

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

- Daan Frenkel (University of Cambridge, UK) wrote a fascinating brief communication, entitled “Order through Entropy”. Referring to earlier studies of athermal systems undergoing transitions that increase both visible order and entropy, he stresses the importance of addressable complexity. Macroscopic “machines” consist of many distinct parts that need to be assembled into a unique spatial pattern. Such systems have been identified and contain an ordered phase with higher entropy than that of the disordered phase at the same density. It is argued that the phase transitions of almost all liquids, vapors, crystals or liquid crystals which are commonly attributed to attractive energetic interactions, can be reproduced by using entropy alone. These insights are of great importance for the design of complex self-assembling structures. *Frenkel, D., Nature Materials, 2015, 14, 9-12.*
- Using vibrational Stark effect spectroscopy, Steven Boxer and coworkers have studied the effect of specific electric fields on the catalytic effect of ketosteroid isomerase (KSI). They found that the active site of the enzyme exerts a strong electric field onto the C=O bond that undergoes a charge rearrangement in KSI’s rate-determining step. The magnitude of the electric field was correlated with the catalytic rate enhancement by the enzyme, indicating that the catalysis is indeed electrostatic in origin. Further measurements are required to substantiate the role of electrostatics in many other enzymes and biomolecular systems. *Fried, S.D., Bagchi, S., Boxer, S.G., Science, 2014, 346, 1510-1514.*
- Scientists from the State Universities of Montana and Ohio (USA) studied the remarkable behavior of Lewis photoacids. Using femtosecond transient absorption and fluorescence upconversion techniques, the quenching mechanism and the identity of the photoproduct of methyl viologen (MV<sup>2+</sup>) were investigated. A long-lived species with a pH-dependent lifetime was formed due to reaction with water at high speed. It is a charge-transfer complex consisting of a ground-state MV<sup>2+</sup> ion and a hydroxide ion, formed when a water molecule transfers a proton to the bulk solvent. There is compelling spectral evidence for MV<sup>2+</sup> as an ion pair and not as a covalent adduct. It is concluded that ultrafast hydrolysis is a general excited-state quenching mechanism for electronically excited Lewis acids and other powerful photooxidants in aqueous media. *Henrich, J.D., Suchyta, S., Kohler, B., J.Phys.Chem.B, 2015, DOI 10.1021/jp510953e.*
- At the Indian Institute of Science in Bangalore, India, a tandem intermolecular nucleophilic and electrophilic vinylation of tosylhydrazones was shown to lead to a regioselective synthesis of vinyl halides, vinyl sulfones, and alkynes. It was demonstrated that a diazo species can be trapped in an intermolecular fashion by attack of two independent ionic species in tandem at the carbene center to install an electrophile and a nucleophile on the same carbon. A gem-dihalide is produced followed by vinyl halides. The metal-free concept appears to be unprecedented. *Ojha, D.P., Prabhu, K.R., Org. Lett. 2015, 17, 18-21.*
- Kjaergaard and coworkers at the University of Copenhagen investigated the ability of phosphorus to participate in P...HO hydrogen bonds. They detected three bimolecular alcohol-trimethylphosphine complexes. OH –stretching frequency red shifts and quantum mechanical calculations showed that P is an acceptor atom, similar in strength to O and S but a weaker acceptor than N. Electrostatic potentials revealed a negative potential area on the electron density surface around P which facilitates the formation of hydrogen

bonds. Hansen, A.S., Du, L., Kjaergaard, H.G., *J.Phys.Chem.Lett.* 2014, 5, 4225-4231.

- Fayer and coworkers at Stanford University, USA, employed 2D IR vibrational echo spectroscopy on a tungsten hexacarbonyl as a vibrational probe to study the bilayer structural fluctuations in vesicular bilayers and in planar bilayers as a function of the cholesterol concentration (0-40%). At all cholesterol concentrations the structural fluctuations are faster in the curved vesicular bilayers. Interestingly, at 10-15% cholesterol in the vesicles, the dynamics are abruptly slowed down, apparently indicating a structural transition. A similar transition occurs at 25-30% cholesterol in the planar bilayers. Kel, O., Tamimi, A., Fayer, M.D., *J.Phys.Chem.B*, 2015, DOI 10.1021/jp503940k.
- “Probing a Hidden World of Molecular Self-Assembly: Concentration-Dependent, Three-Dimensional Supramolecular Interconversions” is the title of a recent paper from the University of Akron, Ohio, USA. Newkome et al. report the synthesis of a 3D supramolecular quasitetrahedron, an elongated molecule with a single S<sub>4</sub> symmetry axis. Unexpectedly, the formation of this molecule is concentration-dependent and could only be detected at solute concentrations below 12 mg.ml<sup>-1</sup>. It was the only observed assembly below 0.5 mg.ml<sup>-1</sup>. Thus, it appears that in the world of 3D supramolecular assemblies different unobserved chemical pathways are possible under high dilution conditions. Such behavior has already been observed for proteins. Lu, X., Li, X., Guo, K., Xie, T-Z., Moorefield, C.N., Wesdemiotis, C., Newkome, G.R., *J.Am.Chem.Soc.*, 2014, 136, 18149-18155.
- Scientists from two research institutes in South Korea reported compositional engineering of perovskite materials for high-performance solar cells. They found that incorporation of MAPbBr<sub>3</sub> into FAPbI<sub>3</sub> resulted in stabilization of the perovskite phase of FAPbI<sub>3</sub> and improvement of the power conversion efficiency of the solar cell to more than 18% under standard illumination of 100 milliwatts per cm<sup>2</sup>. Jeon, N.J., Noh, J.H., Yang, W.S., Kim, Y.C., Ryu, S., Seo, J., Seok, S.I., *Nature*, 2015, DOI 10.1038/nature14133.
- Phosphines can be used as simple organocatalysts for the synthesis of complex spirocyclic compounds. Chiral phosphines gave satisfactory results both in terms of yields and enantioselectivities. A useful review of the field appeared in Synlett and the authors from a Research Institute in Gif-sur-Yvette, France, indicate some key points that need further improvement. Voiturie, A., Marinetti, A., Gicquel, M., *Synlett*, 2015, DOI 10.1055/s-0034-1379251.
- Roughening of a hydrophobic material can make its surface superhydrophobic and superoleophobic. However, until now, no surfaces have been prepared that repel extremely-low-energy liquids such as fluorinated solvents. Two Chinese scientists at the University of California, Los Angeles, have now been able to micro- and nanostructure silica surfaces and make it superomniphobic, which means that it bounces off all available liquids, including perfluorohexane. This very special surface withstands temperatures over 1000°C and resists biofouling. Liu, T.L., Kim, C-J., *Science* 2014, 346, 1096-1100.
- In an extensive review (71 pages!) Peter Nagy of the University of Toledo (USA) has reported the in-solution competition of molecular conformations with intramolecular vs. intermolecular hydrogen bonds for a large number of small organic molecules. In their most stable gas-phase structure, an intramolecular hydrogen bond is often preferred. But in a protic solution, the intramolecular hydrogen bond is disrupted in favor of two solute-solvent intermolecular hydrogen bonds (despite the unfavorable entropy). The new conformer composition in the liquid phase is further determined by a balance between the increased internal energy and the stabilizing effect of the solute-solvent interactions. Nagy, P.I., *Int.J.Mol.Sci.*, 2014, 15, 19562-19633.

Jan Engberts

## **Stratingh Seminars**



**Tuesday, February 10<sup>th</sup>**

**Prof. José Luis Mascarenas** - University of Santiago de Compostela

**Room:** 5111.0022

**Time:** 16:00 hrs

**Title:** Chemical Tools based on Transition Metals: Catalytic Methods and DNA Binders

**Tuesday, February 24<sup>th</sup>**

**Prof. Holger Braunschweig**—Universität Würzburg

**Room:** 5111.0022

**Time:** 16:00 hrs

**Title:** Transfer, Metathesis and Catenation: Reactivity Patterns Emerging from Borylen ecomplexes



## **PhD Defences**

**Friday, February 13<sup>th</sup>**

@ 16:15 **Jort Robertus** will defend his PhD thesis. **Title:** “Photochromic molecular switches—Based on Azobenzenes, Dithienylethenes and Hemithioindigos”. **Promotor:** Prof. dr. B.L. Feringa

**Friday, February 20<sup>th</sup>**

@12:45 **Jens Oelerich** will defend his PhD thesis. **Title:** “Bio-inspired Catalysis in Water”. **Promotor:** Prof. dr. J.G. Roelfes

## **New appointments**



**Ravindra P. Jumde**

1 January—**PostDoc**

Group Harutyunyan



**Annika Borg**

1 January—**Visiting  
Scientist**

Group Roelfes



**Simone Romanini**

1 January—**PhD**

Group Harutyunyan

**Werkbespreking: Thursday morning 8.30 hrs, room 5111.0080**

**February 5<sup>th</sup>—Ramon van der Vlag (Roelfes):** Design and synthesis of ratiometric fluorescent probes

**February 5<sup>th</sup>—Federico Lancia (Browne):** title to be announced

**February 12<sup>th</sup>—Yigit Altay (Otto):** “In Search of Bigger Self-Replicators from Dynamic Combinatorial Libraries”

**February 19<sup>th</sup>—Claudia Poloni (Feringa):** “Photoswitchable peptides”

**February 26<sup>th</sup>— Meniz Tezcan (Otto):** “Controlling complexity and hierarchy of self-replicating peptides”

**March 5<sup>th</sup>—Davide Angelone (Browne):** “Application of DFT methods in the study of metal complexes and their reactivity towards oxidation catalysis”

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