

Gratama Prize for Marthe Walvoort

Dr Marthe Walvoort has been awarded the Gratama Prize this year. She is an internationally renowned specialist in glycochemistry and glycobiology. She is in the vanguard of research on the relationship between sugar and health. The Gratama Prize is for young scientists who stand out for their innovative, socially relevant and important research. The prize amounts €25,000.

By biologically synthesising sugars, Walvoort has gained insight into how mother's milk functions, or rather, why breastfeeding contributes to the health of newborn babies. She has also explored the role of sugar in bacterial infections and in multiple sclerosis. Marthe Walvoort makes her scientific work accessible to a wider audience as a public sugar expert for newspapers, in videos and vlogs, and in public presentations.

She worked as a postdoc at MIT Boston, and she has indicated that she will use part of the prize money to go to San Diego in the USA to work on the health effects of breast milk sugars. Marthe Walvoort was appointed a Rosalind Franklin Fellow at the University of Groningen in 2015 and has received substantial research grants, which have enabled her to found her own research group here in Groningen. She will use the rest of the prize money to cover the research costs of the students participating in her research group.

The Gratama Foundation says that Dr Walvoort's work clearly demonstrates how a young scientist can successfully mix challenging questions, innovative scientific output and socially relevant results, can inspire students and present the results of her research to a general audience.



Sander Wezenberg has been awarded the ERC starting grant

ERC supports talented young researchers in setting up a research team and starting an independent research project. This year Dr. Sander Wezenberg has received the ERC starting grant for a project entitled “From light-stimulated anion receptors to transmembrane carriers and pumps”. The transport of anions across the cell membrane, which is mediated by transport proteins, is essential to many important biological processes. Dysregulation of this transport has been associated to various diseases and therefore, chemists endeavor to develop artificial receptors that mimic the function of natural transporters. Despite much progress over the last decade, the current artificial systems are mostly static, while proteins are able to change their activity dynamically in response to stimuli in the environment. To integrate such stimuli-controlled behavior in synthetic systems is a key contemporary challenge. In view of this, the goal of the proposed research program is to develop anion receptors in which the binding properties can be effectively modulated by light and to apply these receptors as transmembrane carriers and pumps, in order to regulate passive transport (i.e. down a concentration gradient) and to induce active transport (i.e. against a concentration gradient).

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

Time is irreversible! We start a new academic year. I wish all my readers successful scientific work!

I start with a highly interesting study performed by Ben Feringa, Marc Stuart and five colleagues from the Stratingh Institute and Zernike Institute of the University of Groningen, The Netherlands. They examined a molecular motor, containing a rotary core with two bulky aromatic groups, linked by amide groups. It was shown how confinement of the molecular motor affects its rotary motion and that, for bowl-shaped particles, the structures are a direct result of the mixing of a good solvent and a (partial) non-solvent. In other words, no self-assembly takes place, but solvent-driven assembly. The molecular design is rather unimportant, and the spheres are not hollow, micellar or vesicular. The non-solvent induces the formation of droplets with a hardened exterior, because of an increase of the glass transition temperature by the external medium. The droplets also contain an interior that is plasticized by the solvent with an overall result of the formation of stable bowl-shaped particles with a fluid interior, a glass-like exterior and a highly specific shape: dense spheres with a hole in their side. For a bulky first-generation molecular motor, the isomerization behavior could be changed. In addition, the motor showed *in situ* photo-switchable aggregation-induced emission. The thermal helix inversion step is prohibited by strong confinement while altering the energy barriers that determine the rotary motion. As a result, a reverse trans-cis isomerization upon heating is induced. In summary, it is highly interesting that a change in solvent ratio and in the extent of confinement cause a remarkable control of forward and backward rotary motion.

Franken, L.E., Wei, Y., Chen, J., Boekema, E.J., Zhao, D., Stuart, M.C.A., Feringa, B.L., *J.Am.Chem.Soc.*, 2018, DOI 10.1021/jacs.8b03045.

Snieckus and six coworkers at Queen's University, Kingston, Canada and Vertex Pharmaceuticals, Inc., Boston, USA, published a novel and general methodology for the direct *ortho*-arylation of 4-aryl pyrimidines with aryl iodides. The process is mediated by a pyrimidinyl nitrogen directed C-H activation reaction and affords predominantly monoarylated products. Also new reactions for *ortho*-iodination and acetoxylation are provided that are promoted by the

same directing group. The starting 4-aryl pyrimidines are relatively readily available, which helps scale-up processes. The authors anticipate that the novel methodology could be useful in the synthesis of bioactive and material science related molecules.

Gupta, S., Melanson, J.A., Vaillancourt, L., Nugent, W.A., Tanoury, G.J., Schatte, G., Snieckus, V., Org.Lett., 2018, DOI 10.1021/acs.orglett.8b01300.

Suslick, together with four colleagues at the University of Illinois at Urbana-Champaign, USA, wrote a highly interesting review in *Acc.Chem.Res.*, entitled “The Chemical History of a Bubble”. The growth, oscillation, and rapid collapse of bubbles (acoustic cavitation) occurs in all liquids irradiated with a sufficient intensity of sound or ultrasound. The collapse of such bubbles provides a source of, sometimes very high, energy and the resulting local heating can drive chemical reactions. Sonoluminescence (SL) was already observed 85 years ago. The phenomenon has been studied by a variety of physical methods and gave us an understanding of the extraordinary conditions created inside collapsing bubbles. Very high temperatures (exceeding 15,000 K!) can be reached. Within the chemical realm of SL, interesting questions have been solved in the past 40 years, but also many remain to be solved. Secondary reactions from the high energy species that are formed within the collapsing bubble diffuse into the bulk liquid and expand the number of sonochemical reactions, particularly of redox reactions which are relevant for the synthesis of nanomaterials, but also of other important organic and organometallic reactions relevant for biomedical reactions, drug delivery, and pharmaceutical uses.

Suslick, K.S., Eddingsaas, N.C., Flannigan, D.J., Hopkins, S.D., Xu, H., Acc.Chem.Res., 2018, DOI 10.1021/acs.accounts.8b00088.

An interesting and still continuing project in physical organic chemistry involves the structure, binding and dynamics of hexaphenylethane (HPE) and its derivatives with substituents in the phenyl rings. Here I only pay attention to HPE and hexa(3,5-di-*tert*-butylphenyl)ethane (HTBPE), investigated by Schreiner and one coworker from the Justus-Liebig University in Giessen, and one coworker from the University of Padova, Italy. Whereas DPE has not been synthesized yet because of an extremely weak C-C bond and easy formation of two trityl free radicals, HTBPE is a thermally stable compound with a long central C-C bond of 167 pm as compared with a typical C-C bond length of 154 pm. Enthalpy/entropy compensation studies and computational studies can explain these bonding situations. The non-intuitive correlation between increased dimer stability with steric crowding can be attributed to increased rigidity and increased attractive London dispersion interactions that originate from the polarizability of the alkyl moieties.

Rösel, S., Balestrieri, C., Schreiner, P.R., Chem.Sci. 2017, DOI 10.1039/c6sc02727j.

Mai and five coworkers from Jinan University, Guangzhou, China, prepared novel all-inorganic perovskite solar cells recognizing that these structures could be helpful for tackling the problem of thermal instability of organic-inorganic perovskite solar cells (PSCs). The new structures have the formula FTO/NiO_x/CsPbI₂Br/ZnO@C₆₀/Ag in which the ZnO@C₆₀ bilayers were employed as the electron-transporting layers that demonstrate high carrier extraction efficiency and low leakage loss. It was found that the all-inorganic CsPbI₂Br perovskite solar cells yielded a power conversion efficiency (PCE) as high as 13.3% with a V_{oc} of 1.14 V, a J_{sc} of 15.2 mA.cm⁻² and a FF of 0.77. The stabilizing power output (SPO) was about 12% and was remarkably stable within 1000 s. It is clear that the present data demonstrate an important improvement in comparison with the organic-species-

containing PSCs and involve a highly useful step forward toward realizing highly efficient and stable perovskite solar cells.

Liu, C., Li, W., Zhang, C., Ma, Y., Fan, J., Mai, Y., J.Am.Chem.Soc., 2018, DOI 10.1021/jacs.7b13229.

Li, and three coworkers at the University of the Chinese Academy of Sciences in Shanghai, have accomplished the first and asymmetric total synthesis of septedine (SP) and its 7-deoxy analogue (OHSP). These quite complex C₂₀-diterpenoid alkaloids carry an oxygenated heptacyclic scaffold and represent a large family of natural products with a number of biological activities. Previous attempts to prepare SP and OHSP have not been successful. Key steps in the present procedure include a Carreira polyene cyclization, an anionic Diels-Alder cycloaddition, an allylic alcohol isomerization and a Sanford Csp³-H acetoxylation. Much attention was also paid to the late-stage construction of the oxazolidinopiperidine group. The yields were overall good to reasonable. It is clear that the present work will be a basis for further biological studies of this class of interesting alkaloids.

Zhou, S., Guo, R., Yang, P., Li, A., J.Am.Chem.Soc., 2018, DOI 10.1021/jacs.8b03712.

The hydration of ions plays is of great importance for numerous chemical, physical and biological processes. Bakker and three colleagues at the Van 't Hoff Institute, University of Amsterdam and the AMOLF Institute, have recently employed a modified Hubbard-Onsager equation to analyse hydration numbers. This approach does not overestimate the collective nature of water reorientation near ionic species and takes into account the locally reduced Kirkwood factor. New insights were obtained into the effect of ions on water cooperativity. It was found that the reduction in dielectric response (depolarization) in aqueous media, as caused by hydrated ions, is different for water and deuterium oxide. This isotope dependence offers a reliable method to determine the kinetic contribution to the depolarization and is found to be significantly smaller than predicted by the existing theory. The reason can be found in the reduced hydrogen-bond cooperativity in the hydration shell. A quantitative agreement between theory and experiment was obtained by reducing the Kirkwood correlation factor of the solvating water from 2.7 (the bulk value) to about 1.6 for NaCl and about 1 for CsCl (corresponding to completely uncorrelated motion of water molecules). These results are of great importance for quantifying the chemical and physical properties of aqueous solutions.

Cota, R., Ottosson, N., Bakker, H.J., Woutersen, S., Phys.Rev.Lett., 2018, DOI 10.1103/PhysRevLett.120.216001.

I finish this month with a very important paper, written by F. Nicastro of the Universities of Rome and Harvard University, together with twenty coworkers from a number of Universities and published in Nature. As you probably know, we live in a Universe that for only 5% consists of ordinary matter as found in atoms (of the periodic system, baryonic matter) while the rest is “dark” matter and energy that currently cannot be detected directly. Now Nicastro and coworkers have been able to carry out, for the first time, X-ray observations which appear to indicate that dark matter is hidden in the filamentary structure of the cosmic web. X-ray absorption signatures of baryons have been detected in the spectra of a bright background object. It is a great finding!

The original paper is highly theoretical and not easy to understand and therefore I recommend to read first the brief summary, written by Fang (MIT, Cambridge, USA), also published in Nature.

Nicastro, F., Kaastra, J., Krongold, Y., Borgani, S., Branchini, E., Cen, R., Dadina, M., Danforth, C.W., Elvis, M., Fiore, F., Gupta, A., Mathur, S., Mayya, D., Paerels, F., Piro, L., Rosa-Gonzalez, D., Schaye, J., Shull, J.M., Torres-Zafra, J., Wijers, N., Zappacosta, L., Nature, 2018, DOI 10.1038/

New appointments:



Sven van Vliet,
Group Feringa



Marieke J. Veenstra,
Group Harutyunyan



Michiel T. Uiterweerd,
Group Minnaard



Jelte Steen,
Group Otten



George J. Hermens,
Group Feringa



Antonio A. Castillo Garcia,
Group Barta



Michela Ferrari,
Group Walvoort



Hung-Chien Lin,
Group Minnaard



Daisy R. S. Pooler,
Group Feringa

Werkbespreking: Thursday morning 8.30 hrs, room 5111.0080

Sep 6st: Xingchen Yan, "Cu-catalyzed direct asymmetric 1,4-addition of Grignard reagents to α,β -unsaturated carboxylic acids enabled by in situ formation of silyl ester"

Sep 13th: Tjalling Canrinus, "Shedding light on the formation of hydrogels"

Sep 20th: Ruben Andringa, "Synthetic Studies on Archaeal Membrane Spanning Lipids"

Sep 27th: Wojciech Danowski, "Molecular machines and switches in solid state and at the interfaces"

PhD Defences

Beatriz Calvo González from Minnaard Group will defend her thesis on the 07-09-2018 at 9 am

Dorus Heijnen from Feringa Group will defend his thesis on the 07-09-2018 at 16:15 pm

Erik Pinxterhuis from Feringa Group will defend his thesis on the 28-09-2018 at 16:15 pm

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