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Newsletter

Stratingh Institute for Chemistry

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April 2017

Ben Feringa wins Academic Society Award

The Royal Netherlands Society of Engineers (KIVI) has awarded the Academic Society Award to Nobel Prize laureate Ben Feringa, Professor of Organic Chemistry at the University of Groningen. He receives the award in appreciation of the great importance of his research and the appealing manner in which he links science with society. The award ceremony is on 19 April, during Engineers' Day.

'Ben Feringa has managed to achieve breakthroughs in several areas that are fundamental to engineers, such as organic synthesis, catalysis, supra-molecular chemistry and nanotechnology. The Royal Netherlands Society of Engineers has decided to decorate him for his extraordinary research achievements and his excellent clarification of these achievements to the public at large. It is remarkable how he makes time in the media, at schools and in public lectures to make his work accessible to a wide audience', says Micaela dos Ramos, Director of KIVI.

ERC Advanced Grant for Sijbren Otto

Can we synthesise life de-novo in the lab? This is one of the Grand Challenges of contemporary Science. Overall objective of this project is to set important steps in turning chemistry into biology by building fully synthetic chemical systems that contain and integrate some of the essential elements of life: replication, metabolism and compartmentalisation. Functional coupling of any of life's essential elements has not been achieved, at least not without making use of biomolecules. We now aim to achieve such coupling and develop fully chemical systems to become increasingly life-like. Specific aims are:

1. Achieve and explore Darwinian evolution of a fully synthetic system of peptide-based self-replicating molecules.
2. Develop self-replicating molecules that are capable of catalysing not only their own formation, but also other chemical reactions. We will specifically target chemical reactions that result in the production of building blocks which the replicators can utilize to replicate, thereby integrating replication with a rudimentary form of metabolism.
3. Achieve self-reproducing compartments and develop ways to couple replication inside compartments with compartment division. Three parallel approaches will be explored, based on (i) vesicle-type compartments made from self-replicating molecules; (ii) coascervates and (iii) compart-

ments made by surfactants that are produced by catalytically active self-replicators.
4. Extend replication from peptide-based building blocks to ones containing nucleobases. We also plan to investigate reaction networks made from mixtures of peptide- and nucleobase-containing building blocks).
5. Develop kinetic modelling tools that allow an efficient exploration of multi-parameter space of the reaction networks developed in 1-4. Through stochastic computational modelling we will address mechanistic issues that are experimentally intractable. Furthermore, modelling will allow a more efficient exploration of multi-parameter space and will guide further experimental work into the right part of this space.

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

The first and last item in these Highlights will be devoted to two really amazing findings, not directly in organic chemistry, but generally in the chemical sciences.

- The first is a study by Oganov, Zhou, and Wang with an international research team from sixteen Universities in China, the USA, Russia, Italy and Germany, which describes a thermodynamically stable compound of helium and sodium. Although helium has been understood as chemically inert due to its stable closed-shell electronic configuration, zero electron affinity and extremely high ionization potential, they have been able to prepare Na2He which has a fluorite-type structure and is thermodynamically stable at pressures >113 GPa. Sven Lidin said: “The last bastion of inertness has finally fallen”. High pressure synthesis was employed in a diamond anvil cell. The electronic structure of Na2He was investigated. It is an electride in which the presence of the helium atoms causes strong electron localization which makes the material insulating. The authors predict the existence of Na2HeO with a similar structure at pressures higher than 15 GPa. *Dong, X., Oganov, A.R., Goncharov, A.F., Stavrou, B., Lobanov, S., Saleh, G., Qian, G-R., Zhu, Q., Gatti, C., Deringer, V.R., AND Dronskowski, R., Zhou, X-F., Prakapenka, V.P., Konopkova, Z., Popov, I.A., Boldyrev, A.I., Wang, H-T., Nature Chem., 2017, DOI 10.1038/nchem.2716.*

- Studies of soft materials and of supramolecular chemistry have greatly benefitted from the recent technological innovations of transmission electron microscopy (TEM). But, as recently argued by Marc Stuart, together with Egbert Boekema and Linda Franken, technical aspects of sample preparation have often been overlooked. The result is a quite large number of erroneous interpretations of the experimental results, published even in high-quality scientific journals. This is a very serious situation since further research activities can be initiated on the basis of these errors. Stuart’ s paper makes this clear and a warning is expressed and explained against the use of drying. Over-interpretation and mistakes can be avoided by using cryo-TEM. Everybody employing TEM in research, and not being a specialist in the field, should read this paper. *Franken, L.E., Boekema, E.J., Stuart, M.C.A., Adv.Sci, 2017, DOI 10.1002/advs.201600476.*

- A paper, written by nine authors from four University Institutes in Beijing, reports a novel wide band gap donor for efficient fullerene-free all-small-molecule organic solar cells. They designed and prepared an organic small molecule, DRTB-T, containing a two-dimensional trialkylthienyl-substituted benzodithiophene core building block. The compound has a band gap of 2.0 eV with a low-lying highest occupied molecular orbital (HOMO) level of -5.51 eV. Small-molecule solar cells were constructed, consisting of DRTB-T and a nonfullerene acceptor (IC-C6IDT-IC). The morphology of the active layer was fine-tuned by solvent vapor annealing. The device showed an extremely high power conversion efficiency (PCE) of 9.08 percent with a high open-circuit voltage of 0.98 V. The authors claim that this is sofar the highest PCE for a non-fullerene small-molecule organic solar cell that has been found and that there is a great potential for further developments using their approach. *Yang, L., Zhang, S., He, C., Zhang, J., Yao, H., Yang, Y., Zhang, Y., Zhao, W., Hou, J., J.Am.Chem.Soc., 2017, DOI 10.1021/jacs.6b11612.*

- Buxing Han and six coworkers from two academic institutes in Beijing showed that it is possible to switch the chirality in assemblies of bio-based amphiphiles just by varying their alkyl chain length. For this purpose they designed and synthesized a series of sorbitol-alkylamine surfactants (SAAS-Cm)with two alkylamine groups attached to sorbitol and wherein m is the carbon number of the alkyl chains. Self- assembled aggregates were formed in aqueous solutions with supramolecular chirality. Simply by changing the length of the alkyl chains, chirality inversion of the assemblies could be realized. The reason is apparently that a change in the alkyl chains leads to variation of the conformation of the chiral headgroup, which depends on the balance of torsional stress and hydrophobic interaction. Applications are envisaged. *Zhang, P., Ma, J., Kang, X., Liu,*

H., Chen, C., Zhang, Z., Zhang, J., Han, B., Chem.Comm. 2017, DOI 10.1039/c6cc10122d.

- Prof. Gulder, with three coworkers from the Tech.University of München, reported a nice biocatalytic total synthesis of the structurally and stereochemically complex ikarugamycin, a bacterial polycyclic tetramate macrolactam. In order to solve the synthetic challenges, an enzymatic total synthesis was carried out successfully. Employing an iterative PKS/NRPS machinery and two reductases, 15 carbon-carbon and 2 nitrogen-carbon were constructed in a biocatalytic one-pot reaction, overnight and at ambient temperatures. The authors expect further applications of their synthetic approach. *Greunke, C., Glöckle, A., Antosch, J., Gulder, T.A.M., Angew.Chem.Int.Ed., 2017, DOI 10.1002/anie.201611063.*

- A further amazing property of water. A water explosion, found and interpreted by scientists from the Technical University of Enschede, the University of Tsinghua, China, and the Max Planck Institute in Göttingen, Germany. Millimetric water droplets freeze starting with the outside shell and then radially inwards, undergoing fracturing and healing events. Finally the ice drops undergo an explosion with fragment velocities of about 1 m/s. The whole process was studied using a high-speed camera and water droplets of about 1 mm. The ultimate cause of the explosion is, of course, the unusual property of water that it, in contrast to most other materials, expands upon freezing. The detailed explanation for the explosion is worth reading! The results are relevant for understanding the behavior of freezing rain and cloud droplets. *Wildeman, S., Sterl, S., Sun, C., Lohse, D., Phys. Rev.Lett. 2017, 118, 084101-1 – 08101-5.*

- Four professors from Hyogo University (Japan) wrote a useful review of the recent progress in enantioselective radical cyclizations, with particular emphasis on the control of enantioselectivity. Good results have been obtained for radical cyclizations controlled by chiral Lewis acids, chiral metallic reagents, chiral thiols, chiral imidazolidinone catalysts, and chiral non-covalent organocatalysts. These reactions attract much interest because they can be employed for the preparation of highly functionalized compounds with multiple stereocenters. According to the authors,there appear to be many further opportunities for enantioselective radical cyclizations. *Miyabe, H., Kawashima, A., Yoshioka, E., Kohtani, S., Chem.Eur.J., 2017, DOI 10.1002/chem.201603124.*

- The final item is devoted to a great discovery that caused great excitement at Harvard University. Silvera and a colleague were able to produce metallic hydrogen, capable of conducting electricity, at pressures well beyond those in the center of earth and at low temperature. At a pressure of 496 GPa, hydrogen got properties as those of an atomic metal in a Wigner-Huntington transition. Details of the experimental approach and properties of the material are reported in their Science paper and useful comments are given by Service, also in Science. These novel findings may have important impact on physics and may have technological applications. *Dias, R.P., Silvera, I.F., Science, 2016, DOI 10.1126/science.aal1579. Service, R.F., Science, 335 (6323), 332-333 (2017). Wigner, E., Huntington, H.B., J.Chem.Phys. 1935, DOI 10.1063/1.17499590.*

Jan Engberts

New Appointments

Tobias van den Enk

PhD student as of 1/3/2017

Group Feringa

Piermichele Kobauri

PhD student as of 1/3/2017

Group Feringa

Werkbespreking: Thursday morning 8.30 hrs, room 5111.0080

April 6th— Yigit Altay (PhD Otto) - "Novel Self-Replicators from Dynamic Combinatorial Libraries"

Wednesday April 12th—15:00-16:30 Bernoulliborg—Room 5161.0151—Master Symposium Stratingh Institute for Chemistry

- **Jurjen O. Cazemier (Barta) -** "New heterogeneous CuZn catalysts for the reduction and hydrodeoxygenation of 5-(hydroxymethyl)furfural"
- **Ilse Welleman (Szymanski) -** "Development of enzyme-responsive ParaCEST contrast agents for MRI"
- **Marieke Veenstra (Harutyunyan) -** "Sequential copper catalyzed asymmetric conjugate addition and enolate trapping to α,β,-unsaturated amides"

April 13th— Steven (I.C.) Wan (PhD Minnaard) - "Site selective C-C bond formation on monosaccharides by photoredox catalysis"

April 20th— David Komaromy (PhD Otto) - "Triggered self-replication in coupled subsystems"

April 27th— King's Day

May 4th— Guillermo Monreal Santiago (PhD Otto) - "Next steps in peptide based self-replicators: Compartmentalization, metabolism, or cell culture?"

May 11th— Pablo Ortiz (PhD Harutyunyan) - "Catalytic asymmetric alkylation of enolizable ketimines using Grignard reagents"

May 18th—Friederike Reessing (PhD Szymanski) - "Development of light-responsive MRI contrast agents"

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