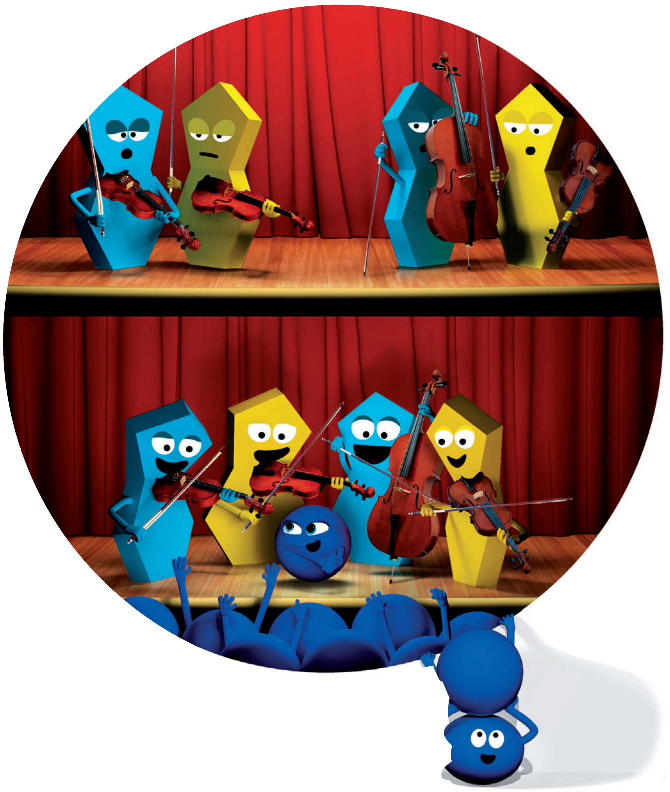
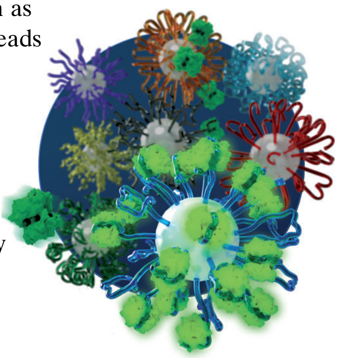
Guanine-rich DNA sequences ...

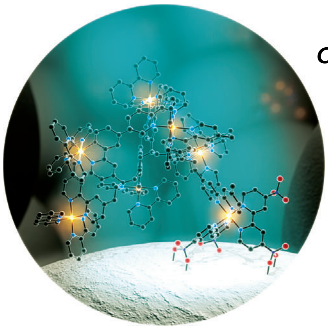


... can self-assemble into specific pre-organized DNA structures, where two-by-two guanine residues shown as "duets" are involved in GG N1-carbonyl symmetric base pairs. In their Communication on page 4881 ff., J. Lah, J. Plavec, and co-workers demonstrate the transition of these "duets" into guanine-quartets, presented as a "string quartet" when interacting with cations, such as potassium ions. This rearrangement consequently leads to formation of G-quadruplex structures.



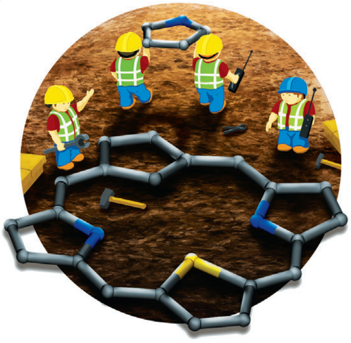
Aptamer Screening

A new particle display method for aptamer screening is described by H. T. Soh and co-workers in their Communication on page 4796 ff. High-quality aptamers can be generated rapidly and economically by this approach.



Oligomer Growth

In their Communication on page 4872 ff., T. J. Meyer et al. describe that ruthenium(II) vinylpolypyridyl complexes can be grown within the cavities of TiO_2 films by electrochemically controlled radical polymerization.



Carbaporphyrinoids

L. Latos-Grażyński and co-workers describe in their Communication on page 4885 ff., the synthesis of 21-carbathiaporphyrin, the first meso-substituted true carbaporphyrin with an unsubstituted cyclopentadienyl moiety.

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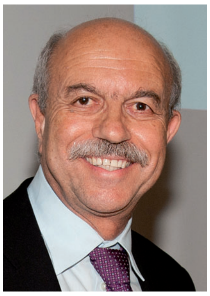
Editorial



"... The pharmaceutical enterprise is facing economic and strategic pressures ... at the same time, academic investigators in basic research are facing their own problems as funding agencies and charitable foundations are shifting their emphasis to more applied and translational programs. These conditions are leading to merging interests and the emergence of partnerships between the two sectors ..."
Read more in the Editorial by K. C. Nicolaou.

Author Profile

"My favorite food is shellfish such as lobster and crab. If I won the lottery, I would take a luxury cruise and travel around the world …"
This and more about Akira Sekiguchi can be found on page 4746.

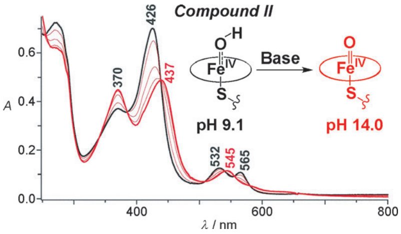
Books

Highlights

Cytochrome P450

A. B. McQuarters, M. W. Wolf, A. P. Hunt, N. Lehnert* ______ **4750 – 4752**

1958–2014: After 56 Years of Research, Cytochrome P450 Reactivity Is Finally Explained

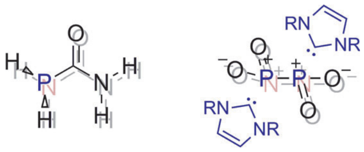


Nature's wisdom in enzyme design: Compounds I and II in the catalytic cycle of the Cytochrome P450 enzymes have been trapped and characterized recently. This work has provided further insight into the electronic structure and reactivity of these crucial intermediates, and key questions regarding the mechanism of these enzymes have finally been answered.

Phosphorus Compounds

D. Gudat* ______ **4753 – 4754**

New Phosphorus Analogues of Nitrogen Classics—No Carbon Copies



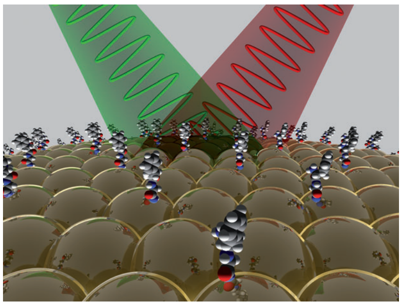
Getting heavy: The recently prepared phosphorus analogues of two old acquaintances, urea and dinitrogen tetroxide, bear some structural resemblance to their archetypes but are no carbon copies. Their syntheses and chemical properties reveal rather certain peculiarities, which back the doctrine that the electronic properties of the heavier elements in a group differ from those of the lightest congener.

Reviews

Spectroscopic Methods

S. Schlücker* ______ **4756 – 4795**

Surface-Enhanced Raman Spectroscopy: Concepts and Chemical Applications



Expanding vibrational spectroscopy: Since its first observation in 1973, surface-enhanced Raman scattering (SERS) has developed into a mature vibrational spectroscopic technique. The number of applications in chemistry as well as the material and life sciences is increasing rapidly. This Review summarizes the key concepts behind SERS and provides an overview of current applications in chemistry.

For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. US mailing agent: SPP, PO Box 437, Emigsville, PA 17318. Periodicals postage paid at Emigsville, PA. US POSTMASTER: send address changes to *Angewandte Chemie*, John Wiley & Sons Inc., C/O The Sheridan Press, PO Box 465, Hanover, PA 17331. Annual subscription price for institutions: US$ 11.738/10.206 (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.

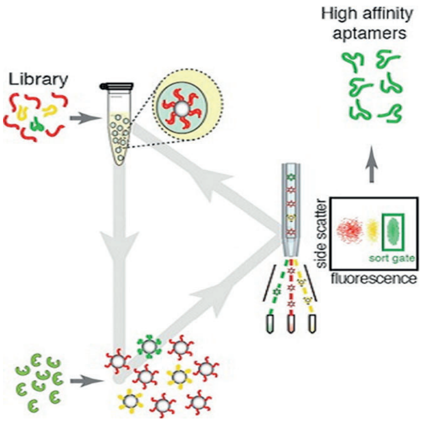
Communications

High-Throughput Aptamer Screening

J. Wang, Q. Gong, N. Maheshwari, M. Eisenstein, M. L. Arcila, K. S. Kosik, H. T. Soh* ______ 4796 – 4801

Particle Display: A Quantitative Screening Method for Generating High-Affinity Aptamers

Frontispiece

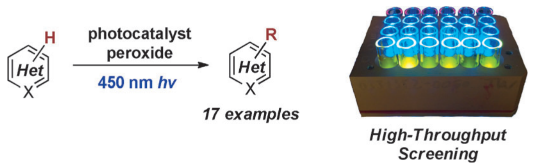


Superior aptamers can be obtained in fewer selection rounds with the particle display method than with the conventional approach. In this new method libraries of solution-phase aptamers are transformed into "aptamer particles", each displaying many copies of a single sequence on its surface. Fluorescence-activated cell sorting is then used to individually measure the relative affinities of $> 10^8$ aptamer particles and sort them in a high-throughput manner.

C–H Functionalization

D. A. DiRocco,* K. Dykstra, S. Krska, P. Vachal, D. V. Conway, M. Tudge ______ 4802 – 4806

Late-Stage Functionalization of Biologically Active Heterocycles Through Photoredox Catalysis

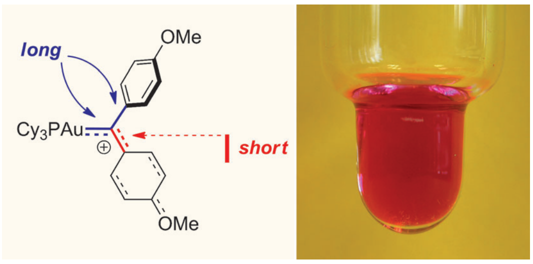


Search and find: A method has been developed for the direct methyl-, ethyl-, and cyclopropylation of biologically active heterocycles using visible-light photoredox catalysis. High-throughput experimentation was used to discover the best catalyst. The simple protocol, mild reaction conditions, and unique tolerability make this method a valuable tool for drug discovery.

Gold Carbenoids

G. Seidel, A. Fürstner* ______ 4807 – 4811

Structure of a Reactive Gold Carbenoid

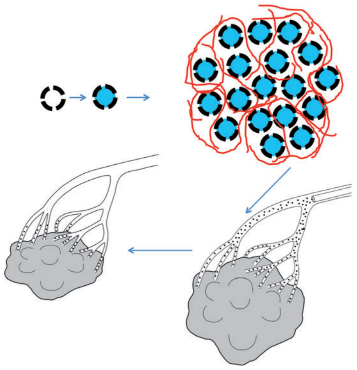


Call me "carbenoid": No signs of significant Au–C double-bond character, but many indications for charge density at carbon distinguish the structure of an only modestly "stabilized" gold carbenoid in the solid state. Because this species is capable of cyclopropanating a styrene derivative under mild conditions, its structural features are relevant for mechanistic discussions of π-acid catalysis in general.

Drug Delivery

Y.-X. J. Wang,* X.-M. Zhu, Q. Liang,
C. H. K. Cheng, W. Wang,*
K. C.-F. Leung* ______ **4812 – 4815**

In Vivo Chemoembolization and Magnetic Resonance Imaging of Liver Tumors by Using Iron Oxide Nanoshell/Doxorubicin/Poly(vinyl alcohol) Hybrid Composites



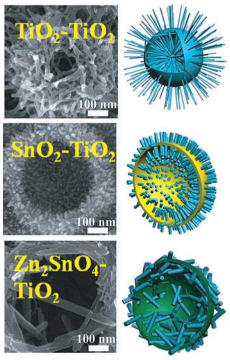
Therapeutic cut off: A hybrid composite based on superparamagnetic iron oxide nanoshells/doxorubicin/poly(vinyl alcohol) (shown in black/blue/red) was used for the in vivo embolization of liver tumor blood vessels. Disassembly of the composite followed, thereby leading to slow and sustained release of the anticancer drug. The composite was relatively noncytotoxic and was responsive to magnetic resonance imaging, thus making it a potential theranostic agent.

Solar Cells

W. Q. Wu, Y. F. Xu, H. S. Rao, H. L. Feng,
C. Y. Su, D. B. Kuang* ______ **4816 – 4821**

Constructing 3D Branched Nanowire Coated Macroporous Metal Oxide Electrodes with Homogeneous or Heterogeneous Compositions for Efficient Solar Cells

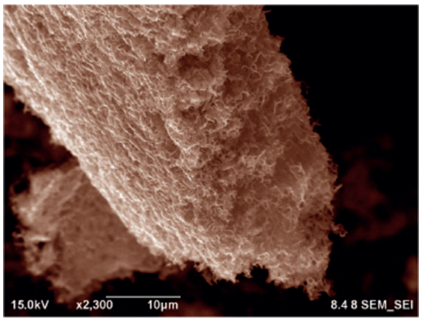
Wired for light: A versatile method allows the preparation of nanowire-coated macroporous material based homo- or heterogeneous metal oxide composite electrodes (TiO_2–TiO_2, SnO_2–TiO_2, and Zn_2SnO_4–TiO_2). Dye-sensitized solar cells based on macroporous TiO_2/TiO_2 nanowire homogeneous electrode show an impressive conversion efficiency as high as 9.51 %, which is much higher than those of pure macroporous material based photoelectrodes used up to date.



Nanoporous Graphene

Y. Ito, Y. Tanabe, H.-J. Qiu, K. Sugawara,
S. Heguri, N. H. Tu, K. K. Huynh, T. Fujita,
T. Takahashi, K. Tanigaki,
M. Chen* ______ **4822 – 4826**

High-Quality Three-Dimensional Nanoporous Graphene

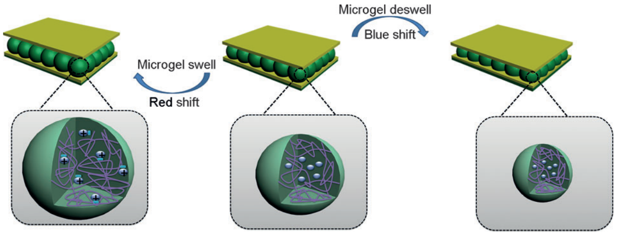


A nickel for your graphene: The title material was synthesized by chemical vapor deposition using nanoporous nickel. The 3D nanoporous graphene preserves 2D electronic properties, such as high electron mobility and massless Dirac fermions.

Smart Materials

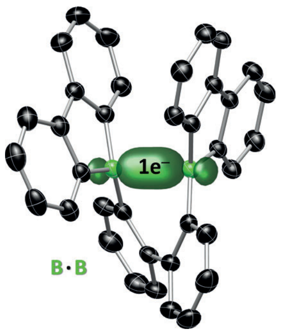
Q. Zhang, W. Xu,
M. J. Serpe* ______ **4827 – 4831**

Optical Devices Constructed from Multiresponsive Microgels



A microgel-based etalon that is capable of changing its optical properties in response to light, solutions of various pHs, and exposure to nerve agents is reported. This investigation showcases the versatility of the etalon construct, which can be made multiresponsive simply by changing the chemistry of its polymer makeup.

Bonding



One is enough: The first structurally characterized radical anion containing a B·B one-electron σ bond shows a significantly shorter B⋯B distance than the uncharged starting material, while the boron centers largely maintain their local planarity.

A. Hübner, A. M. Diehl, M. Diefenbach, B. Endeward, M. Bolte, H.-W. Lerner, M. C. Holthausen,* M. Wagner* ________ **4832 – 4835**

Confirmed by X-ray Crystallography: The B·B One-Electron σ Bond

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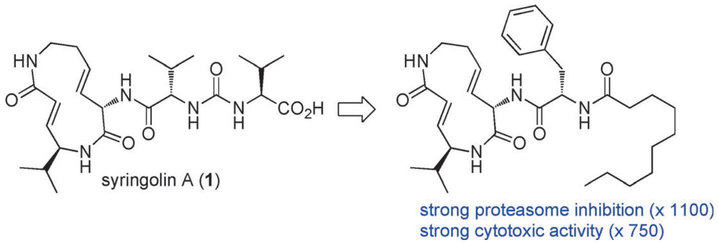
Drug Discovery



Fine-tuned activity: The total synthesis of syringolin A (**1**) was established by an intramolecular Ugi three-component reaction. To improve the moderate biological activities of **1**, analogues having strong proteasome inhibitory and cytotoxic activities comparable to clinically used bortezomib, were prepared.

T. Chiba, H. Hosono, K. Nakagawa, M. Asaka, H. Takeda, A. Matsuda, S. Ichikawa* ________ **4836 – 4839**

Total Synthesis of Syringolin A and Improvement of Its Biological Activity

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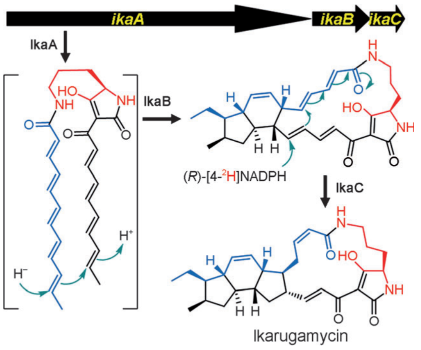
Biosynthesis



Polycycle formation: The mechanism of a five-membered-ring formation in polycyclic tetramate macrolactams (PTMs; see picture) was demonstrated by exploring the IkaC-catalyzed reductive cyclization in ikarugamycin biosynthesis, using a Michael addition-like reaction. This study suggested a general strategy for polycycle formation in PTMs.

G. Zhang, W. Zhang, Q. Zhang, T. Shi, L. Ma, Y. Zhu, S. Li, H. Zhang, Y.-L. Zhao, R. Shi, C. Zhang* ________ **4840 – 4844**

Mechanistic Insights into Polycycle Formation by Reductive Cyclization in Ikarugamycin Biosynthesis

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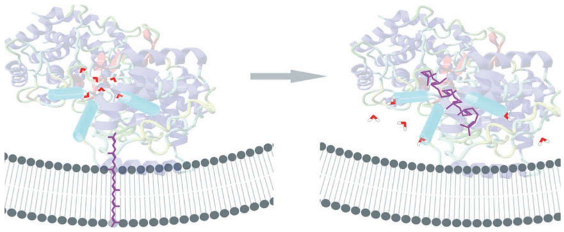
Enzyme Catalysis



Disorderly conduct: Through theoretical and experimental work with a thermophilic triterpene cyclase, it was demonstrated that entropy is key to the polycyclizations that it catalyzes. The release of water molecules (red) through specific channels allows for the prefolding of the polyisoprene substrate (purple) and thus the generation of multicyclic scaffolds by terpene cyclase enzymes.

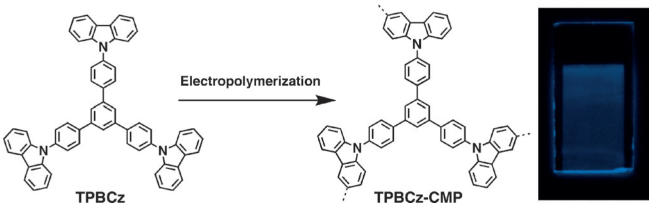
P.-O. Syrén,* S. C. Hammer, B. Claasen, B. Hauer ________ **4845 – 4849**

Entropy is Key to the Formation of Pentacyclic Terpenoids by Enzyme-Catalyzed Polycyclization

Polymer Films

C. Gu, N. Huang, J. Gao, F. Xu, Y. Xu,
D. Jiang* ________ 4850 – 4855

Controlled Synthesis of Conjugated Microporous Polymer Films: Versatile Platforms for Highly Sensitive and Label-Free Chemo- and Biosensing

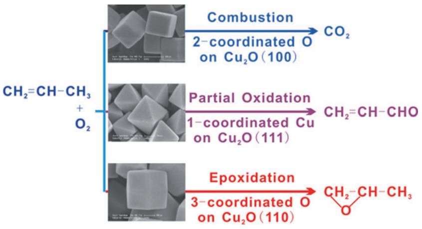


Exceptionally thin: Electropolymerization was employed for the synthesis of conjugated microporous polymer (CMP) films on substrates or as freestanding thin films. The method enables the control of the thickness, size, and shape of the CMP films, which can function as versatile platforms for highly sensitive and label-free chemo- and biosensing, featuring rapid response, excellent selectivity, and reusability.

Surface Chemistry

Q. Hua, T. Cao, X.-K. Gu, J. Lu, Z. Jiang,
X. Pan, L. Luo, W.-X. Li,
W. Huang* ________ 4856 – 4861

Crystal-Plane-Controlled Selectivity of Cu_2O Catalysts in Propylene Oxidation with Molecular Oxygen

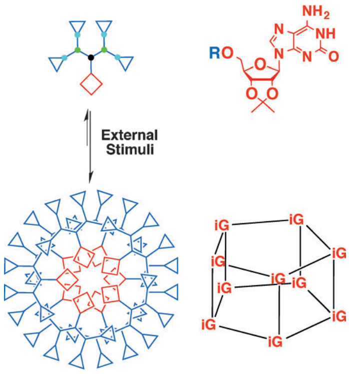


Just plane favoritism: In the catalysis of propylene oxidation with O_2 to acrolein, propylene oxide, and CO_2, Cu_2O octahedra with exposed {111} crystal planes favored the formation of acrolein, Cu_2O cubes with exposed {100} crystal planes gave CO_2 preferentially, and Cu_2O rhombic dodecahedra with exposed {110} crystal planes gave a higher proportion of propylene oxide. The active sites for these reactions were identified as indicated in the scheme.

Supramolecular Chemistry

V. Abet, R. Evans, F. Guibbal, S. Caldarelli,
R. Rodriguez* ________ 4862 – 4866

Modular Construction of Dynamic Nucleodendrimers

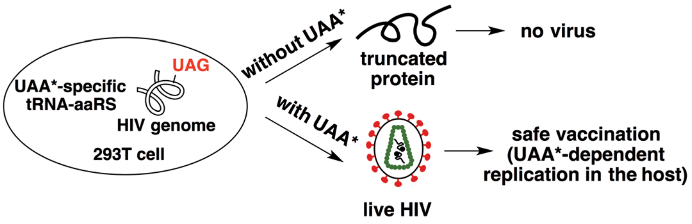


Dendritic macromolecules: Isoguanosine-containing dendritic small molecules self-assemble into isoguanosine-containing dendrimers named nucleodendrimers (see picture). The building blocks alone form pentameric structures while the presence of alkali metals promotes the formation of stable decamers. This system provides a powerful canvas for the rapid and modular assembly of polyfunctional dendritic macromolecules.

Vaccine Engineering

N. Wang, Y. Li, W. Niu, M. Sun, R. Cerny,
Q. Li,* J. Guo* ________ 4867 – 4871

Construction of a Live-Attenuated HIV-1 Vaccine through Genetic Code Expansion

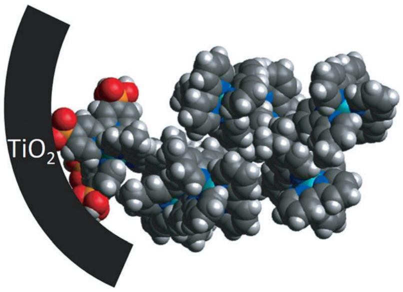


Combat against AIDS: A novel unnatural amino acid (UAA*)-mediated amber codon (UAG) suppression strategy was used to precisely control HIV-1 viability in vitro (see picture). The resulting live-attenuated virus can be potentially used as HIV-1 vaccine.

Oligomer Growth

Z. Fang, S. Keinan, L. Alibabaei, H. Luo, A. Ito, T. J. Meyer* ——— **4872–4876**

Controlled Electropolymerization of Ruthenium(II) Vinylbipyridyl Complexes in Mesoporous Nanoparticle Films of TiO_2



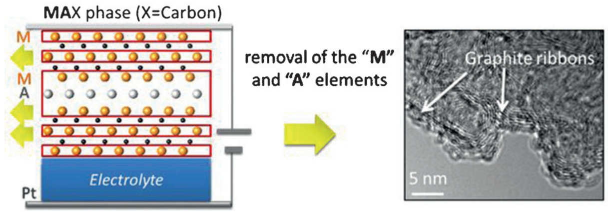
Growth on the surface: Ruthenium(II) vinylpolypyridyl assemblies within the cavities of mesoporous nanoparticle TiO_2 films have been grown from the surface by stepwise, electrochemically controlled radical polymerization. This polymerization was monitored by cyclic voltammetry as well as UV/Vis and X-ray photoelectron spectroscopy.

Inside Back Cover

Carbon

M. R. Lukatskaya, J. Halim, B. Dyatkin, M. Naguib, Y. S. Buranova, M. W. Barsoum, Y. Gogotsi* **4877–4880**

Room-Temperature Carbide-Derived Carbon Synthesis by Electrochemical Etching of MAX Phases



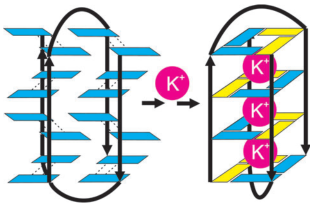
A mild route to carbon: The formation of carbide-derived carbons (CDCs) by electrochemically induced extraction of metal atoms from ternary carbides at room temperature is demonstrated. This approach eschews high temperatures or the use of chlorine gas and allows for the formation of carbon films with quite narrow pore size distributions.

Inside Cover

Oligonucleotides

S. Čeru, P. Šket, I. Prislan, J. Lah,* J. Plavec* ——— **4881–4884**

A New Pathway of DNA G-Quadruplex Formation



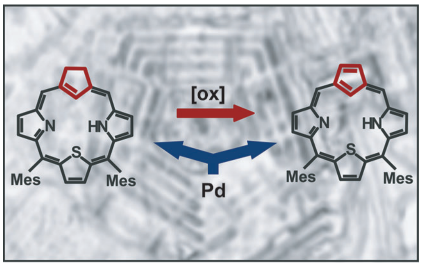
A new folding intermediate of Oxytricha nova telomeric Oxy-1.5 G-quadruplex was characterized in aqueous solution, where all guanine bases are involved in GG N1-carbonyl symmetric base pairs. G-rich DNA sequences can self-assemble into specific pre-organized DNA structures that are predisposed to fold into G-quadruplexes in the presence of cations such as potassium ions (see picture).

Front Cover

Carbaporphyrinoids

A. Berlicka, P. Dutka, L. Szterenberg, L. Latos-Grażyński* ——— **4885–4889**

Towards True Carbaporphyrinoids: Synthesis of 21-Carba-23-thiaporphyrin



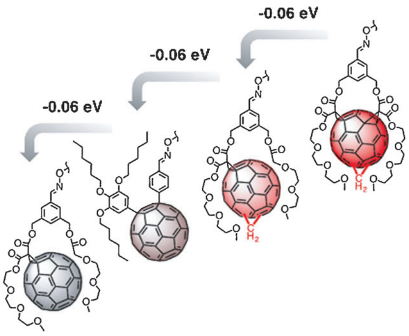
A carbon pentagon in heteroporphyrin: The synthesis of a 21-carbathiachlorin followed by oxidation allowed construction of a 21-carbathiaporphyrin, a meso-substituted true carbaporphyrin with an unsubstituted cyclopentadienyl moiety (Mes = mesityl). Both carbathiaporphyrinoids act as aromatic cyclic ligands, as shown by their coordination to Pd^{2+} ions through their C, N, S donor atoms in the porphyrinic core.

Back Cover

Supramolecular Chemistry

A. Bolag, J. López-Andarias, S. Lascano, S. Soleimanpour, C. Atienza, N. Sakai, N. Martín,* S. Matile* **4890–4895**

A Collection of Fullerenes for Synthetic Access Toward Oriented Charge-Transfer Cascades in Triple-Channel Photosystems

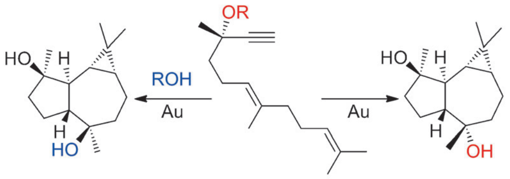


Stacked up: With molecular-level precision, 1,4-diaryl-, methano-, and Bingel fullerenes are engineered into multicomponent architectures by surface-initiated ring-opening disulfide exchange polymerization and templated stack exchange with orthogonal dynamic covalent hydrazone chemistry (see scheme). The results validate the concept of building triple-channel photosystems with oriented strings of fullerenes for directional electron transport.

Natural Product Synthesis

J. Carreras, M. Livendahl, P. R. McGonigal, A. M. Echavarren* **4896–4899**

Gold(I) as an Artificial Cyclase: Short Stereodivergent Syntheses of (−)-Epiglobulol and (−)-4β,7α- and (−)-4α,7α-Aromadendranediols



Aromasynthesis: Aromadendrane sesquiterpenes (−)-epiglobulol, (−)-4α,7α-aromadendranediol, and (−)-4β,7α-aromadendranediol are synthesized in only seven steps from (*E*,*E*)-farnesol by a stereodivergent gold(I)-catalyzed cascade reaction.

DOI: 10.1002/anie.201401127

Flashback: 50 Years Ago …

Anabolic agents and ovulation control are just two uses of non-aromatic 19-norsteroids, which were discussed in a Review by T. B. Windholz and M. Windholz, who outlined total syntheses, aromatization, and intramolecular functionalization reactions.

M. Schlosser continued his series of Reviews on organosodium and organopotassium compounds, and in this issue he discussed the preparation and synthetic applications of these species.

R. W. Hoffmann and H. Häuser reported on the synthesis and cycloaddition reactions of tetramethoxyethylene. This compound is formed by the decomposition of bicyclo[2.2.1]heptadiene derivatives and reacts with compounds containing double bonds to form carbocyclic or heterocyclic four-membered rings. Hoffmann's Essay on the changes in natural product synthesis over time was published in the 125th Jubilee Issue (*Angew. Chem. Int. Ed.* **2013**, *52*, 123).

D. Söll and H. G. Khorana reported on the synthesis of ribodinucleotides with 3'-phosphate end groups in a procedure that avoids the use of an acid-labile protecting group. The target compounds can be polymerized to form ribopolynucleotides. Söll's report on recoding the genetic code with selenocysteine was recently featured on the cover of *Angewandte Chemie* (*Angew. Chem. Int. Ed.* **2014**, *53*, 319–323).

A. Engelbrecht and F. Sladky described the reaction of $BaTeO_4$ and HSO_3F, which they expected to form TeO_2F_2 but instead produced pentafluoro-orthotelluric acid ($HTeOF_5$). The product was a glassy crystalline solid with a melting point of 40 °C and its stability was attributed to Te^{VI} having an octahedral configuration.

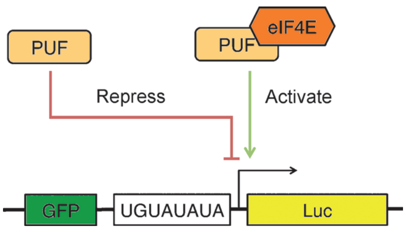
Read more in Issue 5/1964.

Gene Expression

J. Cao, M. Arha, C. Sudrik, D. V. Schaffer,*
R. S. Kane* ______ 4900 – 4904

Bidirectional Regulation of mRNA Translation in Mammalian Cells by Using PUF Domains

One way or another: A genetically encoded system based on the RNA binding domain of PUF proteins was developed for the posttranscriptional regulation of gene expression. The PUF domain was used to tether a translational activation domain (eIF4E) to enhance translation. Alternatively, the PUF domain alone could be used to repress translation. The expression of a reporter could be varied by over 17-fold by using PUF-based activators and repressors.



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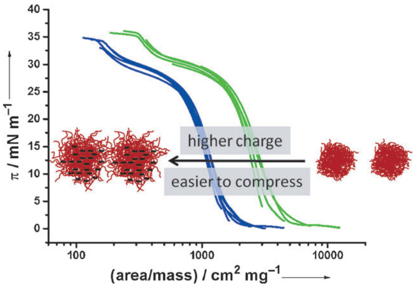
pH-Sensitive Microgels

K. Geisel, L. Isa,
W. Richtering* ______ 4905 – 4909

The Compressibility of pH-Sensitive Microgels at the Oil–Water Interface: Higher Charge Leads to Less Repulsion

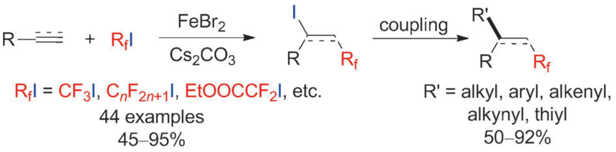


More charge—less repulsion: The influence of electrostatic interactions on microgel-stabilized emulsions has been investigated on flat interfaces. The compressibility of charged microgels was found to be greater than for uncharged microgels, as the former start interacting effectively at a higher microgel density at the interface.

Synthetic Methods

T. Xu, C. W. Cheung,
X. L. Hu* ______ 4910 – 4914

Iron-Catalyzed 1,2-Addition of Perfluoroalkyl Iodides to Alkynes and Alkenes

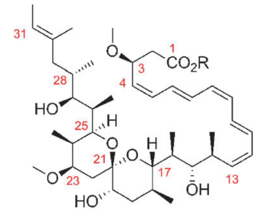


An iron protocol: General and tolerant iron catalysis has been developed for the intermolecular 1,2-addition of perfluoroalkyl iodides to alkynes and alkenes. The resulting perfluoroalkylated alkyl and alkenyl iodides can be further functionalized by cross-coupling reactions.

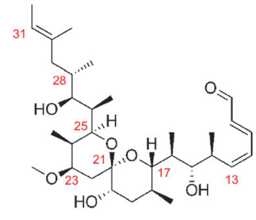
Natural Product Synthesis

S. Newton, C. F. Carter, C. M. Pearson, L. de C. Alves, H. Lange, P. Thansandote, S. V. Ley* ______ 4915 – 4920

Accelerating Spirocyclic Polyketide Synthesis using Flow Chemistry



spirangien A: R = H
spirangien A methyl ester: R = Me



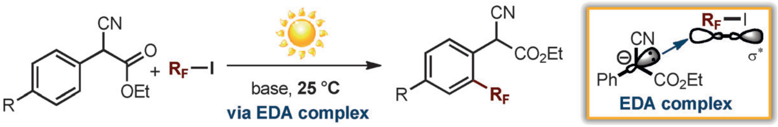
spirodienal A

Rise of the machines: The syntheses of two spirocyclic polyketides, spirangien A methyl ester and spirodienal A, are described. This machine-assisted approach extends the application of flow chemistry to complex natural product synthesis and includes several flow-through processes of transformations commonly encountered in total synthesis.

Photochemical Perfluoroalkylation

M. Nappi, G. Bergonzini,
P. Melchiorre* ____________ **4921 – 4925**

Metal-Free Photochemical Aromatic Perfluoroalkylation of α-Cyano Arylacetates

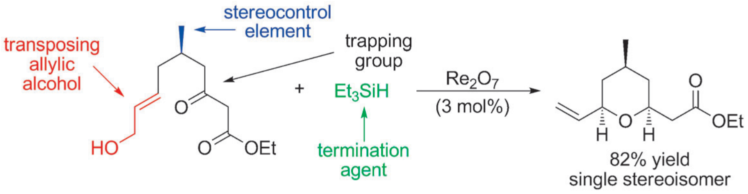


Shining light: An operationally simple protocol for the direct aromatic perfluoroalkylation and trifluoromethylation of α-cyano arylacetates requires the irradiation by visible light at ambient temperature. This metal-free reaction is driven by the photochemical activity of electron donor–acceptor (EDA) complexes, formed in situ by the interaction of transiently generated enolates and perfluoroalkyl iodides.

Synthetic Methods

Y. Xie, P. E. Floreancig* ____ **4926 – 4929**

Heterocycle Synthesis Based on Allylic Alcohol Transposition Using Traceless Trapping Groups

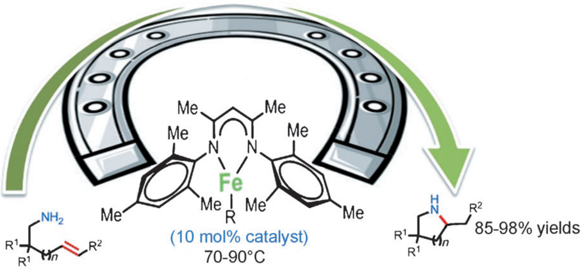


Without a trace: Allylic alcohols transpose in the presence of Re_2O_7 and are trapped by aldehydes or ketones to form hemiacetals. Additional ionization yields oxocarbenium ions, which can be quenched through bimolecular reactions with nucleophiles to provide heterocycles with no trace of the initial trapping group. This method allows stereocontrol in the absence of chiral reagents and without recourse to protecting or leaving groups.

Iron Catalysis

E. Bernoud, P. Oulié, R. Guillot,
M. Mellah,
J. Hannedouche* ___________ **4930 – 4934**

Well-Defined Four-Coordinate Iron(II) Complexes For Intramolecular Hydroamination of Primary Aliphatic Alkenylamines

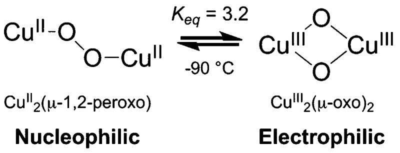


Iron horseshoe: A well-defined four-coordinate β-diketiminatoiron(II) alkyl complex is a precatalyst for the highly selective cyclohydroamination of primary aliphatic alkenylamines at mild temperatures. Its mechanism is also elucidated.

Cu_2O_2 Equilibrium

M. T. Kieber-Emmons, J. W. Ginsbach,
P. K. Wick, H. R. Lucas, M. E. Helton,
B. Lucchese, M. Suzuki,
A. D. Zuberbühler, K. D. Karlin,*
E. I. Solomon* ____________ **4935 – 4939**

Observation of a Cu^{II}_2(μ-1,2-peroxo)/Cu^{III}_2(μ-oxo)$_2$ Equilibrium and its Implications for Copper–Dioxygen Reactivity

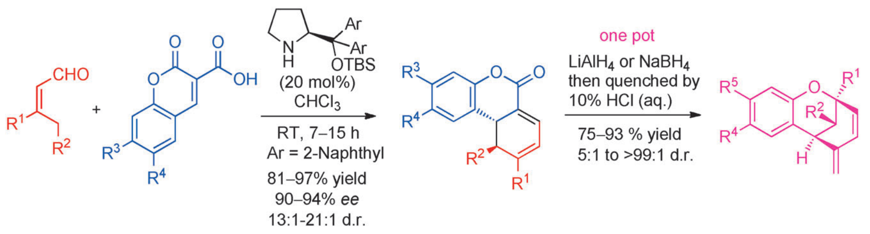


A copper system has been uncovered in which an end-on peroxo [$Cu_2(O_2)$] core is in equilibrium with a bis-μ-oxo [$Cu_2(O)_2$] core. Calibration of computational methods to experimental thermodynamic results suggest that the electrophilic reactivity patterns recently attributed to an end-on-peroxo Cu^{II}_2 species are, in fact, likely a result of an accessible bis-μ-oxo Cu^{III}_2 core, a structural type long associated with electrophilic reactivity.

Synthetic Methods

A.-G. Song, X.-S. Zhang, X.-X. Song, X.-B. Chen, C.-G. Yu, H. Huang, H. Li,* W. Wang* ________ **4940 – 4944**

Construction of Chiral Bridged Tricyclic Benzopyrans: Enantioselective Catalytic Diels–Alder Reaction and a One-Pot Reduction/Acid-Catalyzed Stereoselective Cyclization

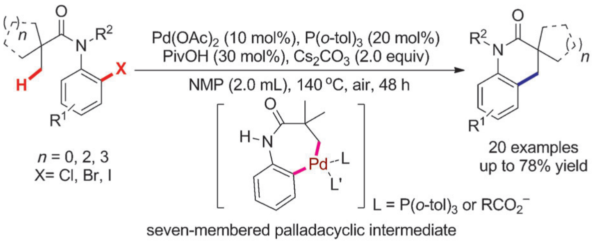


The old one-two: A two-step synthetic strategy was developed for the construction of the bridged benzopyran core present in many natural products. It consisted of an efficient asymmetric catalytic decarboxylative Diels–Alder reaction between enals and coumarin-3-carboxylic acids, and a one-pot protocol for the reduction/acid-catalyzed stereoselective cyclization. TBS = *tert*-butyldimethylsilyl.

C(sp^3)–H Activation

J.-X. Yan, H. Li, X.-W. Liu, J.-L. Shi, X. Wang, Z.-J. Shi* ________ **4945 – 4949**

Palladium-Catalyzed C(sp^3)–H Activation: A Facile Method for the Synthesis of 3,4-Dihydroquinolinone Derivatives

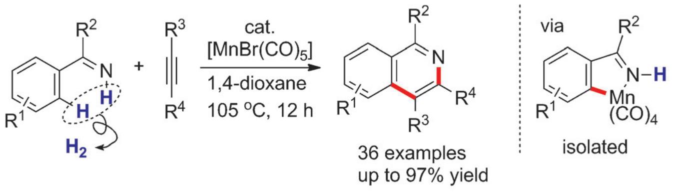


3,4-Dihydroquinolinones were synthesized by the palladium-catalyzed, oxidative-addition-initiated activation and arylation of inert C(sp^3)–H bonds. Pd(OAc)$_2$ and P(*o*-tol)$_3$ were used as the catalyst and ligand, respectively, to improve the efficiency of the reaction. A further advantage of this reaction is that it could be performed in air.

Heterocycles

R. He, Z.-T. Huang, Q.-Y. Zheng, C. Wang* ________ **4950 – 4953**

Manganese-Catalyzed Dehydrogenative [4+2] Annulation of N–H Imines and Alkynes by C–H/N–H Activation

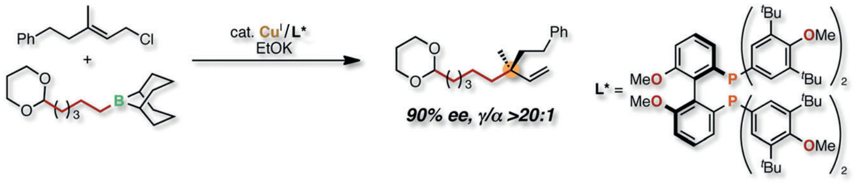


Hidden talents: The ability of manganese(I) to catalytically induce C–H and N–H bond cleavage, and C–C and C–N bond formation, has been recognized using the title reaction. The reaction produces H$_2$ as the major by-product and eliminates the need for any oxidants, external ligands, or additives, and thus tolerating a wide range of functionalities.

Asymmetric Catalysis

K. Hojoh, Y. Shido, H. Ohmiya,* M. Sawamura* ________ **4954 – 4958**

Construction of Quaternary Stereogenic Carbon Centers through Copper-Catalyzed Enantioselective Allylic Cross-Coupling with Alkylboranes

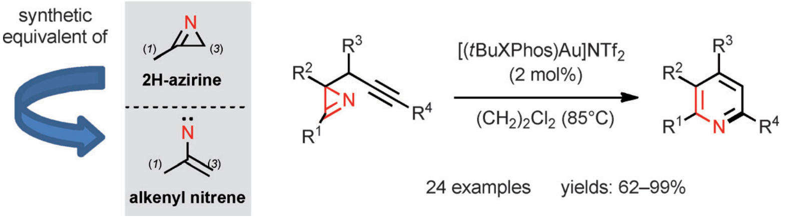


The S$_N$2′-type: A combination of a chiral Cu^I/**L*** catalyst system and EtOK enabled the enantioselective S$_N$2′-type allylic cross-coupling between alkylboranes and γ,γ-disubstituted primary allyl chlorides. The reaction generates quaternary carbon stereogenic centers bearing three sp^3-alkyl groups and a vinyl group. A reaction pathway involving addition/elimination of a neutral alkylcopper(I) species is proposed.

Heterocycles

A. Prechter, G. Henrion, P. Faudot dit Bel, F. Gagosz* ———— **4959 – 4963**

Gold-Catalyzed Synthesis of Functionalized Pyridines by Using 2*H*-Azirines as Synthetic Equivalents of Alkenyl Nitrenes

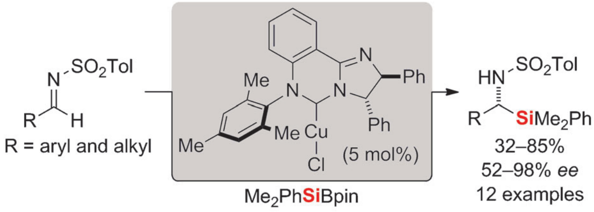


Ringing the changes: A series of easily accessible 2-propargyl 2*H*-azirine derivatives were efficiently converted into the corresponding functionalized pyridines in the presence of a gold catalyst. This transformation, which exhibits a high functional-group tolerance and a wide substrate scope, corresponds to the formal intramolecular transfer of an alkenyl nitrene to an alkyne.

Asymmetric 1,2-Addition

A. Hensel, K. Nagura, L. B. Delvos, M. Oestreich* ———— **4964 – 4967**

Enantioselective Addition of Silicon Nucleophiles to Aldimines Using a Preformed NHC–Copper(I) Complex as the Catalyst



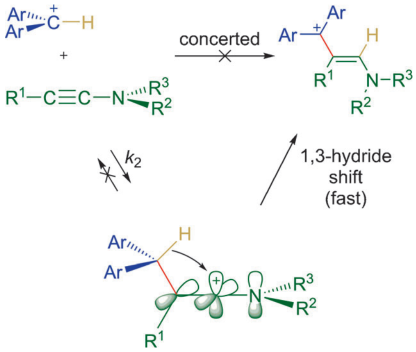
The final chapter: The enantioselective addition of silicon nucleophiles to typical prochiral acceptors is now well-established methodology, except for the 1,2-addition to imines. McQuade's chiral NHC–copper(I) complex catalyzes this elusive transformation with high asymmetric induction, finally allowing for the catalyst-controlled preparation of α-silylated amines from aldimines (see scheme).

Synthetic Methods

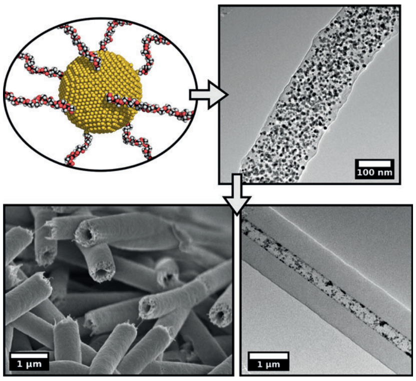
H. A. Laub, G. Evano, H. Mayr* ———— **4968 – 4971**

Hydrocarbation of C≡C Bonds: Quantification of the Nucleophilic Reactivity of Ynamides

Carbenium ions are isoelectronic with boranes, but hydrocarbations analogous to hydroborations usually do not occur. The hydrocarbation of ynamides with benzhydrylium ions and the difference to hydroborations are discussed. Furthermore, kinetic studies allowed the inclusion of ynamides in the comprehensive benzhydrylium-based nucleophilicity scale.



Nanoreactors



Gold-containing polymer nanotubes were prepared by the "tubes by fiber templates" (TUFT) process. For this purpose, electrospun polymer nanofibers with incorporated gold nanoparticles were coated with poly(*p*-xylylene) by chemical vapor deposition and then the inner fiber templates were removed. The resulting tubes, which were utilized as a reusable tea-bag-like catalyst, showed pronounced catalytic activity and resistance to leaching.

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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