university of groningen

Newsletter

Stratingh Institute for Chemistry

133

February 2018

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

It is a bit late, but I wish all my readers a happy, healthy and creative New Year! As we say in The Netherlands, better late than never.

- I start with a quote from Swimme and Tucker: “A machine is a physical system that focuses energies toward satisfying some human desire.” Technological revolution, based on big, macromolecular machines, became the engine of modern progress. Therefore it is so interesting to see that in recent times molecule-sized machines and motors can do mechanical work, with Ben Feringa being one of the leaders in this field. He, with six coworkers, published in Nature Chemistry a fascinating paper which describes an unique artificial supramolecular muscle system. It was found possible to turn molecular motors into muscles. Amphiphilic photoresponsive small-molecule rotary motors (Mw < 1,000 g mol-1) were hierarchically self-assembled in water to give unidirectionally aligned nanofibers inside muscle-like strings that enable mechanical motion upon irradiation. Both in aqueous solution and in air, photocontrolled actuation was achieved, including lifting weight. A tight correlation from nanoscale motion of the motor to macroscopic photoactuation of the string was suggested by in situ SAXS investigations. *Chen, J., King-Chi Leung, F., Stuart, M.C.A., Kajitani, T., Fukushima, T., van der Giessen, E., Feringa, B.L., Nature Chem. 2017, DOI 10.1038/nchem.2887. Swimme, B.T., Tucker, M.E., Journey of the Universe, Yale University Press, New Haven and London, 2011.*
- König and three coworkers from the University of Regensburg reported the first example of single C(sp3)-F functionalization of trifluoromethylarenes via Ir photoredox catalysis merged with Lewis acid activation. Using this method, aryldifluoromethyl moieties with good chemoselectivity control and good functional group tolerance were found. The chemoselectivity of single C (sp3)-F cleavage is controlled by the synergy of steric and electronic factors as revealed by mechanistic studies. An in situ-generated borenium cationic species is a key intermediate in the reaction. The trapping reagent is methacrylamide, which also acts as a proton source. *Chen, K., Berg, N., Gschwind, R., König, B., J.Am.Chem.Soc., 2017, DOI 10.1021/jacs.7b10755.*
- It is well-known that the critical micelle concentration (cmc) of twin-tailed gemini surfactants is quite low. Yethiraj and Jeong, of the University of Wisconsin, Madison, have now studied the driving force for self-assembly of ge-

mini surfactants using computer simulations of the potential of mean force (PMF). Interestingly, it was found that the geminis with sulfonate headgroups have a greater tendency to assemble than those with carboxylate headgroups, as shown by a deeper minimum in the PMF and a PMF occurring at shorter distances. For the carboxylates the driving force is entropic, whereas for the sulfonate headgroups it is energetic. The simulations indicate that the thermodynamic driving force for self-assembly is determined by two factors: the charge density and the size of the surfactant headgroups. The energetic contribution arises largely from electrostatic interactions, which are controlled by the size of the headgroups and which determine the distance of approach. The entropic contributions determine the conformations of the tails of the geminis. The authors suggest that temperature-controlled measurements of the PMF give important insights into the phase behavior of surfactant self-assembly. *Jeong, K-J., Yethiraj, A., J.Phys.Chem.B, 2017, DOI 10.1021/acsjpcb.7b8936.*

- A highly thoughtful essay has been published by Trauner from New York University in Angew. Chem.Int.Ed. Its title is "The Chemist and the Architect". In his words: "to image a structure and then express it in material form is one of the most satisfying of human activities. It is pervasive throughout the arts and crafts and it is one of the most defining features of architecture. It is also at the heart of synthetic chemistry". In his extensive paper he summarizes the many similarities between synthetic chemistry and architecture. Buildings correspond to molecules: both are three-dimensional and have a specific shape, geometry, structure, mass and a definite structure and volume. They are more or less stable, interact with their environment and possess a finite life-time. A variety of molecules have been named after buildings("pagodane", "churchane" etc.). Proteins have a molecular architecture and possess ion channels. Symmetry and chirality are important issues. Molecules and buildings are often called beautiful, and their useful structures are often "esthetically appealing". Many other similarities are described by the author, but he honestly points out that, for example, there are also fundamental differences between the construction of a building and a molecule. Entropy plays a more important role in chemical synthesis than in architecture. However, I conclude that the similarities between synthetic chemists and architects are very worthy of exploring! *Trauner, D., Angew.Chem.Int.Ed., 2017, DOI 10.1002/anie.201708325.*
- It is already known for some time that organic-inorganic halide perovskites are potential materials for highly efficient solar cells with power conversion efficiencies (PCE) of more than 22%. However, density (J)-voltage (V) hysteresis in these cells have remained an unsolved problem. Now Park and six coworkers from the Sungkyunkwan and Pohang Universities in Suwon and Pohang, South Korea, have shown that defect engineering can be applied as a universal approach for obtaining hysteresis-free perovskite solar cells. Substantial reductions in low-frequency capacitance and bulk trap density were measured for KI-doped perovskites, indicating trap-hysteresis correlation. Experiments with alkali metal iodides of LiI, NaI, KI, RbI and CsI reveal that the potassium ion is the best element for hysteresis-free perovskites. A series of theoretical studies suggest that the hysteresis of the solar cells is caused by the formation of iodide Frenkel defects. Potassium ions can prevent these defects because K+ energetically prefers the interstitial site. The novel KI doping methodology can be universially applied and is not depending on perovskite composition and device structure. *Son, Dae-Yong, Kim, Seul-Gi, Seo, Ja-Young, Lee, Seon-Hee, Shin,*

H., Lee, D., Park, Nam-Gyu, J.Am.Chem.Soc., 2018,DOI 10.1021/jacs.7b10430.

- A remarkable review article appeared in Nature Chemistry, written by chemists from Pennsylvania State University, Indiana University, Tulane University and the University of California. They argue that the supramolecular and physical science communities should combine their expertise in a detailed examining of the solvation, and particularly the hydration, of nonpolar surfaces and ions. Since water is ubiquitous and essential to life on our planet Earth, these studies will allow novel insights into how water controls the chemical and physical properties of proteins, nucleic acids, carbohydrates and lipid membranes, and also of ion transport. Much attention should go to the hydrophobic effect, but a long list of other very interesting and important properties is given that also need much further attention. Kinetic, computational and spectroscopic studies are particularly recommended, but above all a collaboration of supramolecular and physical experts can help "clarify what are still very murky waters". *Cremer, P.S., Flood, A.H., Gibb, B.C., Mobley, D.L., Nature Chem., 2017, DOI 10.1038/nchem.2894.*
- A new, facile, and efficient protocol for the synthesis of polysubstituted conjugated 1,3-dienes was published by three chemists from the Lanzhou Institute of Chemical Physics, the University of Science and Technology of China at Hefei, and the Academy of Sciences in Beijing. The method involves a Ni-catalyzed tandem dimerization/cross-coupling reaction of diarylacetylenes and arylboronic acids with a small amount of bis(pinacolato)diboron (B2pin2) as the reductant. Screening of the Ni precursors indicated that Ni(OAc)2 gave the best results. Successful results were obtained with a whole series of arynes and arylboronic acids with different substituents. Two disadvantages are the high temperature (120oC) and rather long reaction time (9 h) that are required. A likely reaction mechanism was proposed. Further studies of the reaction are in progress. *Liu, Y., Zhang, G., Huang, H., Org.Lett. 2017,DOI 10.1021/acs.orglett.7b03398.*
- "Material witness: How does it feel?" is the title of a fascinating paper written by Philip Ball and published in Nature Materials. He is considering the question "is there any systematic way of understanding links between materiality and affective association?" Examples are: people can be described as "warm", a reply can be sharp, gold implies wealth, a piece of music can be cold, etc. People have mapped perceptual dimensions like temperature, texture and taste onto a variety of emotional states and even a material toolkit has been developed, named PhysFeel, for exploring the above-mentioned connections. Whatever its philosophical appeal, according to Donald (1991) we cannot have a science of mind that disregards material culture as we cannot have an adequate science of material culture that leaves out cognition. As Ball suggests: asking the question "if you were a material, which material would you be?" is not such a trivial question after careful thinking about it! *Ball, P., Nature Materials 2017, DOI 10.1038/nmat5062. Donald, M., "Origins of the Modern Mind: Three Stages in the Evolution of Culture and Cognition", Havard University Press, 1991.*

Jan Engberts

New appointments

Renze Sneep

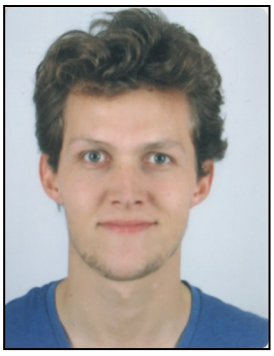
Research Technician

Chromatography

Linda Ofori Atta

PhD—group Roelfes

1/12/2017



Johann Bartold Kasper

PhD—group Browne

1/12/2017

Linda Eijsink

PhD—group Browne

1/1/2018

Manas Das

PostDoc—Group Harutyu-nyan

Werkbespreking: Thursday morning 8.30 hrs, room 5111.0080

February 8th—Simone Romanini (PhD Harutyunyan) - "Title to be announced"

February 15th—Fransesca Milocco (PhD Otten) - "Electronic and structural properties of iron complexes with formazanate ligands"

February 22nd—Selim Sami (PhD Hummelen) - "Dielectric properties of organic photovoltaics"

March 1st—Jim Ottele (PhD Otto) - "Chance Emergence of Catalysis by a Self-Replicator"

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

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 corse. 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