Newsletter

120

Stratingh Institute for Chemistry

September 2016

Ben Feringa wins the 2016 Tetrahedron Prize



The Board of Executive Editors of Elsevier's Tetrahedron journal series have announced that the 2016 Tetrahedron Prize for Creativity in Organic Chemistry has been awarded to Professor Ben L. Feringa of the Stratingh Institute for Chemistry, University of Groningen. He receives the award for his outstanding contributions to organic chemistry. Former winners of the prestigious prize are from Cambridge University, Stanford University and the Max-Planck-Institut.

Professor Stephen Martin, Chairman of the Editorial Board of the Tetrahedron journals, said on announcing this year's winner: "Professor Feringa has performed truly ground-breaking research in the diverse fields of

dynamic molecular systems, catalysis, and stereochemistry. His contributions to molecular nanotechnology, including molecular switches and rotors, have played a major role in shaping the field of nanomachines. Similarly, his discoveries in catalysis, particularly of enantioselective transformations, have had a profound influence in synthetic organic chemistry and its applications to natural product chemistry."

Syuzanna Harutyunyan wins KNCV Gold Medal

On December 7 the KNCV Gold Medal will be awarded to associate professor Syuzanna R. Harutyunyan of the Stratingh Institute for Chemistry (University of Groningen). The KNCV Gold Medal is the most prestigious, Dutch recognition for chemical talent. The medal will be awarded during the chemical conference CHAINS, which takes place from 6th December until 8th December 2016 in Veldhoven, the Netherlands.

Harutyunyan is currently an Associate Professor in Synthetic Organic Chemistry at the University of Groningen. Her research aims at the development of new catalytic methods and concepts in asymmetric synthesis. Before joining the Stratingh Institute of Chemistry in Groningen, she carried out research in Armenia, Russia, Poland, Belgium, both in academia and in industry. In 2011 Harutyunyan won the prestigious Solvias Ligand Contest Prize. Furthermore, she received a NWO Vidi grant in 2012 and two NWO ECHO grants in 2014 and 2016.



Veni grant awarded to Marthe Walvoort

Marthe Walvoort from the Stratingh Institute for Chemistry has been awarded a Veni grant as part of the Innovational Research Incentives Scheme run by the Netherlands Organisation for Scientific Research (NWO), the Royal Netherlands Academy of Arts and Sciences (KNAW) and the universities. The personal Veni grants are worth up to a maximum of € 250,000 and enable talented researchers who have just completed a PhD to conduct research of their own choice.

Marthe's projects is about : Attacking the bacterial sweet spot

Bacteria display a diverse array of exotic sugars that are absent from humans. These sugars play a crucial role in infection and bacterial survival. Using chemistry and biology, the researchers will explore a novel sugar modification with the aim to attack this bacterial sweet spot in the fight against infection.



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

A new academic year! And certainly a lot of novel beautiful science!

- A highly interesting two-faced polar molecule has been prepared by chemists from Canada, France and England: all-cis 1,2,3, 4,5,6 hexafluorocyclohexane. The dipole moment of the molecule was calculated to be as high as 7 D as a consequence of the differentially polarized faces of the molecule. The compound shows an extraordinary propensity to bind both cations and anions. The fluorine face binds sodium ions, whereas the hydrogen face binds chloride ions. These complexes are among the most strongly bound complexes of Na+ and Cl-, and, not unexpectedly, the bonding has a high electrostatic contribution. Applications in supramolecular chemistry are anticipated. *Ziegler,B.E., Lecours, M., Marta, R.A., Featherstone, J., Fillion, E., Scott Hopkins, W., Steinmetz, V., Keddie, N.S., O'Hagan, D., McMahon, T.B., J.Am.Chem.Soc., 2016, DOI 10.1021/jacs.6bo2856*.
- For the first time strong evidence has been obtained that a natural enzyme can catalyze a Diels-Alder reaction. Scientists from two British universities published a molecular-level description of the reaction mechanism of the spirotetronate cyclase AbyU, that has an active site capable to facilitate a transannular pericyclic reaction. The enzyme is relatively simple and can also catalyze conversions of non-natural substrates. The authors claim that it may be a compelling and practical target for engineering. *Byrne, M.J., Lees, N.R., Han, L-C., van der Kamp, M.W., Mulholland, A.J., Stach, J.E.M., Willis, C.L., Race, P.R., J.Am.Chem.Soc., 2016, 138, 6095-6098*.
- A study performed at several American universities recorded a new approach, departing from traditional electrolyte design, for obtaining strongly correlated perovskite fuel cells. Perovskite nickelate was used as an electrolyte with high initial ionic and electrolyte conductivity. Electronic conduction can be suppressed through a filling-controlled Mott transition induced by spontaneous hydrogen incorporation. With the nickelate as the electrolyte in free-standing membrane geometry, a low temperature micro-fabricated solid oxide fuel cell with a high performance was demonstrated. The ionic conductivity is comparable to that of the best-performing solid electrolytes in the same temperature range with a very low activation energy. *Zhou, Y., Guan, X., Zhou, H., Ramadoss, K., Adam, S., Liu, H., Lee, S., Shi, J., Tsuchiya, M., Fong, D.D., Ramanathan, S., Nature, 2016, DOI 10.1038/nature17653*.
- This month again a highlight from our own Institute. Prof. Syuzanna Harutyunyan and three of her coworkers reported in Science a highly chemoselective and enantioselective catalytic transformation of a large number of conjugated alkenyl-N-heteroaromatics to their corresponding chiral alkylated products. The relatively simple methodology allows the introduction of linear, branched, and cyclic alkyl chains, and also a phenyl group, at the Important for the success of the method is the enhancement of the reactivity of the alkenyl-heteroaromatics by Lewis-acid activation, which is coupled with the use of highly reactive Grignard reagents and a copper catalyst which is coordinated by a chiral diphosphine ligand. *Jumde, R.P., Lanza, F., Veenstra, M.J., Harutyunyan, S., Science 352 (issue 6284), 433-437 (2016)*.
- Philip Ball wrote a fascinating one page article in Nature Physics entitled "How Wet Can You Get?" The emphasis is on hydrophobicity, how difficult it is to give a general definition of this property and to design wetting and hydration properties of molecules and materials. For example, for proteins, and presumably also for synthetic macromolecules, hydrophobicity should be seen as a multi-dimensional property. However, hydra-

tion may be qualitatively different at different length scales for more extended surfaces and distinctly non-additive for chemically non-uniform surfaces. Ball gives an interesting explanation why so many definitions are needed for what it means to be wet. Understanding the peculiar nature of water is a continuing scientific challenge. *Ball, P., Nature Physics, 2016, 12, 718*.

- An interesting discovery at the Universty of California, Merced. Heterocycle C-H functionalization can be performed using unprotected bench-stable α-amino acids as stable radical precursors. With 1 equiv. of TFA, 10 mol % of AgNO3, 5 equiv. of (NH4)2S2O8 and dichloroethane/water (1:1) as the solvent a variety of electron-deficient heterocycles were functionalized in reasonable to good yields and high levels of selectivity. Preliminary mechanistic studies indicate that an aldehyde intermediate is formed in situ, which then undergoes a Minisci-type radical substitution reaction via a decarbonylative process. The procedure was effective for several natural and unnatural α-amino acids. More detailed mechanistic studies are in progress. *Mai, D.N., Baxter, R.D., Org.Lett., 2016, 18, 3738-3741*.
- A study, performed at the University of Wisconsin-Madison has shown that $n-\pi^*$ interactions can be competitive with hydrogen bonds. This has been investigated in a single molecule. They found that enhancement of an amide $n-\pi^*$ interaction can reduce the ability of β -keto amides to tautomerize to the enol, apparently because of a decreased hydrogen-bonding capacity of the amide carbonyl group. It is concluded that an $n-\pi^*$ interaction can have a significant effect on the strength of a hydrogen bond to the same carbonyl group. *Newberry*, *R.W.*, *Orke*, *S.J.*, *Raines*, *R.T.*, *Org.Lett.*, 2016, 18, 3614-3617.
- David MacMillan (our Backer lecturer 2015) and two coworkers at Princeton University wrote an extensive perspective on photoredox catalysis in organic chemistry. Irradiation with visible light at wavelengths where common organic molecules do not absorb, anables selective excitation of the photoredox catalyst. The excited species can than act as both a strong oxidant and a strong reductant simultaneously, thereby providing access to a reaction environment that is unique for organic chemistry and that leads to novel redox-neutral reaction platforms. A wide and often unprecedented array of novel synthetic methodologies have been developed by this approach and are discussed in this paper. *Shaw, M.H., Twilton, J., MacMillan, D.W.C., J.Org.Chem., 2016, DOI 10.1021/acs.joc.6bo1449*.
- It is well-known that, quite generally, carbonyl compounds and alkenes do not react with each other. A recent contribution by Schindler and coworkers at the University of Michigan has now shown that a simple Lewis acid (for example FeCl3) can catalyze metathesis between these functional groups. Both five- and sixmembered rings can be synthesized with different substitution patterns and functional groups. The carbonyl component is currently limited to electron-rich and electron-poor aryl ketones. Two limiting mechanisms have been suggested for the formation of a novel cyclic alkene. This important advance in carbonyl-olefin metathesis chemistry has been reviewed by Hennessy and Jacobsen. *Ludwig, J.R., Zimmerman, P.M., Gianino, J.B., Schindler, C.S., Nature 2016, 533, 374-379. Hennessy, E.T., Jacobsen, E.N., Nature Chem., 2016, 8, 741-742.*
- A shocking paper appeared in Nature. A survey of 1576 researchers revealed that 52% of those surveyed believe that there is a significant crisis of reproducibility of published scientific results. More than 70% of researchers have tried and failed to reproduce another scientist's experiments, and, perhaps still more remarkable, more than 50% have failed to reproduce their own experiments. Chemistry is at the top of the list, followed by biology and physics. Reasons for these results include pressure to publish, selective reporting, poor use of statistics and finicky protocols, but several other reasons can be given. Respondents were also asked what could be done to improve this situation. More than 1000 scientists replied: "more robust experimental design", "better statistics", and "better mentorship". About 80% of the respondents believes that funders and publishers should do more to improve reproducibilty. Since the ability to reproduce experiments is at the heart of science, the recommendations should be taken seriously! *Baker, M., Nature, 2016, 533, 452-454.*

Jan Engberts

New Appointments



Johannes Ottelé

As of 1/8/2016 PhD student Group Otto

Werkbespreking: Thursday morning 8.30 hrs, room 5111.0080

September 8th— **Olga Castañeda Ocampo** (PhD Chiechi): "How sunlight and algae could potentially power our world"

September 15th— **Stefano Pizzolato** (PhD Feringa): "Biaryl-functionalized molecular switches: switching properties of overcrowded alkenes with a versatile biaryl-core"

September 22nd— **Anouk Lubbe** (PhD Feringa): "Solvent effects on the thermal isomerisation of a molecular motor"

September 29th— Mickel Hansen (PhD Feringa): "A Direct and Versatile Synthesis of Red-shifted Azobenzenes"

October 6th— Boris Bartolec (PhD Otto): "Self-replication and compartment formation in dynamic combinatorial libraries"

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