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:

C. Costentin, M. Robert, J. Savéant, C. Tard
Inserting a Hydrogen Bond Relay between Proton Exchanging Sites in Proton-Coupled Electron Transfers

*A. Wilbuer, D. H. Vlecken, D. J. Schmitz, K. Kräling, K. Harms, C. P. Bagowski, E. Meggers**
Iridium Complex with Antiangiogenic Properties

J. M. Slattery, A. Higelin, T. Bayer, I. Krossing**
A Simple Route to Univalent Gallium Salts of Weakly Coordinating Anions

*R. Rose, S. Erdmann, S. Bovens, A. Wolf, M. Rose, S. Hennig, H. Waldmann, C. Ottmann**
Identification and Structure of Small-Molecule Stabilizers of 14-3-3 Protein–Protein Interactions

*A. Schlossbauer, S. Warncke, P. E. Gramlich, J. Kecht, A. Manetto, T. Carell, T. Bein**
A Programmable DNA-Based Molecular Valve for Colloidal Mesoporous Silica

*M. Walz, M. Schirmer, F. Vollnhals, T. Lukasczyk, H.-P. Steinrück, H. Marbach**
Electrons as "Invisible Ink"!

*A. Takaoka, L. C. H. Gerber, J. C. Peters**
Access to Well-Defined Ruthenium(I) and Osmium(I) Metalloradicals

*J. Zhang, X.-J. Wu, Z. Wang, Yu Chen, X. Wang, M. Zhou, H. Scheer, K. Zhao**
Single Fused Gene Approach to Photoswitchable and Fluorescent Biliproteins

Author Profile

"My most exciting discovery to date has been the functionalization of endohedral metallofullerenes. My biggest motivation is to realize that where there is a will, there is a way …"
This and more about Takeshi Akasaka can be found on page 3408.

Takeshi Akasaka ____ 3408

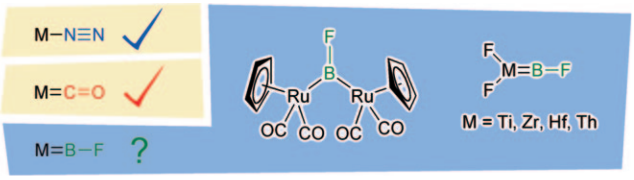
Books

Concepts of Nanochemistry — Ludovico Cademartiri, Geoffrey A. Ozin — *reviewed by N. Korber* ____ 3409

Click Chemistry for Biotechnology and Materials Science — Joerg Lahann — *reviewed by R. Hoogenboom* ____ 3410

Highlights

Borylene Complexes



B and F become BFFs: The last of the neutral first-row main group diatomics, BF, has conspicuously eluded synthetic chemists and their attempts to stabilize it by transition metals. After decades of near misses, two contrasting families of fluoroborylene transition metal complexes have been definitively synthesized by the research groups of Aldridge and Andrews.

H. Braunschweig,*
R. D. Dewhurst ____ 3412 – 3414

Fashionably Late: Synthesis and Characterization of Transition-Metal–Fluoroborylene Complexes

© 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

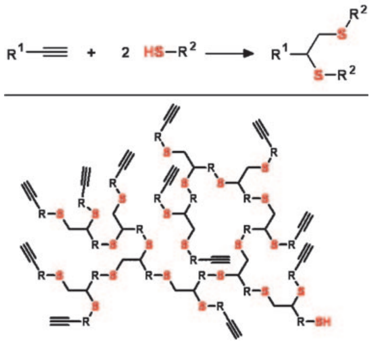
WILEY InterScience® DISCOVER SOMETHING GREAT

Synthetic Methods

R. Hoogenboom* ________ **3415 – 3417**

Thiol–Yne Chemistry: A Powerful Tool for Creating Highly Functional Materials

Branching out: Thiol–yne chemistry is emerging as new tool for polymer chemists, as it represents a unique and efficient coupling procedure to create highly branched structures (see scheme). This method can be used to prepare highly functional dendrimers and hyperbranched polymers.



Minireviews

Cyclopamine

P. Heretsch, L. Tzagkaroulaki,
A. Giannis* ____________ **3418 – 3427**

Cyclopamine and Hedgehog Signaling: Chemistry, Biology, Medical Perspectives

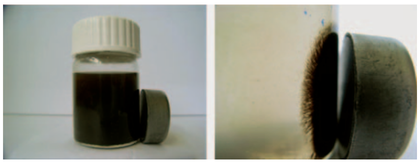
The freaky molecule: From Odysseus' encounter with the cyclops and the appearance of cyclops-like sheep in Idaho more than 3000 years later, to the discovery of cyclopamine and the hedgehog signaling pathway as well as a highly selective anticancer therapy—this sometimes creepy but always interesting story is told in this Minireview.

Reviews

Nanocatalysts

S. Shylesh,* V. Schünemann,
W. R. Thiel* ____________ **3428 – 3459**

Magnetically Separable Nanocatalysts: Bridges between Homogeneous and Heterogeneous Catalysis



An attractive concept: Quasihomogeneous magnetic nanoparticles and magnetic nanocomposites have found increasing application in organic synthesis; for example, they are ideal supports for the heterogenization of homogeneous catalysts (the picture shows a catalyst that can be removed with a simple magnet). This Review summarizes recent developments in the synthesis, characterization, and applications of these materials.

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*, Journal Customer Services, John Wiley & Sons Inc., 350 Main St., Malden, MA 02148-5020. Annual subscription price for institutions: US$ 9442/8583 (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.

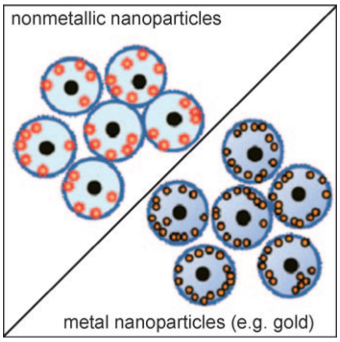
Communications

Cell Mass Spectrometry

H.-C. Lin, H.-H. Lin, C.-Y. Kao, A. L. Yu,
W.-P. Peng,* C.-H. Chen* ___ **3460 – 3464**

Quantitative Measurement of Nano-/Microparticle Endocytosis by Cell Mass Spectrometry

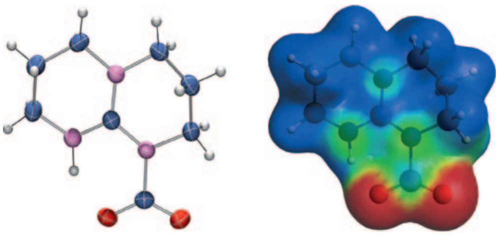
All present and accounted for? Cell mass spectrometry was used to determine the quantity of both gold and polystyrene nano-/microparticles taken up into cells (see picture). The uptake amounts measured for gold nanoparticles were similar to those determined by inductively coupled plasma mass spectrometry, a technique which can not be used to measure the cellular uptake of nonmetal particles.



CO_2 Binding

C. Villiers,* J. P. Dognon,* R. Pollet,
P. Thuéry, M. Ephritikhine* **3465 – 3468**

An Isolated CO_2 Adduct of a Nitrogen Base: Crystal and Electronic Structures

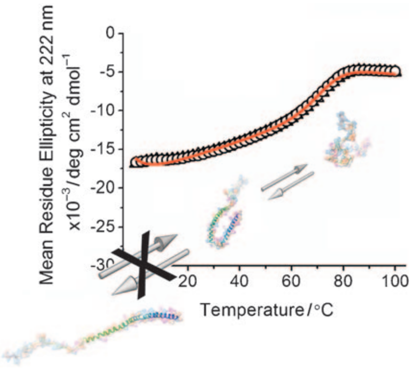


In a crystal at last: CO_2 binds reversibly to the guanidine molecule TBD. The zwitterionic structure of the adduct is demonstrated by X-ray diffraction analysis and computational methods (see picture; left: C blue, H white, N pink, O red), while its fluxionality in solution is revealed by NMR spectroscopy.

Protein Folding

A. C. M. Ferreon, C. R. Moran,
J. C. Ferreon, A. A. Deniz* ___ **3469 – 3472**

Alteration of the α-Synuclein Folding Landscape by a Mutation Related to Parkinson's Disease



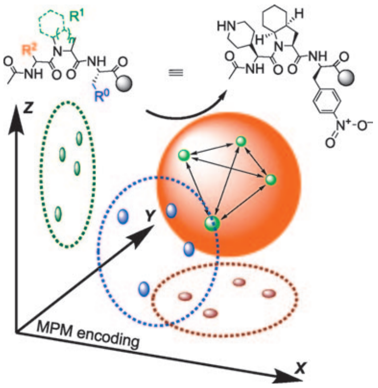
Shape shifting linked to disease: A single-molecule fluorescence technique was used to probe structures of an intrinsically disordered brain protein. A mutation was found to tilt the coupled binding–folding energy landscape of the protein and inhibited switching between induced ordered structures (see picture). The observations provide fundamental insight into the molecular basis of Parkinson's disease.

Combinatorial Chemistry

M. Meldal,*
S. F. Christensen ___________ **3473 – 3476**

Microparticle Matrix Encoding of Beads

Reloaded matrix: Facile optical encoding of polyethylene glycol (PEG) based resins provides a direct identification of compounds in combinatorial libraries, and the structures may be correlated with bioactivity. The new technique, microparticle matrix (MPM) encoding (see picture), circumvents some problems often encountered in solid-phase combinatorial chemistry and is extremely simple to implement.

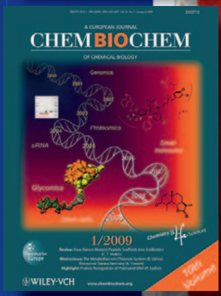


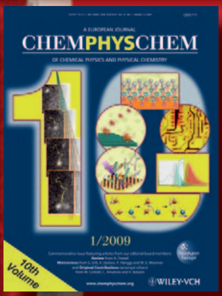
© 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Frontiers of Chemistry:
From Molecules to Systems

A One-Day Symposium

Celebrating 10 Years of





On 21st May 2010 in Paris

at the Maison de la Chimie
(near the Eiffel Tower and Les Invalides)

Speakers

Gerhard Ertl
Nobel Prize 2007

Jean-Marie Lehn
Nobel Prize 1987

Roger Y. Tsien
Nobel Prize 2008

Ada Yonath
Nobel Prize 2009

Luisa De Cola

Alan R. Fersht

Marc Fontecave

Michael Grätzel

Michel Orrit

Nicolas Winssinger

Scientific committee

E. Amouyal, M. Che,
F. C. De Schryver,
A. R. Fersht, P. Gölitz,
J. T. Hynes, J.-M. Lehn

Posters

will be displayed also online from 1st April

www.chembiophyschem.org

Topics

catalysis, biochemical imaging, chemical biology, bionanotechnology, proteomics, spectroscopy, solar cells

Organized by

ChemPubSoc Europe

Société Chimique de France

Partner of the event sanofi aventis
Because health matters

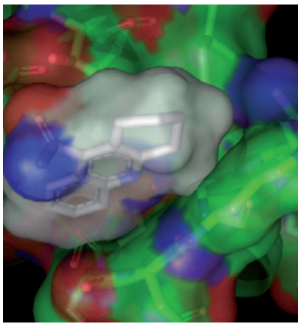
WILEY-VCH

557101001

Protein Purification

J. E. Rasmussen,* C. B. Schiødt,
S. F. Christensen, L. Nørskov-Lauritsen,
M. Meldal, P. M. St. Hilaire,*
K. J. Jensen* __________ **3477 – 3480**

Small-Molecule Affinity Ligands for Protein Purification: Combined Computational Enrichment and Automated In-line Screening of an Optically Encoded Library

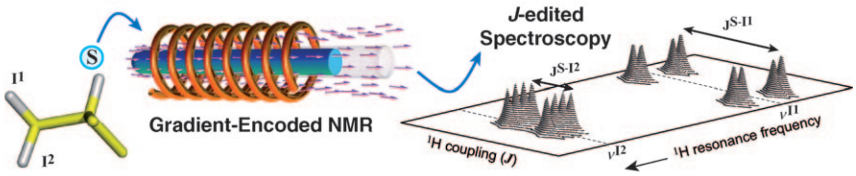


Screening with codes: A versatile methodology for the development of small-molecule affinity chromatography ligands for protein targets is presented. The combination of computational enrichment with automated screening and affinity mapping of an optically encoded combinatorial library allows identification of a novel set of ligands for the single-step purification of human growth hormone (see picture).

NMR Techniques

N. Giraud, L. Béguin, J. Courtieu,
D. Merlet* __________ **3481 – 3484**

Nuclear Magnetic Resonance Using a Spatial Frequency Encoding: Application to *J*-Edited Spectroscopy along the Sample

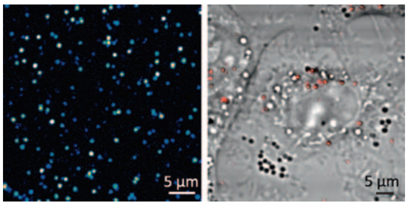


Finger on the pulse: Selective experiments can be simultaneously run on different parts of the sample when NMR sequences based on a spatial encoding are used. This approach was applied to a gradient-encoded selective refocusing sequence. The resulting data provide a collection of all the couplings that involve a given proton spin, which can be conveniently assigned and measured from only one spectrum.

Imaging Agents

L. Tong, C. M. Cobley, J. Chen, Y. Xia,*
J.-X. Cheng* __________ **3485 – 3488**

Bright Three-Photon Luminescence from Gold/Silver Alloyed Nanostructures for Bioimaging with Negligible Photothermal Toxicity

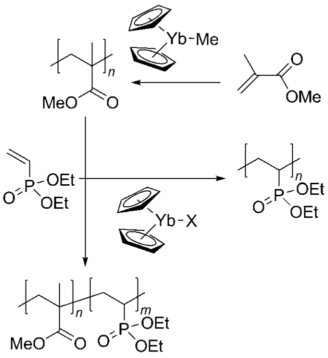


Au/Ag alloyed nanostructures exhibit a bright three-photon luminescence (3PL; see picture, left) upon excitation by a femtosecond laser at 1290 nm, with an intensity level one order of magnitude higher than pure Au or Ag nanoparticles. As the excitation is outside the range of plasmon resonance, 3PL enables bioimaging (right) with negligible photothermal toxicity.

Phosphorus-Containing Polymers

U. B. Seemann, J. E. Dengler,
B. Rieger* __________ **3489 – 3491**

High-Molecular-Weight Poly(vinylphosphonate)s by Single-Component Living Polymerization Initiated by Rare-Earth-Metal Complexes



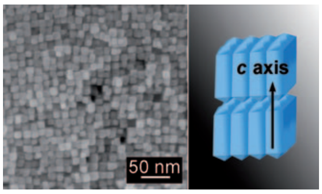
Transfer ticket: A group transfer polymerization (GTP) reaction mechanism operates in the living polymerization of diethyl vinylphosphonate, in which high-molecular-weight homo- and copolymers are produced using simple rare-earth-metal complexes (see scheme). The mechanism is consistent with the well-known and established mechanism for polar monomers such as acrylates, and opens up a new approach toward phosphorus-containing polymeric materials.

Nanorod Arrays

J. F. Liu, L. L. Wang, X. M. Sun,*
X. Q. Zhu ______ **3492 – 3495**

Cerium Vanadate Nanorod Arrays from Ionic Chelator-Mediated Self-Assembly

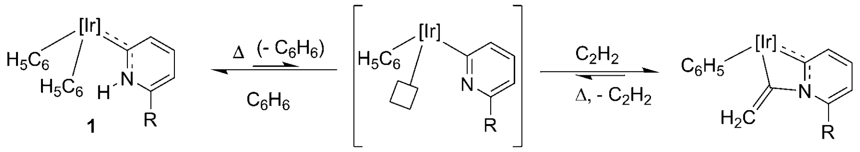
Line them up: Uniform $CeVO_4$ nanorod arrays (see picture) were synthesized in a self-assembly approach assisted by ethylenediaminetetraacetic acid (EDTA) molecules in aqueous media. EDTA is important not only in controlling anisotropic growth by restricting the active points of certain faces, but also in mediating the assembly by forming intermolecular hydrogen bonds.



Cycloaddition Reactions

E. Álvarez, Y. A. Hernández,
J. López-Serrano, C. Maya, M. Paneque,
A. Petronilho, M. L. Poveda,* V. Salazar,
F. Vattier, E. Carmona* ______ **3496 – 3499**

Metallacyclic Pyridylidene Structures from Reactions of Terminal Pyridylidenes with Alkenes and Acetylene

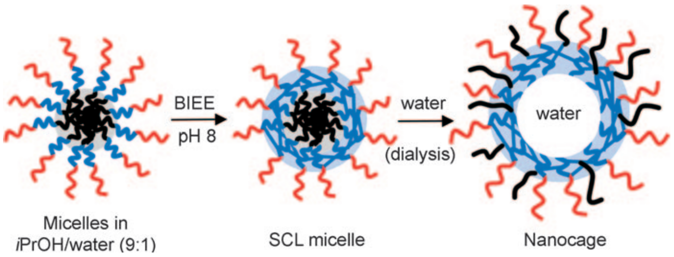


Iridium pyridyl species are key intermediates in the title reactions. Thermal elimination of benzene from complexes **1** (R = Me, Ph) creates a vacant coordination site accessible to unsaturated hydrocarbons. Subsequent intramolecular nucleophilic attack by the pyridyl nitrogen atom to the alkene or vinylidene leads to iridacyclic pyridylidene structures (see scheme).

Polymers

S. Sugihara,* S. P. Armes,*
A. L. Lewis ______ **3500 – 3503**

One-Pot Synthesis of Biomimetic Shell Cross-Linked Micelles and Nanocages by ATRP in Alcohol/Water Mixtures



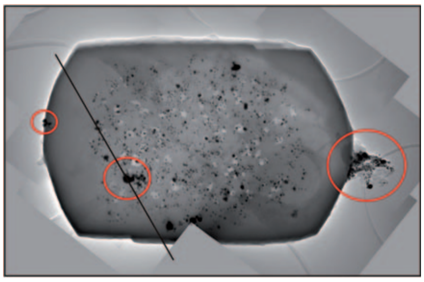
Shell shock: The one-pot synthesis of shell cross-linked (SCL) micelles was achieved using an ABC triblock copolymer in a 9:1 alcohol/water mixture. These SCL micelles were dialyzed against water, leading to solvation of the core-forming PMPC chains. If the cross-linking is not too high, these chains migrate through the inner shell to join the coronal PEO chains, hence forming nanocages.

Hybrid Materials

A. B. Laursen, K. T. Højholt,
L. F. Lundegaard, S. B. Simonsen,
S. Helveg, F. Schüth, M. Paul,
J.-D. Grunwaldt, S. Kegnæs,
C. H. Christensen,*
K. Egeblad* ______ **3504 – 3507**

Substrate Size-Selective Catalysis with Zeolite-Encapsulated Gold Nanoparticles

The Dark Crystal: A hybrid material is reported that is comprised of 1–2 nm sized gold nanoparticles, accessible only through zeolite micropores in a silicalite-1 crystal, as shown by three-dimensional TEM tomography (see picture). Calcination experiments indicate that the embedded nanoparticles are highly stable towards sintering.

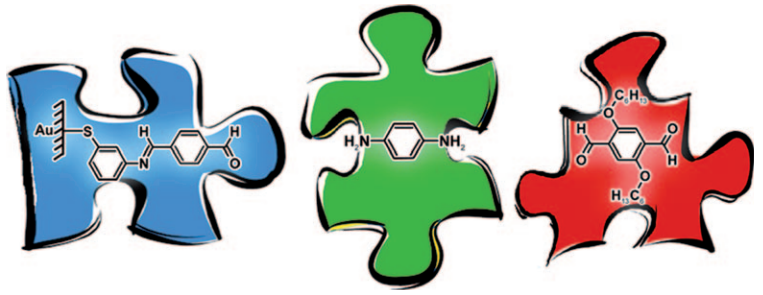


© 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Molecular Electronics

G. J. Ashwell,* B. Urasinska-Wojcik, L. J. Phillips ______ 3508 – 3512

In Situ Stepwise Synthesis of Functional Multijunction Molecular Wires on Gold Electrodes and Gold Nanoparticles

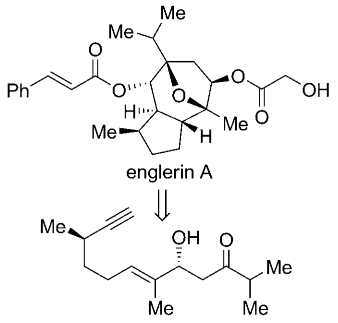


Tunneling through: The sequencing of electron-donating and electron-accepting components that are separated by a σ-electron bridge has resulted in the highest rectification ratio to date from a molecular diode.

Natural Product Synthesis (1)

Q. Zhou, X. Chen, D. Ma* _ 3513 – 3516

Asymmetric, Protecting-Group-Free Total Synthesis of (−)-Englerin A

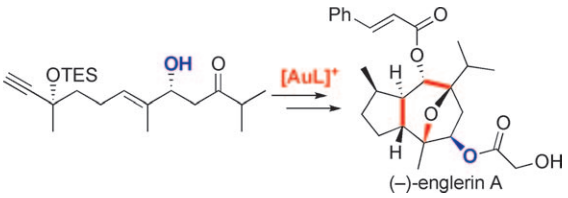


The golden touch: Total synthesis of natural (−)-englerin A from (*R*)-citronellal has been achieved using a gold-catalyzed cyclization as the key step (see scheme). No protecting-group manipulations were required in the synthetic sequence.

Natural Product Synthesis (2)

K. Molawi, N. Delpont, A. M. Echavarren* ________ 3517 – 3519

Enantioselective Synthesis of (−)-Englerins A and B

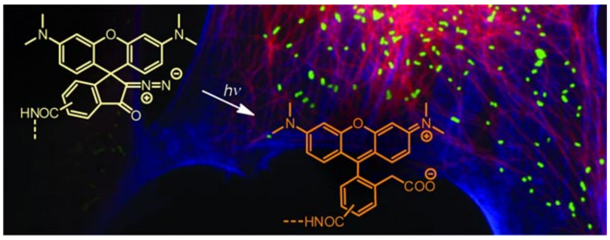


All that glitters is gold: The total synthesis of the natural enantiomers of englerins A and B has been completed using a gold-catalyzed stereoselective domino alkyne/alkene/carbonyl cyclization of an enyne with an unprotected alcohol group at a stereogenic allylic position (see scheme; TES = triethylsilyl).

Caged Fluorescence

V. N. Belov,* C. A. Wurm,* V. P. Boyarskiy, S. Jakobs, S. W. Hell* _____ 3520 – 3523

Rhodamines NN: A Novel Class of Caged Fluorescent Dyes



A bright future: The reaction of diazomethane with acid chlorides obtained from *N*,*N*,*N*′,*N*′-tetraalkylrhodamines affords 2-diazo-2,3-dihydro-1*H*-indenespiro[1,9′]-9*H*-xanthen-3-ones—a novel class of caged rhodamines. These dyes allow new imaging procedures based on the step-wise activation and detection of several fluorescent markers (see picture).

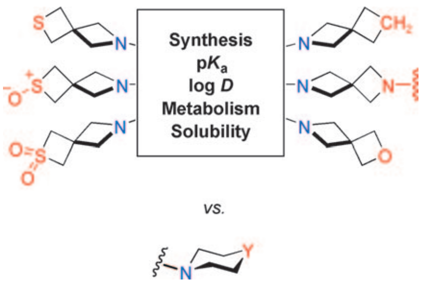
© 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Contents

Drug Design

J. A. Burkhard, B. Wagner, H. Fischer,
F. Schuler, K. Müller,*
E. M. Carreira* ____________ **3524–3527**

Synthesis of Azaspirocycles and their Evaluation in Drug Discovery

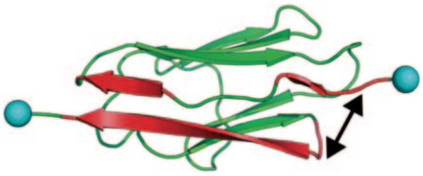


Make it spiro! Readily synthesized heteroatom-substituted spiro-[3.3]heptanes generally show higher aqueous solubility than their cyclohexane analogues, and show a trend towards higher metabolic stability. The novel framework can be mounted onto scaffolds of druglike structures, such as fluoroquinolones, to afford active compounds with similar or even improved metabolic stability.

Protein Folding

J. M. Nunes, U. Hensen, L. Ge,
M. Lipinsky, J. Helenius, H. Grubmüller,*
D. J. Muller* ____________ **3528–3531**

A "Force Buffer" Protecting Immunoglobulin Titin



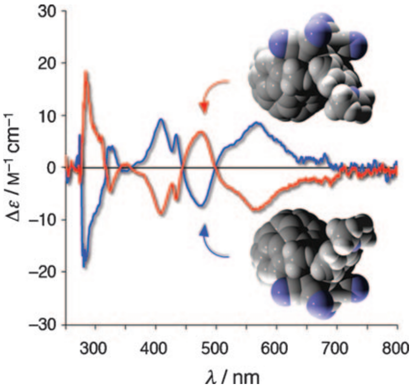
The adventures of titin: in vertebrates, titin filaments control the extendibility of the muscle sarcomere. The titin immunoglobulin 27 unfolds through an intermediate (see structure; arrow: hydrogen bonds ruptured to reach intermediate) that it is highly independent of the force load applied. It is shown that this intermediate acts as a "force buffer" that protects immunoglobulin from unfolding at physiologically applied forces.

Hindered Rotation

M. Yamada, P. Rivera-Fuentes,
W. B. Schweizer,
F. Diederich* ____________ **3532–3535**

Optical Stability of Axially Chiral Push–Pull-Substituted Buta-1,3-dienes: Effect of a Single Methyl Group on the C_{60} Surface

A new spin on C_{60}: Axially chiral, push–pull buta-1,3-diene chromophores conjugated to vicinally methylated fullerenes (see picture) have high barriers of rotation about their chiral axes. These high barriers allowed their optical resolution and the determination of the absolute configuration by comparison of experimental and calculated circular dichroism spectra. The methyl group is rigidly fixed upon the surface of the carbon sphere and is responsible for the high rotational barriers.

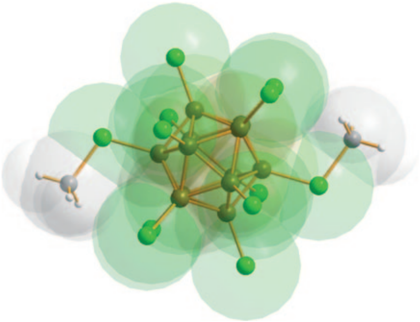


Dodecaborates

C. Bolli, J. Derendorf, M. Keßler,
C. Knapp,* H. Scherer, C. Schulz,
J. Warneke ____________ **3536–3538**

Synthesis, Crystal Structure, and Reactivity of the Strong Methylating Agent $Me_2B_{12}Cl_{12}$

Give Me strength: Methylation of the easily accessible weakly coordinating dianion $[B_{12}Cl_{12}]^{2-}$ affords $Me_2B_{12}Cl_{12}$ (see picture). This neutral compound is a stronger methylating agent than commonly used methyl triflate, and it even methylates benzene. The synthesis, crystal structure, and reactivity of $Me_2B_{12}Cl_{12}$ in solution and the gas phase are discussed.



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).

© 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Sources

Product and Company Directory

You can start the entry for your company in "Sources" in any issue of *Angewandte Chemie*.

If you would like more information, please do not hesitate to contact us.

Wiley-VCH Verlag – Advertising Department
Tel.: 0 62 01 - 60 65 65
Fax: 0 62 01 - 60 65 50
E-Mail: MSchulz@wiley-vch.de

Service

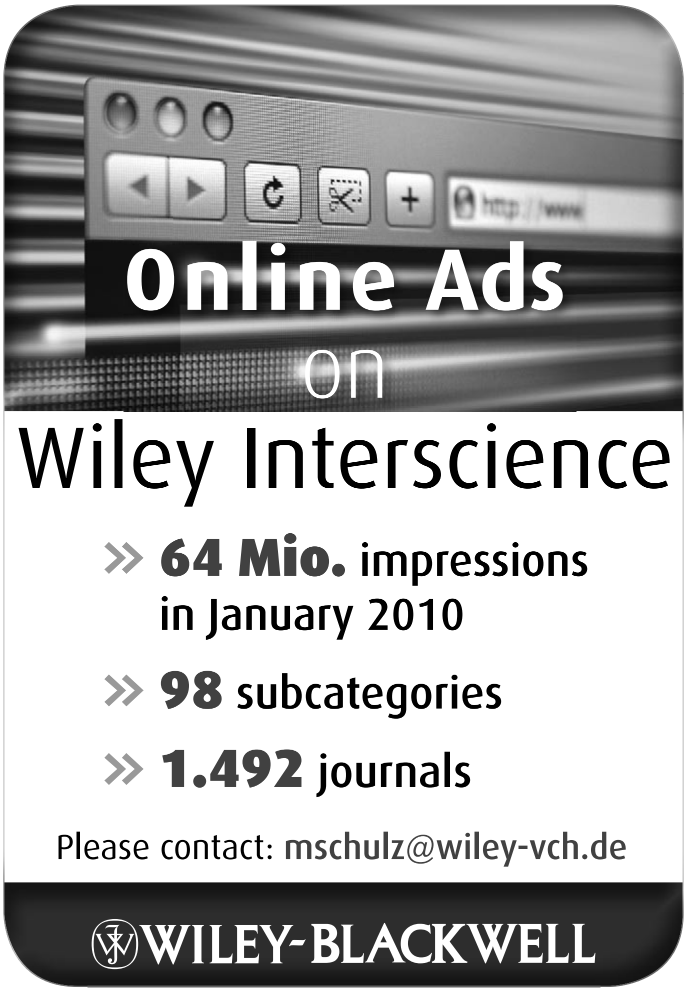
Spotlight on Angewandte's Sister Journals ____ *3404 – 3406*

Keywords ____ *3540*

Authors ____ *3541*

Preview ____ *3543*

The issues for April 2010 appeared online on the following dates
Issue 15: March 26 · Issue 16: March 30 · Issue 17: April 1 · Issue 18: April 9



Online Ads
on
Wiley Interscience

» **64 Mio.** impressions in January 2010

» **98** subcategories

» **1.492** journals

Please contact: mschulz@wiley-vch.de

WILEY-BLACKWELL

www.iciqsummerschool.com

2010

ICIQ summer school

Tarragona, July 19-23, 2010
contact information:
iciqsummerschool@iciq.es

intecat

Consolider

ICIQ Institut Català d'Investigació Química

Av. Països Catalans 16
43007 Tarragona (Spain)
Phone: +34 977 920 200
Fax: +34 977 920 225
www.iciq.es

Speakers:

Prof. Veronique Gouverneur
University of Oxford

Prof. Amir Hoveyda
Boston College

Prof. David A. Leigh
University of Edinburgh

Prof. Benjamin List
Max-Planck-Institut für Kohlenforschung

Prof. Cristina Nevado
University of Zürich

Prof. Tobias Ritter
Harvard University

Prof. Eric J. Sorensen
Princeton University

Prof. Dirk Trauner
University of Munich

Prof. Helma Wennemers
University of Basel

Directors:

Prof. Miguel Ángel Sierra
Universidad Complutense de Madrid

Prof. Antonio M. Echavarren
Institut Català d'Investigació Química (ICIQ)

© 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim