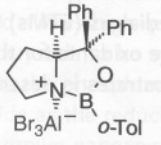
Contents

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

News

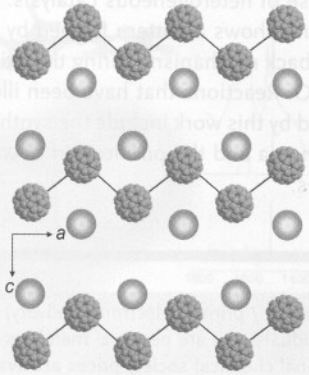
Books

Highlights



More and more applicable: The adduct of an oxazaborolidine and aluminum tribromide (see picture) turns out to be an efficient catalyst not only for enantioselective Diels–Alder reactions but now also for enantioselective [2+2] cycloadditions. The products are important enantiomerically pure building blocks for the synthesis of complex organic compounds.

Asymmetric Catalysis



Nuggets and buckyballs: Cationic small molecular gold clusters linked together by anions form ionic crystals. The cutting edge of such intercluster compounds involves combinations of Au_7 and Au_8 clusters and fullerides obtained by the reaction of KC_{60} with $[Au_8(PPh_3)_8](NO_3)_2$ in MeCN/THF. The picture shows a simplified view of the crystal structure of $[Au_7(PPh_3)_7]C_{60}\cdot THF$ in the direction of [010] (C gray, Au yellow).

Gold Clusters

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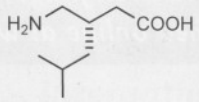
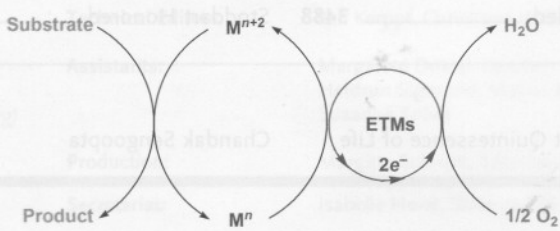
Essays



The anticonvulsant drug (*S*)-(+)-3-isobutyl-γ-aminobutyric acid ((*S*)-(+)-3-isobutyl-GABA, Lyrica; see structure) was developed from a study of fundamental science, which took an unexpected course. The activity of Lyrica was found to be unrelated to the originally anticipated activation of L-glutamic acid decarboxylase and the increase in the inhibitory neurotransmitter GABA; instead, it antagonizes a calcium ion channel, which inhibits the release of the excitatory neurotransmitter L-glutamate. The ultimate effect, however, is the same.

Reviews



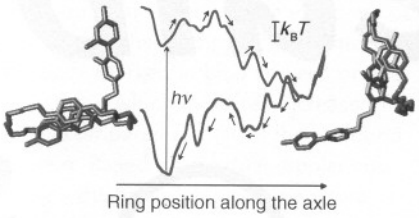
Going green: The use of environmentally friendly oxidation materials such as O_2 or H_2O_2 is a very important goal in organic chemistry, particularly for oxidations in industrial chemistry. The use of electron-transfer mediators (ETMs) to facilitate the use of these oxidants for the oxidation of organic substrates is described.

The spatio–temporal formation of patterns on the surface during a chemical reaction is one phenomenon that can now be understood and modeled thanks to the Nobel Prize winning research on the course of heterogeneous catalysis. The picture shows a pattern formed by a feedback mechanism during the oxidation of CO. Reactions that have been illuminated by this work include the synthesis of ammonia and the purification of waste gases.

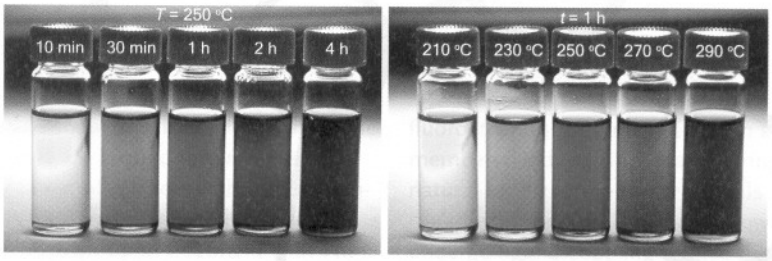
For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. 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.

Communications

On the move: A computational investigation of the photo-triggered shuttling of a multicomponent bistable rotaxane in solution has shown that decomplexation of the counterions from the positively charged stations may be the efficiency-limiting step of the nanomachine. The picture shows the free-energy profile as a function of the ring position for the oxidized (ground) state (blue) and the reduced state (red) generated by photoexcitation.

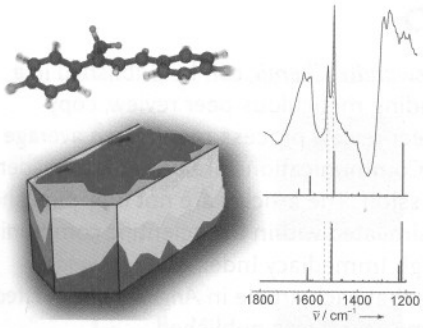


Molecular Machines



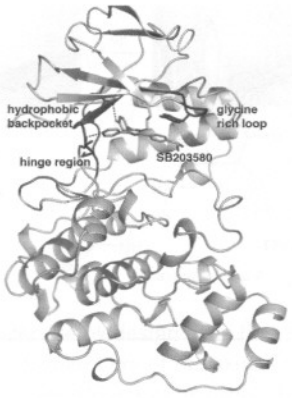
Finding the little InP particles: A coreduction method allows high-quality colloidal InP nanocrystals to be synthesized by using PCl_3 as the phosphorus source and superhydride as the reducing agent. Etching the as-grown nanocrystals with HF leads to high-efficiency photoluminescence. The synthetic strategy can be extended to the preparation of other III–V nanocrystals with the corresponding pnicogen halides.

Nanocrystal Synthesis

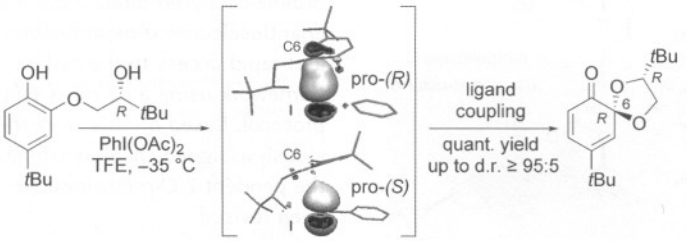


CSI: Carbocation species identification: The nonhomogeneous distribution of the reaction products of styrene oligomerization on large ZSM-5 crystals was mapped with in situ IR microspectroscopy. Diffraction-limited spatial resolution was achieved with synchrotron light. IR spectra for possible reaction products were calculated with DFT/B3LYP; by comparison with experimental results carbocationic reaction species formed in zeolite channels could be singled out.

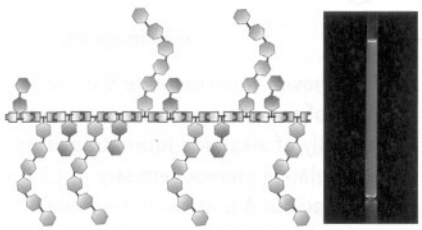
Heterogeneous Catalysis



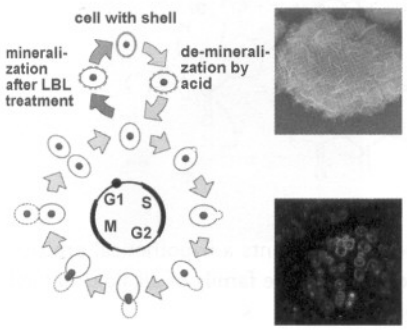
Added flexibility: NMR data for p38α MAP kinase in a complex with the SB203580 inhibitor show intermediate exchange of residues in the binding pocket (affected residues marked in blue and red on the structure), which indicates increased flexibility compared to that of the unbound protein. Based on residual dipolar couplings, the overall solution structure of p38α is very similar to the crystal structure. Thus, the increased mobility in solution is an effect of the inhibitor that is not reflected in the crystal structure.



Versatile chiral substrates for asymmetric synthesis are formed through the spiroketalization of phenols with a chiral substituted ethanol unit O-tethered to the *ortho* position upon treatment with $PhI(OAc)_2$ (see example; TFE = 2,2,2-trifluoroethanol). Intermediates with a six-membered iodine(III)-containing ring (the natural localized molecular orbitals associated with the I–C6 bond are shown) undergo ligand coupling to give the spiroketals.



A change in the constitution: Dynamic glycopolymers based on a poly(acylhydrazone) main chain bearing lateral oligosaccharide groups have been obtained and their structure has been characterized as a bottlebrush type (see picture) by cryo-TEM and small-angle neutron scattering studies. They have remarkable fluorescence with emission wavelengths which are tunable by exchange/incorporation of components which modify the polymer constitution.



Inspired by eggshells in nature, living yeast cells were conferred with an artificial mineral coat by using a combination of the layer-by-layer (LBL) treatment with functional polymers and in situ biomimetic mineralization. The resulting hard inorganic shells have a tremendous effect on the storage, protection, delivery, and modification of the cells.

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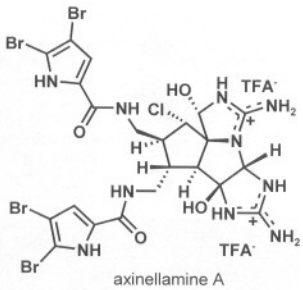
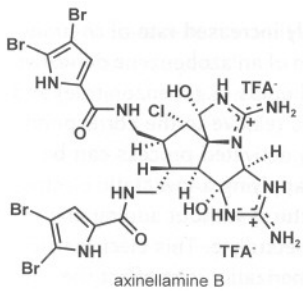
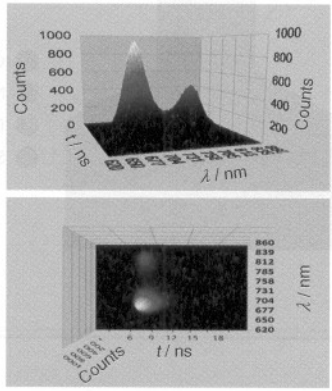




Chemoselective by design: The first total synthesis of members of the axinellamine/palau'amine/massadine class of pyrrole–imidazole alkaloids features unconventional transformations on completely unprotected polyamino and hydroxylated substrates and a new method for chemoselective oxidations in such settings.

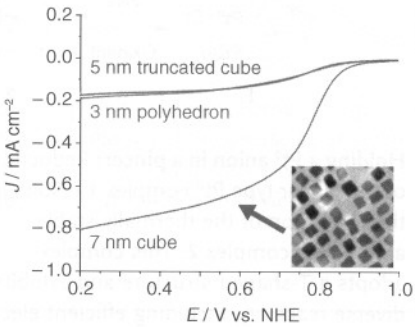
Natural Products

Bilingual fluorescent molecules: An array of asymmetric carbocyanines capable of dual fluorescence emissions in the near-infrared region is described (see image). The fluorescent molecules are robust in different pH and solvents. Additionally, each fluorescence peak possesses a distinct fluorescence lifetime. These properties are retained after conjugation of the dyes with small bioactive peptides.

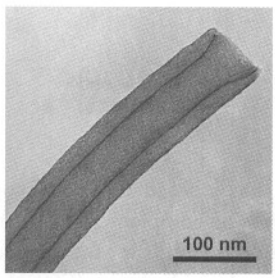


Dichromic Molecules

Catalytic cobblestones: Monodisperse platinum nanoparticles were prepared with controlled sizes (3–7 nm) and shapes (polyhedron, truncated cube, or cube). The cubic nanoparticles are a much more active cathode catalyst for the oxygen reduction reaction: the current density J from 7 nm cubes is four times that of the other shapes (see picture), indicating great potential for fuel cell applications.



O_2 Reduction



Controlled growth: A non-aqueous approach inspired from sol–gel chemistry and adapted to the formation of metal oxide thin films by means of atomic layer deposition is presented. The process is based on the reaction of a carboxylic acid with an alkoxide. Growth of metal oxides is achieved at temperatures as low as 50 °C on various supports including carbon nanotubes (see TEM picture). The as-grown films show excellent uniformity and possess good dielectric properties.

Thin Films

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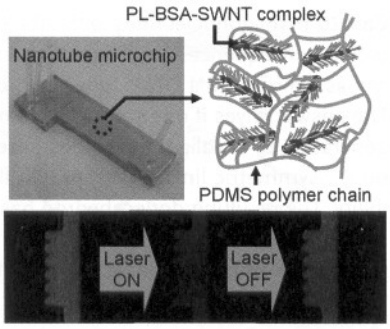
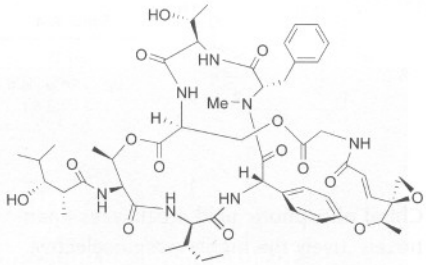


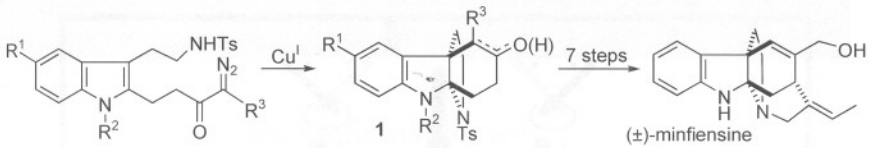
Rapid temperature control: A phospholipid–bovine serum albumin functionalized single-walled carbon nanotube complex (PL–BSA–SWNT) was found to be readily dispersible in poly(dimethylsiloxane) (PDMS). A photoinduced PDMS microchip encapsulating this complex is capable of achieving ultrarapid control of the temperature of a solution contained in one of its microchannels (see image).

Nanotube–Polymer Composites

It's swell! The first total synthesis of potent anti-inflammatory agent salinamide A was achieved. This synthesis features a concise elaboration of the phenylglycine-derived epoxide fragment and the identification of two possible macrolactamization sites (see scheme).

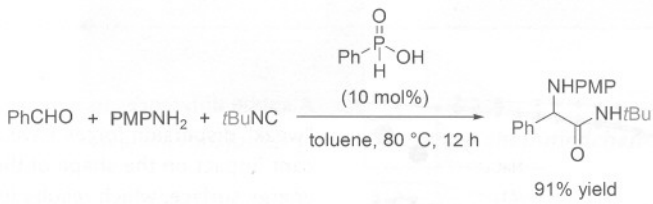


Natural Products



Cascading into (±)-minfiensine: An efficient method was developed for the assembly of tetracyclic skeleton **1** by a three-step, one-pot cascade reaction including cyclopropanation, ring opening, and ring closure (see scheme; Ts = *p*-toluenesulfonyl). The concise total synthesis of the (±)-minfiensine was completed in about a 4% overall yield.

Natural Products



Perfect atom economy characterizes a novel catalytic three-component Ugi reaction (see example). Different α-amino amides are formed in good yields from aldehydes, primary amines, and isocyanides in the presence of phenyl phosphinic acid as the catalyst. The products will be useful for the synthesis of α-amino acid derivatives and in diversity-oriented synthesis.

Multicomponent Reactions

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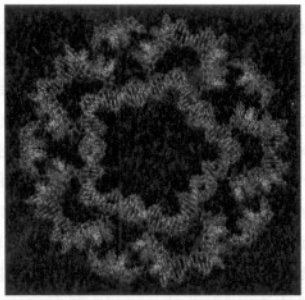
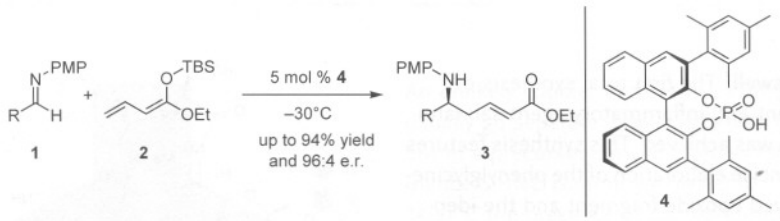
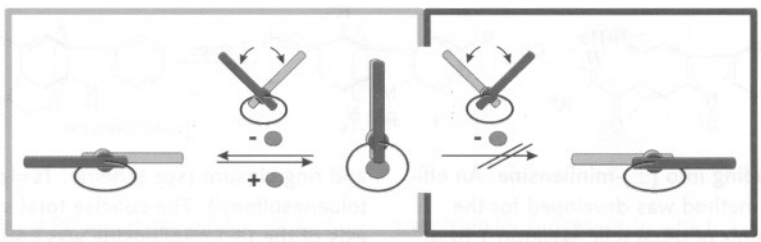


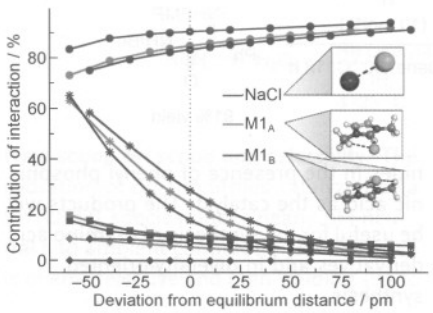
Can 20 trisoligonucleotides with 20×3 individual sequences be programmed to self-assemble into a DNA dodecahedron? The answer is yes if one starts from a new generation of trisoligonucleotides based on C_{3h}-symmetric linkers with proper flexibility. The resulting dodecahedron has C_1 symmetry and may facilitate the construction of multimodular scaffolds in the future.



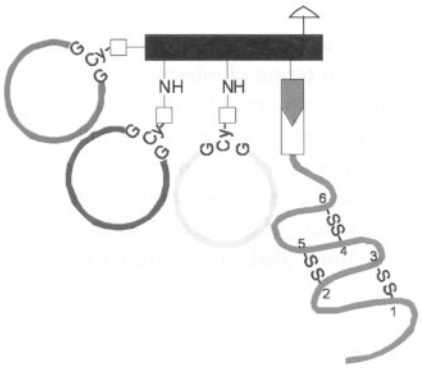
Chiral phosphoric acid 4 catalyzes enantioselectively the highly γ-regioselective addition of a silyl dienolate **2** to imines **1** in good yields and furnishes α,β-unsaturated δ-amino carboxylic esters **3** in one step. The reaction may also be carried out as a direct three-component coupling (PMP = *para*-methoxyphenyl; TBS = *tert*-butyldimethylsilyl).



An open-and-closed case: When a chiral clamp is attached to a molecular hinge the open–close motion induced by coordination to a metal ion becomes unidirectional (see scheme). The large change in amplitude caused by the unidirectional rotation and the relatively simple preparation of the hinge open up the possibility of using this concept for even more-complex molecular machines.



A subtle difference: In ionic liquids the "weak" dispersion forces have a significant impact on the shape of the potential energy surface, which results in a shallow profile when all of the contributions are considered. Such findings are commonly accepted to determine the liquid state.



The synthesis of a 23-kDa protein that mimics the ligand-binding extracellular part of a G-protein-coupled receptor shows the potential of a combined recombinant, enzymatic, and chemical synthesis (CRECS) strategy. The mimic of the corticotropin-releasing factor receptor, synthesized from single domains by chemical ligation and sortase A-mediated coupling, has a high affinity for natural ligands.

Protein Mimics

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).

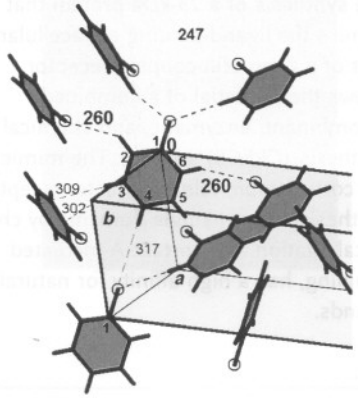
Service

Supramolecular Chemistry

P. Ganguly,* G. R. Desiraju*

Van der Waals and Polar Intermolecular Contact Distances: Quantifying Supramolecular Synthons

Chem. Asian J.
DOI: **10.1002/asia.200700343**



Sizing it up: Crystal structures are considered in terms of intermolecular distances, which are determined by environment-dependent atomic sizes. The supramolecular synthons that make up an organic crystal are quantified in terms of the nature of the weak intermolecular interactions (distances shown are in ppm).

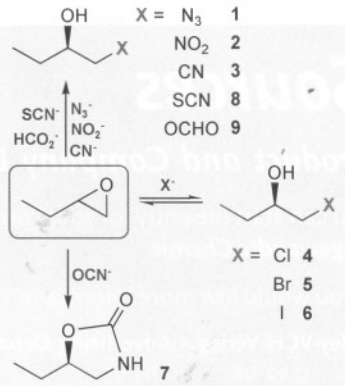
Protein Engineering

G. Hasnaoui-Dijoux, M. Majerić Elenkov, J. H. Lutje Spelberg, B. Hauer, D. B. Janssen*

Catalytic Promiscuity of Halohydrin Dehalogenase and its Application in Enantioselective Epoxide Ring Opening

ChemBioChem
DOI: **10.1002/cbic.200700734**

Easy virtue: Halohydrin dehalogenase is a highly promiscuous enzyme that can catalyze enantioselective epoxide ring opening with at least nine different anionic nucleophiles (see scheme). Its capacity to form carbon–nitrogen, carbon–oxygen, carbon–sulfur, and carbon–carbon bonds makes it possible to use this enzyme for the preparation of a range of highly enantioenriched β-substituted alcohols or derivatives thereof, including cyanoalcohols, nitroalcohols, and oxazolidinones.

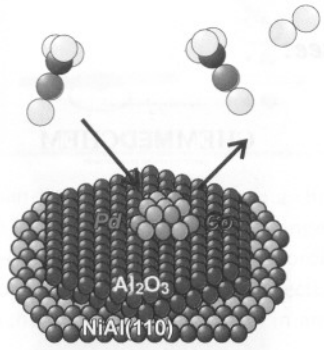


Catalysts

T. Nowitzki, H. Borchert, B. Jürgens, T. Risse, V. Zielasek, M. Bäumer*

UHV Studies of Methanol Decomposition on Mono- and Bimetallic CoPd Nanoparticles Supported on Thin Alumina Films

ChemPhysChem
DOI: **10.1002/cphc.200700663**



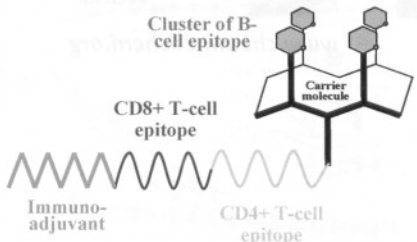
One metal or two? Adsorption and reaction studies on well-defined model systems are important to understand the complex surface processes on real catalysts. This fundamental study of the decomposition of methanol on metal clusters (see picture) results in syngas and/or carbon deposits on the particle surfaces depending on their composition.

Antitumor Agents

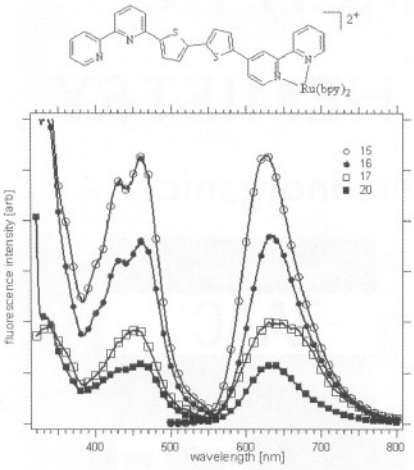
O. Renaudet, L. BenMohamed, G. Dasgupta, I. Bettahi, P. Dumy*

Towards a Self-Adjuvanting Multivalent B and T cell Epitope Containing Synthetic Glycolipopeptide Cancer Vaccine

ChemMedChem
DOI: **10.1002/cmdc.200700315**



A new generation of synthetic cancer vaccine: the first self-adjuvanting vaccine prototype combining a cluster of B cell epitope, a CD4+ T helper cell epitope, a CD8+ T cell epitope, and an immunoadjuvant has been synthesized by a chemoselective strategy. Vaccination of mice with this molecularly defined construction induces a strong protection against tumors.



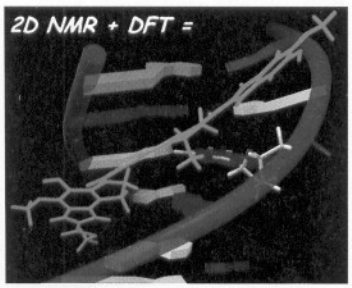
A range of mono- and bis(bidentate) 2,2′-bipyridine-capped oligothiophene-bridged Ru^{II} complexes based on the 6-(2-thienyl)-2,2′-bipyridine motif and the 4-(2-thienyl)-2,2′-bipyridine motif have been synthesized, and the luminescence lifetimes and electrochemical potentials have been measured.

Photophysics

R. O. Steen, L. J. Nurkkala, S. J. Angus-Dunne, C. X. Schmitt, E. C. Constable, M. J. Riley, P. V. Bernhardt, S. J. Dunne*

The Role of Isomeric Effects on the Luminescence Lifetimes and Electrochemistry of Oligothienyl-Bridged Dinuclear Tris(2,2′-bipyridine)-ruthenium(II) Complexes

Eur. J. Inorg. Chem.
DOI: **10.1002/ejic.200701118**



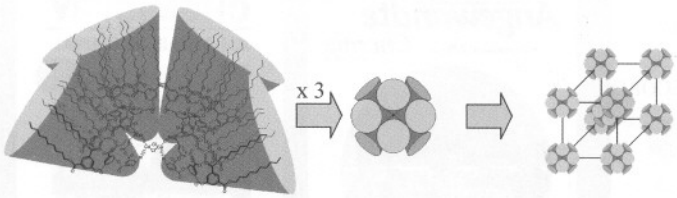
A hybrid approach based on 2D-NMR spectroscopy and quantum mechanical calculations of ^1H chemical shifts at the DFT/MPW1PW91 level was used for the characterization of the covalent complex formed by (+)-yatakemycin and d(GACTAATTGAC)–(GTCAATTAGTC), showing that calculation of NMR parameters can be a useful tool for the structural characterization of ligand–receptor interactions.

Ligand–Receptor Interactions

S. Di Micco, D. L. Boger, R. Riccio, G. Bifulco*

Structural Features of the (+)-Yatakemycin/d(GACTAATTGAC)-(GTCAATTAGTC) Complex – Quantum Mechanical Calculation of NMR Parameters as a Tool for the Characterization of Ligand/DNA Interactions

Eur. J. Org. Chem.
DOI: **10.1002/ejoc.200701212**



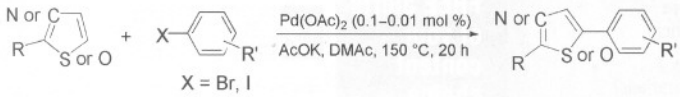
Branching out! Stable metallodendrimers made from monodendrons with an isocyanide group in the focal point have been prepared. Although the molecules of the metallodendrimers prepared are structurally very different, consisting of one, two, or four monodendrons, the structures of the mesophases are similar and consist of the packing of micellar aggregates in a three-dimensional cubic $Im\bar{3}m$ lattice (see scheme).

Metallodendrimers

S. Coco,* C. Cordovilla, B. Donnio, P. Espinet,* M. J. García-Casas, D. Guillon

Self-Organization of Dendritic Supermolecules, Based on Isocyanide–Gold(I), –Copper(I), –Palladium(II), and –Platinum(II) Complexes, into Micellar Cubic Mesophases

Chem. Eur. J.
DOI: **10.1002/chem.200800128**



How low can Pd go? The direct arylation of heteroaryl compounds under very low loadings of $Pd(OAc)_2$ as catalyst and in the absence of any added ligand proceeds in high yield. Turnover numbers up to 10000 are observed for the coupling of activated aryl bromides with thiazole, thiophene or furan derivatives (see scheme; DMAc = *N*,*N*-dimethylacetamide).

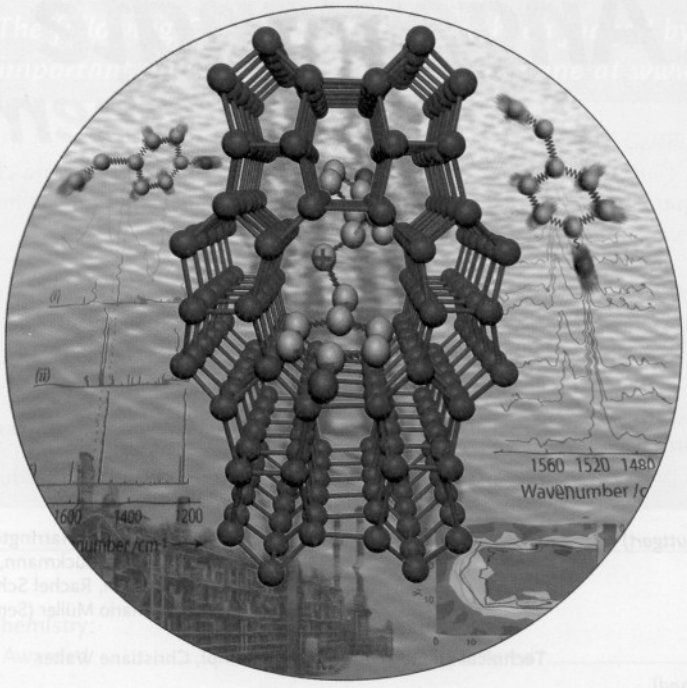
Homogeneous Catalysis

F. Požgan, J. Roger, H. Doucet*

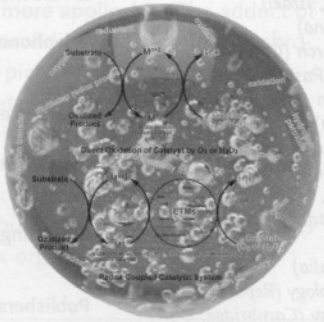
Ligand-Free Palladium-Catalysed Direct Arylation of Heteroaromatics Using Low Catalyst Loadings

ChemSusChem
DOI: **10.1002/cssc.200700166**

Heterogeneous catalysis through infrared goggles:

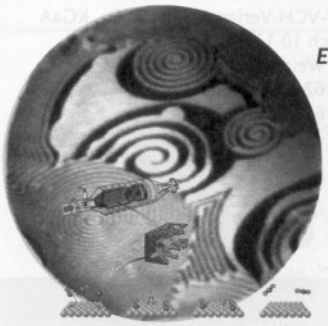


In their Communication on page 3543 ff., B. M. Weckhuysen and co-workers use synchrotron-based IR microspectroscopy with diffraction-limited spatial resolution to map the catalytic activity of ZSM-5 zeolite crystals in styrene oligomerization and identify the carbocationic reaction products entrapped in zeolite pores. They propose a combined three-pronged microspectroscopic approach for in-depth spatially- and time-resolved characterization of catalytic processes taking place within catalyst grains.



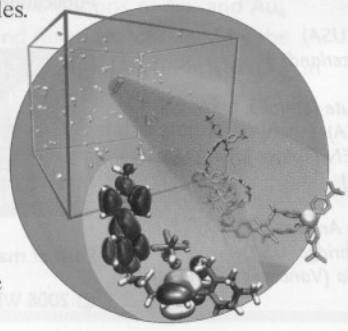
Oxygen as an Oxidant

J.-E. Bäckvall and J. Piera describe in their Review on page 3506 ff. how the combination of transition-metal catalysts and electron-transfer mediators enable the use of oxygen or hydrogen peroxide as oxidants.



Elementary Reaction Steps (Nobel Lecture)

In the Review on page 3524 ff., G. Ertl describes for a broad audience his research on heterogeneous catalysis, for which he was awarded the 2007 Nobel Prize in Chemistry. The synthesis of ammonia and automotive catalytic converters are used as examples.



Rotaxanes

Fast-switching nanomachines can exist in solution. Raiteri, Credi et al. show in their Communication on page 3536 ff. by using free-energy calculations that ring displacement in a photocontrollable molecular shuttle may occur on the nanosecond timescale.

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