

May 2018

FameLabNL audience award goes to Groningen!



Photo courtesy of Joost Weddephol

Last week the national final of FameLab was held in Utrecht. FameLab is the biggest science communication competition in the world. The idea behind FameLab is that young scientists (students, PhD's, postdocs and starting professors) have to present a scientific topic to an audience of laymen in under 3 minutes without using powerpoint.

This year the audience award was awarded to Marcel Eleveld, who gave a presentation about the Eigen paradox of the origin of life (“Machinery for accurate (molecular) self-replication needs a lot of information to be encoded - but how do you obtain such machinery before the associated information can be accurately copied?”). Marcel is a Nanoscience master student who is working in the group of Sijbren Otto.

The jury award was awarded to Jair Santanna (assistant professor at the TU Twente) who spoke about DDoS attacks and how they can be prevented.

Sijbren Otto wins prestigious Royal Society of Chemistry Award



Professor of Systems Chemistry Sijbren Otto is the 2018 recipient of the Royal Society of Chemistry (UK) Supramolecular Chemistry Award. This biennial award is in recognition of Otto's contribution to the science of molecular networks and systems chemistry. The main theme of his current work is chemical evolution. As recipient of the award, Otto will give a number of lectures in Britain.

'I feel very honoured to receive this award', says Otto. 'It is nice to receive such recognition from my colleagues.' Each year, the Royal Society of Chemistry presents awards to a number of chemists in a range of fields. 'Previous winners of the Supramolecular Chemistry Award are leading scientists in the field, so it is great to be on that same list.' The award, which will be presented later this year, includes a medal, £ 2000 and a lecture tour.

New PhD coordinator for the Stratingh Institute: Marzia Nuzzolo

Marzia Nuzzolo is taking over from Cristina D'Arrigo the task of PhD coordinator. From now onwards, please refer to Marzia for any question you may have

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

- The energy landscape of chemical reactions can be modified by mechanical stimuli and also chemical reactions can be enabled. A pulling force can stretch chemical bonds, thereby initiating a reaction. Melosh from the Stanford Institute for Materials and Energy Sciences together with seventeen coworkers from the USA, China, Mexico, Germany and the Ukraine, have now shown that mechanochemistry through isotropic compression is possible by molecularly engineering structures that are able to translate macroscopic isotropic stress into molecular-level anisotropic strain. These molecules contain mechanically heterogeneous components – a compressible mechanophore and incompressible ligands. In these molecules isotropic stress can induce relative motions of the rigid ligands, resulting in the activation of bonds. In a combination of experimental and DFT computational work the

authors could demonstrate hydrostatic-pressure-driven redox reactions in metal-organic chalcogenides which incorporate molecular elements that possess molecular elements that have heterogeneous compressibility. In these structures bending of bond angles or shearing of adjacent chains activates the metal-chalcogen bonds, resulting in the formation of the elemental metal. This new reaction mechanism appears to suggest strategies for high-specificity mechanosynthesis. Yan, H., Yang, F., Pan, D., Lin, Y., Hohman, J.N., Solis-Ibarra, D., Li, F.H., Dahl, J.E.P., Carlson, R.M.K., Tkachenko, B.A., Fokin, A.A., Schreiner, P.R., Galli, G., Mao, W.L., Shen, Z-X., Melosh, N.A., *Nature*, 2018, DOI 10.1038/nature25765.

- A recent minireview, written by Enders and three colleagues from the University of Aachen, Germany, summarizes the developments and new advances in N-heterocyclic carbene (NHC)-catalyzed asymmetric cycloadditions involving azolium dienolate intermediates. These intermediates have been employed only very recently in asymmetric synthesis, particularly in cycloadditions dealing with remote functionalization. The azolium dienolate intermediates can be readily generated from α,β -unsaturated aldehydes, functionalized enals, α,β -unsaturated acid derivatives, and cyclobutenones in the presence of NHCs as catalysts. It is a very practical strategy for remote functionalizations affording valuable asymmetric molecules, such as δ -lactones, δ -lactams, γ -amino acids, cyclohexenones, and seven-membered dinitrogen-fused heterocyclic derivatives. It is argued that the present work will lead to important further studies which will reveal the synthetic potential of NHC organocatalysis. Chen, X-Y., Liu, Q., Chauhan, P., Enders, D., *Angew.Chem.Int.Ed.*, 2018, DOI 10.1002/anie.2017709684.
- The single C-C bond is perhaps the most familiar covalent bond in organic chemistry. Their typical length is 1.54 Å, but they can be elongated a little bit in molecules with special properties. Now Suzuki with four coworkers at the Hokkaido University in Japan, have established a world record by preparing a dihydropyrycene that contains a C-C bond with a length of 1.806 Å. This compound has a highly strained core and two spirocyclic units which are forced to face each other and helping to stretch out the central C-C bond. Of course they asked the question “when is a bond a bond?” But the presence of the C-C bond was confirmed by observing its stretching vibration (587 cm⁻¹, compare ethane, 993 cm⁻¹) through Raman spectroscopy and by employing X-ray crystallography. Previously a theoretical limit of 1.803 Å was proposed for the alkane bond length in caged dimer compounds. It is the bond length at which the bond has a dissociation energy of zero. The molecule prepared at Hokkaido appears to deviate from this theoretical relation. Ishigaki, Y., Shimajiri, T., Takeda, T., Katoono, R., Suzuki, T., *Chem.*, 2018, DOI 10.1016/j.chempr.2018.01.011.
- Wang, together with twelve coworkers from the Universities of California, San Diego and Wuhan, China, published a further contribution aimed at understanding the intelligent communication between synthetic nanomotors. In general, a chemical message was sent from a moving activator motor to a nearby activated receiver motor by release of Ag⁺ ions from a Janus polystyrene/Ni/Au/Ag activator motor to the activated Janus SiO₂/Pt nanomotor. A dramatic speed change resulting from the enhanced catalytic activity of the activated motor then comes from the transmitted silver signal. Thus, sequential localized chemical communications provide selective and successive activation of multiple nanomotors. The authors conclude that chemical communication between different nanomotors can pave the way to developing intelligent nanoscale robotic systems which can cooperate with each other. Chen, C., Chang, X., Teymourian, H., Ramirez-Herrera, D.E., Esteban-Fernández de Avila, B., Lu, X., Li, J., He, S., Fang, C., Liang, Y., Mou, F., Guan, J., Wang, J., *Angew.Chem.Int.Ed.*, 2018, DOI 10.1002/anie.201710376.
- Yorimitsu and three colleagues from Kyoto University, Japan, have accomplished the aminati-

on of diaryl sulfoxides with anilines and alkylamines under palladium/N-heterocyclic carbene (NHC) catalysis. Because of its electron deficiency, the leaving arenesulfenate anion is readily released from the palladium center, resulting in smooth catalyst turnover under milder reaction conditions in comparison with the previous C-S bond amination. Regioselective amination of unsymmetrical diaryl sulfoxides could also be carried out by means of steric bias. According to its mild reaction conditions, the present amination could also be carried out with potentially reactive functional groups such as silyl, boryl, methylsulfanyl, and halogen moieties. *Yoshida, Y., Otsuka, S., Nogi, K., Yorimitsu, H., Org.Lett., 2018, DOI 10.1021/acs.orglett.8b00060.*

- Proton transfers via hydronium and hydroxide ions is an important reaction in organic chemistry and biochemistry. The mechanism is, however, not fully understood. Car and Wu, and six coworkers from Temple University and Princeton University, have now modelled water and hydrated water ions, employing state-of-the-art density-functional-theory-based molecular dynamics, with corrections for non-local van der Waals interactions, and self-interaction in the electronic ground state. It is shown that the structural diffusion of hydronium ions preserves the previously assumed concerted behavior. Proton transfers are frequent via H_3O^+ and mostly concerted. But proton transfers via the solvated hydroxide ion are more rare and with much fewer concerted jumps. It is shown that the unique solvation shell of this ion discourages proton transfer. A rational explanation has now been found as to why hydroxide diffuses slower than hydronium in water. The asymmetry in the temporal correlation of proton transfer appears to be the explanation why hydroxide is diffusing slower than the hydronium ion. *Chen, M., Zheng, L., Santra, B., Ko, H-Y., DiStasio Jr., R.A., Klein, M.L., Car, R., Wu, X., Nature Chem. 2018, DOI 10.1038/s41557-018-0010-2.*
- Hydrophobic molecules and surfaces usually do not interact with biologically relevant hydrophilic molecules because of their different hydration properties. But sometimes differences are found: Akita with four scientists at the Tokyo Institute of Technology at Yokohama reported that the hydrophobic cavity of a polyaromatic capsule can encapsulate hydrophilic oligo(lactic acid)s in aqueous solution. X-ray crystallographic and ITC analyses indicated that this highly unusual host-guest behavior is the result of enthalpic stabilization by multiple CH- π and hydrogen-bonding interactions. The binding constants are up to $K_a=3.105 M^{-1}$, not very high, but nevertheless remarkable. *Kusaba, S., Yamashina, M., Akita, M., Kikuchi, T., Yoshizawa, M., Angew.Chem.Int.Ed., 2018, DOI 10.1002/anie.201800432.*

Jan Engberts

New appointments:



Lukas Pfeifer—PostDoc
Feringa Group



Ankush Sood - PhD
Group Otto

Werkbespreking: Thursday morning 8.30 hrs, room 5111.0080

May 24th — Xiaoming Miao

May 31st— Ji Zhang—"Palladium-catalyzed regioselective oxidation and reduction of glucosamine, and its application in chemical biology"

Jun 7th—Beibei Guo

Jun 14th— Anastasia Afasanenko—"New catalytic systems for efficient N-alkylation of amines with alcohols"

Monday July 2nd Stratingh Day

On Monday July 2nd, the Stratingh Institute will hold its first Stratingh Day.

The Stratingh day will take place at the Biotop, Vleugel F, Kerklaan 30 9751NN Haren.

During the morning there will be several talks, followed by a poster session and another talk by Prof. Henry Rzepa, from Imperial College, London.

All PhD students who started their PhD before January 1, 2018 must present a poster in the poster session.

The afternoon will be dedicated to different activities and the day will end with a BBQ, always at the Biotop.



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