

May 2016

Vidi grants for Katalin Barta and Martin Witte



Dr. Katalin Barta: Lignin waste to valuable chemicals

Lignin is the largest renewable source of aromatics on the planet. Still, its chemical conversion is a real challenge. This research will find ways to break down the robust structure of lignin and convert this aromatic biopolymer into valuable chemicals.

Recent video on Barta's research Sustainable alternative to fossil fuels and chemicals in the making

Dr. Martin Witte: Molecular tools for phospholipases

Enzymes that model the phospholipid cell membrane play an important role in the transmission of signals and the formation of organelles. The research will focus on developing molecular tools to study these processes.



Marthe Walvoort in the YAG



The Young Academy of Groningen is a club for the University's most talented, enthusiastic and ambitious young researchers of all fields and disciplines. Operating independently within the University, the Young Academy aims to actively promote interdisciplinary research, engage the University's young researchers of all faculties in the Young Faculty Forum, develop viewpoints on science policy and talent development and advise the University on these and related topics and organise inspiring activities for the public to boost the relationship between science and society.

The Young Academy is currently being established. The first generation Young Academy members have the unique opportunity to set the agenda for the club's organisation and activities.

Faces of Science: Dowine de Bruijn

Dowine from the Roelfes' group was selected by KNAW to be one of the "faces of science". She has now officially been "launched" and will regularly blog about her experiences.

See: <http://www.kennislink.nl/facesofscience/wetenschappers/dowine-de-bruijn>



Paper in Science for Syuzi Harytyunyan



Cool combination produces easier carbon bonds

By combining two century-old techniques in organic chemistry, Syuzanna Harutyunyan is able to make organic compounds with greater ease and precision. Such compounds are important for drug discovery and development. Harutyunyan's method is described in a paper that published by the journal Science on 22 April.

<http://science.sciencemag.org/content/352/6284/433.full.pdf+html>

Almost 90 percent of known active pharmaceutical ingredients contain one or more 'heterocyclic aromatic rings', structures that contain atoms of at least two different elements. Most of these rings contain carbon and nitrogen atoms. 'Connecting two carbon atoms is a crucial step in synthesizing heterocycle-containing molecules', explains University of Groningen Associate Professor of Synthetic Organic Chemistry Syuzanna Harutyunyan. But carbon-carbon bonds are notoriously difficult to make. An intermediary step is often required, but this makes the synthetic process longer and thus less efficient. Furthermore, many pharmaceutically relevant heterocyclic molecules are chiral, which means they are present in two mirror-image versions. These versions often exhibit different biological activities. 'So we need a way to create the right chiral version as well', says Harutyunyan. In the Science paper, Harutyunyan and her team describe just that: the efficient creation of carbon-carbon bonds with a high chiral selectivity for a wide range of nitrogen-containing heterocyclic molecules. For this breakthrough, Harutyunyan reverted to methods from the early twentieth century. Grignard reagents, originally developed by Victor Grignard, the first laureate of the Nobel Prize for Chemistry in 1912, are still an important tool in creating carbon-carbon bonds.

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

- In a highly interesting feature article, Mihail Barbolu, staff member at two research institutes, one in France and one in Romania, has discussed the properties of biological water channels (aquaporins, AQP) and the possible preparation of artificial water channels (AWC) with a similar high water permeability and rejecting ion and proton transport. The incorporation of such AWCs in artificial lipid bilayer membranes could lead to effective desalination and water-purification applications. The most popular procedure for the construction of ACWs is a bottom-up supramolecular strategy, involving the synthesis of biomimetic architectures via the self-assembly of molecular precursors through non-covalent bonding. But other approaches are also possible and their success depends strongly on a detailed understanding of the structural and dynamic features that are required for rapid and selective water transport in molecular channels. *Barbolu, M., Chem.Comm., 2016, DOI 10.1039/C6CC017243.*
- Chemists from Nanjing University, China and Southern Methodist University, USA, described for the first time the B-H... π interaction, a novel type of nonclassical hydrogen bonding. In the gas phase, at reduced temperatures, the interaction has been observed, both experimentally and quantum chemically, in the B₂H₆...benzene ($\Delta E = -5.07$ kcal/mol) and the carborane...benzene complex ($\Delta E = -3.94$ kcal/mol). Structural features have been investigated by X-ray diffraction and by ¹H-NMR experiments. The H... π distances are 2.40-2.76 Å. Quantum chemical calculations suggest that the interaction is electrostatic. *Zhang, X., Dai, H., Yan, H., Zou, W., Cremer, D., J.Am.Chem.Soc. 2016, DOI 10.1021/jacs.6b01249.*
- In a joint project of Boston College and MIT it was shown that previously unknown halo-substituted molybdenum alkylidene species possess a great reactivity and are able to participate in high-yielding olefin metathesis reactions to provide acyclic 1,2-disubstituted Z-alkenyl halides. The transformations are promoted by small quantities of a catalyst that is generated in situ and used with unpurified, commercially available and easy-to-handle liquid 1,2-dihaloethene reagents. The reactions proceed to high conversions at ambient temperatures within four hours. A number of alkenyl chlorides, bromides and fluorides were obtained in yields up to 91 per cent and with complete Z selectivity. The method can be employed in a number of synthetic processes including the preparation of biologically active materials. *Koh, M.J., Nguyen, T.T., Zhang, H., Schrock, R.R., Hoveyda, A.H., Nature 2016, 531, 459-465.*

- Susanta Sen Gupta (Banaras Hindu University) wrote a review about proton transfer reactions in apolar, aprotic solvents. In these media there are only small solute-solvent interactions, and proton transfer occurs directly. General acid/base catalyzed kinetics is observed with timescales of microseconds to minutes. A thorough understanding of the mechanism of these processes is relevant for a number of applications such as coupling of proton transfer with electron transfer which is involved in the development of renewable energy devices. *Sen Gupta, S.K., J.Phys.Org.Chem., 2016, DOI 10.1002/poc.3524.*
- A molecular dynamics simulation was carried out of the reaction of dimethyldioxirane (DMDO) with isobutene. The simulations were performed by Ken Houk (University of California, our Backer lecturer this year) and two coworkers. Oxygen-rebound and radical pair separation were both identified, with relative percentages strongly medium dependent. The life-time of the radical pairs is 30-150 fs. The solvent influences the oxygen rebound by response to the polarity change during hydroxyl group transfer. An analysis of oxygen rebound trajectories shows that both dynamically concerted and stepwise mechanisms do occur. *Yang, Z., Yu, P., Houk, K.N., J.Am.Chem.Soc. 2016, 138, 4237-4242.*
- A paper in Science, written by 13 authors from Cambridge University, UK, reports the use of a lateral-contact perovskite solar cells with selective electron- and hole-collecting contacts in which charge extraction for photoexcitation >50 micrometers away from repeated recycling between photons and electron-hole pairs was observed. This indicates that electron transport is not limited by diffuse charge transport but can take place over long distances through multiple absorption-diffusion-emission events. In this way high excitation densities are created within the perovskite layer, allowing high open-circuit voltages. *Pazos-Outon, L.M., Szumilo, M., Lamboll, R., Richter, J.M., Crespo-Quesada, M., Abdi-Jalebi, Beeson, H.J., Vrucinic, M., Alsari, M., Snaith, H.J., Ehler, B., Friend, R.H., Deschler, F., Science, 2016, 351, 1430-1433.*
- A perhaps unexpected observation. Researchers from three Chinese Institutes and from Rice University in Houston, Texas, examined isotope effects on the formation and dissociation kinetics of hydrogen bonds in real time with ultrafast chemical exchange spectroscopy. The experimental data showed that substitution of H for D in a phenol hydrogen-bond donor had only negligible effects on the hydrogen bond kinetics. This result was further confirmed by density functional theory (DFT) calculations. Further studies are necessary to see whether these results are also valid for other donor systems. *Ge, C., Shen, Y., Deng, G-H., Tian, Y., Yu, D., Yang, X., Yuan, K., Zheng, J., J.Phys.Chem.B 2016, 120, 3187-3195.*
- Phorbol has been called the flagship member of the tricyclic diterpene family. It is a very complex molecule with an unusual placement of oxygen atoms. Although the compound is known for more than 80 years, purely synthetic enantiopure phorbol has remained elusive. Access to useful quantities of the compound has relied on isolation from natural sources and semisynthesis. Chemists from The Scripps Research Institute in La Jolla, California, have now been able to perform a two-phase terpene synthesis strategy to achieve the enantio-specific total synthesis of (+)-phorbol in 19 steps, starting from the abundant monoterpene (+)-3-carene. The synthetic route can also be employed to prepare analogues with a unique placement of oxygen atoms that are otherwise not accessible. *Kawamura, S., Chu, H., Felding, J., Baran, P.S., Nature 2016, 532, 90-93.*
- The Journal of Chemical Education published a special issue, containing 26 papers, focussed on how chemical information is produced, distributed, discovered, managed, shared, and preserved. In the past two decades these issues underwent important changes. An example is the question how to navigate the digital landscape, an essential issue for students, educators, and researchers who like to use their time effectively and efficiently. The Editorial has been written by Grace Baysinger (Stanford University) and gives an introduction to all contributions. *Baysinger, G., J.Chem.Educ. 2016, DOI 10.1021/acs.jchemed.6b00113.*

Jan Engberts

New Appointments



Mira Holtzheimer

As of 16/3/2016

PhD student

Group Walvoort

PhD Defences

Friday, May 20th

@ **11:00 Zhiyuan Zhao** will defend his PhD thesis. Title: "Applications of High-Aspect-Ratio Gold Nanowires Fabricated by Nanoskiving". Promotor: Prof. dr. R. Chiechi

Stratingh Lectures



Dr. Roman Boulatov

Dept. of Chemistry, University of Liverpool

Title: **The Force of Mechanochemistry**

Day: Tuesday, May 10th, 2016

Room: 5111.0022

Time: 16:00

Contact: Ryan Chiechi (r.c.chiechi@rug.nl)

Werkbespreking: Thursday morning 8.30 hrs, room 5111.0080

May 19th —**Arjan Geersing** (PhD Roelfes): "Title to be announced"

May 26th —**Leticia Monjas Gomez** (PhD Hirsch): "Exploring hit-identification strategies for energy-coupling factor transporters"

June 2nd— **Sandeep Padamati** (PhD Browne): "Title to be announced"

June 9th— **Jenny Douvogianni** (PhD Hummelen): "Organic semiconductors with high-k side groups"

June 16th— **Raquel Travieso Puente** (PhD Otten): "Formazan: a new versatile ligand platform"

June 23rd— **X iaoming Miao** (PhD Otto): "Selective functionalization of magnetical nanoparticles by dynamic imine chemistry"

June 30th— **Juan** Chen (PhD Browne): "The mechanistic study of the reaction of FeII(N₄Py) complex with H₂O₂ in methanol"

If you have items for the next issue of this Newsletter, please send an e mail to the Stratingh Institute office: Stratingh@rug.nl