



Swiss Science Concentrates

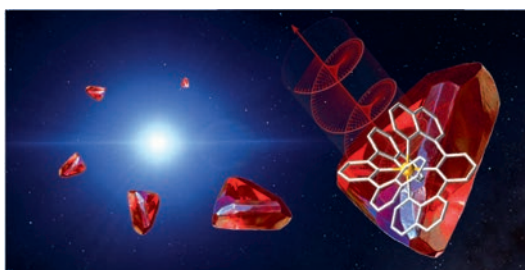
A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

Chiral Molecular Ruby $[\text{Cr}(\text{dqp})_2]^{3+}$ with Long-Lived Circularly Polarized Luminescence

J.-R. Jiménez,* B. Doistau, C. M. Cruz, C. Besnard, J. M. Cuerva, A. G. Campaña,* and C. Piguet,* *J. Am. Chem. Soc.* **2019**, *141*, 13244. University of Geneva and University of Granada

The use of molecular Cr(III)-based coordination complexes to construct cheap emissive chiral materials is of great interest for many applications. The authors report the chiral resolution of the kinetically inert complex $[\text{Cr}(\text{dqp})_2]^{3+}$, formed with two chelating 2,6-di(quinolin-8-yl)pyridine (dqp) ligands, by cation-exchange chromatography and salt-metathesis. The dissymmetry factors measured by circularly polarized luminescence, which shows two emission bands within the NIR region due to the metal-centered spin-flip, were exceptionally high and comparable to values reported for lanthanides. Moreover, an extremely long-lived room temperature phosphorescence (1.2 ms) was observed in water, together with a high quantum yield (5.2%).



Ni-Catalyzed Enantioselective Intermolecular Hydroamination of Branched 1,3-Dienes Using Primary Aliphatic Amines

G. Tran, W. Shao, and C. Mazet,* *J. Am. Chem. Soc.* **2019**, *141*, 14814, doi: 10.1021/jacs.9b07253. University of Geneva

The stereocontrolled addition of amines to olefins *via* transition-metal catalysis provides a direct and atom-economical access to valuable chiral nitrogen-containing molecules, but also poses several issues associated with regio-, diastereo-, and enantio-control. In this paper, Mazet and co-workers describe a highly regioselective and enantioselective Ni-catalyzed intermolecular hydroamination of 2-substituted 1,3-dienes with linear and α -branched aliphatic primary or secondary amines. The reaction displays excellent yields and functional group tolerance. Kinetic studies revealed a Ni- π -allyl catalyst resting state and rate-determining outer-sphere attack of H-bonded amine aggregates. This work represents a major advance in the enantioselective synthesis of chiral amines.

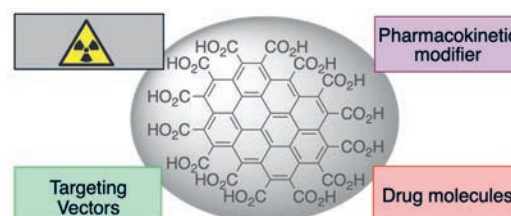


- ◆ mild conditions
- ◆ high enantioselectivity
- ◆ broad scope
- ◆ high regioselectivity
- ◆ 1° and 2° amines
- ◆ mechanistic study

Multi-functionalised graphene nanoflakes as tumour-targeting theranostic drug-delivery vehicles

J. Lamb, E. Fischer, M. Rosillo-Lopez, C. G. Salzmann, and J. P. Holland,* *Chem. Sci.* **2019**, *10*, 8880, doi: 10.1039/c9sc03736e. University of Zurich and University College London

Graphene nanoflakes (GNFs) are composed of a graphene sheet with a pristine aromatic system and carboxylic acid groups on the edge. They represent a potential new scaffold for theranostic agents due to their high water solubility and ease of functionalization. In this work, J. P. Holland and co-workers prepared multi-functionalized GNFs with an array of pharmacophores, and evaluated their performance *in vitro* and *in vivo*. For instance, GNFs functionalized with the antimetabolic drug ispinesib remained pharmacologically active and showed enhanced water solubility. This work demonstrates that GNFs are promising versatile platforms for theranostic drug development.



Long-Lived, Strongly Emissive, and Highly Reducing Excited States in Mo(0) Complexes with Chelating Isocyanides

P. Herr, F. Glaser, L. A. Büldt, C. B. Larsen, and O. S. Wenger,* *J. Am. Chem. Soc.* **2019**, *141*, 14394, doi: 10.1021/jacs.9b07373. University of Basel

Many photophysical and photochemical applications are based on the long-lived luminescent metal-to-ligand charge transfer (MLCT) of precious d^6 metal complexes. Wenger and co-workers introduce a new family of photoactive Mo(0) complexes with chelating diisocyanide ligands displaying luminescent quantum yields up to 0.20 and microsecond excited state lifetimes in solution at room temperature, which are significantly better than for $[\text{Ru}(\text{bpy})_3]^{2+}$. The new complexes were shown to promote light-driven aryl-aryl coupling reactions which are thermodynamically too challenging for precious metal-based complexes such as the widely employed *fac* $[\text{Ir}(\text{ppy})_3]$.

