

March 2018



Major Vici grant for Syuzanna Harutyunyan

NWO awards a Vici grant of 1.5 million euros to Prof. dr. Syuzanna Harutyunyan. She will be doing research into new chemical reactions using Lewis acids.

Lewis acids can be used to either make unreactive molecules chemically active, or conversely to selectively block reactive groups and direct the outcome of reactions. Combining this concept with copper catalysts Harutyunyan and her team will develop efficient and environmentally friendly alternatives to existing chemical processes for the production of pharmaceutically relevant

compounds.

First European Chemistry Gold Medal awarded to Prof. Ben Feringa

The very first European Chemistry Gold Medal has been awarded to Professor Ben Feringa for exceptional achievements in the field of chemistry in Europe. Professor Feringa will be presented with the Gold Medal during the 7th EuCheMS Chemistry Congress in Liverpool this year, where he will also give a plenary lecture.



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

- The first issue of Nature Catalysis was published last January. I think a wise decision and important for the Stratingh Institute. John Thomas wrote the first editorial with the title “The enduring relevance and academic fascination of catalysis”. An interesting and extensive review article (with 115 references) was written by Bornscheuer of the University of Greifswald with five co-authors from Hoffman-La Roche, Basel, Novartis, Basel, Bielefeld University and the University of Vienna. They describe the opportunities and challenges for a combination of chemo- and biocatalysis, two different worlds of catalysis. Among the first examples is the work by van Bekkum (Univ. of Delft) on

the preparation of D-mannitol. Some challenges have been daunting, as the requirement to employ water as the solvent, the preferred solvent for enzymes. A number of concepts have been discussed in some detail: the combination of biocatalysis, with metalcatalysis, with organocatalysis, and with photo-/electro- (chemistry and catalysis). Of particular importance is also the use of reaction engineering to combine catalytic steps. Two further developments are the creation of enzymes that are able to catalyse novel chemical reactions not found in nature's repertoire, and the use of surfactant technology on a large scale and in multistep processes in aqueous media. The authors have no doubt that further applications will be found for an effective combination of chemo- and biocatalysis, and photocatalysis employing a frequency range different from IR. *Thomas, J.M., Nature Catalysis, 2018, DOI 10.1038/s41929-017-0014-0. Fudroff, F., Mihovilovic, M.D., Gröger, H., Shajdrova, R., Iding, H., Bornscheuer, U.T., Nature Catalysis, 2018, DOI 10.1038/s41929-017-0010-4.*

- The development of efficient methods for functionalization of inert C-H bonds remains an important research theme. Arndtsen and five colleagues from McGill University in Montreal, Canada, published a novel Pd-catalyzed C-H bond functionalization via the generation of high-energy electrophiles from aryl iodides with carbon monoxide. This reaction leads to ketones through aroyl triflates, which are extremely reactive electrophiles. This process is confirmed by mechanistic studies. Thus, metal-catalyzed arene C-H bond functionalization (employing stable and available reagents) can be coupled with electrophilic arenes (broad scope and selectivity). No directing groups are necessary and low palladium-catalyst loadings are sufficient. *Kinney, R.G., Tjutrins, J., Torres, G.M., Liu, N.J., Kulkarni, O., Arndtsen, B.A., Nature Chem., 2018, DOI 10.1038/nchem.2903.*
- Nazeeruddin, of the Ecole Polytechnique Fédérale de Lausanne, Switzerland, with nine coworkers from two Technical Institutes in Spain and Germany and from the Humboldt University in Berlin, have shown that it is possible to prepare solar cells with a lead iodide perovskite-like crystal structure and containing a large organic cation, guanidinium, with a photovoltaic performance of 20% and improved stability compared with CH₃NH₃⁺ ions. Calculations suggest that the increased stability of these materials is caused by the possible formation of more hydrogen bonds. There are still a number of theoretical questions that have to be solved and further research is required. *Jodlowski, A.D., Carmona, C.R., Grancini, G., Salado, M., Ralaiarisoa, M., Ahmad, S., Koch, N., Camacho, L., de Miguel, G., Nazeeruddin, M.K., Nature Energy, 2017, DOI 10.1038/s41560-017-0054-3.*
- It is known that the interstellar medium contains a large number of aromatic molecules, including polycyclic aromatic hydrocarbons (PAHs). But unfortunately, so far it has not been possible to identify specific aromatics by infrared spectroscopy because the spectra cannot be distinguished adequately. The only molecule that has been identified with 100% certainty is benzene. Now a second aromatic, benzonitrile, has been detected with great certainty by Brett McGuire (from the National Radio Astronomy Observatory, Charlottesville, USA) and six coworkers (from other Astronomy and Chemical Laboratories in the USA and Russia) using the 100-m Robert C-Byrd Green Bank Telescope with a frequency range different from IR. Hyperfine-resolved transitions were seen in emissions from the molecular cloud TMC-1. It is argued that benzonitrile has possibly been formed from benzene via reaction with the cyanopolyynes that occur in TMC-1, but further research is clear-

ly necessary. Simple aromatics like benzonitrile are likely precursors for the formation of polycyclic aromatics. *McGuire, B.A., Burkhardt, A.M., Kalenskii, S., Shingledecker, C.N., Remijan, A.J., Herbst, E., McCarthy, M.C., Science, 2018, DOI 10.1126/science.aao4890.*

- In a recent JACS communication, Peters and Fu, with two coworkers from Cal Tech, Pasadena, remember us that selective monoalkylation of aliphatic amines by unactivated, hindered halides is still a largely unsolved challenge in organic synthesis. They have now largely solved this problem by using a combination of visible light and a copper catalyst for a transition-metal catalyzed alkylation of aliphatic amines by unactivated secondary alkyl halides. Employing their optimized method, C-N bond formation occurs without significant over-alkylation (<1%) under mild conditions (-100C) in the presence of a number of functional groups. Irradiation is carried out by blue-LED lamps of a catalyst prepared from commercially available components. Preliminary mechanistic studies suggest the formation of an alkyl radical that is engaged in out-of-cage C-N bond formation. The yields are between 34 and 83%, largely depending on steric effects. *Mattier, C.D., Schwaben, J., Peters, J.C., Fu, G.C., J.Am.Chem.Soc., 2018, DOI 10.1021/jacs.7b09582.*
- Not a very recent review, but I think sufficiently interesting to call your attention to. Written by Bakshi, from the Wilfrid Laurier University, Waterloo, Canada, it summarizes how the fine-tuning of the desired morphologies of nanomaterials can be achieved by interaction with surfactants, monomeric, micellar, vesicular, wormlike and as microemulsions. Surfactants are excellent shape directing agents due to their unique ability of interfacial adsorption. Special attention is given to the effects of surfactant tail and headgroup structure. For example, strongly hydrophobic surfactants which produce wormlike micelles, vesicles and liquid crystalline phases, are suitable templates for the production of long nanrods or wires. Headgroup modification is also important, particularly changes in the hydrophobicity of the headgroup. Cetyltriethylammonium bromide-stabilized seeds produce gold nanorods in high yields compared to that in the presence of cetyltrimethylammonium bromide. Important future perspectives include the design of biologically sustainable nanomaterials for their possible application in nanomedicine. *Bakshi, M.S., Cryst.Growth.Des. 2016, DOI 10.1021/acs.cgd.5b01465.*
- In Chem.Eng.News appears already for some time a series of brief articles entitled "What will be Chemistry's next big thing?" In the issue of Febr.1, 2018 my attention was attracted to the work of Zare (Stanford University). He has shown that water droplets (measuring about 1-5 μm) can be used for chemical analysis, for understanding chemical reactions and for synthetic reactions in ways rather different from those in bulk water solutions. He was recently been called the "microdroplet evangelist". In a recent paper in *Angew.Chem.Int.Ed.* he and two coworkers have now shown that the $[2\sigma+2\sigma+2\pi]$ cycloaddition of diethyl azodicarboxylate and quadricyclane in aqueous microdroplets is accelerated by a factor of 102 compared to the already rapid "on-water" reaction previously reported by Sharpless. The authors suggest that "on-droplet" chemistry, similar to "on-water" chemistry, is now becoming a general process of synthetic interest. *Bain, R.M., Sathyamoorthi, S., Zare, R.N., Angew.Chem.Int.Ed., 2017, DOI 10.1002/anie.201708413. Narayan, S., Muldoon, J., Finn, M.G., Fokin, V.V., Kolb, H.C., Sharpless, K.B., Angew.Chem.Int.Ed., 2005, DOI 10.1002/anie.200462883.*

Jan Engberts

PhD defences

Friday, March 9th

@ 14:30 **Paul Dockerty** will defend his PhD thesis. Title: "Nature-inspired molecules containing multiple electrophilic positions". Promotor: Prof. dr. A.J. Minnaard Co-promotor: Dr. M. Witte

Werkbespreking: Thursday morning 8.30 hrs, room 5111.0080

March 8th—Andreas Hussain (PhD Otto) - "Adaptation and Catalysis in Self-Replicating Systems"

March 15th—Marco Carlotti (PhD Chiechi) - "Structure vs. Function: What Matters in Molecular Tunneling Junctions Comprising Conjugated Molecules"

March 22nd—Nabil Tahiri (PhD Minnaard) - "Total Synthesis of Mycolic Acid Diastereomers"

March 29th—Stella Verkhnyatskaya (PhD Walvoort) - "Fucosylated Cyclodextrins as Novel Antiadhesives"

Keep the date: Monday July 2nd Stratingh Day

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

More information about the organization of the day will follow in due course. Please make sure you block the day in your diary.

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