university of groningen

Newsletter

Stratingh Institute for Chemistry

114

December 2015—January 2016

To all members of the Stratingh Institute for Chemistry

I just saw that it is warmer in Groningen these days than in many Mediterranean cities (including Venice, Florence, Trieste…). Nevertheless, the winter break is approaching and we are optimistic that we will see at least some traces of what used to be a winter in The Netherlands. Personally, I take no risks and I head to the Austria Alps.

The present academic community is part of a world where several high impact developments are taking place at the same time. Different as the problems may seem, they may be related, even having a common origin, according to some. While on the one hand I think we should be a bit modest in thinking that we can improve life or even save the planet simply by progress in science and technology only, we chemists have an almost unique and key position in making this happen. Remember US president Obama quoting one of his governors: "We are the first generation to feel the impact of climate change and the last generation that can do something about it." I am convinced that if we are able to stop global warming, improve everyone's health level, and arrange sufficient local and sustainable energy sources for everybody, the world would become a much better and safer place for everybody in all respects. We all work on those goals within the Stratingh Institute! Think about it: within our institute, we develop better catalysts for cleaner and more energy efficient chemical processes, we develop new bio-based and bio-inspired chemical processes and products, we develop methods for a much more cyclic economy building on natural starting materials and working towards recyclable materials, we develop new and affordable medicines, including new targeting strategies, we search for sustainable molecular building blocks for affordable and large scale application in photovoltaics, we develop testing and sensing devices for monitoring and analysis, etc. And, last but not least: we generate new fundamental scientific knowledge to do all of these things better and more efficiently. Do not hesitate to enjoy the fact that you are working on shaping the future for the better. Let's do what we can and what we are good at.

In order to do keep on doing so, we need a home. We are working on the final details of our new home, the Zernikeborg. The process has not always been easy during the past year, but it seems that, in the end, we will have a great building. Thanks to Wim, Wesley, Adri, Theodora for their continuous efforts in this matter. Starting January 1st, Adri Minnaard will take over as scientific director of the Stratingh Institute. We wish him luck, wisdom and a clear vision for the coming years. He will be the person that will lead us into this new place, our home during these following and decisive decades.

Please join us in the Institute's festivities on Wednesday December 16! Let's party, let's celebrate our successes of last year, take your chance to meet the new staff members if you haven't already, pour your colleagues a glühwein or a soda, feast on an oliebol, whatever you prefer. Tradition promises an unforgettable gathering before we go off for a short holiday.

Merry Christmas and a happy new year!

Kees Hummelen

Advanced Research Centre: Chemical Building Blocks Consortium

AkzoNobel, BASF, Shell, the Ministry of Economic Affairs, Top Sector Chemistry, the Netherlands Organisation for Scientific Research (NWO) and Utrecht University, the Eindhoven University of Technology and Groningen University on Monday December 7th presented their plans for setting up the new Advanced Research Center Chemical Building Blocks Consortium (ARC CBBC). This national research centre will tackle important energy and chemistry issues associated with the growing depletion of the finite supply of raw materials. The partners have made a commitment for several years and are aiming to jointly invest EUR 11 million a year, or 80 - 100 jobs in the knowledge industry. “This will also reinforce our competitive position,” Economic Affairs Minister Henk Kamp points out. “It will promote economic growth and generate new jobs.” Please read more about CBBC here.

Ben Feringa receives Chemistry for the Future Solvay Prize

Ben Feringa, Professor of Organic Chemistry at the Stratingh Institute for Chemistry, was presented with the Chemistry for the Future Solvay Prize by Queen Mathilde of Belgium on Thursday November 19th. He is awarded the prize, which includes prize money of € 300,000, for his pioneering research into molecular motors. You can find more information about the prize here.

Katalin Barta is awarded an ERC Starting Grant

Dr. Katalin Barta of the Synthetic Organic Chemistry group (Stratingh Institute for Chemistry) has been awarded an ERC Starting Grant of 1.5 million EUR. During this research she will develop novel, fully sustainable catalytic methods for the conversion of renewable resources to industrially relevant bulk and fine chemicals. The approach combines several disciplines including homogeneous and heterogeneous catalysis in order to address key fundamental challenges in the field . The ERC Starting Grant enables researchers to establish their team to further develop their research lines.

2015 Backer Lecture by Prof David W.C. MacMillan

This year the H.J. Backer lecture was presented by Prof. David W.C. MacMillan, from Princeton University in the USA. In his group the application of photoredox catalysis is developed and applied in novel transformations in organic synthesis.

In my opinion the lecture brought a clear message for synthetic organic chemists: for a long time we knew already that the comfort zone of polar reaction processes (and yes, yes, pericyclic reactions as well) did no longer hold and radical (chain) reactions and photochemistry make important contributions to synthesis. Photoredox catalysis, however, with hydrogen atom transfer as a pars pro toto, is going to make a big impact on the way we prepare molecules. We will need to know how this works, with the same ease as drawing an aldol reaction, and teach it our students.

Adri Minnaard

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

- An interesting review, written by chemists from a University in Taiwan, is devoted to the asymmetric synthesis of natural products and medicinal drugs through one-pot reaction strategies. This procedure has several advantages, such as its efficiency, versatility and expediency, particulary for complicated polycyclic ring systems, especially those with a sustainable and catalytic aspect. The review describes a number of successful and imaginative applications. The authors suggest that one-pot strategies for the preparation of complex molecules will assume a key role in chemical synthesis for decades to come. *Hong, B-C., Raja, A., Sheth, V.M., Synthesis 2015, DOI 10.1055/s-0035-1560344.*

- For the first time it was found possible to prepare esters from an acyl chloride and a halohydrocarbon in a single step. The reaction is carried out with dimethylaminopyridine (DMAP, 2 mol %) and using Cs2CO3 (0.7 equiv.) as the oxygen source. A preliminary study of the reaction mechanism suggests that the reaction proceeds via a free radical mechanism. The Chinese scientists at Dalian and Beijing found that the methodology has a wide scope and can be scaled up. The yields varied from 63 to 96 %. *Ren, L., Wang, L., Lv, Y., Li, G., Gao, S., Org.Lett. 2015, DOI 10.1021/acs.orglett.5b02479.*

- Houk and coworkers at the University of California, Los Angeles, performed a detailed study, using density functional theory, of the high rates of transannular Diels-Alder (TADA) reactions for substrates with 10-18 membered rings. The rates were compared with those of bimolecular and intramolecular Diels-Alder reactions, particularly looking at the effects of tether length, heteroatoms, and alkynyl dienophiles. Tether length played an important role (12-membered rings are most reactive due to a favorable enthalpy), but also heteroatoms and alkynyl moieties enhanced the rates significantly. Reasons for these effects are proposed. *He, C.Q., Chen, T.Q., Patel, A., Karabiyikoglu, S., Merlic, C.A., Houk, K.N., J.Org.Chem. 2015, 80,11039-11047.*

- Angew.Chemie published a thoughtful review, written by John Sutherland, entitled "The Origin of Life – Out of the Blue". Looking at the large number of suggestions in the literature regarding the early stages of the "chemistry of life", he concludes that the first building blocks of biology correspond to products of hydrogen cyanide chemistry, suggesting that life emerged "out of the blue". This means that it is likely that organic synthesis started from an environmentally available C1 feedstock molecule, crucial to the origin of life. *Sutherland, J.D., Angew.Chem.Int.Ed.2015, DOI 10.1002/anie.201506585.*

- Scientists from research institutes in the UK and Switzerland made an extensive study of the diffusion of water nanodroplets on graphene. Generally, diffusion across surfaces occurs via motion on a vibrating but otherwise stationary substrate. MD studies now showed that the motion of water nanodroplets on graphene is extremely fast (hundred to thousand times faster than the self-diffusion of water molecules in liquid water) and that the motion of adsorbate and substrate is strongly coupled. A new mechanism has been identified wherein the water droplets co-move with ripples of the underlying substrate. A number of applications of these diffusion processes have been suggested. *Ma, M., Tocci, G., Michaelides, A., Aeppli, G., Nature Materials, 2015, DOI 10.1038/NMAT4449.*

- Tunge and his coworker at the University of Kansas have found that the decarboxylative benzylation of acetylides is highly stereospecific. Interestingly, the stereochemistry of a secondary alcohol is effectively transferred to generate a tertiary stereogenic center. The sp-sp3 coupling does not require strongly basic conditions or preformed organometalics and produces CO2 as the sole byproduct. Thus, the synthetic procedure involves the transfer of stereochemical information from secondary benzyl alcohols to generate enantio-enriched tertiary diarylmethanes. *Mendis, S.N., Tunge, J.A., Org.Lett.2015, DOI 10.1021/acs.orglett.5b02410.*

- In biological rotary motors, the control of the direction of motion results from the intrinsic chirality of the α-amino acids from which the motors are composed. In his studies of synthetic autonomous light-driven synthetic rotary motors, Ben Feringa and three members of his group, have now found that in an achiral molecular system the presence of a pseudo-asymmetric carbon atom was sufficient for inducing exclusive autonomous disrotary motion of two appended rotor moieties. In fact the system resembles wheels on an axle, since isomerization around the two double bonds enables both rotors to move in the same direction with respect to their surroundings. This is an important finding: autonomous unidirectional rotary motion can occur in a symmetric system. *Kistemaker, J.C.M., Stacko, P., Visser, J., Feringa, B.L., Nature Chem.,2015, DOI 10.1038/nchem.2362.*

- Linker and his colleague at the University of Potsdam, Germany, prepared donor/acceptor systems for the first succesful intramolecular singlet oxygen (1O2) transfer. The migration of this reactive species within the molecule was evidenced by UV/vis, NMR, and quenching experiments and by competition reactions. An optimal balance of transfer rates and 1O2 yield was observed at about 315 K, which fits well with increased body temperature. This could make the novel singlet oxygen donors suitable for the treatment of cancer by the release of 1O2 in the dark. *Klaper, M., Linker, T., J.Am.Chem.Soc.2015, 137, 13744-13747.DOI 10.1021/jacs.5b07848.*
- Chemists at reseach institutes in Hong Kong, Xi'an, Guangzhou and Nanshan, Shenzhen reported a series of difluorobenzothiadizole (ffBT) and oligothiophene-based polymers.Three oligothiophene units were employed: quaterthiophene (T4), terthiophene (T3) and bithiophene (T2). A polymer based on ffBT and T3 with an asymmetric arrangement of alkyl chains provided 10.7% efficiency thick-film polymer solar cells (PSCs) without using any processing additives.Rather extensive studies were made of the effects of structural changes of the PSCs on their performance. *Hu, H., Jiang, K., Yang, G., Liu, J., Li, Z., Lin, H., Liu, Y., Zhao, J., Zhang, J., Huang, F., Qu, Y., Ma, W., Yan, H., J.Am.Chem.Soc.2015, DOI 10.1021/jacs.5b08556.*
- Multicomponent reactions (MCRs) represent a powerful chemical tool for the synthesis of complex molecules. Important factors are atom and step economy as well as the highly effective generation of complex molecules. One of the oldest MCRs is the Passerini reaction which provides a multifunctional α-acyloxyamide with the generation of a stereogenic center. Chemists at the University of Shenzhen, China, have now performed the Passerini reaction in the presence of a chiral phosphoric-acid catalyst under metal-free conditions. High asymmetric induction was found by concurrent activation of the aldehyde, carboxylic acid, and isocyanide under mild reaction conditions. A whole series of widely useful complex molecules has been prepared. *Zhang, J., Lin, S-X., Cheng, D-J., Liu, X-Y., Tan, B., J.Am.Chem.Soc., 2015, DOI 10.1021/jacs.5b09117.*
- Na+-activated K+ channels belong to the Slo family of large conductance K+ channels which are widely expressed in the brain. Their opening regulates neuronal activity that is determining the functioning of our brain. The channels possess intriguing biophysical properties such as extremely high conductance levels and gating sensitivity to intracellular Na+. Scientists from the Rockefeller University and the Harvard Medical School have now determined the structure of a complete channel by cryo-electron microscopy at a nominal resolution of 4.5 A°. The structural details make it possible to explain the extremely high conductance as well as how contraction of the cytoplasmic gating ring closes the pore. *Hite, R.K., Yuan, P., Li, Z., Hsuing, Y., Walz, T., MacKinnon, R., Nature 2015, DOI 10.1038/nature14958.*

Jan Engberts

PhD Defences

Friday, November 13th

@ 14:30 Tiziana Masini defended her PhD thesis. **Title:** "The enzyme DXS as an anti-infective target". Promotores: Prof. dr. A.K.H. Hirsch and Prof. Dr. A.J. Minnaard

Friday, December 18th

@ 9:00 Mathieu Colomb-Delsuc will defend his PhD thesis. **Title:** "Mechanistic studies on a peptidebased self-replicating system ". Promotor: Prof. S. Otto

New appointments

Filippo Tosi
As of 1/11/2015
PhD—Group Feringa

Ramon van der Vlag
As of 1/11/2015
PhD—Group Hirsch

Adele Faulkner
As of 1/11/2015
PostDoc—Group Feringa

Bin Liu
As of 1/11/2015
PhD—Group Otto

Werkbespreking: Thursday morning 8.30 hrs, room 5111.0080

December 10th—Dorus Heijnen (PhD Feringa): "Cross-coupling reactions with organolithium reagents"

December 17th—Mu-Chieh Chang (PhD Otten): "Title to be announced"

January 7th—Giulia Leonetti (PhD Otto): "Title to be announced"

January 14th—Thomas Voortman (PhD Chiechi): "Conjugated Polymers with Ionic, Water-Soluble Backbones"

January 21st—Ivica Cvrtila (PhD Otto): "Title to be announced"

January 28th—Difei Zhou (PhD Hummelen): "Title to be announced"

February 4th—Matea Vlatkovic (PhD Feringa): "Dynamic control of chiral space"

Stratingh Christmas Borrel

The traditional Stratingh Christmas Borrel will take plane on Wednesday December 16th, starting at 16:00 in 16.0215. You are all welcome!!

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