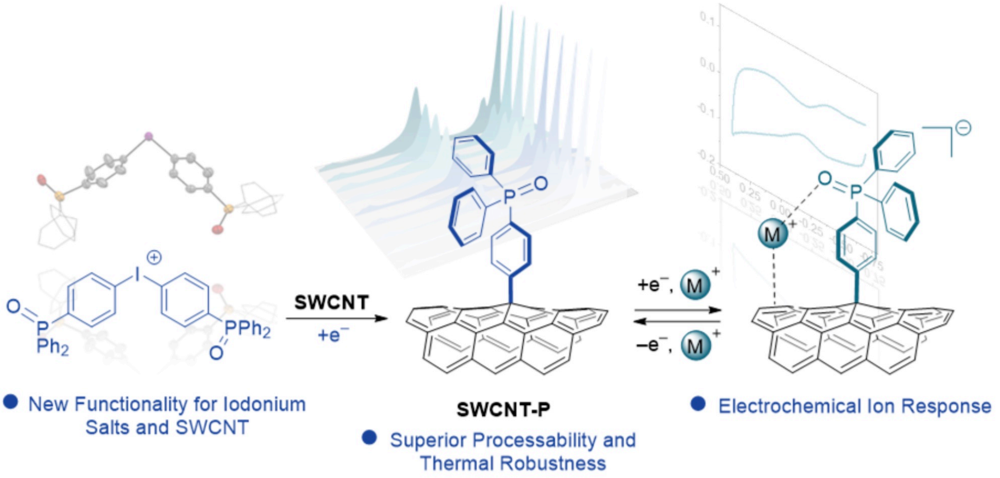
Single-walled carbon nanotubes (SWCNT) are a promising class of nanomaterials for application as sensors, batteries, spintronics and heterogeneous catalysts owing to their excellent physical, mechanical and electronic properties.[1] To successfully implement SWCNTs in such applied settings, surface functionalization is necessary to tune their chemical and physical properties.[2] Among various modification approaches, covalently functionalized SWCNTs feature long-term stability and therefore continue to attract research interest. However, efficient and controllable covalent modification methods remain limited due to the inertness and poor dispersibility of SWCNTs that hinder the incorporation of new functionalities and the exploration of new applications.[3] In particular, phosphorus-containing functional groups are virtually unexplored compared to their well-developed nitrogen/oxygen-based counterparts[4] in the context of SWCNT surface chemistry.

Herein we present the synthesis and characterization of a new series of phosphine oxide- functionalized diaryliodonium salts, which served as convenient aryl transfer reagents for accessing novel phosphorus-enriched carbon nanotubes (**SWCNT-P**). A suite of spectroscopic characterization methods combined with electron microscopy and thermogravimetric analysis supported the atomically precise covalent attachment of triphenylphosphine oxide in **SWCNT- P** as well as its superior processability and thermal robustness. Electrochemical studies were conducted and suggest that **SWCNT-P** exhibits a response to Lewis acidic cations, representing a proof-of-concept for its utility as a robust ion sensing platform.[5]



[1] V. Schroeder, S. Savagatrup, M. He, S. Lin, T. M. Swager, *Chem. Rev.* **2019**, *119*, 599-663.
[2] D. Tasis, N. Tagmatarchis, A. Bianco, M. Prato, *Chem. Rev.* **2006**, *106*, 1105-1136.
[3] X. Lu, Z. Chen, *Chem. Rev.* **2005**, *105*, 3643-3696.
[4] S. X. L. Luo, R. Y. Liu, S. Lee, T. M. Swager, *J. Am. Chem. Soc.* **2021**, *143*, 10441-10453.
[5] Y. Pan, D. Baster, D. Käch, J. Reger, L. Wettstein, F. Krumeich, M. El Kazzi, M. J. Bezdek, *Submitted*.

Nanoscopic mechano-imaging in polymers

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The stress application on polymers often leads to their fracture and failure, and this can be an obstacle towards the preparation of “sustainable polymeric materials”. The origin of macroscopic failure is the presence of nanoscopic defects in polymeric materials. Precise visualization of the evolution of these nanoscopic defects to microcracks and their propagation will help us study the dynamics of polymer failure. This knowledge will not only help us to predict polymer failure in advance but also to design polymers with enhanced mechanical properties. Mechanochromic mechanophores are a class of molecules that give out an optical signal when they experience force. Using sensitive force-reporting mechanophore motifs, one can sense and image the distribution of stress in polymer networks.To achieve this at a nanoscale resolution, we aim to exploit the highly promising technique of single-molecule localization microscopy. This requires the judicious development of force sensors that give out stochastically fluctuating fluorescent signals when they are mechanically activated. Semiconductor quantum dots exhibit intrinsic fluorescence blinking, which has enabled their wide use as labels for super-resolution imaging. Harnessing this property, we aim to combine quantum dots with mechanophores to assemble a FRET-based SMLM probe. The probe will be applied to perform nanoscopic mechano-imaging of filled polymer nanocomposites.

[1] H. Traeger, D. Kiebala, C. Calvino, Y. Sagara, S. Schrettl, C. Weder and J. M. Clough, *Mater Horiz*, 2023, **10**, 3467–3475.
[2] H. Li and J. C. Vaughan, *Chem Rev*, 2018, **118**, 9412–9454.
[3] J. Xu, K. F. Tehrani and P. Kner, *ACS Nano*, 2015, **9**, 2917–2925.