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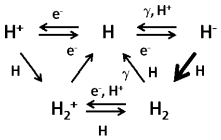
VIP ***The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:***

Author Profile

"When I was eighteen I wanted to be a professional baseball player. The biggest challenge facing scientists is to convince the funding agencies that what they do is meaningful …" This and more about Steven P. Nolan can be found on page 2212.

Books

Highlights



A star is born: The formation of H_2 was crucial to the generation of the first stars and possibly the first galaxies. The rate of H_2 generation by associative detachment (thick arrow in the scheme of the reactions of hydrogen in the early universe) has now been determined experimentally and may provide a more detailed understanding of the birth of the first stars.

Astrochemistry

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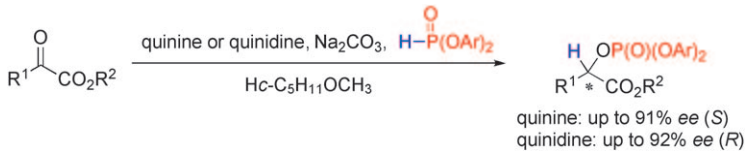
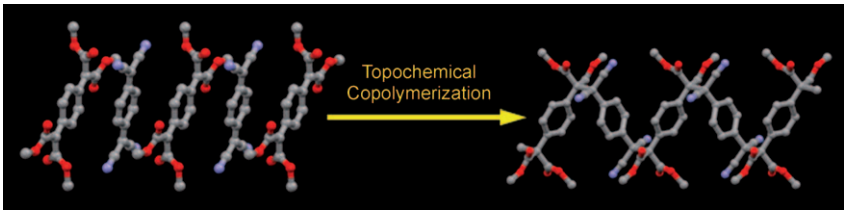


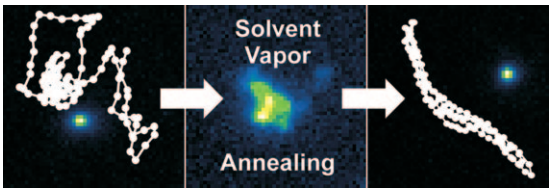
Phosphonates go chiral: The organocatalytic enantioselective reaction of α-ketoesters with phosphites using cinchona alkaloids and Na_2CO_3 has afforded α-phosphonyloxy esters with high enantioselectivities (see scheme). This process allows the formation of both enantiomers of the product. A catalyst loading of as low as 2 mol% does not result in a significant decrease of the enantioselectivity.

Asymmetric Synthesis



From single crystal to single crystal: A crystalline charge-transfer complex of the title compounds underwent topochemical polymerization through a radical mechanism under UV irradiation or upon heating. This *cis*-specific solid-state copolymerization of the substituted quinodimethanes required the alternating monomers in the cocrystal to tilt (see picture).

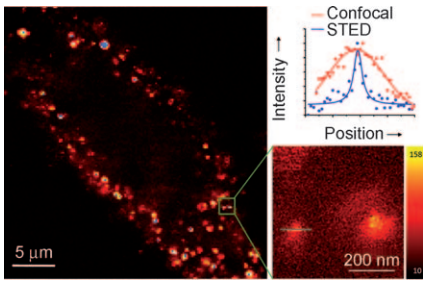
Solid-State Photopolymerization



An inside job: By using single-molecule spectroscopy (SMS) several effects of solvent vapor induced annealing (SVA) were studied directly on single conjugated polymers, e.g.: SVA-induced translocations, folding/unfolding dynamics, and changes in the morphological order. It is shown that single chains can be trapped by spin-coating in a disordered conformation and subsequent SVA leads to an equilibrated, highly ordered conformation (see picture).

Single-Molecule Studies

A bunch of loners: Fluorescent nanodiamonds (FNDs) noncovalently conjugated with bovine serum albumin (BSA) or α-lactalbumin exhibited good dispersibility in a buffer with only minor or no agglomeration. They are useful as photostable fluorescent markers in cells for superresolution imaging by STED (see confocal fluorescence image of an FND-labeled cell (left) and STED image of single BSA-conjugated FNDs (right)).



Biolabeling

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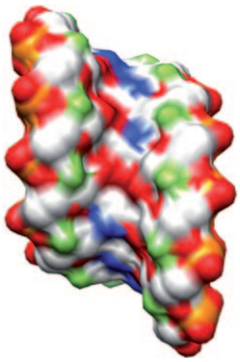
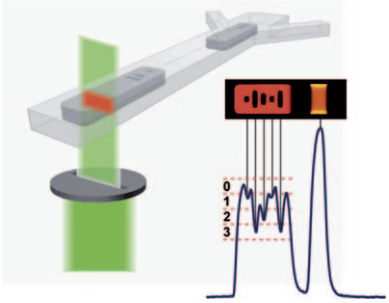
With little or no negative impact on the activity of small interfering RNAs (siRNAs), regardless of the number of modifications or the positions within the strand, the 2′-deoxy-2′-fluoro (2′-F) modification is unique. Furthermore, the 2′-F-modified siRNA (see crystal structure) was thermodynamically more stable and more nuclease-resistant than the parent siRNA, and produced no immunostimulatory response.

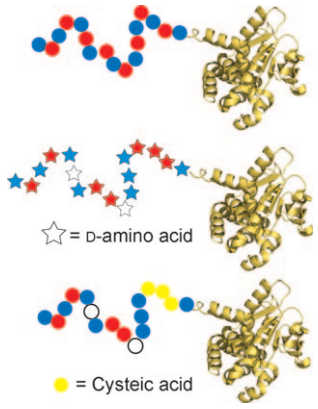


RNA Interference

Sensitive, flexible, and rapid: A post-hybridization labeling scheme was combined with a high-throughput microfluidic scanning system to demonstrate the use of graphically encoded gel particles for rapid microRNA quantification (see picture). A versatile particle encoding scheme allows for scalable multiplexing that provides attomole sensitivity with a simple and efficient workflow.

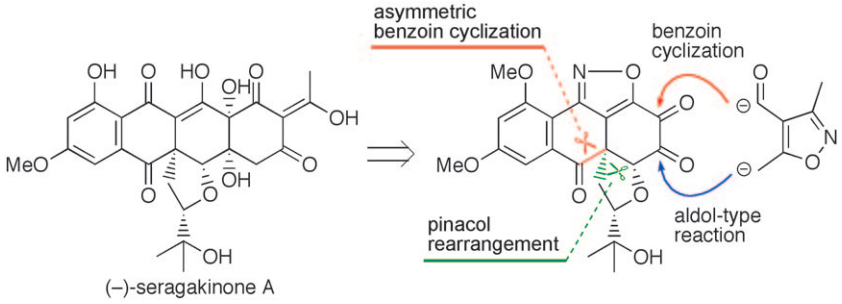


Bioanalytical Methods



Through the pore: The N-terminal domain of the lethal factor of anthrax toxin was modified to probe protein translocation through the toxin pore. Replacing acidic residues with cysteic acid inhibited translocation, whereas introduction of D-amino acids or an alternating Lys–Glu sequence had no effect. The findings demonstrate independence of translocation from stereospecificity and strict sequence, and dependence on the charge state of acidic residues.

Protein Translocation



Cyclic transformation: The key transformations of the asymmetric total synthesis of the marine-derived natural product seragakinone A are two N-heterocyclic carbene catalyzed benzoin cyclizations that result in the construction of two rings and a pinacol-type rearrangement to install the angular prenyl substituent.

Natural Product Synthesis

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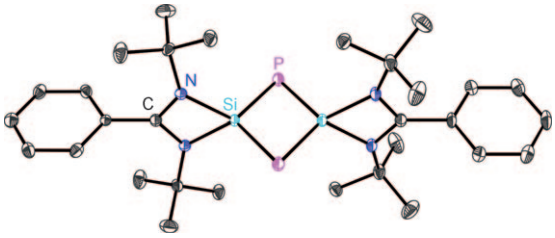
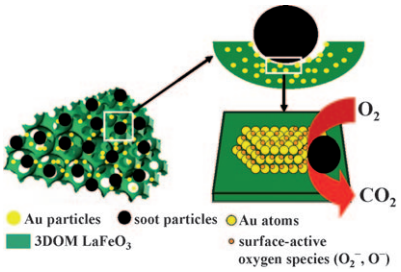


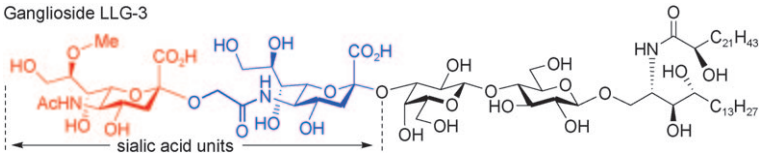
It's hip to be square: The reaction of amidinato chlorosilylene (PhC-(N*t*Bu)$_2$SiCl) with adamantyl phosphaalkyne and white phosphorus affords the formation of Si-C-Si-P and Si-P-Si-P (see picture) four-membered rings. Both compounds were characterized by single-crystal X-ray studies and by solution and solid-state NMR spectroscopy. DFT calculations elucidated the bonding situation.

Silicon Chemistry



The catalyst support 3DOM $LaFeO_3$ contains highly ordered macropores that are connected with each other by small windows. 3DOM $LaFeO_3$ supported gold catalysts, which combine the advantages of good contact by the macroporous support and highly active sites for activation of O_2 by gold clusters, exhibit super catalytic performance for soot oxidation.

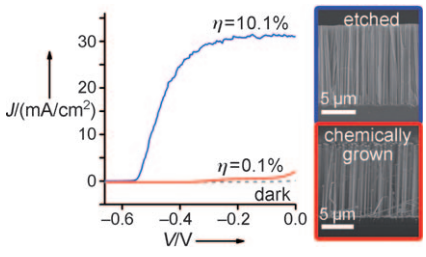
Heterogeneous Catalysis



A gift from the star: The title compound, which was identified in starfish, contains two sialic acid units and was constructed utilizing a sialic acid derivative as a pivotal precursor. The potentially difficult conjugation of the phytoceramide portion with the glycan portion was achieved through the glucosyl ceramide cassette approach.

Oligosaccharides

Wired: Electrochemical impedance spectroscopy (ESI) reveals that high energy-conversion efficiencies are attainable on vertically aligned Si nanowires obtained by electroless etching (see picture). The key reason for the low performance of chemically grown Si nanowires lies in the mid-gap traps as a result of growth chemistry.



Nanowire Solar Cells

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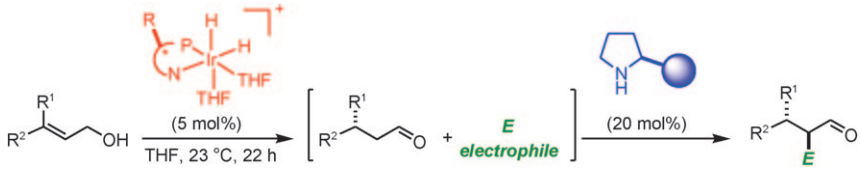
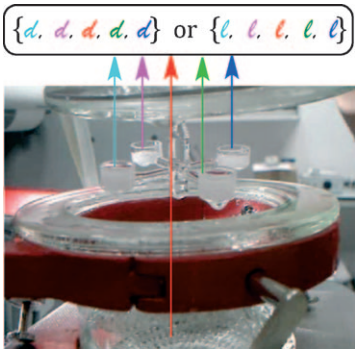


Independent workers with team spirit: A catalytic sequence that exploits the compatibility of (chiral) cationic iridium catalysts for the isomerization of primary allylic alcohols to aldehydes with organocatalysts has been developed for the highly enantioselective α functionalization of aldehydes (see scheme: up to 66% yield, d.r. 49:1, 99% *ee*). The reaction displayed useful generality with respect to both the nucleophile and the electrophile.

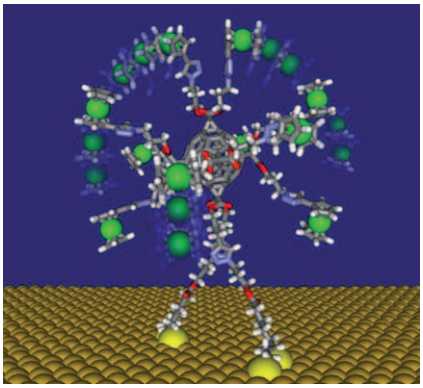
Sequential Catalysis

This way or that: Analysis of the chiral composition of the crystal mixture obtained from samples of boiling solutions of $NaClO_3$ (see picture) indicates that symmetry breaking towards homochiral compositions may begin in the metastable stage preceding crystallization, that is, at the level of subcritical clusters.

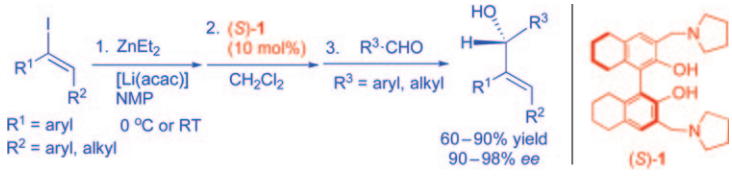


Chirality

A rigid 3D scaffold in a 2D world! A mixed [5:1] fullerene hexaadduct that bears ten peripheral ferrocene redox subunits has been anchored onto a gold surface (see picture, green: iron, black: carbon, white: hydrogen, red: oxygen, blue: nitrogen). Ultrafast cyclic voltammetry investigations revealed that both intramolecular electron hopping and molecular motions influence the electron transfer from the ferrocene moieties to the electrode.



Electron Transfer



Mild and tolerant: Vinylzinc reagents were directly prepared from the reaction of vinyl iodides with $ZnEt_2$ under mild reaction conditions. The compound (*S*)-**1** was found to catalyze the addition of the vinylzinc reagents to a variety of aldehydes to generate structurally diverse allylic alcohols with high yields and enantioselectivities. This catalytic process can tolerate functional groups such as esters, chlorine, ethers, and silyl ethers on the substrates. acac = acetylacetonate, NMP = *N*-methyl-2-pyrrolidone.

Asymmetric Catalysis

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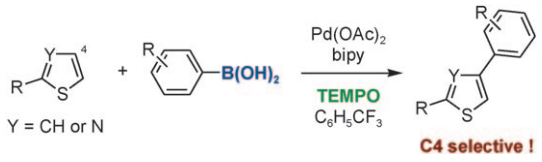
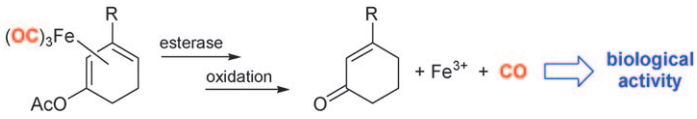


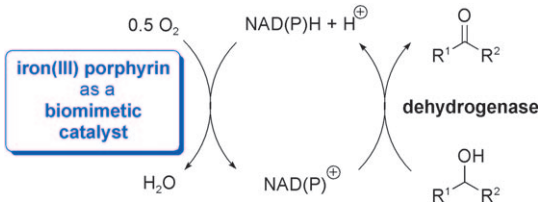
It adds up to 4! Thiophenes and thiazoles can be arylated in the 4- rather than the expected 5-position in a new C–H functionalization reaction (see scheme; TEMPO: 2,2,6,6-tetramethylpiperidine-N-oxyl). The boronic acid proved to be the key to achieving the otherwise difficult C4 selectivity. The method was applied to a concise synthesis of a key pharmacological structure with potential for treatment of Alzheimer's disease.

Oxidative C–H Arylation



Molecular hazardous materials transport: Enzyme-triggered CO-releasing molecules (ET-CORMs) offer new options for the delivery of CO. The cleavage of dienylester iron tricarbonyl complexes by an esterase under mild oxidative conditions generates CO, which causes a strong inhibiting activity of the compounds to inducible nitric oxide synthase as shown in a cellular assay.

Carbon Monoxide Release



An enzyme substitute: A synthetic Fe^{III} porphyrin was used as a catalyst for the activation and reduction of O_2 into H_2O with the cofactor NAD(P)H in aqueous solution. The catalyst is compatible with different preparative enzymatic oxidation reactions. Thus, a new method is provided for the in situ regeneration of the oxidized cofactor $NAD(P)^+$ with help from a non-enzymatic, synthetic catalyst (see scheme).

Metalloporphyrins

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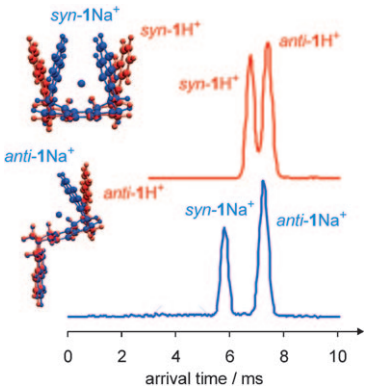

Increased mobility is observed for the sodiated *syn* and *anti* isomers of bis-Tröger base **1** relative to that of the protonated variants. Ion-mobility measurements further demonstrate that the pseudo-epimerization of the bis-Tröger base proceeds by a proton-mediated ring opening rather than a retro-Diels–Alder sequence.

Supporting information is available on www.angewandte.org (see article for access details).

A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

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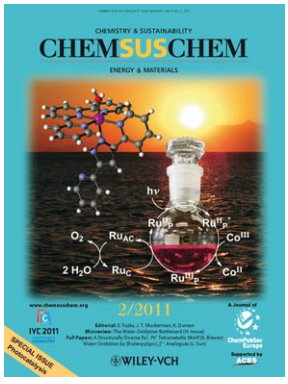

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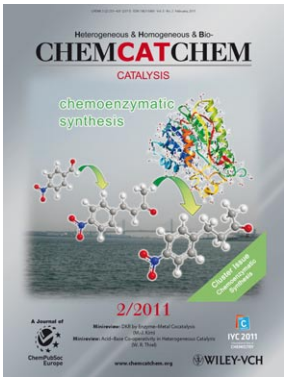

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