university of groningen

Newsletter

Stratingh Institute for Chemistry

105

December 2014/January 2015

To all members of the Stratingh Institute for Chemistry

The warmest one in three hundred years is coming to an end. A last working week, with our yearly lab cleaning event on Monday, the institute's Christmas party, including the announcement of the prestigious 'Groningen Center for Brilliant Students' (GCCB) trophy on Wednesday, and the election of the Teacher of the Year (two Stratingh staff members nominated!) and subsequent chemistry Christmas dinner on Thursday, is going to be a really heavy one! Please do not forget to come to this election event, because students have to vote on the spot for one of our two guys –ok, I admit I am one of them, together with Gerard- to keep that trophy within the institute. So, it is going to be a lot of fun, next week, but that is in quite sharp contrast to what seems to be happening in the Dutch scientific landscape, certainly including that of chemistry, biology, and physics. What is going to happen precisely is not clear yet, but major changes in the organization of the Dutch national science foundation are projected. Some see opportunities, but others are quite worried, especially when it comes to the aspect of who is going to decide what kind of academic research we are going to do in this country. Much of these issues will be resolved in the upcoming year. Next year, we will also finalize the design of our new building, the Zernikeborg. Especially Wim Kruizinga is putting in a lot of effort to get us a new situation which is to last at least for the next 40 or so years, which seems to be more of a challenge than anticipated a few years ago, since we now know that we live in an interesting earthquake area….

In the past year, we have welcomed new support staff members Annette Witter-Waalkens and Erik Jan Lindeboom. It has taken us a while to find a successor of legendary Ebe Schudde. I think the fact that we found Erik Jan at the opposite face of the earth serves as an indication of the efforts we've gone through to find the right guy. With Annette in the institute, we now have a full scale secretarial support team for all groups in the institute. Welcome, both of you!

Wesley Browne will be the new head of the MOLAN group, starting January 1st. We are all very excited about that move and we are confident that this will put the basiseenheid in a vital position. Due to this move, the institute will now go ahead defining a new scientific staff position, most likely in the form of a tenure track appointment.

Looking back, we have seen a great number of successes, last year. A VICI grant for Gerard Roelfes, Edwin Otten teacher of the year, Ben Feringa passing the magic number of 100 PhDs, the Theodor Föster Award and the Cope Scholar Award (2015), a Marie Curie fellowship for Giovanni Bottari, the Strating prize for Antonio Rizzo, the Gratama Science Award and an ECHO-STIP grant for Anna Hirsch, a VIDI grant for Tati Fernández, an NWO-TOP grant for Adri Minnaard, an NWO-ECHO grant for Syuzi Harytyunyan, the Backer prize 2013 for Danny Geerdink, a VENI grant for Sander We-

zenberg, and Ryan Chiechi became assistant professor: all of these were highlights for the people within institute, this year.

All in all, things are going well. It is time to enjoy the holidays and relax a bit.

Merry Christmas and a happy new year!

Kees Hummelen

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

- The "dance of lipids" in an idealized mammalian plasma membrane was analyzed by Siewert Marrink, Alex de Vries (GBSB and Zernike Institute) and colleagues at the Universities of Erlangen, Germany and Calgary, Canada, by large-scale MD simulations. The membrane contained 63 different lipid species, combining 14 types of headgroups and 11 types of tails asymmetrically distributed across the two leaflets. An enrichment of cholesterol occurs in the outer leaflet. Transient domains with liquid-ordered character form and disappear on a microsecond time scale. Of course, lipid mobility in bilayers is common knowledge, but the present study provides a rather detailed view of the dynamic lateral organization of lipids in the cell membrane. The next step will be to include membrane proteins into the bilayer membrane. *Ingolfsson, H.I., Melo, M.N., van Eerden, F.J., Arnarez, C., Lopez, C.A., Wassenaar, T.A., Periole, X., de Vries, A.H., Tieleman, D.P., Marrink, S.J., J.Am.Chem.Soc., 2014, 136, 14554-14559.*
- A paper by David Leigh and coworkers in Nature Chemistry has the challenging title "A Star of David Catenane". It describes the synthesis of a [2]catenane that consists of two triply entwined 114-membered rings. The structure is confirmed by NMR, mass spectrometry and X-ray crystallography. The woven scaffold is a hexameric circular helicate generated by the assembly of six tris(bipyridine) ligands with six iron(II) cations, with the size of the helicate promoted by the use of sulfate counterions. The synthetic protocol may provide a strategy for the synthesis of molecular topologies of ever-increasing complexity. *Leigh, D.A., Pritchard, R.G., Stephens, A.J., Nature Chem. 2014, 6, 978-982.*
- Scientists from three Universities in Japan performed a kinetic study of the Diels-Alder (DA) reaction of Li+- encapsulated [60]fullerene with 1,3-cyclohexadiene. The reaction product is [Li+@C60(C6H8)](PF6-). Interestingly, the complex Li+@C60 reacted 2400 times faster than empty C60 at 303 K, a lowering of the energy of activation by 24.2 kJ mol-1. The reason for the rate enhancement was investigated by DFT calculations. It is suggested that the encapsulated Li+ ion catalyses the DA reaction by lowering the LUMO of Li+@C60. This is the first detailed kinetic study of a DA reaction catalyzed by an encapsulated Lewis-acid catalyst. *Ueno, H., Kawakami, H., Nakagawa, K., Okada, H., Ikuma, N., Aoyagi, S., Kokubo, K., Matsuo, Y., Oshima, T., J.Am.Chem.Soc. 2014, 136, 11162-11167.*
- A Science paper reported that in single-junction polymer solar cells fulleropyrrolidines with amine(C60-N) or zwitterionic(C60-SB) substituents as cathode-independent buffer layers can be solution-based incorporated. For example, a thin layer of C60-N reduced the effective work function of Ag, Cu, and Au electrodes to 3.65 eV. Also high power conversion efficiency values were obtained, not requiring precise control over interlayer thickness. *Page, Z.A., Liu, Y., Duzhko, V.V., Russell, T.P., Emrick, T., Science, 2014, 346, 441-444.*
- A German-Chinese joint project resulted in a successful asymmetric photoredox transition-metal catalysis, activated by visible light. Already for some time visible light has been re-

cognized as an environmentally friendly and sustainable form of energy for triggering chemical transformations and catalytic chemical processes. Quite generally, photoredox catalysis generates highly reactive radical-ion intermediates which, under suitable conditions, lead to useful chemical reactions. In this paper, it is shown that a chiral iridium complex can serve both as a sensitizer for photoredox catalysis and as a complex providing effective asymmetric induction for the enantioselective alkylation of 2-acyl imidazoles. The process offers novel opportunities for the "green" synthesis of chiral molecules. *Huo, H., Shen, X., Wang, C., Zhang, L., Röse, P., Chen, L-A., Harms, K., Marsch, M., Hilt, G., Meggers, E., Nature 2014, 515,100-103.Review: Skubi, K.L., Yoon, T.P., Nature, 2014, DOI 10.1038/515045a.*

- A fundamental study appeared in PNAS. Greg van Anders and colleagues revealed how shape can exert an entropic influence. They defined a shape-dependent directional entropic force based on the concept that shape can maximize the entropy of dense packings. For example, it can manifest itself for polyhedral as a repulsion between corners and an attraction between faces. We can now understand why self-assembled systems do not necessarily adopt the densest packing. Of course, shape entropy competes with intrinsic shape effects. The paper is not easy to read, but the brief review written by Phil Ball may be helpful! *van Anders, G., Klotsa, D., Ahmed, N.K., Engel, M., Glotzer, S.C., Proc. Natl. Acad. Sci., 2014, DOI 10.1073/pnas.1418159111. Ball, P., Nat. Mater., 2014, DOI 10.1038/nmat4142.*
- Andrew Ashley and coworkers (Imperial College, London) found that the hydrogenation of a variety of aliphatic and aromatic aldehydes and ketones can be carried out with solutions of the Lewis acid B(C6F5)3 in 1,4-dioxane. It is claimed that this is the first entirely metal-free catalytic hydrogenation of carbonyl groups under relatively mild reaction conditions. The reaction is believed to occur via a "frustrated Lewis pair" mechanism in which 1,4-dioxane, a weak Brönsted base yet a moderately strong donor, plays a pivotal role. Further investigations of the hydrogenation of more challenging carbonyl substrates are ongoing. *Scott, D.J., Fuchter, M.J., Ashley, A.E., J.Am.Chem.Soc., 2014, DOI 10.1021/ja506936f.*

Two brief references to interesting synthetic studies published in Org.Lett.:

- Organocatalytic enantioselective Michael- Michael. Michael-Aldol condensation reactions: control of five stereocenters in a quadrupole-cascade asymmetric synthesis of highly functionalized hexahydrophenanthrenes. *Raja, A., Hong, B-C., Lee, G-H., Org.Lett., 2014, DOI 10.1021/ol502821e.*
- Highly enantioselective one-pot synthesis of chiral β-hydroxy sulfones via asymmetric transfer hydrogenation in an aqueous medium. *Zhang, D., Cheng, T., Zhao, Q., Xu, J., Liu, G., Org.Lett., 2014, DOI 10.1021/ol502832a.*

- A novel mechanism has been suggested for ion permeation in K+ channels in living cells. These processes are highly efficient. In the past it was assumed that a superposition of alternating ion- and water-occupied states was involved. Detailed MD simulations have now suggested that permeation occurs via ion-ion contacts between neighboring K+ ions. The reason for the high efficiency of K+ conduction is Coulomb repulsion between adjacent ions. The directly neighboring K+ ions in the selectivity filter are consistent with crystallographic data. *Köpfer, D.A., Song, C., Gruene, T., Sheldrick, G.M., Zachariae, U., de Groot, B.L., Science, 2014, DOI 10.1126/science.1254840.*
- Finally some beautiful results obtained by Gerard Roelfes and his coworkers in our Institute who created the first examples of artificial metalloenzymes with in vivo incorporated unnatural α-amino acids capable of binding a Cu2+ ion. The site-specifically insertion of the α-amino acid into a protein was accomplished by using the "amber stop codon suppression" method called "Lactoccocal multidrug resistance Regulator (LmrR). The new materials are able to ca-

talyze asymmetric vinylogous Friedel-Crafts alkylation reactions to yield products with up to 83% ee. This novel approach, design and protocol makes it ultimately possible to augment cellular biosynthesis with unnatural catalytic transformations. The work has been briefly reviewed in Nature Chemistry. *Drienovska, I., Rioz-Martinez, A., Draksharapu, A., Roelfes, G., Chem.Sci. 2014, DOI 10.1039/c4sc01525h. Johnson, R., Nature Chem., 2014, DOI 10.1038/nchem.2127.*

Jan Engberts

Stratingh Seminars

Tuesday, December 9th

Prof. Lee Cronin, University of Glasgow
Room: 5111.0022
Time: 16:00 hrs

Title: Towards the evolutionary genesis engine

PhD Defences

Friday, December 5th

@ 9:00 Francesca Caprioli will defend her PhD thesis. **Title:** "Enantioselective Auto and Cross Catalytic Reactions". **Promotor:** Prof. dr. S.R. Harutyunyan

Friday, January 9th

@11:00 Saleh Hamieh will defend his PhD thesis. **Title:** "Synthetic receptors for ammonium ions using Dynamic Combinatorial Chemistry". **Promotor:** Prof. dr. S. Otto

@12:45 Hugo Fanlo Virgos will defend his PhD thesis. **Title:** "Catalysis and Communication in Dynamic Molecular Networks". **Promotor:** Prof. dr. S. Otto

Friday, January 30th

@11:00 Jiawen Chen will defend his PhD thesis. **Title:** "Advanced Molecular Devices Based on Light-driven Molecular Motors". **Promotor:** Prof. dr. B.L.Feringa

@ 14:30 JiaJia Dong will defend her PhD thesis. **Title:** "Selective catalytic oxidations by palladium and manganese—Selectivity, reactivity and mechanistic studies". **Promotor:** Prof. dr. W.R. Browne, Prof. Dr. B.L. Feringa

New appointments

Ruben Maaskant

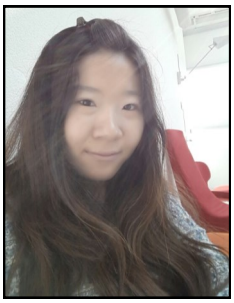
1 November

Group Roelfes

Wojciech Danowski

1 December

Group Feringa



Di Zhu

1 October

Group Hirsch

Werkbespreking: Thursday morning 8.30 hrs, room 5111.0080

December 4th—Douwe Zijlstra (MSc, Otten): Study of the Michael addition on unsaturated nitriles using a ruthenium pincer complex

December 4th—Mehrnoosh Jahani Bahnamiri (PhD, Hummelen): Fullerene derivatives with increased dielectric constant

December 11th— Niek Eisink (PhD, Minnaard): Selective modifications of unprotected carbohydrates

December 18th—Niels van Velzen (PhD, Harder): Pentaarylcyclopentadienyl lanthanide complexes

January 8th—Peter Deuss (Barta): Lignin as renewable feedstock for aromatic chemicals

January 15th—Steven Wan (Minnaard): new biphosphine monoxide ligand for asymmetric Heck reaction

January 22nd—Yan Tao (Barta): Redox Complex for casde reaction

January 29th—Peter Kroon (Hirsch): Efficient fragment based drug design using dynamic combinatorial chemistry and NMR

January 29th— Yanxi Zhang (Hummelen): title to be announced

February 5th—Ramon van der Vlag (Roelfes): Design and synthesis of ratiometric fluorescent probes

February 5th—Federico Lancia (Browne): title to be announced

The traditional Stratingh Christmas Borrel will take place in room 5116.0116, 1st floor, on Wednesday December 17th starting at 16:00.

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