

Newsletter

Stratingh Institute for Chemistry

June 2016

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M. Yagiz Unver Best Poster Prize, VI EWDSy



M. Yagiz Unver, a PHD student under supervision of Prof. Anna Hirsch, was awarded for the best poster prize in 6thEuropean Workshop in Drug Synthesis. This years' workshop was held in Certaso di Pontignano, Siena, Italy in 15th -19thof May 2016 and main focus of the workshop was on novel synthetic procedures in medicinal chemistry, HIV research, neglected diseases and ADMET. The aim of this unique workshop was to provide a fertile background for young scientists from universities and pharmaceutical industries to share and exchange knowledge.

Adri Minnaard awarded a TOP_PUNT grant

Finding Mycobacterium tuberculosis' Achilles heel using chemical immunology

Tuberculosis, which is caused by infection with Mycobacterium tuberculosis (Mtb), is responsible for millions of deaths annually. The Mtb cell wall is a complex mixture of compounds that has strong effects on the immune system. Thanks to genomics, proteomics, metabolomics, and lipidomics of Mtb, we now know the identity of many components of the Mtb cell wall. Unfortunately, purification of these cell wall constituents in order to unravel the role of the individual components, provides insufficient amounts for in depth immunological study, and does not result in sufficiently pure preparations for clinical application.



Adri Minnaard, together with his colleague G. A. Van der Marel are awarded a TOP_PUNT grant where they propose to synthesize the most important M. tuberculosis cell wall components in sufficient amounts, and to study their role in the host immune response in molecular detail.

You can read <u>here</u> more information about this grant.

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

A group of Japanese chemists reported for the first time a synthetic strategy leading to the encapsulation of just one or two water molecules inside fullerene C70. A selective generation of a genuine water dimer has never been achieved before. These new species were studied by X-ray diffraction and 1H-NMR spectroscopy. Insights were obtained into the intrinsic pro-

perties of a single water molecule without hydrogen bonding interactions as well as into a water dimer with a single hydrogen bond between the two water molecules. Theoretical calculations showed a peculiar cis-linear conformation of the dimer due to confinement effects inside C70. *Zhang, R., Murata, M., Aharen, T., Wakamiya, A., Shimoaka, T., Hasegawa, T., Murata, Y., Nature Chem., 2016, 8, 435-441.*

- Chemists from the University of California at Berkeley reported regioselective, transition metal-free C-O coupling reactions that occur via aryne intermediates. These conversions between various aryl halides and alkoxides can be performed under mild, ambient conditions. Aryl bromides and iodides give the best results. The yields are often in the range between 85 and 92 %. The reaction is particularly useful for the introduction of alkoxy substituents meta to an inductively electron-withdrawing group for a relatively wide range of aryl halides. Reactions with other nucleophiles are presently under study. It is likely that the mechanistic pathway involves an aryne intermediate. The regioselectivity is most likely controlled by the electron-withdrawing substituents in the aryl ring. *Dong, Y., Lipschutz, M.I., Tilley, T.D., Org.Lett.*, 2016, 18, 1530-1533.
- Chemists at the University of Minnesota reported a new type of reaction: the formal [4+2] cycloaddition of an allenyne with a pendant alkyne (or nitrile) to give an α,3-dehydro(aza) toluene derivative. This may be called a pentadehydro-Diels-Alder (PDDA) reaction. Previously, hexadehydro-Diels-Alder (HDDA) reactions have been described, but the PDDA reactions proceed more rapidly. The likely mechanism has been discussed in some detail. Remarkably, nitriles do not participate in HDDA processes, but form readily pyridine-containing products in PDDA reactions. *Wang, T., Naredla, R.R., Thompson, S.K., Hoye, T.R, Nature 2016, 532, 484-488*.
- At the University of Tokyo it was found that the presence of small amounts of acidic sulfamic acid (SA) exerts beneficial effects on the fabrication of perovskite for solar cell fabrication on glass and flexible plastic films. The mechanism of the effects of SA has been elucidated and solar cells with a reproducible power conversion efficiency of 16.02% have been obtained. This is considerably higher than for devices without SA. *Guo*, *Y.*, *Sato*, *W.*, *Shoyama*, *K.*, *Nakamura*, *E.*, *J.Am.Chem.Soc.*,2016, *DOI* 10.1021/jacs.6b02130.
- Stephen Goldup, at the University of Southampton, has prepared, for the first time, an enantioselective catalyst that is chiral solely due to a mechanical bond between the two components and not as a result of being encoded in the covalent connectivity of the components themselves. Respectable enantioselectivities have been observed for a relevant mechanically chiral [2]rotaxane. It is suggested that chiral reaction fields generated by a mechanical bond in rotaxanes and catenanes may have a bright future in asymmetric catalysis. *Goldup, S.M., Nature Chem., 2016, 8, 404-406.*
- The next item is concerned with a world record. Pichler at the University of Vienna, together with an international group of coworkers, prepared a linear carbon chain of more than 6000 carbon atoms, the longest known sofar. It is a long acetylenic carbon chain of sp-hybridized carbon atoms (a carbyne), protected by thin double-walled carbon nanotubes with specific inner diameters of ca. 0.7 nm. The synthesis of these very long arrangements is confirmed by transmission electron microscopy, X-ray diffraction and (near-field) resonance Raman spectroscopy. There will be a strong interaction between the tubes and the chains. For an understanding of the properties of these long chains it is therefore necessary to extract the linear chain molecules from the carbon nanotubes, a considerable challenge. Shi, L., Rohringer, P., Suenaga, K., Niimi, Y., Kotakoski, J., Meyer, J.C., Peterlik, H., Wanko, M., Cahangirov, S., Rubio, A., Lapin, Z.J., Novotny L., Ayala, P., Pichler, T., Nature Materials, 2016, DOI 10.1038/nmat4617.
- A commentary in Nature Chemistry is devoted to an unusual topic: "One-world chemistry and systems thin-king". It is argued that chemistry needs a major overhaul in order to be fit for purpose in the twenty-first century and beyond. Stephen Matlin, at Imperial College London, and colleagues from India, Germany and Belgium, stress the interconnectedness of chemistry and related chemical sciences with local and global systems, including the biosphere, the environment, human and animal health, economics, politics, psychology and the law, which is summed up in the concept of one-world chemistry. Novel approaches are required that cross disciplinary boundaries. The paper summarizes in some detail the essential roles for future chemistry and demonstrates that many factors should be brought together, including ethics and sustainability. The authors express the hope that the global chemistry community will take up the challenge, since it will be for the benefit of the field and the society that it serves. *Matlin, S.A., Mehta, G., Hopf, H., Krief, A., Nature Chem., 2016, 8, 393-398*.

Dear readers of the highlights: I wish you all a relaxing and pleasant summer holiday!

Jan Engberts

New Appointments



Francesca Milocco

As of 15/5/2016 PhD student Group Otten

PhD Defences

Friday, June 10th

@ 16.15 Jeffrey Buter will defend his PhD thesis. Title: "On the total synthesis of terpenes containing quaternary stereocenters". Promotor: Prof. dr. A.J. Minnaard

Tuesday, June 28th

@ 11.00 Thomas Pieter Voortman will defend his PhD thesis. Title: "Conjugated Polyions: Polymers with ionic, water-soluble backbones". Promotor: Prof. Dr. R.C. Chiechi and Prof. dr. J.C. Hummelen

Thursday, June 30th

@ 9.00 Fatemeh Jahani Bahnamiri will defend her PhD thesis. Title: "Synthetic strategies for modifying dielectric properties and the electron mobility of fullerene derivatives". Promotor: Prof. dr. J.C. Hummelen

Werkbespreking: Thursday morning 8.30 hrs, room 5111.0080

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