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Swiss Science Concentrates

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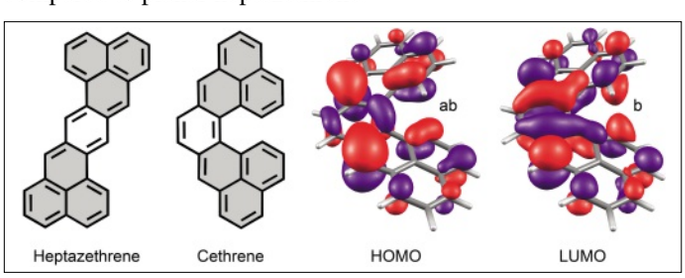
Short Abstracts of Interesting Recent Publications of Swiss Origin

Cethrene: A Helically Chiral Biradicaloid Isomer of Heptazethrene

P. Ravat, T. Šolomek, M. Rickhaus, D. Häussinger, M. Neuburger, M. Baumgarten, and M. Juríček*, *Angew. Chem. Int. Ed.* **2016**, *55*, 1183. University of Basel

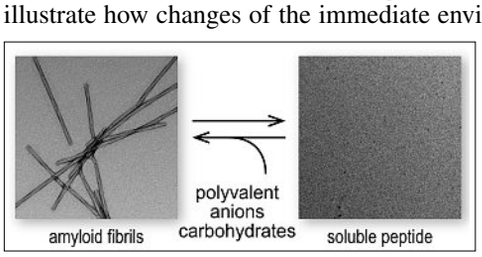
Neutral polycyclic aromatic hydrocarbons containing one or more unpaired electrons, such as phenalenyl, often possess an intriguing electronic structure due to delocalized spin density. Heptazethrene and its isomers formally contain two phenalenyl units (gray) fused to a central benzene ring (white). Juríček and collaborators report the synthesis and properties of the hitherto elusive 'cethrene', the only helically chiral isomer of heptazethrene with a biradicaloid singlet ground state. Cethrene undergoes an intramolecular cyclization within several hours at room temperature. It gives a well-resolved EPR spectrum at room temperature and its structure was confirmed by 2D NMR and absorption spectroscopies. The authors show that the helical twist affects the electronic properties of cethrene, as a result of antibonding (ab) and bonding (b) interactions within the HOMO and the LUMO, and decreases the singlet–triplet energy gap compared to planar heptazethrene.



Dynamic Assembly and Disassembly of Functional β-Endorphin Amyloid Fibrils

N. Nespovitaya, J. Gath, K. Barylyuk, C. Seuring, B. H. Meier, and R. Riek*, *J. Am. Chem. Soc.* **2016**, *138*, 846. ETH Zürich

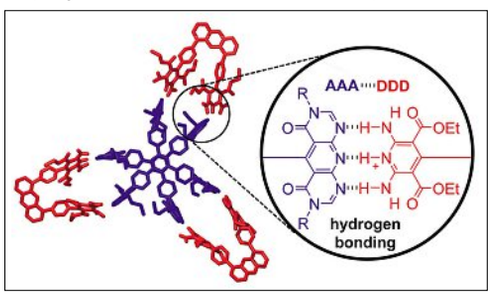
Neuropeptides and peptide hormones are stored in the amyloid state in dense-core vesicles of secretory cells. The molecular mechanisms of amyloid formation during packing of peptides into secretory vesicles and amyloid dissociation upon release remain unknown. Using fluorescence and solid-state NMR spectroscopy, Riek and coauthors studied the reversible aggregation of β-endorphin *in vitro* at near-physiological conditions. They found that both assembly and disassembly of amyloids strongly depend on the presence of salts of polyprotic acids (such as phosphate and sulfate) and low-molecular-weight carbohydrates. The data illustrate how changes of the immediate environment can affect the mechanisms of reversible hormone/neuropeptide aggregation.



Molecularly Defined Nanostructures Based on a Novel AAA–DDD Triple Hydrogen-Bonding Motif

M. Papmeyer, C. A. Vuilleumier, G. M. Pavan, K. O. Zhurov, and K. Severin*, *Angew. Chem. Int. Ed.* **2016**, *55*, 1685. EPF Lausanne

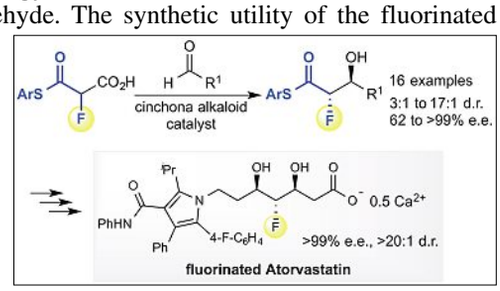
Molecularly defined nanostructures based on multiple AAA–DDD interactions are largely unknown, primarily due to limited synthetic access of the required polytopic building blocks. Severin and coworkers now describe a facile and flexible method for the synthesis of a new AAA–DDD triple hydrogen-bonding motif. The process gives access to polytopic building blocks with precisely oriented hydrogen bond donor and acceptor groups in just a few steps with high yields. Tetrameric macrocycles from bent, ditopic building blocks, and a macrobicyclic complex from five components, including a tritopic acceptor, were prepared. The newly described methodology should enable the formation of novel cage structures, crystalline molecular networks, and novel supramolecular polymers.



Enantioselective Aldol Reactions with Masked Fluoroacetates

J. Saadi and H. Wennemers*, *Nat. Chem.* **2016**, *8*, 276. ETH Zürich

Despite the growing importance of organofluorines as pharmaceuticals and agrochemicals, the stereoselective introduction of fluorine into biologically active compounds remains difficult. One long-standing unsolved challenge is the enantioselective aldol reaction of fluoroacetate to enable access to fluorinated analogues of medicinally relevant acetate-derived compounds, such as polyketides and statins. Saadi and Wennemers present a decarboxylative aldol reaction with fluoromalonic acid halfthioesters and their use in highly stereoselective aldol reactions in the presence of a Cinchona alkaloid catalyst. They further show that the methodology can be extended to formal aldol reactions of fluoroacetaldehyde. The synthetic utility of the fluorinated aldol products is illustrated by the synthesis of a fluorinated derivative of the anti-hypercholesterolaemia drug atorvastatin.



Prepared by Caroline D. Bösch, Markus Probst, Yuliia Vyborna, Mykhailo Vybornyi, Simon M. Langenegger and Robert Häner*

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Please contact robert.haener@dcb.unibe.ch