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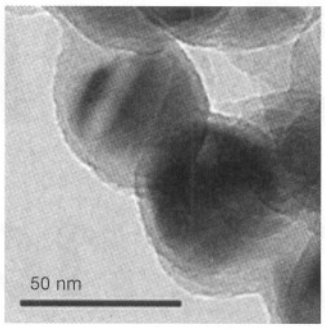
Reviews

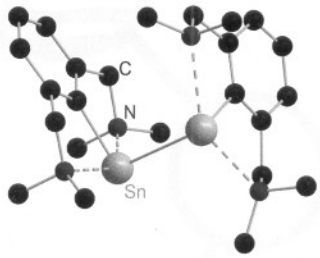
Communications

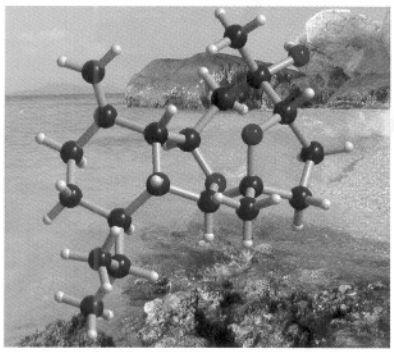
For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Wiley-VCH, 111 River Street, Hoboken, NJ 07030. Annual subscription price for institutions: US$ 7225/6568 (valid for print and electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

Full charge ahead: Hydrothermal carbonization of glucose in the presence of Si nanoparticles yields a Si@SiO_x/C nanocomposite that has high reversible lithium-storage capacity, excellent cycling performance, and high rate capability. This material shows promise as an anode material in lithium-ion batteries.

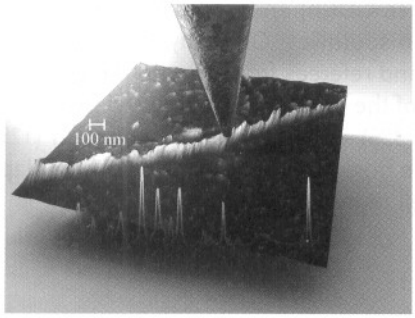


Not only steric protection by bulky substituents but also intramolecular N→Sn coordination makes possible the isolation and characterization of dimeric organotin(I) compounds such as [{2,6-$(Me_2NCH_2)_2C_6H_3$}Sn]$_2$ (see structure), which according to a crystallographic study exhibits a Sn–Sn bond length of 2.9712(12) Å.

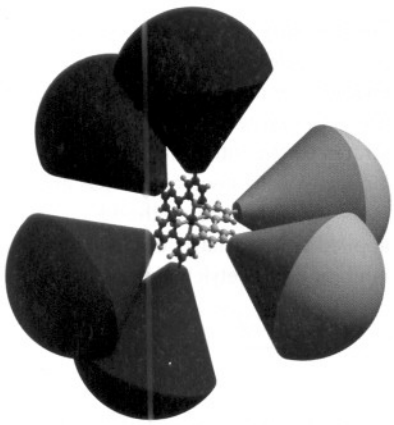




A crystal from the China sea: The asymmetric total synthesis of (+)-vigulariol (see picture: red O, blue C, white H) has been accomplished in eight linear steps starting from (*R*)-cryptone, which is readily available from eucalyptus oil. Key steps involve an asymmetric homoaldol reaction of chiral allyl carbamates and THF cyclocondensation. Ring-closing metathesis led to the tricyclic framework of the cladiellin diterpenes.

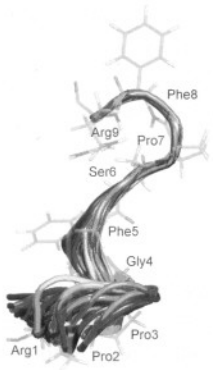


Walking the strand: Tip-enhanced Raman scattering (TERS) with precision probe positioning has been used to obtain high-quality Raman spectra of the nucleobases in a single RNA strand (see picture: foreground Raman spectrum, background atomic-force microscope tip positioned over the RNA strand). This procedure represents the first step towards direct and label-free single-biomolecule sequencing.



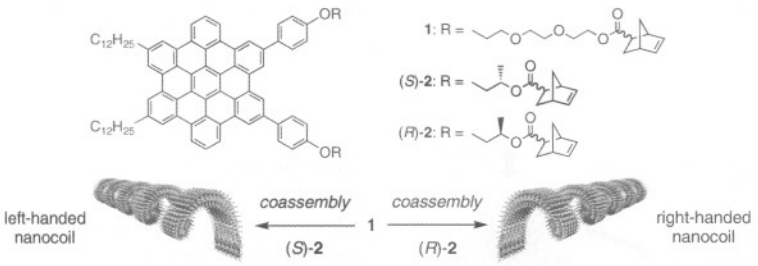
Cores for thought: Dendrimers based on an octahedral symmetry and with a central positively charged transition-metal complex have been prepared up to the third generation (see schematic representation). The shape-persistent dendrimers with a high density of aromatic rings are accessible by either a partly convergent synthesis or a divergent strategy in which the metal complex proved to be stable to high-temperature Diels–Alder reactions.

Dendrimers



Triggering the signal: The backbone structure of the nine amino acid neuropeptide bradykinin (see picture) bound to the human G-protein coupled bradykinin subtype 2 receptor has been determined by solid-state NMR spectroscopy. Torsion-angle constraints based on ^{13}C chemical shifts were used for structure calculation, which revealed an elongated conformation with an α-helical turn at the N terminus and a β turn at the C terminus.

Protein Structures



One-handed military discipline: The hexabenzocoronene (HBC) derivative **1** can coassemble with the chiral HBCs (*S*)- or (*R*)-**2** to yield graphitic nanocoils (see picture). Self-assembly of **2** alone gives noncoiled fibrous assemblies. A sergeants-and-soldiers effect leads to the formation of one-handed nanocoils. These can be covalently stabilized by post-surface ROMP of the pendant norbornene groups to give a uniform cast film. Upon doping with I_2, this film becomes electroconductive without any detectable morphological disruption.

Helical Nanocoils

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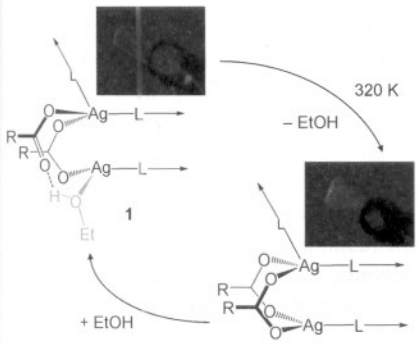
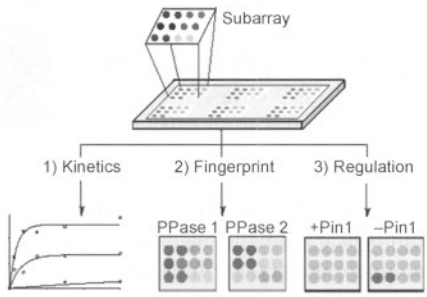


How does it fit? The one-dimensional coordination polymer $[Ag_4L_3\{O_2C(CF_2)_3CF_3\}_4(EtOH)_2]_n$ (**1**; L = tetramethylpyrazine, see scheme) eliminates coordinated ethanol in an intramolecular substitution reaction. The reaction occurs in a single-crystal-to-single-crystal transformation and leads to extrusion of ethanol from the nonporous crystals. The reverse reaction involving uptake of ethanol vapor has been verified using X-ray powder diffraction.

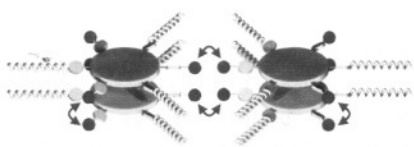
Solid–Gas Reactions

Identifying phosphatase substrates: A peptide microarray has been developed for the high-throughput study of Ser/Thr phosphatases. Putative peptide substrates, upon immobilization onto a glass slide, could be used to obtain kinetic information and identify the substrate preferences of a Ser/Thr phosphatase (see schematic representation); with this information, new biology of the enzyme could be discovered.

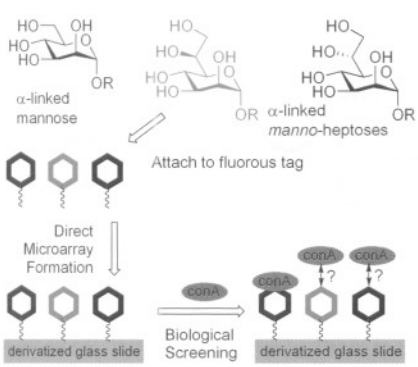


Substrate Fingerprinting

Every second counts: Enhanced control over the self-organization of discotic compounds has been obtained by introducing alternating arrays of apolar (alkyl) and polar (ester) substitutents on to C_3-symmetric hexa-*peri*-hexabenzocoronenes. The local dipole moments and the nanophase separation between the polar and apolar sites significantly influence the self-assembly in solution and in the solid state (see schematic representation).



Supramolecular Chemistry



Fooling conA? Fluorous microarrays allow not only qualitative, but also quantitative assessment of binding to show that conA can accept modifications to its usual mannose ligand at the C-6 position and bind to bacterial seven-carbon mannose analogues.

Carbohydrate Microarrays

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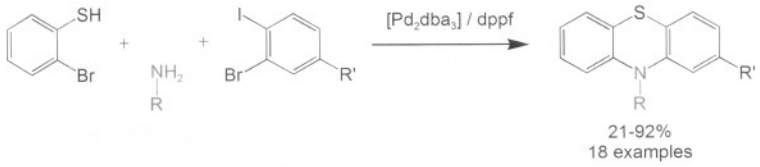
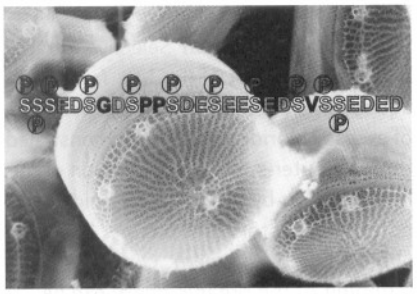


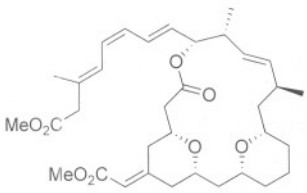
Zip it up! The use of a Pd/dppf catalyst gives access to the tricyclic phenothiazine scaffold starting from 1-bromo-2-iodobenzenes, aliphatic or aromatic amines, and 2-bromothiophenols in a single reaction flask (see scheme; dppf = 1,1′-bis(diphenylphosphanyl)ferrocene; dba = dibenzylidineacetone). This transformation involves thioether formation and subsequent intermolecular and intramolecular aryl amination reactions. The reaction occurs in good overall yield and selectivity.

Promazine Synthesis



More decorative than wallpaper: Silica biomineralization in diatoms leads to intricate structures in the cell wall (see SEM image) and depends on structure-directing templates formed by the electrostatically driven assembly of positively charged polyamine derivatives and polyanions. The title peptides are a family of biologically relevant polyanions present in diatom biosilica and composed mainly of serine phosphate and acidic amino acid residues.

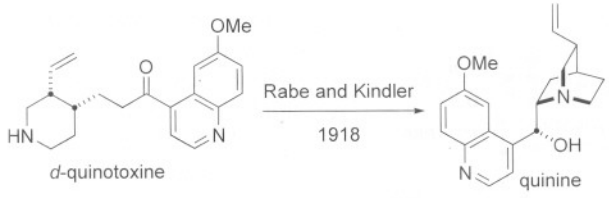
Biomineralization



(+)-exiguolide (**1**)

The unique 16-membered macrolide (+)-exiguolide (**1**) was the target of a total synthesis featuring radical and Prins cyclizations of β-alkoxyacrylates, along with ring-closing olefin metathesis. The structure incorporates two *cis*-2,6-disubstituted oxane rings where one of the rings has an exocyclic enoate group. The successful synthesis of **1**, isolated from a marine sponge, led to the unambiguous determination of its absolute stereochemistry.

Natural Product Synthesis



Put to rest: The three-step conversion of *d*-quinotoxine into quinine, as originally reported by Rabe and Kindler in 1918, has been experimentally verified. This conversion serves to reaffirm the formal total synthesis of quinine reported by Woodward and Doering in 1944.

Quinine: Controversy in Synthesis

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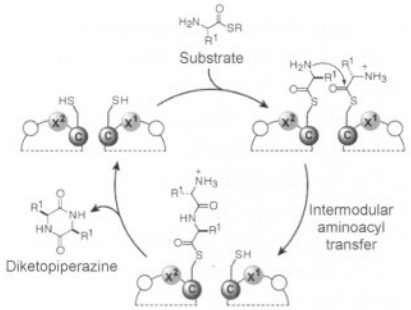
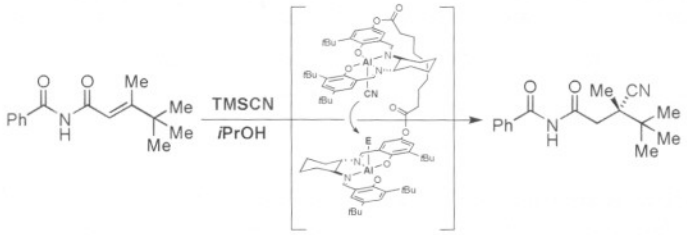


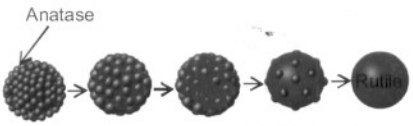
Modular supramolecular catalysts with a coiled-coil peptide scaffold, designed to mimic nonribosomal peptide synthetases, catalyze the formation of diketopiperazines and linear dipeptides for several aminoacyl substrates (see scheme). The nature of the active-site residues in the peptide catalysts can be used to effect directed intermodular aminoacyl transfer processes and govern the relative yields of diketopiperazine, linear dipeptide, and hydrolyzed substrate.

Peptidic Catalysts



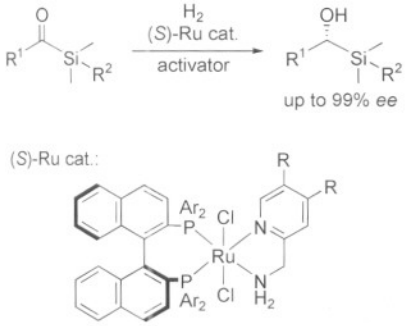
Al together: Covalently linked dinuclear {(salen)Al} complexes catalyze the conjugate cyanation of α,β-unsaturated imides with several orders of magnitude greater reactivity over the mononuclear analogue, and with comparable enantioselectivity. Imides that were completely unreactive with homo- and heterobimetallic combinations of mononuclear catalysts can now be converted into the corresponding cyanation products with high enantiomeric excess.

Cyanation Catalysis



The junction boosts the function: With a combination of surface-sensitive techniques, the photocatalytic activity of TiO_2 was found to be directly related to the surface-phase structure, and can be greatly enhanced when anatase TiO_2 nanoparticles are highly dispersed on the surface of rutile TiO_2 to form anatase–rutile surface-phase junctions (see picture for calcination progression).

Surface-Phase Junctions



A catalytic system of Ru^{II} complex (see scheme; Ar = 4-$CH_3C_6H_4$; R = H, *t*-C_4H_9) and *t*-C_4H_9OK or $NaBH_4$ activator has been used in the hydrogenation of aromatic and aliphatic acyl silanes to give α-hydroxysilanes with high enantioselectivity (R^1 = aryl, alkyl, alkenyl; R^2 = *t*-C_4H_9, C_6H_5). Optically active allylic α-hydroxysilanes are obtained in the 1,2-reduction of α,β-unsaturated acyl silanes. These chiral α-hydroxysilanes are converted into 4-substituted 2-cyclopentenones without loss of enantioselectivity.

Asymmetric Hydrogenation

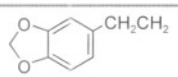
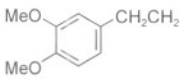
Contents

Service

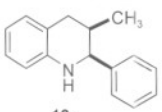
Corrigendum

In Table 3 of this Communication, the chemical structures of the substituents of products **8q** and **8r** were inadvertently switched. The correct entries are shown here.

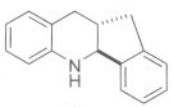
Table 3: Catalytic asymmetric hydrogenation of quinoline derivatives.[a]

Entry	R	Product	Yield [%]	*ee* [%]	Config
17		**8q**	>99[c]	90	*R*
18		**8r**	>99[c]	95	*R*

In Table 4, the structures of the major isomers **12a** and **12c** were printed incorrectly. The correct structures are shown here.



12a



12c

The editorial office apologizes for these oversights.

The Development of Double Axially Chiral Phosphoric Acids and Their Catalytic Transfer Hydrogenation of Quinolines

Q.-S. Guo, D.-M. Du,* J. Xu ___ **759–762**

Angew. Chem. Int. Ed. **2008**, *47*

DOI 10.1002/anie.200703925