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:*

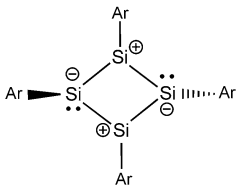
Author Profile

"What I look for first in a publication is architecturally beautiful structures.
My favorite piece of research is R. B. Woodward's total synthesis of reserpine …"
This and more about Masayuki Inoue can be found on page 9016.

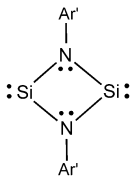
Books

Highlights

Silicon Chemistry



1'

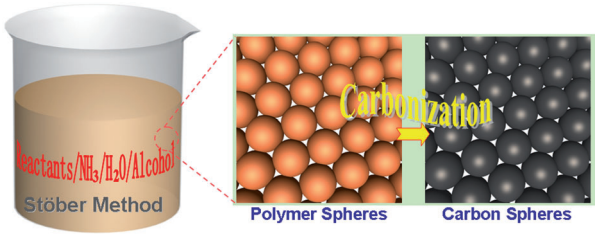


2

Ar = novel bulky aryl group
Ar' = Power-type terphenyl group

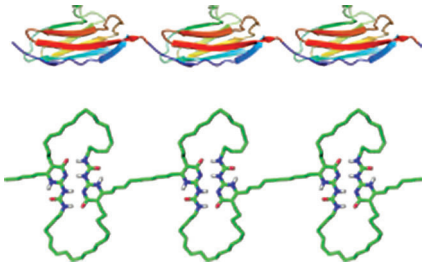
The fundamental question of how silicon handles antiaromaticity in four-membered ring systems has been answered by the synthesis and characterization of the first tetrasilacyclobutadiene Si_4Ar_4 (**1**) and by the first dimeric silaisonitrile $Si_2(NAr')_2$ (**2**). Compound **1** is best described by the charge-separated resonance structure **1'** and **2** by a structure with π-type lone pairs at the nitrogen atoms and vacant π orbitals at the silicon atoms.

Contents



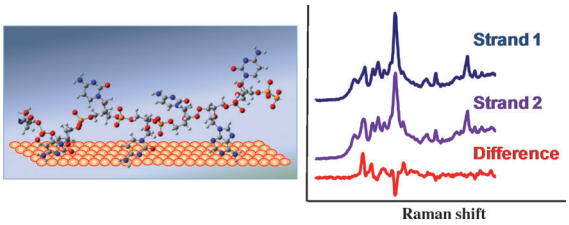
The Stöber method is an authoritative approach for the synthesis of monodisperse colloidal silica spheres; this method has now been extended to the synthesisis of monodisperse resorcinol-formaldehyde resin polymer and carbon spheres.

Reviews



Nature's bounty: Recent advances in analytical and synthetic tools are facilitating the development of materials inspired by nature. This Review highlights the history and the state-of-the-art in the quest to understand the molecular mechanisms behind nature's most remarkable peptide-based materials, as well as the attempts to apply that understanding to design biomimetic materials.

Communications



Singles only: DNA sequences can be induced to spontaneously adsorb to the surfaces of Ag colloids through their nucleotide side chains (see picture). The SERS spectra of these nonspecifically bound strands are sufficiently reproducible that they can be used to identify single-base mismatches in short (25-mer and 23-mer) strands. Subtracting the spectra of different DNA sequences results in difference spectra that contain features corresponding to the exchanged nucleotides.

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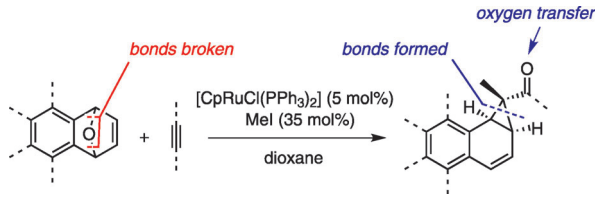
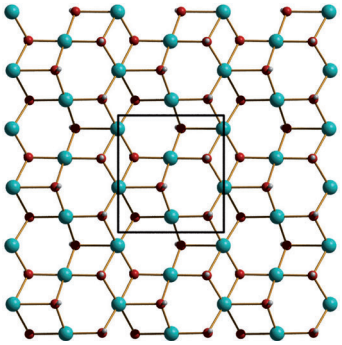


Stereodefined: The title reaction provides an atom-economic route to benzonorcaradienes. The diastereoselectivity of the coupling relies upon the structure of the alkene; unsubstituted bicyclic alkenes afforded exclusively *exo*-benzonorcaradienes (see scheme) whereas the bicyclic alkenes with substituents at the bridgehead positions resulted in *endo*-benzonorcaradienes.

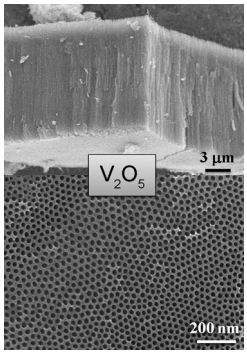
Ruthenium Catalysis



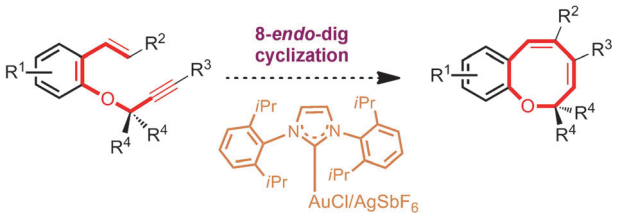
Cationic layers: Copper hydroxide ethanedisulfonate consists of cationic sheets (see structure of a $[Cu_4(OH)_6]^{2+}$ layer; Cu green, O red, H white) with ethanedisulfonate as extraframework counteranion. This material shows excellent anion exchange properties for both organics and metal oxo anion pollutants, with over five times higher adsorption capacity for permanganate than hydrotalcite.

Layered Compounds

Vanadium oxide layers with homogeneous nanoporous nanotubular morphology (see picture) were successfully fabricated by direct anodization of vanadium in fluoride electrolytes such as $[TiF_6]^{2-}$ or $[BF_4]^-$. The pore size and layer thickness can easily be controlled by tailoring the electrochemical conditions. Such nanotubular or porous structures are promising for the fabrication of lithium-ion insertion electrodes.



Metal Oxides



A golden dig! Gold-catalyzed direct access to functionalized 2*H*-1-benzoxocines, eight-membered-ring ethers, is described. This unprecedented synthesis of benzoxocines occurs by an 8-*endo*-dig cyclization of the 1,7-enyne substrates.

Gold Catalysis

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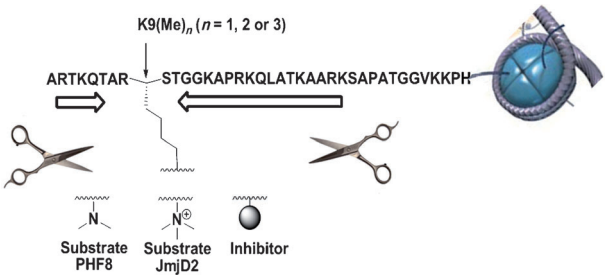
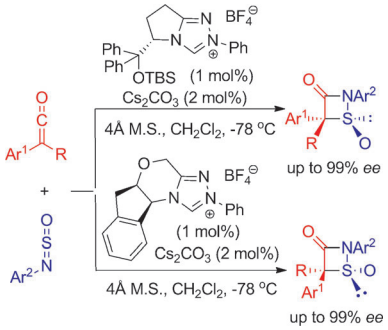


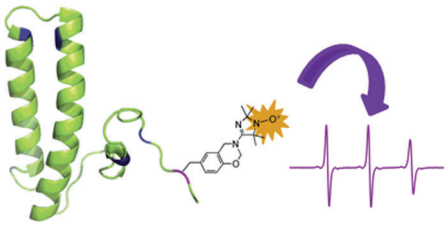
How low can you go? The natural substrate for the epigenetic regulators PHF8, JmjD2A, and JmjD2C (lysine demethylases), a peptide consisting of 39 amino acid residues, can be truncated to 14, 8, and 4 amino acids, respectively, while maintaining catalytic activity (see picture). Inhibitors were prepared by attaching small molecules to the truncated substrates. Selective inhibition of JmjD2C over JmjD2A and PHF8 was possible.

Inhibitors



Sultam of swing: Both enantiomers of 1,2-thiazetidin-3-one oxides were obtained in very good yields with excellent enantioselectivities when using N-heterocyclic carbene catalysts (see scheme; M.S. = molecular sieves, TBS = *tert*-butyldimethylsilyl). The products were easily converted into 3-oxo-β-sultams, α-mercapto amides, and β-mercapto amines through oxidation or reduction.

Asymmetric Catalysis



Keeping tabs on tyrosine: A three-component Mannich-type reaction extends the scope of site-directed spin labeling by selectively labeling the unique tyrosine residue of CP12 protein (see picture), as was confirmed by mass spectrometry. EPR spectroscopy of the labeled protein showed a very high mobility of the probe, which remained very mobile after complex formation with GAPDH.

Protein Labeling

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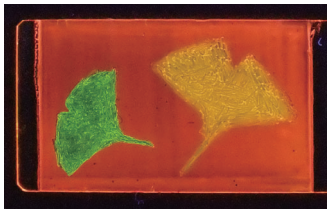
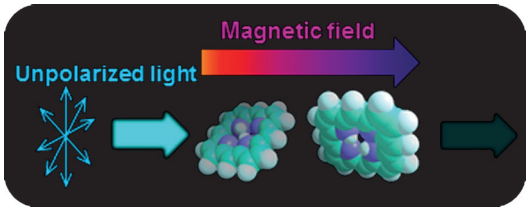


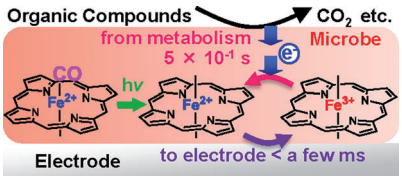
A glowing image: The photoluminescent colors reddish-orange, yellow, and green, are generated from a single liquid-crystalline mixture containing one luminophore (see picture). The colors are easily distinguished by the naked eye and can be reversibly written and erased. Moreover, these luminescent colors can be switched by mechanical and thermal stimuli.

Materials Chemistry



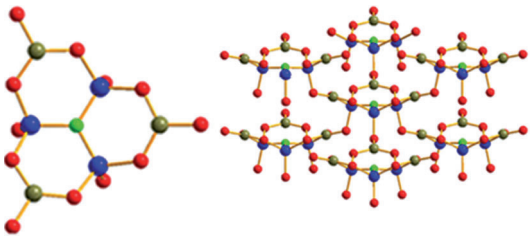
Direction decides: Magneto-chiral dichroism describes the dependence of the absorbance of a chiral molecule on the direction of a magnetic field to which it is exposed, and it may help to explain the homochirality of life. This phenomenon was now observed in organic compounds using porphyrin J-aggregates.

Chirality



Morning light: In vivo photodissociation of CO from bacterial *c*-type cytochromes yields a redox-active Fe^{2+} form, which can be oxidized at an electrode surface to the Fe^{3+} form. Reduction by electrons from the metabolic pathway regenerates the Fe^{2+} form (see picture). Spectroscopic monitoring of this process yields information on the in vivo respiratory electron-transport dynamics.

In Vivo Electron Transport



Structure matters: Owing to the structure and arrangement of the $[Be_3B_3O_{12}F]^{10-}$ group (see picture, left, Be blue, B olive, F green, O red), the mixed-cation fluorine beryllium borate $NaSr_3Be_3B_3O_9F_4$ (right) exhibits a large second harmonic generation effect and a short UV absorption edge. Its crystals show no layering tendency, making it promising for applications in deep-UV nonlinear optics.

Structure–Property Relationships

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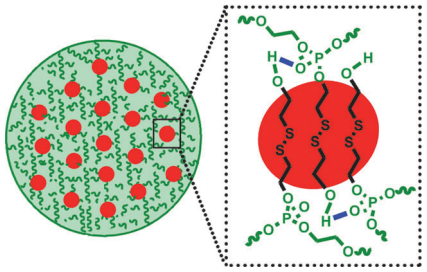
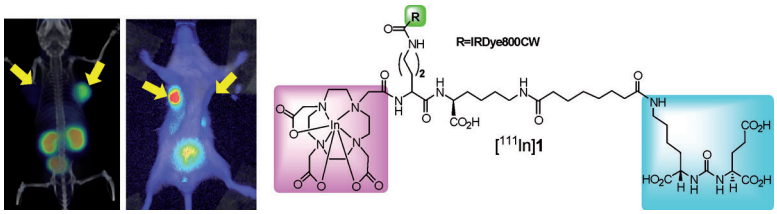
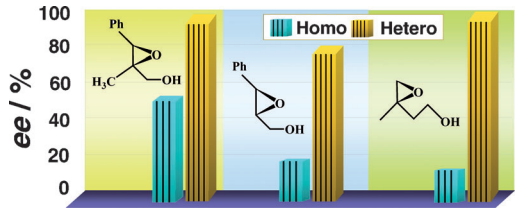


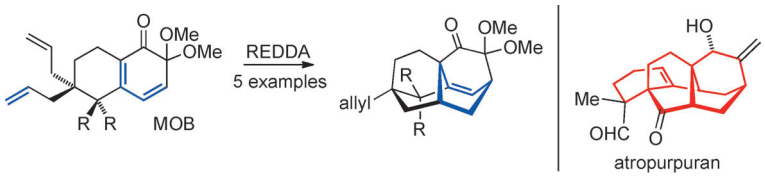
The best of both worlds: A novel amphiphilic homopolymer synthesized from a monomer consisting of a hydrophobic group (see picture, red) and a hydrophilic moiety (green) self-assembles in aqueous solution. The resulting micelles have a multi-core/shell structure and exhibit smart redox-responsive properties, thus providing a favorable drug delivery platform for cancer therapy.



One reagent for two techniques: Compound [^{111}In]**1** provides a platform for sequential radionuclide and optical imaging of prostate cancer through targeting of the prostate-specific membrane antigen. Because the same subject can be dual-imaged after one injection of the agent, these findings support rapid clinical translation.



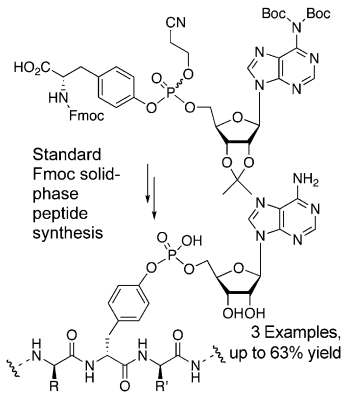
Layered catalyst: The attachment of α-amino acid ligands to inorganic nanosheets for use as ligands to vanadium, resulted in a catalyst that enhanced the enantioselectivity of the epoxidation of allylic alcohols (see picture) . The catalyst can be colloidized, allowing for the catalytic reactions to be carried out under pseudo-homogeneous reaction conditions and also the catalysts to be directly recycled by simple liquid/liquid separation.



Masked talent: A tetracyclo-[5.3.3.$0^{4,9}$.$0^{4,12}$]tridecane skeleton can be accessed by an intramolecular reverse-electron-demand Diels–Alder (REDDA) reaction of masked *ortho*-benzoquinone (MOB; see scheme). This reaction gives access to the pentacyclic framework of atropurpuran, and also enables the construction of other anti-Bredt and cage-like complex molecules.

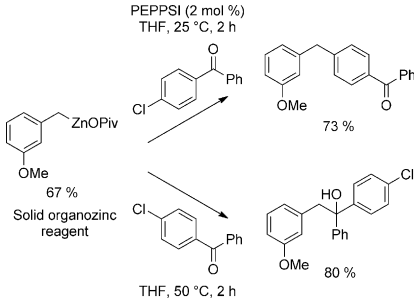
Contents

The enzyme DrrA of the human pathogen *Legionella pneumophila* adenylylates specifically a tyrosine of the GTPase Rab1. An efficient synthesis route using Fmoc solid phase peptide synthesis led to Tyr-adenylylated peptides and allowed the generation of mono-selective polyclonal antibodies against this post-translational modification.



Post-Translational Modification

Powdered organozinc reagents: Various aryl and heteroaryl bromides as well as benzylic chlorides react with Mg and $Zn(OPiv)_2 \cdot 2\,LiCl$ (OPiv = pivalate) to provide solid organozinc reagents after solvent evaporation. These powders can be stored at room temperature under argon for months and can be manipulated in air for a short time. They undergo smooth Negishi cross-coupling and carbonyl addition reactions (see scheme).



Organozinc Reagents

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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Service