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Swiss Science Concentrates

A CHIMIA Column

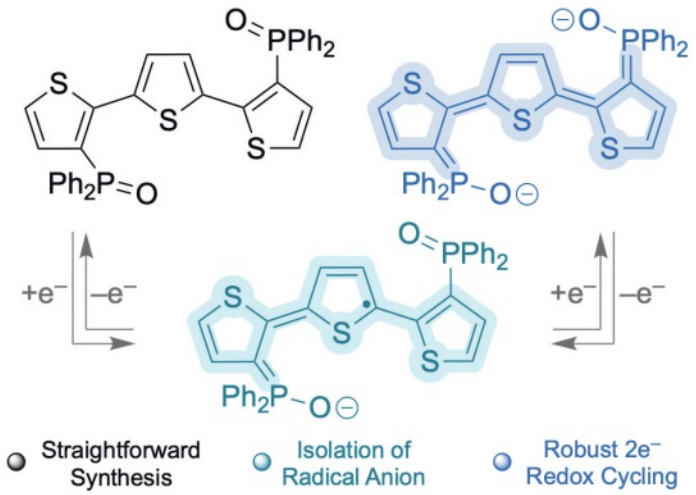
Short Abstracts of Interesting Recent Publications of Swiss Origin

Phosphine Oxide-Functionalized Terthiophene Redox Systems

Daniel Käch, Aurelio C. Gasser, Lionel Wettstein, Clara Schweinzer, and Máté J. Bezdek*
Angew. Chem. Int. Ed. **2023**, *62*, e202304600
https://doi.org/10.1002/anie.202304600
ETH Zürich, Zurich, Switzerland

Redox systems based on main group elements are attractive for various applications, including energy storage, but their long-term stability has been a challenge. The authors demonstrate that phosphine oxide functionalization of terthiophenes enables them to function as robust two-electron acceptors at very low potentials, expanding the parameter space for stable main group redox systems with high cell voltages. The researchers synthesized a phosphine oxide-functionalized terthiophene and characterized its redox properties using various techniques. They found that the compound exhibited reversible two-electron reduction at extreme negative potentials (lower than –2.0 V *vs.* Fc/Fc^+), while retaining high stability. The electronic structure of the compound and its reduced forms were investigated using density functional theory calculations. The authors also explored the effect of substituents on the terthiophene backbone to modulate the electrochemical properties. Overall, this study presents a new strategy for designing stable main group redox systems with high cell voltages, which could have significant implications for the development of next-generation energy storage devices and other organic electronics applications.

Authors' comments:
"Oligothiophenes are among the most well-investigated structural motifs in organic electronics yet remain underutilized in energy storage due to their redox instability. Unlocking terthiophene redox chemistry by phosphine oxide functionalization opens new parameter space for molecular energy storage media."

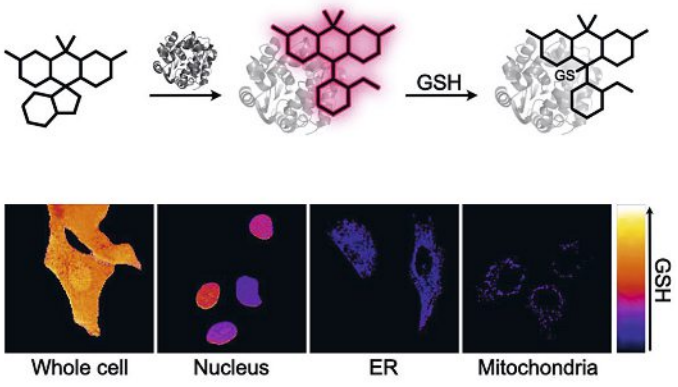


A locally activatable sensor for robust quantification of organellar glutathione

Sarah Emmert, Gianluca Quargnali, Sebastian Thallmair, and Pablo Rivera-Fuentes*
Nat. Chem. **2023**
https://doi.org/10.1038/s41557-023-01249-3
Institute of Chemical Sciences and Engineering, EPFL, Lausanne, Switzerland; Department of Chemistry, University of Zurich, Zurich, Switzerland; Frankfurt Institute for Advanced Studies, Frankfurt am Main, Germany

A new glutathione (GSH)-sensing platform called TRaQ-G has been developed for live-cell imaging, allowing for a detailed understanding of intracellular GSH homeostasis. This platform enables mapping of GSH compartmentalization and intra-organelle fluctuations. TRaQ-G is a chemogenetic sensor based on a silicon rhodamine-HaloTag conjugate. The sensor selectively responds to GSH in specific locations due to its unique reactivity turn-on mechanism. It can be combined with a fluorescent protein, resulting in a ratiometric response. With a TRaQ-G-mGold fusion, the study demonstrates independent regulation of nuclear and cytosolic GSH pools during cell proliferation. When used simultaneously with a redox-sensitive fluorescent protein, both redox potential and GSH concentration could be measured at the same time in the endoplasmic reticulum. By swapping the fluorescent protein, a near-infrared, targetable, and quantitative GSH sensor was created. This advancement offers a powerful tool for investigating GSH dynamics and its involvement in cellular signaling pathways.

Authors' comments:
"Glutathione is a key regulator in the context of cellular redox homeostasis and stress. We developed a glutathione sensor with subcellular targetability, robustness and a dynamic read-out for live-cell imaging."



Prepared by Cesare Berton, Patrick A. Cieslik, Fan Liu, Samy Kichou, Dominik Roth, Stanislav Prytuliak, Simon Klinger, Jonas Genz, Eda Nisli, and Jason P. Holland*

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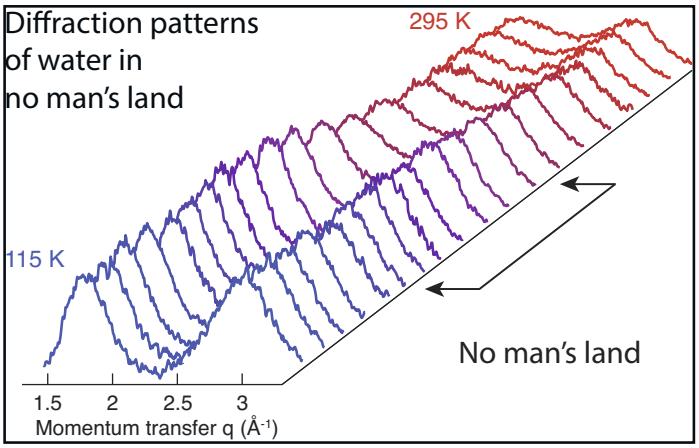
Electron diffraction of deeply supercooled water in no man's land

Constantin R. Krüger, Nathan J. Mowry, Gabriele Bongiovanni, Marcel Drabbels, and Ulrich J. Lorenz*
Nat. Commun. **2023**, *14*, 2812
https://doi.org/10.1038/s41467-023-38520-7
Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland

In this paper, the authors aimed to characterize water systematically in the deeply supercooled regime to understand its anomalous properties. Previous studies have been limited by the rapid crystallization of water between 160 K and 232 K, referred to as 'no man's land'. To overcome this challenge, the authors present an experimental approach that involves rapidly preparing deeply supercooled water at a well-defined temperature and probing it with electron diffraction before crystallization occurs. Their experiments show that as water is cooled, its structure evolves smoothly and approaches that of amorphous ice below 200 K. This experimental approach narrows down the possible explanations for the origin of water anomalies and opens new avenues for studying supercooled water. Additionally, there is potential application of their approach in investigating the dynamics of supercooled water and its relevance to cryo-electron microscopy in structural biology.

Authors' comments:
"We believe that our method for rapidly preparing water in no man's land and probing it before crystallization sets in should be quite general. We hope that this will enable others to use our approach to study deeply supercooled water with a variety of probes."



Seeking Brightness in Molecular Erbium-Based Light Upconversion

Inès Taarit, Filipe Alves, Amina Benchohra, Laure Guénée, Bahman Golesorkhi, Arnulf Rosspeintner, Alexandre Fürstenberg, and Claude Piguet*
J. Am. Chem. Soc. **2023**, *145,* 8621
https://doi.org/10.1021/jacs.3c01331
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Near-infrared (NIR) to visible light upconversion is an important phenomenon in the development of deeply penetrating biological probes and optical limiting devices. It relies either on the nonlinear optical properties of materials or the successive absorption of several photons. The latter occurs *via* two mechanisms: excited-state absorption (ESA) and energy transfer upconversion (ETU). In this work, the authors developed a compact erbium binding ligand that carries a sulfur bridge between the dye and the chelating moiety, thus forming stable complexes capable of efficient ETU. Detailed photophysical studies show an unprecedented conversion efficiency of the near-infrared (801 nm) into visible green (525–545 nm) light. These discoveries could lead to the development of the novel biological probes and NIR-sensitive photocatalysts.

Authors' comments:
"Shifting from difficult-to-reproduce doped solid-state materials toward stable and well-defined single molecular entities opens remarkable perspectives for pushing linear upconversion within the frame of innovative optical applications."