

Stratingh Award 2015



The prestigious Stratingh Award for the best colloquium for the year 2014 was awarded on June 15. The award ceremony started with the presentation of Prof. Jan Engberts about the history of the prize. After, the selection committee announced the winners. The selection committee consisted of 2 staff members and 2 PhD students from various disciplines: Katalin Barta, Martin Witte, Michael Lerch and Ivica Cvrtila.

The third prize went to a colloquium which provided a great

introduction to rheology for beginners and an enjoyable piece of reading for experts as well. The third place went to Luuk Kortekaas for "Rheology as versatile tool in rational gelator design". There was big competition for the first place. The second place was awarded to a colloquium that was very scholarly presented and revealed a lot of knowledge in organic chemistry: Rik Oost for "Applications of the [1,2]-Brook rearrangement in tandem carbon-carbon bond formation". The first price was given to the colloquium which provided great insight into the field of photocleavable protecting groups in general, and was certainly not lacking a balanced, but critical own opinion on the subject. The title of the winning work by Mickel Hansen is: "Wavelength-selective cleavage of protecting groups." The event was finished with delicious cakes and coffee, followed by a nice lunch with the members of the Baker foundation, the reading committee and of course the winner!

Summer school "Spectroscopy of Spin in Catalysis, Bioinorganic and Materials Chemistry: spinning a web of theory and practice"

Last July, the summer school "Spectroscopy of Spin in Catalysis, Bioinorganic and Materials Chemistry: spinning a web of theory and practice" took place in Groningen. The school was aimed at PhD and Postdoctoral researchers with backgrounds ranging from inorganic chemistry, theory and spectroscopy attracting 40 participants from all over Europe including several members of the Gravity Program FMS. The summer school is a joint venture between the Summer Schools program, Molecular Inorganic Chemistry, Theoretical Chemistry at the University of Groningen and the COST (Cooperation on Science and Technology) Action ECOSTbio CM1305 (ecostbio.eu). The aim of the summer school was to bring together theorists and practitioners in the field of (bio)inorganic chemistry and in particular does dealing with spin systems. The 7 day event involved lectures on research topics, introductions to theory and spectroscopy as well as four afternoons of laboratory sessions to give hands on experience in NMR, MCD, EPR, Raman

and resonance Raman spectroscopies as well as theory (DFT and EPR simulations).

The lectures were provided by experts from all over Europe, including Sam de Visser (University of Manchester), Marcel Swart (University of Girona), Jana Roithnova (Charles University Prague), Ricardo Louro (IQBT, Lisbon) Carole Duboc (UJF, Grenoble) and Maylis Orio (CNRS, Marseille) together with several University of Groningen Staff, including Wesley Browne, Remco Havenith, Thomas la Cour Jansen and Ria Broer and the entire school was chaired by Edwin Otten.

The organisers of the summer school are deeply indebted to the assistance of Hilda Biemold for organisation support, Peter van der Meulen and Wim Kruizinga for support in the NMR Practicals, Shaghayegh Abdolazadeh, Juan Chen, Luuk Kortekaas, Tjalling Canrinus, Duenpen Unjaroen and Sandeep Padamati for their help in the spectroscopy practicals and Davide Angelone and CIT, in particular, Bob Droge, for ensuring that the theoretical sessions could take place. Massimo Boomi is thanked for catering.

Netherlands Award for Supramolecular Chemistry for Prof. Jean-Marie Lehn

During the last two decades the Netherlands have been recognized for their outstanding contributions to the field of Supramolecular Chemistry. With this in mind the Research Center for Functional Molecular Systems to which the Stratingh Institute belongs has initiated the Netherlands Award for Supramolecular Chemistry with the intention to recognize and reward outstanding scientists in the Supramolecular Chemistry field, and provide researchers in The Netherlands the opportunity to meet leading scientists in this field. The award will be presented every year to an internationally renowned senior or junior scientist working in the field of Supramolecular Chemistry. The awardee will be invited to undertake a lecture tour of The Netherlands and present his/her work at several universities.

The first Netherlands Award for Supramolecular Chemistry could only be given to one person: Professor Jean-Marie Lehn, by many regarded as the founding father of Supramolecular Chemistry. This prize is in recognition of his lifetime contribution to the field. From 25 to 30 September 2015 Jean-Marie Lehn will be visiting several universities in the Netherlands as part of the lectureship connected to the award. The award ceremony will take place in Nijmegen on 30 September .

Prof. Jean-Marie Lehn will give a lecture at the Stratingh Institute for Chemistry on Friday, September 25th, at 15:00 in room 5111.0022.

In memoriam Hepke Hogeveen

Prof. dr. Hepke ('Heppie') Hogeveen, 15/08/1935 – 28/08/2015



Hepke Hogeveen studied chemistry and obtained his PhD in 1961 with Prof. Hans Wynberg in Groningen. After a period of industrial research in Bologna, Amsterdam, and London (Shell), he returned to Groningen and became professor of Organic Chemistry in 1971. During his academic career, until 1992, he published more than 160 scientific papers. His most influential scientific work was on the structure and reactivity of carbocations in general, and on non-classical carbon mono- and dications in particular. There has been quite a bit of (famous, strong and very interesting) scientific discussion on the precise structure of certain carbocations, (the classical versus non-classical carbocation debate) in the second half of the 20th century. His work did not fully escape from

that as well. Later on, he was also active in stereochemistry, specifically on enantioselective and diastereoselective reactions. Hepke Hogeveen was a very open, cheerful and life-celebrating person, an enthusiastic and well-appreciated teacher and a very inspiring scientist to his students and group members. This is the time when the Department of Organic Chemistry at the RuG consisted of his group, together with those of professors Hans Wynberg, Jan Engberts, Dick Kellogg, and Albert van Leusen. At the end of the 80's, he decided to make a major move in his life, quitted chemistry completely, started performing with his melodeon, went through a psychotherapeutic phase, and obtained a degree in Gestalt therapy. Since the 90's, making a second and major move, he fully developed the visual artist in himself, producing a wide variety of paintings and sculptures. He specifically liked to play and investigate at what he called 'the area between the second and third dimension of reality'. His artwork was exhibited publically a number of times.

Stratingh Institute co-ordinating office

The Stratingh Office is located on the ground floor of building 16—Nijenborgh 4— and it consists of Hilda, Alphons and Cristina. We handle a range of responsibilities and provide help and advice on various aspect of University regulations.



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

- Paul von Ragué Schleyer († Nov.21,2014) and four colleagues from the USA, China and Germany) published a fascinating review about four decades of research on planar tetracoordinate carbon (ptC). Since 1874 the possibility of ptC was considered highly implausible, both experimentally and computationally. About 200 years of organic chemistry resulted in the synthesis of 14.000.000 carbon compounds, all with traditional sp, sp², and sp³ hybridization. But the seemingly unlikely planar hypercoordinate carbon compounds are now well established, and these have now been reviewed in some detail. These structures include small molecules to clusters, nanospecies and bulk solids. Factors which can overcome the high energy of ptC materials include strain and electronic (e.g. multicenter bonding) strategies. The paper has been written in memory of Hans Wijnberg. *Yang, L-M., Ganz, E., Chen, Z., Wang, Z-X., von Ragué Schleyer, P., Angew. Chem. Int.Ed. 2015, 9468-9501.*
- A group of scientists from Israel, England and Germany reported a conceptually novel procedure to assemble nanoparticles (NP) reversibly using light but not with particles functionalized with light-responsive ligands. This could be accomplished by using a photoswitchable medium that responds to light and thereby modulating the interparticle interactions. A quantitative NP assembly was observed both in gels and in solution. Many further applications are being considered, particularly for nanofabrication and controlled drug delivery. Examples include the behavior of mixtures of inorganic NPs and proteins. *Kundu, P.K., Samanta, D., Leizrowice, R., Margulis, B., Zhao, H., Börner, M., Udayabhaskararao, T., Manna, D., Klajn, R., Nature Chem. 2015, DOI 10.1038/nchem.2303.*
- Niu and Buchwald of the Massachusetts Institute of Technology reported the design of a modified type of amine transfer reagent, containing a 4-(dimethylamino)benzoate group, that can participate in a CuH-catalyzed synthesis of chiral secondary amines using a variety of amine coupling partners. The latter include those derived from α -amino acid esters, carbohydrates, and steroids. The novel procedure can be applied in the synthesis of pharmaceutically important drugs and can be useful in the design and development of other CuH-catalyzed processes. *Niu, D., Buchwald, S.L., J.Am.Chem.Soc.2015, DOI 10.1021/jacs.5b05446.*
- Henk Hiemstra and coworkers (University of Amsterdam) described the first total synthesis of the sesquiterpene lactone aquatolide, a natural product isolated from plants native to the Mediterranean countries. The procedure involved 16 steps and the overall yield was 2.2%. The intramolecular [2+2]-photocycloaddition of

an allene onto an α ,-unsaturated δ -lactone is a key step. The lactone is closed by an intramolecular Horner-Wadsworth-Emmons reaction whereas the eight-membered ring is cyclized using an intramolecular Mukaiyama-type aldol reaction. Preparative HPLC was employed to resolve the racemic aquatolide. An enantioselective synthesis is in progress. *Saya, J.M., Vos, K., Kleinnijenhuis, R.A., van Maarseveen, J.H., Ingemann, S., Hiemstra, H., Org.Lett.2015, DOI 10.1021/acs.orglett.5b01888.*

- Scientists from the University of Massachusetts have observed that finely tuned polymer interlayers can enhance the solar cell efficiency. They synthesized three conjugated polymer zwitterions (CPZs), containing thiophene, diketopyrrolopyrrole (DPP), and naphthalene diimide (NDI) backbones with pendant zwitterions, specifically sulfobetaine groups. The CPZs were incorporated into polymer solar cells as interlayers between the photoactive layer and the Ag cathode. Large power conversion efficiencies were found (5-10 %). Physical techniques provided insights into the specific function of the CPZ interlayers and the CPZs may be useful in conjunction with high-performing polymer-active layers and stable, high-work-function, metal cathodes. *Liu, Y., Page, Z.A., Russell, T.P., Emrick, T., Angew. Chem.Int.Ed.2015, DOI 10.1002/anie.201503933.*
- Five chemists from the CBI Institute in Paris have demonstrated that trifluoroacetic acid (TFA) is able to promote direct C-H sulfenylation of electron-rich arenes using readily available N-(arylthio)- and N-(alkylthio) succinimides as the sulfenylating reagents. This metal-free procedure is highly regioselective and moderate to excellent yields have been obtained at room temperature and in the presence of TFA. Aryl sulfides are important building blocks in organic synthesis and can be employed in material science and in the pharmaceutical industry. *Hostier, T., Ferey, V., Ricci, G., Pardo, D.G., Cossy, J., Org.Lett. 2015, DOI 10.1021/acs.orglett.5b01889.*
- Hydration water around a protein surface plays a key role in the structure, folding and dynamics of proteins. Physical chemists at the University of Delhi have now performed MD simulations on globular and partially/completely disordered proteins and it appears that the latter types of proteins bind a larger number of waters as compared to the globular proteins, due to the exposure and abundance of charged residues. These water molecules are more tetrahedrally ordered. Furthermore, water molecules around intrinsically disordered proteins/regions depict slower dynamics with longer residence times than those around globular protein/regions. It will be clear that these results are relevant for understanding the different biomolecular properties of both types of proteins. *Rani, P., Biswas, P., J.Phys.Chem.B 2015, DOI 10.1021/jp511961c.*
- Kay and Leigh wrote an interesting and thoughtful brief review about “the rise of molecular machines”. It is mentioned that over the last two decades a number of molecular architectures have been designed and synthesized which can be viewed as pistons, clutches, windmills, elevators, wheelbarrows and nanocars. The appearances and modes of operation of these systems are inspired by the corresponding macroscopic machines. Their importance has already been formulated by Richard P. Feynman in 1959: “I can’t see exactly what would happen, but I can hardly doubt that when we have some control of the arrangement of things on a small scale we will get an enormously greater range of possible properties that substances can have, and of different things that we can do”. I recommend to look up this stimulating brief review. *Kay, E.R., Leigh, D.A., Angew.Chem.Int.Ed.2015, DOI 10.1002/anie.201503375.*
- David O’Hagan and his coworkers at the University of St.Andrews prepared a unique molecule. It is all-cis-1,2,3,4,5,6-hexafluorocyclohexane (**1**), a facially polarized, “Janus-headed” molecule with one hydrocarbon face and one fluorocarbon face. It has the largest reported molecular dipole moment ($\mu = 6.2$ D) of any alkane reported so far. The molecule has a classic cyclohexane chair-like conformation with three axial C-F bonds as confirmed by X-ray structural analysis. The crystal shows facial polarization of the individual molecules, also revealed by quantum-mechanical calculations. Using NMR studies, the thermodynamic data for degenerate ring flip of **1** were determined. The entropic contribution was found to be negative, in contrast with the positive value for cyclohexane. This can most likely be explained by a rigidified transition state for the fluorinated compound. Possible applications of the special properties of **1** have been suggested. *Keddie, N.S., Slawin, A.M.Z., Lebl, T., Philp, D., O’Hagan, D., Nature Chem.2015, DOI 10.1038/nchem.2232. For a brief discussion of this paper, see Santschi, N., Gilmour, R., Nature Chem.2015,7,467-468.*
- The number of recognized bases in DNA has recently been extended to seven by researchers at the University of Bath (UK). The well-known ones are adenine, uracil, guanine, thymine and cytosine. But after finding 6-methyladenine as base number 6, 5-formylcytosine (5fC) has now been found as number 7. It is a rare base found in mammalian DNA and likely involved in active DNA demethylation. Using stable isotope labelling in vivo, it was shown that 5fC can be a stable DNA modification, and suggests that 5fC has functional roles in DNA, going beyond being a demethylation intermediate. Although it is known that 5fC can alter the structure

of the DNA double helix, the exact biological function of 5fC has still to be demonstrated. *Bachman, M., Uribe-Lewis, S., Yang, X., Burgess, H.E., Lurlaro, M., Reik, W., Murrell, A., Balasubramanian, S., Nature Chem.Biol.2015, DOI 10.1038/nchembio.1848.*

- The homochirality of biomolecules is a signature of life but its origin is still under discussion. Yun and Gellman from the Carnegie Mellon University in Pittsburgh have now shown that for gas-phase mixtures of D- and L-aspartic acid, when exposed to an achiral Cu(III) surface, a small e.e. in the gas phase leads to an amplification of the e.e. on the surface under equilibrium conditions. Adsorption-induced chiral auto-amplification can be explained by the formation of homochiral clusters on the achiral surface. These findings may have implications for the role of inorganic surfaces in the processes that lead to the homochirality of life on Earth. It is suggested that these auto-amplification processes have relevance for our understanding of enantioselective chemical processes, such as adsorption, separation and catalysis, in ways that have not been considered previously. *Yun, Y., Gellman, A.J., Nature Chem.2015, DOI 10.1038/nchem.2250.*

Jan Engberts

Stratingh Lectures



Tuesday, September 15th, 2015

Prof. Giuseppe Graziano

Department of Science and Technology—University of Sannio

Title: **A molecular mechanism for the hydrophobic effect**

Room: **5111.0080**

Time: **16:00 hs**

Friday, September 25th, 2015

Prof. Jean-Marie Lehn

Nobel Prize in Chemistry

Title: **Perspectives in Chemistry: Towards Complex Matter**

Room: **5111.0022**

Time: **15:00 hs**



New appointments



Vasha R. Jumde

As of 16/7/2015

PostDoc—Minnaard group



Viktor Ivasyshyn

As of 16/8/2015

PhD—Chiechi Group

Werkbespreking: Thursday morning 8.30 hrs, room 5111.0080

September 3rd— Thijs Krijger (PhD Hummelen) "The soft molecular landing machine"

September 10th— Mannathan Subramanian (Postdoc Minnaard) "Palladium-Catalyzed Reductive Heck Reaction of Aryl halides with Enones"

September 17th—Yagiz Unver (PhD Hirsch) "Expanding the toolbox of protein-templated reactions for hit identification"

September 24th— Jean Baptiste Gualtierotti (Postdoc Feringa) "On the Formation and Transformation of α -Iminonitriles, the Desymmetrization of Bicyclic Bislactones and Total Synthesis of (-)-Leucomidine B and (-)-Rhazinilam"

October 1st—Andreas Hussain (PhD Otto) "Replication in a Formation Destruction Regime"

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