

New research coordinator for CBBC

From November 1st, Mickel Hansen will be the research coordinator of the CBBC in Groningen (Advanced Research Center Chemical Building Blocks Consortium) which is a nationwide close collaboration between academia (7 research groups in Groningen) and industry (Akzo Nobel, BASF, Shell) in the Netherlands. The research focus in Groningen will mainly be on homogeneous catalysis, materials and synthesis. Mickel's main role will be to develop and coordinate the new CBBC research hub within the University of Groningen. Welcome (back) Mickel!



PhD students involved in the “Weekend van de Wetenschap”



Marcel Eleveld and Jim Ottelé (both PhD students in the Otto group) were invited on October 6th by Bidfood (a wholesale company for food professionals). They performed a couple of experiments and told the audience more about the pH of food and the density of ice, water and oil. One highlight was a reaction of hydrogen peroxide with chicken liver (that contains peroxidase and thus forms an "elephant's toothpaste").

A (beautiful) picture taken by Dusan Kolarski features in C&EN

C&EN's Chemistry in Pictures was launched in early 2014 to showcase the beauty of chemistry and chemical engineering. Through visually compelling photos and images, it provides a window into the fascinating world of scientific research and discovery.

The picture shown here, taken by Dusan Kolarski (Feringa group), was selected to feature in one of the latest editions of C&EN ([link](#)).



The vials shown here contain a molecule that can be activated with light to affect biological processes in mammals. It's part of a class of potential smart drugs that are under development to treat ailments including diabetes, blindness, and the side effects of chemotherapy. Because the molecules turn on only when hit with a certain wavelength of light, researchers can control when and where the compounds are active in the body.

Well done Dusan!

Explaining the Origin of Life to high school teachers

Jim Ottelé (again!) will teach a masterclass at the Woudschoten Chemie Conferentie 2018. This meeting gathers once a year around 300 high school teachers (“havo” and “vwo”) from the Netherlands and is aimed at keeping chemistry education “in motion” by continuous update on new course content and teaching methods.

Jim’s presentation will be about the various theories describing the origin of life and the most recent developments in the journey towards *de novo* life.



Highlights by Prof. dr. Jan B.F.N.Engberts

Recently Prof. Hummelen called my attention to two interesting papers in the area of organic photovoltaic cells (OPVs). One of them, published in *Science*, reports a world record of 17.29% power conversion accomplished by Chen, Ding and Wan, with ten coworkers, from the South China University, in Guangzhou, the National Center for Nanoscience in Beijing and Nankai University in Tianjin, all in China. OPVs possess many advantages, but their performance is often much lower than that of other photovoltaic platforms. Their low charge mobility leads to a limit on the active layer thickness and efficient light absorption. These disadvantages were now largely removed guided by a semi-empirical model analysis and employing a tandem cell strategy. In addition to these features, advantage was taken of the high diversity and easily tunable band structure of organic materials. The very high power conversion (PCE) of 17.29% was accomplished for a 2-terminal monolithic solution processed tandem OPV. The authors even argue that a PCE of >25% should be achievable. Taking into account other advantages, OPVs should be competitive as other solar cell technologies for industrial applications in the future in case their stability could be addressed.

Meng, L., Zhang, Y., Wan, X., Li, C., Zhang, X., Wang, Y., Ke, X., Xiao, Z., Ding, L., Xia, R., Yip, H-L., Cao, Y., Chen, Y., *Science*, 2018, [DOI 10.1126/science.aat2612](https://doi.org/10.1126/science.aat2612).

A recent publication by Yu and three colleagues at The Scripps Research Institute in La Jolla, California, describes a Pd(II)-catalysed enantioselective C(sp³)-H fluorination using a chiral transient directing group. They used a bulky, amino amide transient directing moiety for critically controlling the stereochemistry of the C-H insertion step and for selectivity promoting the C(sp³)-F reductive elimination pathway from the Pd(IV)-F intermediate. A stereochemical analysis showed that the desired C(sp³)-F formation occurs via an inner-sphere pathway with retention of configuration, while the undesired C(sp³)-O formation takes place via an S_N2-type mechanism. A careful study of this dual mechanism made it possible to rationalize the profound ligand effect on controlling the selectivity of reductive elimination selectivity from high-valent Pd compounds.

Park, H., Verma, P., Hong, K., Yu, J-Q., *Nature Chem.*, 2018, [DOI 10.1038/s41557-018-0048-1](https://doi.org/10.1038/s41557-018-0048-1).

Kraus, of the Philips-University in Marburg with four colleagues from Marburg and from the Aalto University in Aalto, Finland, reported the synthesis and characterization of rather unique poly-halogen cations that contain μ -bridging fluorine atoms. Two types of cations were described, the $[\text{Br}_2\text{F}_5]^+$ cation with a symmetric $[\text{F}_2\text{Br}-\mu\text{-F}-\text{BrF}_2]$ bridge and the $[\text{Br}_3\text{F}_8]^+$ cation with asymmetric $\mu\text{-F}$ bridges. Raman and ^{19}F -NMR spectroscopy, single-crystal X-ray diffraction and quantum mechanical calculations were employed to study these fluoronium ions. Population analyses indicate that the Br atoms of the cations possess a positive partial charge as expected on the basis of the differences in electronegativity of the atoms involved. The μ -bridging F atoms have the highest negative partial charge. The molecular cations apparently also exist in the melts of the compounds with the F atoms having a high mobility. Further studies are in progress.

Ivlev, S.I., Karttunen, A.J., Buchner, M.R., Conrad, M., Kraus, F., Angew.Chem.Int.Ed., 2018, DOI [10.1002/anie.201803708](https://doi.org/10.1002/anie.201803708).

Chalcogens are the chemical elements in group 16 of the periodic table and are also known as the oxygen family. The members are oxygen, sulfur, selenium, tellurium and the radioactive element polonium (Po). Often oxygen has been excluded from the chalcogens because its chemical properties are rather different from those of the other members. In a recent communication by Yan from the Fudan University of Shanghai and three coworkers from the University of Sherbrooke, Canada, it was shown that chalcogen interactions can be viewed as novel non-covalent forces in supramolecular chemistry. They describe a new class of supra-amphiphiles formed by $\text{Te}\dots\text{O}$ or $\text{Se}\dots\text{O}$ chalcogen-bonding interactions, and their self-assembly to form vesicles and nanofibers. A quasi-calix[4] chalcogenadiazole as a macrocyclic donor and a tailed pyridine N-oxide surfactant as a molecular acceptor are designed to construct the donor-acceptor complex via chalcogen-chalcogen connection between the chalcogenadiazole groups and an oxide anion. The geometry of the supra-amphiphiles is dictated by the affinity of the chalcogen-bonding. Several self-assembled nanostructures can be formed. The reverse disassembly can be initiated by competing halide ions or by a decreasing systemic pH.

Chen, L., Xiang, J., Zhao, Y., Yan, Q., J.Am.Chem.Soc. 2018, DOI [10.1021/jacs.8b04569](https://doi.org/10.1021/jacs.8b04569).

A recent paper in *Org.Lett.* reports a novel procedure for the synthesis of sulfonamides. It was written by Ball and twelve coworkers from Pfizer Research in Connecticut, and Pomona College, Claremont. They employed calcium triflimide $[\text{Ca}(\text{NTf}_2)_2]$ as a Lewis acid for the activation of sulfonyl fluorides toward nucleophilic addition with amines. Good to excellent yields were obtained with a large number of sterically and electronically diverse sulfonyl fluorides and amines. Further mechanistic studies are required, but preliminary results show that divalent cations and the triflimide anion are necessary for an efficient conversion. The authors suggest that sulfonyl fluorides will become the preferred sulfonyl halide for the preparation of sulfonamides. In 2016 it was found that sulfonamides represented 15% of the top 100 most prescribed drugs. Until now, the most popular method for the synthesis of sulfonamides requires the oxidation of sulfides or nucleophilic addition to sulfonyl chlorides, but these procedures possess several limitations.

Mukherjee, P., Woroch, C.P., Cleary, L., Rusznak, M., Franzese, R.W., Reese, M.R., Tucker, J.W., Humphrey, J.M., Etuk, S.M., Kwan, S.C., am Ende, C.W., Ball, N.D., Org.Lett., 2018, DOI [10.1021/acs.orglett.8b01520](https://doi.org/10.1021/acs.orglett.8b01520).

C-H functionalization is a promising technique for preparing complex molecules. But usually C-H bonds are unreactive functional groups in a molecule and it is a major challenge to prepare catalysts for site- and stereoselectivity of the desired C-H functionalization. But Davies and six coworkers (among them Ken Houk) at Emory University, Atlanta, The University of California, Los Angeles and Zhejiang University, Hangzhou, developed dirhodium catalysts with different selectivity profiles for C-H functionalization. The reactive intermediates are donor/acceptor carbenes. Site-selective C-H functionalization at the most accessible primary C-H bond could be accomplished. This selectivity is the most challenging for donor-acceptor carbenes since it goes against the normal electronic preference of these intermediates. The authors argue that the present study can most likely be extended to a range of different types of metal carbenes beyond donor/acceptor carbenes and also to metal-nitrene and metal-oxo intermediates.

Liao, K., Yang, Y-F., Li, Y., Sanders, J.N., Houk, K.N., Musaev, D.G., Davies, H.M.J., Nature Chem. 2018, DOI [10.1038/s41557-018-0087-7](https://doi.org/10.1038/s41557-018-0087-7).

A relatively simple procedure to prepare molecular knots and links was recently published by Cougnon and four colleagues from the University of Geneva and the Universitat de les Illes Balears, Palma de Mallorca, Spain. Whereas the conventional techniques rely on metal templation, the novel approach uses the hydrophobic effect as the driving force for the synthesis of complicated interlocked structures in aqueous solution. The formation of specific topologies, as determined by the size, geometry and rigidity of the building blocks, is employed to prepare a specific topology. This technique, simple, cheap, and high-yielding, is illustrated for a number of examples of topologically complex systems. There appears to be no doubt that the hydrophobicity of the building blocks represents the main feature that drives the formation of metal-free molecular links and knots in water. But a synergetic combination of hydrophobic effects with donor-acceptor interactions or metal templation may also prove useful.

Cougnon, F.B.L., Caprice, K., Pupier, M., Bauzá, A., Frontera, A., J.Am.Chem.Soc., 2018, DOI [10.1021/jacs.8b05220](https://doi.org/10.1021/jacs.8b05220).

The final paper that I like to mention this month was recommended to me by Prof. Barta. It is a study published in Nature Energy and carried out by Dusselier and Sels with eight coworkers from the Catholic University of Leuven and from the Hungarian Academy of Sciences Centre for Energy Research in Budapest. A novel process was developed, called liquid phase cellulose-to-naphtha (LPCtN) technology. They employed the LSR naphtha cut of petroleum (the C₅-C₆ alkane fraction) as part of a biphasic reaction medium in which cellulose is converted to mainly C₆ alkanes and which leads to enrichment of the original alkane mixture with virtually identical, but bio-based, components. Central to this process is a biphasic catalytic system that consists of an aqueous and an organic phase. The aqueous layer contains a soluble heteropolyacid catalyst which is responsible for “cutting” the cellulose into smaller monosaccharide units, as well as their further dehydration, mostly to furanics such as 5-hydroxymethyl furfural (5-HMF). These cyclic oxygenated intermediates then partition into the organic phase and undergo complete hydrodeoxygenation to C₆ alkanes via a series of hydrogenation and dehydration steps promoted by a bifunctional acid-metal catalyst (polyacid-modified Ru/C). This catalytic strategy is elegant as it allows for reaction pathways from cellulose to C₆ alkanes with minimal C-C bond cleavage and taking advantage of catalyst compartmentalization in a biphasic reaction medium where one of the phases is light naphtha itself. The reaction product is bio-enriched light naphtha, which can be integrated into existing infrastructures.

Deneyer, A., Peeters, E., Renders, T., Van den Bosch, S., Van Oeckel, N., Ennaert, T., Szarvas, T., Korányi, T.A., Dusselier, M., Sels, B.F., *Nature Energy*, 2018, [DOI 10.1038/s41560-018-0245-6](https://doi.org/10.1038/s41560-018-0245-6).

Text in part adopted from Barta, K., *Nature Energy*, 2018, [DOI 10.1038/s-41560-018-0264-3](https://doi.org/10.1038/s-41560-018-0264-3).

A selection of recent publications from Stratingh members

- Chen, J., Browne, W.R., "[Photochemistry of iron complexes](#)" *Coordination Chemistry Reviews* **2018**, 374, pp. 15-35
- Hansen, M.J., Feringa, F.M., Kobauri, P., Szymanski, W., Medema, R.H., Feringa, B.L., "[Photoactivation of MDM2 Inhibitors: Controlling Protein-Protein Interaction with Light](#)" *Journal of the American Chemical Society* **2018**, 140 (41), pp. 13136-13141.
- Jia, C., Famili, M., Carlotti, M., Liu, Y., Wang, P., Grace, I.M., Feng, Z., Wang, Y., Zhao, Z., Ding, M., Xu, X., Wang, C., Lee, S.-J., Huang, Y., Chiechi, R.C., Lambert, C.J., Duan, X., "[Quantum interference mediated vertical molecular tunneling transistors](#)" *Science Advances* **2018**, 4 (10), art. no. aat8237
- Guo, Y., Kootstra, J., Harutyunyan, S.R., "[Catalytic Regio- and Enantioselective Alkylation of Conjugated Dienyl Amides](#)" *Angewandte Chemie International Edition* **2018**, 57 (41), pp. 13547-13550
- Chen, J., Draksharapu, A., Angelone, D., Unjaroen, D., Padamati, S.K., Hage, R., Swart, M., Duboc, C., Browne, W.R., "[H₂O₂ Oxidation by Fe^{III}-OOH Intermediates and Its Effect on Catalytic Efficiency](#)" *ACS Catalysis* **2018**, 8 (10), pp. 9665-9674

Upcoming PhD Ceremonies

- **November 2nd** at 12:45 - **Dowine de Bruijn** (Roelfes group) - "Bio-orthogonal metal catalysis for selective modification of dehydroalanine in proteins and peptides"
- **November 16th** at 11:00 - **Liliana Cozzoli** (Roelfes group) - "Controlling the self-assembly of amphiphiles using DNA G-quadruplexes"

Werkbespreking

Thursday morning at 8:30 am - room 5111.0080

- **November 1st** - **Alessandra de Santi** (PhD Barta) - "Exploring sustainable value chains from renewable resources"
- **November 8th** - **Ivana Maric** (PhD Otto) - "Self-assembly and self-replication in systems with one or two dynamic covalent chemistries"
- **November 15th** - **Liubov Yakovlieva** (PhD Walvoort) - "Unusual protein glycosylation enzymes as antimicrobial targets"
- **November 22nd** - **Balint Fridrich** (PhD Barta) - "Walking alone the value chain by catalytic C-C bond formation"
- **November 29th** - **Simona Bianca** (PhD Minnaard) - "Novel catalysis for the late stage modification of complex antibiotics"

New appointments



David Villarón Salgado (PhD)
Group Wezenberg



Srikanth Birudula (PhD)
Group Hummelen



Xianyuan Wu (PhD)
Group Barta



Sarina Massmann (PhD)
Group Minnaard



Cosimo Boldrini (PhD)
Group Harutyunyan



Jinyu Sheng (PhD)
Group Wezenberg



Niklas Thiel (Post-doc)
Group Feringa



Nadja Simeth (Post-doc)
Group Feringa

*If you have items for the next issue of this Newsletter, please send an email to the Stratingh Institute Office:
Stratingh@rug.nl*