

## Molecular Machines Nobel Prize Conference



"for the design and synthesis of molecular machines"

It is a pleasure to invite and welcome you to the international Molecular Machines Nobel Prize Conference to be held in Groningen, The Netherlands, on 19 to 22 November 2017. The conference is in honor of the 2016 Nobel Laureates in Chemistry, Prof. J.-P. Sauvage, Prof. J. Fraser Stoddart and Prof. B.L. Feringa, all of whom will participate fully and deliver lectures. The scientific program celebrates their achievements with top speakers covering the various topics in the fields of research of the laureates. This conference is a unique opportunity to learn about the latest developments relating to the 2016 Nobel Prize in Chemistry. We strongly encourage students to apply for a poster presentation to be viewed by and discussed with the top scientists!

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

- This month I start with a world record in carbohydrate synthesis. Xin-Shan Ye with one graduate student and three undergraduates synthesized, in 2.5 years, a polysaccharide, a mycobacterial arabinogalactan, containing 92 monosaccharide units. This is the largest polysaccharide prepared so far. Previously the largest was synthesized by Peter Seeberger which contained 50 monosaccharide units. The compound synthesized by Ye et al. was made at Peking University and the work was published in Nature Comm. It is an important cell-wall component in mycobacterium tuberculosis, the bacterium causing tuberculosis. The Chinese chemists developed an efficient preactivation-based one-pot glycosylation protocol to put the carbohydrate units together which will stimulate further research in large-glycan synthesis. *Wu, Y., Xiong, D-C., Chen, S-C., Wang, Y-S., Ye, X-S., Nature Comm. 2017, DOI 10.1038/ncomms14851.*
- Kjaergaard and two coworkers from the University of Copenhagen made an interesting comparison of the hydrogen-bonding ability of tert-butyl hydroperoxide and tert-butanol em-

ploying dimethyl ether as the hydrogen-bond acceptor. Using both Fourier-transform infrared spectroscopy and quantum mechanical calculations, they found that t-BuOOH is a significantly better H-bond donor than t-BuOH by about 4 kJ/mol in Gibbs energy. It is explained by a weaker OH bond in the hydroperoxide. A similar trend in H-bond strength was found for trimethylamine (with nitrogen as the acceptor atom) and dimethyl sulfide (sulfur as the acceptor atom). These results are of particular importance for chemical processes in the atmosphere. *Möller, K.H., Tram, C.M., Kjaergaard, H.G., J.Phys.Chem. 2017, DOI 10.1021/acs.jpca.7b01323.*

- Ballester and a post-doc at the Institute of Chemical Research of Catalonia in Spain published a feature article on light-responsive molecular containers. The encapsulation of small molecules in molecular containers, with the ability to release them in a controlled way, can recently be performed employing light as an external stimulus for controlling the behavior of molecular capsules. This technique is particularly useful for drug delivery and catalysis. In many cases photocontrol can allow reversibility of the supramolecular processes and the technique is clean and reliable. Many further studies still need to be performed and the mechanistic details are vital for a deeper understanding of the effect of light on these molecular containers. *Diaz-Moscoso, A., Ballester, P., Chem.Comm.2017, DOI 10.1039/C7CC015668b.*
- Burkhard König (University of Regensburg) wrote a brief but interesting review of the past, present and future of photocatalysis in organic synthesis. There is great interest in the use of visible light as a catalyst in organic reactions because these reactions are efficient in energy, green and have benefitted from the development of light-emitting diodes as convenient sources of visible light. The first applications were by Ciamician and Silber who ran reactions catalyzed by sunlight on the balcony of the chemical institute of the University of Bologna. Photoredox catalysts have now been used for a large range of organic transformations, including oxidations, reductions and cycloadditions. There is, however, room for further improvement. Reaction mechanisms should be further investigated, reaction times can be reduced and the quantum efficiencies have to be drastically enhanced. *König, B., Eur.J.Org.Chem. 2017, DOI 10.1002/ejoc.201700420.*
- Sugiyasu (University of Tsukuba, Japan) and eight coworkers from four Universities have studied molecular self-assembly under kinetic control. This leads to nanostructures which are inaccessible through a spontaneous thermodynamic process. They report the capacity of a metastable porphyrin supramolecular assembly to differentiate into nanofiber and nanosheet structures. A mechanistic study has been made of this unique kinetic behavior and the results made it possible to control the differentiation phenomena so that both one- and two-dimensional living supramolecular polymerization could be achieved using an identical monomer. The material properties are clearly pathway-dependent and the results show unprecedented control over synthetic supramolecular self-assembly. *Fukui, T., Kawai, S., Fujinuma, S., Matsushita, Y., Yasuda, T., Sakurai, T., Seki, S., Takeuchi, M., Sugiyasu, K., Nature Chem., 2017, DOI 10.1038/nchem.2684.*
- The performance of solar cells can be improved by optimizing the morphology of metal halide perovskite films when these materials are employed as light harvesters. The reason is that film homogeneity is correlated with photovoltaic performance. Many techniques have been used for this purpose but the main factors that play a role are only poorly understood. In a recent study, Grätzel at the University of Lausanne (Switzerland) and six coworkers from different Institutes in England, Japan and Germany, describe that light has a strong effect on both the rate of perovskite formation and on film morphology when using the main deposition methods, namely sequential deposition and the anti-solvent method. They studied lead iodide in combination with methylammonium iodide with two microscopic techniques and found that the formation of perovskite via sequential deposition is strongly accelerated by light. A doubling of solar-cell efficiency is found induced by light. By contrast, using the anti-solvent method, best results are found in the dark. The discovery of light-activated crystallization may open new ways of tuning morphology and structuring perovskites for different applications. *Ummadisingu, A., Steier, L., Seo, J-Y., Matsui, T., Abate, A., Tress, W., Grätzel, M., Nature, 2017, DOI 10.1038/nature22072.*
- Dong (University of Chicago) and two coworkers from the Universities of Chicago and Texas published the first examples of catalytic couplings between unsaturated hydrocarbons and unactivated C-H bonds via a metal-hydride reaction path. It involves a Rh(I)-catalyzed site-selective coupling between ketone  $\beta$ -C(sp<sup>3</sup>)-H bonds and aliphatic alkynes and employing an in situ-installed directing group. Several  $\beta$ -alkylation or  $\beta$ -aldol derivatives of the ketones are obtained with a broad functional group tolerance. A most likely mechanism involves the involvement of a Rh-H intermediate, formed via oxidative addition of Rh(I) into the  $\beta$ -C-H

bonds. The yields are often above 80%. Xu, Y., Young, M.C., Dong, G., *J.Am.Chem.Soc.*, 2017, DOI 10.1021/jacs.7b02020.

- Sijbren Otto called my attention to a highly interesting discovery in bio-organic chemistry which was published by Markus Ralser (University of Cambridge, UK) and three colleagues from the UK and Austria. They found that a mutually compatible, efficient, non-enzymatic catalyst was able to interconvert Krebs (TCA) cycle intermediates. The reactions were enabled by sulfate radicals that were produced upon activation of peroxydisulfate. The resulting chemical network covered the topology of the oxidative part of the Krebs cycle and resulted in more than 90% carbon efficiency. It is argued that the Krebs cycle may have emerged from a non-enzymatic precursor that could have been formed in the presence of sulfate radicals. Keller, M.A., Kampjut, D., Harrison, S.A., Ralser, M., *Nature Ecology & Evolution*, 2017, DOI 10.1038/s41559-017-00831.

I wish all my readers a most pleasant and relaxing summer holiday!

Jan Engberts

## New Appointments



Katalin Barta

Associate Professor

1/6/2017



Alessandra de Santi

PhD student—group Barta

1/5/2017



Bian Corbet

PhD student  
group Feringa

1/6/2017



Jana Volaric

PhD student  
group Feringa

1/6/2017

## PhD defence

Friday, June 26<sup>th</sup>

@ 12:45 Ivana Drienovská will defend her PhD thesis. Title: "Designing artificial enzymes with unnatural amino acids". Promotor: Prof. dr. J.G. Roelfes

## Werkbespreking: Thursday morning 8.30 hrs, room 5111.0080

**June 15<sup>th</sup>— Henrieke Heideman (PhD Feringa)** - "Directional Movement of Light-Driven Molecular Motors on Surfaces"

**June 22<sup>nd</sup>— Master students Nanoscience (Feringa): Michael A. Muller** "Catalysis in Confined Space: Exploiting MOFs as Heterogeneous Medium", **Chen Yao** "Governing the Enantioselective Adsorption in MOFs by Light"

**June 29<sup>th</sup>— Cora Gutiérrez de Souza (PhD Roelfes)** - "Artificial metalloenzymes by in vivo incorporation of unnatural amino acids"

**July 6<sup>th</sup>—Tao Yan (PhD Barta)** - "Catalytic N-alkylation of unprotected amino acids with alcohols"

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