



Newsletter

Stratingh Institute for Chemistry

130

October 2017



Molecular Machines Nobel Prize Conference

From November 19th to 22nd 2017, Groningen and the University will host the [Molecular Machines Nobel Prize Conference](#). The conference is in honour of the 2016 Nobel Laureates in Chemistry, [Prof. J.-P. Sauvage](#), [Prof. J. Fraser Stoddart](#) and [Prof. B.L. Feringa](#), all of whom will participate fully and deliver lectures. The [scientific program](#) celebrates their achievements with top speakers covering the various topics in the fields of research of the laureates. This conference wishes to offer the unique opportunity to learn about the latest developments relating to the 2016 Nobel Prize in Chemistry. The conference social program will culminate in a festive dinner at the Martini Church on November 21st.



Marthe Walvoort features in the New Investigators in Glycoscience article—Journal “Carbohydrate Research”.

The Stratingh Institute is proud to announce that Marthe Walvoort, Assistant Professor and Rosalind Franklin fellow in Chemical Biology at the Stratingh Institute for Chemistry features in the New Investigators in Glycoscience article ([here](#)). This article highlights the excellent research being undertaken by the rising stars of the molecular glycoscience field from across the globe.

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

- An interesting editorial in *Nature Cell Biology*. What constitutes the ideal referee report? Scientists are expected to have different opinions about this question, but it will be clear that the referee has to be an expert in the field of the reported research and should be able to review studies fairly and objectively. A good and justified assessment of the potential significance of the work coupled with a justified evaluation of the technical merits are among the main requirements of a peer review. Gaps in the report and logical avenues for further investigations might be noted but the referee should refrain from raising requests that are peripheral to the central message of the manuscript. But several other aspects are clearly described in the editorial. There is no doubt that refereeing is a time-consuming endeavor. A mutual trust is necessary: the authors entrust their unpublished work to the editors of the journal and then the editors entrust the paper to usually at least two expert referees. Good principals of refereeing are very much defining the general scientific quality of the journal! *Nature Cell Biology*, 2017, DOI 10.1038/ncb3606.
- Methane is a prime example of a hydrophobic compound. The gas is a model system for studying hydrophobic interactions which are of crucial importance in biological processes such as protein folding, the functioning of proteins and cell membrane formation. At 1000°C and at 100 bar (10 MPa) its maximum aqueous solubility is 6.10⁻³ mol %. But now Loveday and three colleagues at the University of Edinburgh made a very remarkable observation: at 2 GPa and at 1000°C the maximum solubility of methane in water exceeds 35 mol %! At 330 K liquid methane droplets were observed in water but at pressures above 2 GPa the droplets disappeared and methane became soluble in water. The authors speculate about the reason for this behavior. A possibility could be that at the elevated pressures the molecules become smaller and fit better into the hydrogen-bond network of water. It is also suggested that the methane molecules not only become more soluble but also more reactive that might increase the possibility to make methanol or a halogen compound from methane. Other possibilities for green chemistry, based upon the new data, are also suggested. *Pruteanu, C.G., Ackland, G.J., Poon, W.C.K., Loveday, J.S., Science Advances* 2017, DOI 10.1126/sciadv.1700240.
- A facile and scalable synthesis of lead-free Cs₃Bi₂X₉ (X=Cl,Br,I) perovskite nanocrystals (NCs) was reported by Keli Han and nine coworkers from research institutes at Dalian, Beijing and Lund. The excited state dynamics of these as-synthesized compounds were investigated by time-resolved photoluminescence and transient absorption measurements. It was found that the fast trapping process (2-20 ps) leads to a low photoluminescence (PL) quantum efficiency (QE) of ligand-free Cs₃Bi₂Br₉NCs (0.2%). However, the PLQE can be enhanced to 4.5% when extra oleic acid is added during the synthesis processes. The reason is passivation of the fast trapping process (2-20 ps). The trap states can also be passivated under humid conditions. The NCs show then a high stability towards air exposure exceeding 30 days. *Yang, B., Chen, J., Hong, F., Mao, X., Zheng, K., Yang, S., Li, Y., Pullerits, T., Deng, W., Han, K., Angew.Chem.Int.Ed.* 2017, DOI 10.1002/anie.201704739.
- Noy, from the Lawrence Livermore National Laboratory, Livermore (USA) and five colleagues have shown that skinny nanotubes can break aquaporin's record for moving water across lipid membranes. The nanotubes in the new system are just 0.8 nm in diameter, and consequently the water molecules must slide through them single file, which speeds the

transport of the molecules. A similar process occurs in the biological protein aquaporin, but the α -amino acids on the inside of its channel form hydrogen bonds to the water molecules, thereby slowing their transit compared to that in the molecularly smooth nanotube's interior. It is, of course, remarkable that now a man-made system has been found that is more efficient than the biological system of aquaporin. Despite obvious challenges, nanotubes are amenable to different types of processing, unlike the delicate aquaporin, and could be strong contenders for desalination membrane components. *Tunuguntla, R.H., Henley, R.Y., Yao, Y-C., Pham, M.W., Noy, A., Science 2017, DOI 10.1126/science.aan2438.*

- Yitzhak Apeloig and five coworkers from the Technion-Israel Institute of Technology published the first spectroscopic observation of a triplet diradical state of a cyclobutadiene. This triplet diradical electronic state, stabilized by trimethylsilyl groups, was obtained from tetrakis (trimethylsilyl)cyclobuta-1,3 diene and characterized by a temperature-dependent EPR study. The structure was confirmed by a singlet \rightarrow triplet energy gap of 13.9 kcal mol $^{-1}$ in agreement with calculated values. Interestingly, the triplet radical is thermally accessible at moderate temperatures and is not an intermediate in the thermal cycloreversion of cyclobutadiene to two acetylene molecules. It is explained that double-bonded carbon and silicon anions and radicals have different structures and properties, with silicon radicals being thermodynamically more stable than carbon radicals. *Kostenko, A., Tumanskii, B., Kobayashi, Y., Nakamoto, M., Sekiguchi, A., Apeloig, Y., Angew.Chem.Int.Ed.2017, DOI 10.1002/anie.201705228.*
- A total synthesis in 14 steps of Nannocystin Ax was reported by Kalesse (University of Hannover) and Poock (Helmholtz Center in Braunschweig). This natural product is a cytotoxic 21-membered depsipeptide (a peptide in which one or more amide linkages are replaced by ester functions) which was previously isolated from the myxobacterial genus *Nannocystis* sp. Key-steps in the construction of the polyketide fragment were a vinylogous Horner-Wadsworth-Emmons (HWE) reaction and a vinylogous Mukaiyama (VMAR) aldol reaction. Closure of the macrocycle was carried out via a macrolactamization reaction employing COMU (1-cyano-2-ethoxy-2-oxoethylidenaminoxy)dimethylamino-morpholino-carbenium hexafluorophosphate). The overall yield was 11%. The stepwise introduction of the three peptide fragments opened the possibility to incorporate modified fragments leading to derivatives that might be used for further biological investigations. *Poock, C., Kalesse, M., Org.Lett. 2017, DOI 10.1021/acs.orglett.7b02112.*
- Ir-catalyzed enantioselective, intramolecular silylation of unactivated primary methyl C-H bonds was reported by Hartwig (our Backer lecturer in 2014) and a coworker from the University of Berkeley, California. Dihydrobenzosiloles are formed in high yields and high enantioselectivities by functionalization of enantiotopic methyl groups under mild conditions. Catalysis is provided by an iridium complex generated from [Ir(COD)OMe] and chiral dinitrogen ligands. Further transformation of the C-Si bonds in the enantioenriched dihydrobenzosiloles gave the C-Cl, C-Br, C-I, and C-O bonds in the final products. The potential of this reaction was shown by sequential silylations and functionalization of the C(sp 3)-H and C(sp 2)-H bonds, as well as diastereoselective C-H silylations of a chiral, natural-product derivative containing multiple types of C-H bonds. The authors suggest that C-H bond cleavage is the rate-determining step. *Su, B., Hartwig, J.F., J.Am.Chem.Soc. 2017, DOI 10.1021/jacs.7b06679.*
- A remarkable new finding: molecular motors can open biological cell membranes! Molecular machines have previously been employed for biomedical applications, but Tour (Rice Universi-

ty) and coworkers from North Carolina State University and Durham University have now physically absorbed, specifically designed molecular motors onto lipid bilayers and after activation of the motors by ultraviolet light, holes are drilled into the cell membranes. Molecular motors and complementary experimental protocols were designed that use nanomechanical action to induce the diffusion of chemicals out of synthetic vesicles, to enhance the diffusion of traceable molecular machines into and within live cells, to induce necrosis and to induce chemical species into live cells. Furthermore it was shown that by using molecular machines bearing short peptide addends, nanomechanical action can selectively target specific cell-surface recognition sites. It is suggested that both in-vitro and in-vivo application of molecular machines can be used as their design progresses to allow two-photon, near-infrared and radio-frequency activation. *Garcia-Lopez, V., Chen, F., Nilewski, L.G., Duret, G., Aliyan, A., Kolomeisky, A.B., Robinson J.T., Wang, G., Pal, R., Tour, J.M., Nature 2017, DOI 10.1038/nature23657.*

Jan Engberts

New Appointments



Johan Kemmink

Head of NMR facility

1/9/2017



Nittert Marinus

PhD –group Minnaard

1/9/2017



Jorn Steen

PhD–group Browne

1/9/2017



Kirill Kulish

PhD-group Harutyunyan

1/9/2017

H.J. Backer Lecture 2017.



Wilfred A. van der Donk

University of Illinois at Urbana-Champaign

Title: **Biosynthesis and Engineering of Cyclic Peptide Antibiotics**

Time **16.00**

Date **31 October 2017**

Place **5161.0151**

Drinks will be served after the lecture

PhD defences

Friday, October 6th

@ 9:00 **Niek Eisink** will defend his PhD thesis. Title: “Regioselective oxidation of carbohydrates - Scope, Limitations and Origin of Selectivity”. Promotor: Prof. dr. A.J. Minnaard, Co-promotor: Dr. M.D. Witte

Friday, October 13th

@ 11:00 **Rachel Travieso Puente** will defend her PhD thesis. Title: “Exploring coordination chemistry and reactivity of formazanate ligands”. Promotor: Prof. dr. E. Otten

Friday, October 13th

@ 14:30 **Niels van Velzen** will defend his PhD thesis. Title: “Superbulky penta-aryl cyclopentadienyl ligands in lanthanide chemistry”. Promotores: Prof. dr. S. Harder

Werkbespreking: Thursday morning 8.30 hrs, room 5111.0080

October 5th—**Kaja Sitkowska (PhD Feringa)** - "Towards uncaging amines with red light"

October 12th—**Yanxi Zhang (PhD Chiechi)** - "Gating and Conjugation in Nano-gap Tunneling Junctions"

October 19th—**Ramon van der Vlag (PhD Hirsch)** - “Acylhydrazones as potent inhibitors of human 15-lipoxygenase-1”

October 26th—**Dusan Kolarski (PhD Feringa)** - “Towards the control of circadian rhythm with light”

November 2nd—**Verena Böhmer (PhD Feringa)** - “Development of 18F-PET Tracers for Prostate Cancer using Click Chemistry”

November 9th—**Bin Liu (PhD Otto)** - "Foldamers and self-replicators from aminoacid-nucleobase conjugates"

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