university of groningen

Newsletter

Stratingh Institute for Chemistry

108

April 2015

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

- "Reinventing Chemistry". The challenging title of a 14-page article by George Whitesides (Harvard University) in Angew. Chem Int. Ed. He makes an attempt to answer the question "What must chemistry be in the future"? He argues that a particularly profilic era of chemistry is now over and that chemistry is now facing entirely different but even more interesting classes of opportunities. He is honest enough to admit that he is just offering ideas and opinions, not facts. The article summarizes 24 priorities for future research, some of them already being considered in the Stratingh Institute. I recommend reading this paper. Let me just tell you what Whitesides' reply is when somebody asks him "What is it that chemists do, anyway"? He likes to answer "We change the way you live and die". *Whitesides,G.M.,Angew.Chem.Int.Ed.,2015,DOI 10.1002/anie.201410884.*

- Four chemists from Nagoya University, Japan, described a programmed protocol for the synthesis of hexaarylbenzenes carrying five or six different substituents. C-H activation, cross coupling and [4+2] cycloadditions were employed and made it possible to obtain hexaarylbenzenes with distinctive aryl substituents at all positions in the benzene molecule. The novel synthetic approach can also be used for the synthesis of tetraarylnaphthalenes and pentaarylpyridines. *Suzuki, S., Segawa, Y., Itami, K., Yamaguchi, J., Nature Chem., 2015, DOI 10.1038/nchem.2174.*

- The characterization and prediction of the interactions between biomolecules hinges in part on an understanding of the hydrophobicity of complex heterogeneous molecular assemblies. In a joint project of the Universities of Maryland and Pennsylvania, a novel electrostatics-based mapping of aqueous interfaces was developed, focused on the collective, long-wavelength electrostatic response of water to the presence of nearby surfaces. The authors claim that their novel technique can find use in predicting the location of possible water-mediated hydrophilic interactions in addition to the more commonly emphasized hydrophobic interactions. *Remsing, R.C., Weeks, J.D., J.Phys.Chem.B, 2015, DOI 10.1021/jp509903n.*

- René Janssen and coworkers at the University of Technology, Eindhoven, and the Academy of Sciences, Beijing, successfully designed and synthesized several solar cells based on the conjugated polymer diketopyrrolopyrrole (DPP), serving as the electron-deficient unit. By bridging DPP units to electron-rich units using thiazoles, conjugated polymers were obtained with both a high ionization potential and a high electron affinity. The material has an efficient charge generation (>50%) and a minimum amount of energy loss between optical band gap and open-circuit voltage for such a material (<0.6 eV).*Li, W., Hendriks, K.H., Furlan, A., Wienk, M.M., Janssen, R.A.J., J.Am.Chem.Soc., 2015, DOI 10.1021/ja5131897.*

- Chemists from the Chinese Academy of Sciences in Beijing, proposed a new class of ion-ion interactions, the Z-bond, that occurs in ionic liquids (ILs).The general model is +[A-H….B]- in which A and B are heavy atoms, O, N, F, but also C, P, Cl, Br, I, and S atoms. The middle atom is not restricted to hydrogen and may be replaced by halogen or other atoms. These Z-bonds arise from the coupling interactions of the induced and existed

eletrostatic interactions. The bonding characteristics differ from those of conventional hydrogen bonds, and the bonding energies are usually 10 times larger. The A-H…-Z bond shows a zig.zag motif, therefore the name Z-bond. The Z-bonds play a vital role in the peculiar catalytic properties of ILS and in a number of properties of bio-systems in ILs. *Dong, K., Zhang, S., Wang, Q., Science China, Chemistry, 2015, DOI 10.1007/s11426-014-5147-2*.

- The first terpene cyclization catalyzed inside a self-assembled cavity was reported by Tiefenbacher and coworker at the Technical University of München. In nature, complex terpene natural products are formed by a tail-to-head terpene (THT) cyclization in complex enzyme pockets acting as catalysts. The reaction has now been mimicked successfully for cyclase enzymes inside a supramolecular structure and a catalytic non-stop THT was achieved using geranyl acetate as the substrate. These results have implications for the postulated mechanism in cyclase enzymes. *Zhang, Q., Tiefenbacher, K., Nature Chem., 2015, DOI 10.1038/NCHEM.2181*.

- Although the Diels-Alder reaction is a most important synthetic transformation, the intramolecular dehydro-Diels-Alder reaction (IMDDA), employed for the preparation of naphthalene and dihydronaphthalene substrates, has not been studied in detail. A joint mechanistic study of three American Universities has now provided novel insights, including the observation that the thermal IMDDA of styrene-ynes produces a naphthalene product via loss of hydrogen gas from the initially formed tetraenyl intermediate. The dihydronaphthalene compound originates via a radical isomerization process. Conditions have been identified to achieve efficient, high-yielding, and selective IMDDA reactions of styrene -ynes substrates. The authors also claim that the synthetic protocol is environmentally benign. *Kocsis, L.S., Kagalwala, H.N., Mutto, S., Godugu, B., Bernhard, S., Tantillo, D.J., Brummond, K.M., J.Org.Chem., 2015, DOI 10.1021/acs.joc.5b00200*.

- A one-pot synthesis of aryl sulfones from organometallic reagents and iodonium salts has been developed by chemists from the Goethe University in Frankfurt, Germany. The process involves a transition-metal-free arylation of lithium, magnesium, and zinc sulfinates with diaryliodonium salts. The required sulfinates were prepared from a reaction of an organometallic reagent and sulfur dioxide. Combination of the preparation of the organometallic compound, the formation of the sulfinate, and the arylation in a practical one-pot sequence then leads to the aryl sulfones in reasonable to high yields. Reactions with magnesium and zinc sulfinates are inherently limited because of side-reactions. *Margraf, N., Manolikakes, G., J.Org.Chem., 2015, DOI 10.1021/jo5027518*.

- The final item this month is not so much a scientific highlight but is concerned with the impact and opportunities of undergraduate research. Marcia Linn and four colleagues of the University of California at Berkeley discuss in a seven-page review in Science the best possibilities for students to benefit from undergraduate research experiences. In our Department we have a long tradition to bring students in contact with research at an early stage, but in the USA this has been a bit different. Linn and colleagues believe that research experiences provide a window on science and allow students to participate in scientific practices, to expand conceptual understanding and to communicate the nature of science, recognizing creativity in research and teaching. Much attention is also paid to the question how mentors can be best prepared for efficient guiding of students. Most colleges in the USA offer Undergraduate Research Experiences (UREs) and/or Course-based Undergraduate Research Experiences (CUREs). Their impact on persistence in science and intention to pursue graduate school has been investigated. The authors propose that there is a need for greater emphasis on integration of research experiences with the beliefs and expectations of undergraduates. When research experiences introduce novel ideas, these ideas should

not remain isolated and fragmented. Linn, M.C., Palmer, E., Baranger, A., Gerard, E., Stone, E., Science, 2015, DOI 10.1126/science.1261757.

Jan Engberts

PhD Defences

Friday, April 17th

@ 11:00 Massimo Giannerini will defend his PhD thesis. **Title:** "Advancing selectivity control with highly reactive organometallic reagents". **Promotor:** Prof. dr. B.L. Feringa

New appointments

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1 February—**PhD**

Group Browne

Werkbespreking: Thursday morning 8.30 hrs, room 5111.0080

April 2—Apparao Draksharapu "In situ formation of NiII-OCl and NiIII-OH species with NaOCl and their relevance to catalytic oxidation"

April 9—Sander Wezenberg "Regulating the anion binding affinity of a light- and heat-responsive bis-urea receptor"

April 16—Oleg Kozlov "Title to be announced"

April 23—Anne Schoonen "Title to be announced"

April 30—Dávid Komáromy "Diversity and self-replication in a solvent-and mechanosensitive dynamic combinatorial library"

May 7—Francesco Lanza "Synthesis of Substituted Tetrahydroisoquinoline via Morita-Bailys-Hillman Reaction"

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