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A CHIMIA Column

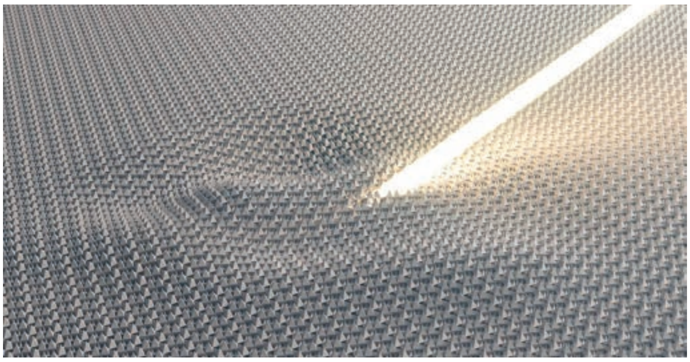
Short Abstracts of Interesting Recent Publications of Swiss Origin

Quantifying Photoinduced Polaronic Distortions in Inorganic Lead Halide Perovskite Nanocrystals

Oliviero Cannelli, Nicola Colonna, Michele Puppin, Thomas C. Rossi, Dominik Kinschel, Ludmila M. D. Leroy, Janina Löffler, James M. Budarz, Anne Marie March, Gilles Doumy, Andre Al Haddad, Ming-Feng Tu, Yoshiaki Kumagai, Donald Walko, Grigory Smolentsev, Franziska Krieg, Simon C. Boehme, Maksym V. Kovalenko, Majed Chergui*, Giulia F. Mancini*, *J. Am. Chem. Soc.* **2021**, *143*, 9048-9059. https://doi.org/10.1021/jacs.1c02403
École Polytechnique Fédérale de Lausanne, Paul Scherrer Institute, Argonne National Laboratory, ETH Zurich

Understanding the interplay of charge carriers and the polar lattice in out-of-equilibrium conditions in lead halide perovskites is crucial for the development of next-generation perovskite-based optoelectronic devices. While it is known that the flexibility of the Pb-Br framework is key in their light-activated functionality, in $CsPbBr_3$ perovskites, the mechanisms of local structural rearrangements require further elucidation. Here, the authors elegantly illustrate that photoinduced lattice changes in the system are due to a specific polaronic distortion, associated with the activation of a longitudinal optical phonon mode, and show that carrier recombination reversibly unlocks structural deformation at both Br and Pb sites. These results provide a thorough description of the $CsPbBr_3$ perovskite's photophysics, offering novel insights on the light-induced response of the system.

Authors' comments:
"This work clarifies the difference between optically- and temperature-induced thermal effects in $CsPbBr_3$ perovskites, showing the importance of combining different approaches (X-ray and optical spectroscopy, X-ray diffraction) in order to unravel details of photoinduced processes in these materials" says Giulia Mancini.

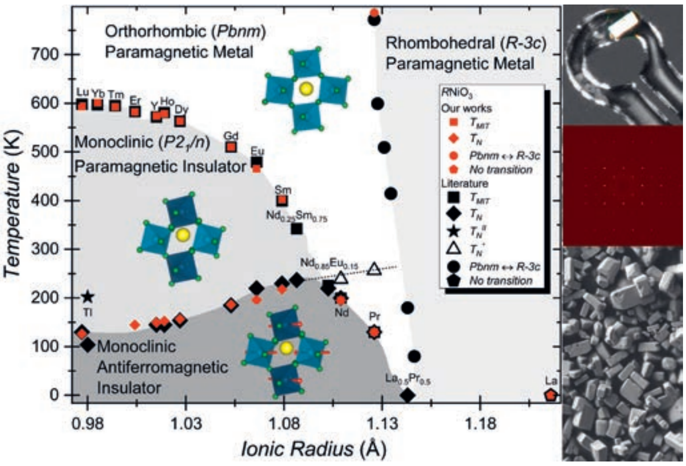


*RE*NiO$_3$ Single Crystals (RE = Nd, Sm, Gd, Dy, Y, Ho, Er, Lu) Grown from Molten Salts under 2000 bar of Oxygen Gas Pressure

Yannick Maximilian Klein,* Mirosław Kozłowski, Anthony Linden, Philippe Lacorre, Marisa Medarde,* and Dariusz Jakub Gawryluk*, *Cryst. Growth Des.* **2021**, *21*, 4230–4241, https://doi.org/10.1021/acs.cgd.1c00474
Paul Scherrer Institute, University of Zurich

In this work the authors report on the first-ever successful growth of rare earth nickelates (*RE*NiO$_3$) single crystals with *RE* = Nd, Sm, Gd, Dy, Y, Ho, Er and Lu, a family of oxides with fascinating magnetic and electronic properties. Their unusually high Ni formal valence (3+) requires oxygen pressures up to 60 kbar and high temperature to obtain stoichiometric ceramic samples, making the growth of single crystals extremely challenging. Using a novel approach involving solvothermal growth, a high temperature gradient, and much lower oxygen gas pressures (2 kbar) the authors managed to obtain *RE*NiO$_3$ single crystals of excellent quality covering the full 4*f* series. The availability of such crystals, with physical properties identical to those reported for ceramic samples, should pave the way to advanced measurements impossible to conduct in the past, hopefully contributing to a better understanding of the physicochemistry of oxides with highly correlated electrons.

Authors' comments:
"This novel, technically challenging crystal growth route eliminates one of the main stoppers for the understanding the unusual properties of *RE*NiO$_3$ perovskites, one of the rare oxide families with spontaneous metal-to-insulator transitions with a huge potential for optoeletronics and neuromorphic applications".



Prepared by David Lim, Pablo Diaz Kruik, Lucia Robustini, Stefania Gianolio, and Francesca Paradisi*
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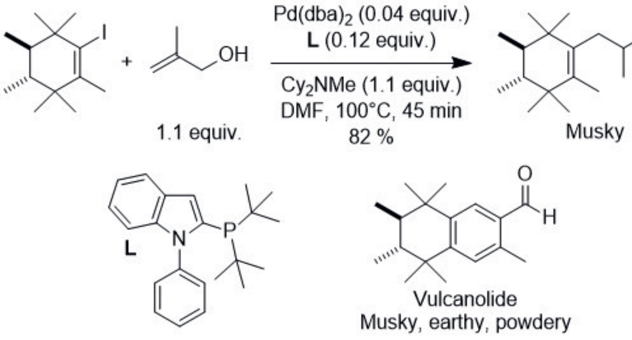
Relay-Heck Cross-Coupling Between Alkenyl Halides and Unsaturated Alcohols in the Synthesis of Open-Chain Analogues of Musk Odorant Vulcanolide

Anthony Lenormand, Lucía Reyes Méndez, and Julien Coulomb*, *Chem. Eur. J.* **2021**, *27*, 9276-9280, https://doi.org/10.1002/chem.202101080
Firmenich SA

Vulcanolide is a polycyclic aromatic musk odorant with earthy and powdery facets, which is more tenacious and at least 10 times stronger than benchmark molecules of the same family. The (*S*)–enantiomer of Vulcanolide is responsible for the musky scent and a double bond at the ring junction seems to be a structural requirement for this typical smell. In this work, the synthesis of open-chain analogues with retained key olfactory activity was investigated. This process involved a palladium-catalyzed relay-Heck cross-coupling between an unactivated alkenyl halide with a series of allylic alcohols, forming unsaturated aldehydes and ketones. Attempts to broaden the scope of the coupling reaction with homoallylic and longer chain unsaturated alcohols, provided a straightforward access to a whole range of unsaturated carbonyl compounds.

Authors' comments:
"This reaction gives an instant access to compounds that previously required multi-step syntheses, including patented odorant molecules. We also discovered the first cyclohexenylpropanal derivatives with a musky smell, as previously known analogues were lily of the valley odorants."



Rules of Nucleophilic Additions to Zigzag Nanographene Diones

Peter Ribar, Leoš Valenta, Tomáš Šolomek,* and Michal Juríček*, *Angew. Chem. Int. Ed.* **2021**, *60*, 13521–13528, https://doi.org/10.1002/anie.202016437
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Molecular graphene-based materials are crucial for the development of organic electronics. Functionalization of their periphery is key to controlling their electronic structure, solubility, stability, and self-assembly behaviour. Although nucleophilic additions of carbon-based nucleophiles to readily available ketone precursors represent a straightforward method for selective functionalization of zigzag nanographenes, it is rarely found in the literature.
In this article, the authors investigated nucleophilic additions to prototypical diones, triangulenedione and anthanthrone. With the help of DFT calculations, they derived four general rules that govern the selectivity of these reactions: 1) A directing group is needed, 2) ketone conjugation topology affects the electronic preference for 1,2- versus 1,4- selectivity, 3) size of the π-electron cloud of the ketone and the nucleophile favors 1,4-addition, and 4) non-planarity of ketones may alter the expected selectivity. These rules enable installation of substituents at a late stage of the synthesis as well as addressing positions which would not be accessible otherwise.

Authors' comments:
"A vast number of nanographene ketones have been reported since the pioneering work of Eric Clar. Our method can therefore enable synthesis and exploration of hitherto unknown functionalized nanographenes."