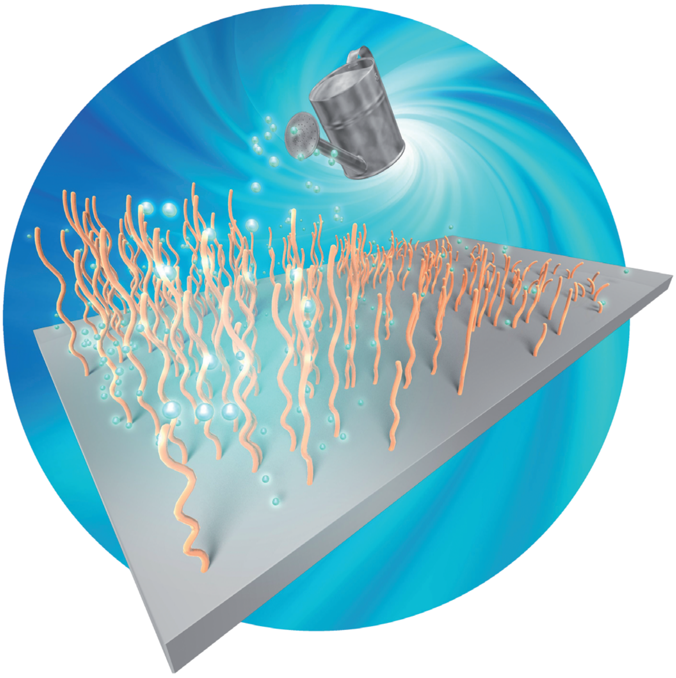
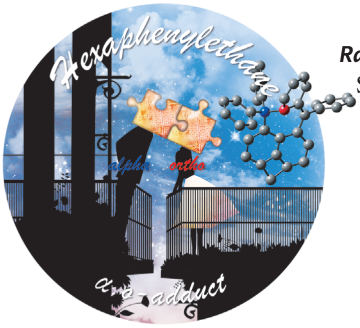
Gradient growth ...



… of poly(NIPAM) brushes from an initiator-modified substrate surface was achieved by electrochemically mediated atom-transfer radical polymerization (eATRP). In their Communication on page 3922 ff., S. Inagi et al. show that setting the surface close to a bipolar electrode results in a potential gradient, which leads to a concentration gradient of the Cu^I polymerization catalyst on the substrate. The polymer brushes could be fabricated in three-dimensional gradient shapes with control over thickness, steepness, and modified area.

Quantum Dots

The self-protection of semiconductor quantum dots against oxidation by transient escape into the Auger recombination cycle is reported by V. Biju et al. in their Communication on page 3892 ff.



Radicals

Since the discovery of triphenylmethyl by Gomberg in 1900, its dimerization has been extensively studied. In their Communication on page 4010 ff., T. Suzuki et al. report the generation of the α,*o*-adduct for the first time.

Radical Reactions

In their Communication on page 4041 ff., B. Tan, X.-Y. Liu, and co-workers realize the first phosphine-catalyzed radical tandem route for the concomitant functionalization of an alkene and the remote β-C(sp^3)-H bond of amine derivatives.

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Author Profile

“My favorite saying is ‘Curiosity makes us young’. My favorite drink is green tea from Japan, Taiwan, or China …”
This and more about Tamio Hayashi can be found on page 3854.

Books

Highlights

Crystal Growth

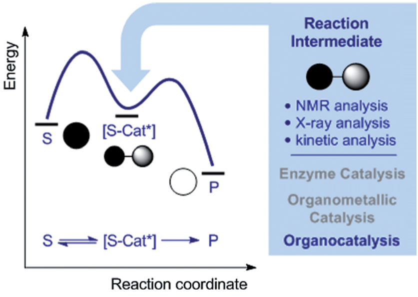
Learning from classics: Crystal growth is a complex process, and there are multiple paths for going from dissolved ions to solid crystals. Highlighted herein is the application of traditional chemistry concepts to new ways for increasing the complexity of nanocrystals while maintaining a high degree of symmetry.

Minireviews

Organocatalysis

M. C. Holland, R. Gilmour* **3862 – 3871**

Deconstructing Covalent Organocatalysis



In recent years, interest in organocatalytic intermediates has intensified. Through their study, various mechanistic anomalies have been illuminated, new reaction manifolds have been identified, and the intermediates themselves have proven to be valuable platforms for the study of many noncovalent interactions more commonly found in complex biomolecules. Cat = catalyst, P = product, S = substrate.

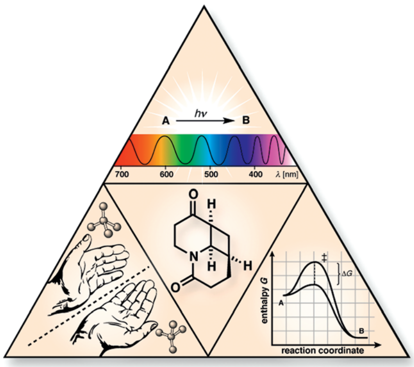
Reviews

Enantioselective Photocatalysis

R. Brimioulle, D. Lenhart, M. M. Maturi, T. Bach* **3872 – 3890**

Enantioselective Catalysis of Photochemical Reactions

All good things come in threes: With catalysis, light, and chirality, three of the most important scientific phenomena merge in the field of the enantioselective catalysis of photochemical reactions. This Review introduces the main concepts and provides an overview of the key findings in this area.



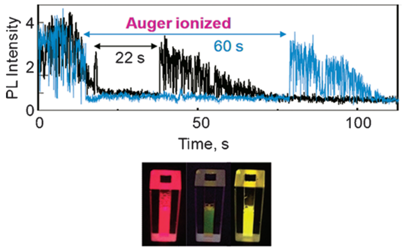
Communications

Photochemistry

S. Yamashita, M. Hamada, S. Nakanishi, H. Saito, Y. Nosaka, S. Wakida, V. Biju* **3892 – 3896**

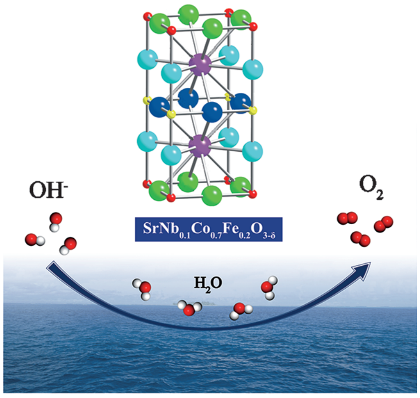
Auger Ionization Beats Photo-Oxidation of Semiconductor Quantum Dots: Extended Stability of Single-Molecule Photoluminescence

Preventing oxidation: Single semiconductor quantum dots escape from photoluminescence (PL; see picture) loss, which is due to the self-sensitized oxidation by singlet oxygen, by the transient escape into the Auger-ionized state. The ultrafast nonradiative recombination processes of carriers in the trion state of such quantum dots shut down the energy transfer pathway to molecular oxygen.



Frontispiece

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.



The perovskite $SrNb_{0.1}Co_{0.7}Fe_{0.2}O_{3-\delta}$ shows remarkable activity and stability as an electrocatalyst for the oxygen evolution reaction in alkaline solutions. This catalyst has a smaller Tafel slope and better stability than the state-of-the-art precious-metal IrO_2 catalyst and the well-known BSCF perovskite. The mass activity and stability are further improved by ball milling. Sr purple, Co(Fe,Nb) red/yellow, O green/pale and dark blue.

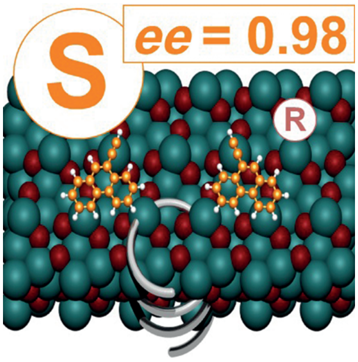
Electrocatalysis

Y. L. Zhu, W. Zhou, Z. G. Chen, Y. B. Chen, C. Su, M. O. Tadé, Z. P. Shao* ———— **3897 – 3901**

$SrNb_{0.1}Co_{0.7}Fe_{0.2}O_{3-\delta}$ Perovskite as a Next-Generation Electrocatalyst for Oxygen Evolution in Alkaline Solution

---

Intermetallic compounds as chiral templates: PdGa has a chiral crystal structure. Adsorption of prochiral molecules on single-crystal surfaces leads to the formation of only one of the two possible enantiomeric complexes at room temperature. This proof-of-principle is highly promising for applications of chiral intermetallics as stable and enantioselective catalytic materials.



Interactions on Surfaces

J. Prinz, O. Gröning, H. Brune, R. Widmer* ———— **3902 – 3906**

Highly Enantioselective Adsorption of Small Prochiral Molecules on a Chiral Intermetallic Compound

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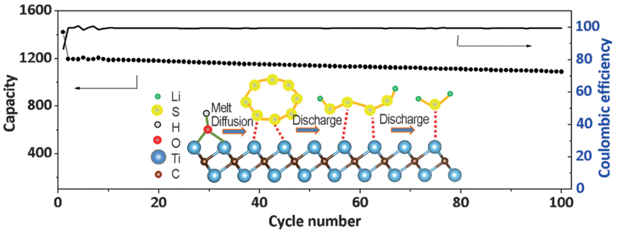

Efficient energy storage: 2D early transition-metal carbide MXene phases performed as excellent sulfur battery hosts. Sulfur–titanium carbide composites with a sulfur content of 70 wt% showed stable cycling performance because of strong interactions of the polysulfide species with the surface Ti atoms.

Electrochemistry

X. Liang, A. Garsuch, L. F. Nazar* ———— **3907 – 3911**

Sulfur Cathodes Based on Conductive MXene Nanosheets for High-Performance Lithium–Sulfur Batteries

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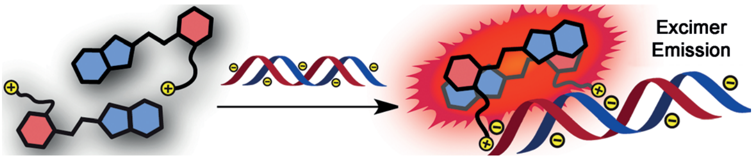


Let there be light: Cyanovinylene-based dyes form red-emitting excimers that surpass pyrene excimers as optical reporters of proximity. The application of a cationic derivative to the label-free detection of DNA and as a staining agent for DNA in gel electrophoresis is demonstrated.

Chromophores

G. Han, D. Kim, Y. Park, J. Bouffard,* Y. Kim* ———— **3912 – 3916**

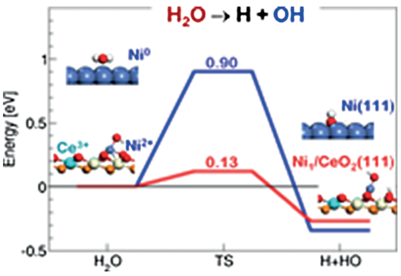
Excimers Beyond Pyrene: A Far-Red Optical Proximity Reporter and its Application to the Label-Free Detection of DNA

Metal–Support Interactions

J. Carrasco, D. López-Durán, Z. Liu, T. Duchoň, J. Evans, S. D. Senanayake, E. J. Crumlin, V. Matolín, J. A. Rodríguez,* M. V. Ganduglia-Pirovano* _ **3917 – 3921**

In Situ and Theoretical Studies for the Dissociation of Water on an Active Ni/CeO$_2$ Catalyst: Importance of Strong Metal–Support Interactions for the Cleavage of O–H Bonds

By accommodating electrons in localized f-states, ceria stabilizes Ni^{2+} species that possess unique activity for the cleavage of O—H bonds. These species play an important role in the water-gas shift reaction and the steam reforming of alcohols over Ni/CeO$_2$ catalysts.



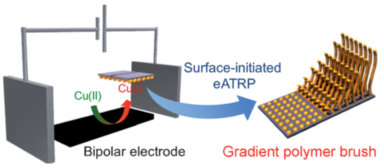
Electrochemistry

N. Shida, Y. Koizumi, H. Nishiyama, I. Tomita, S. Inagi* ________ **3922 – 3926**

Electrochemically Mediated Atom Transfer Radical Polymerization from a Substrate Surface Manipulated by Bipolar Electrolysis: Fabrication of Gradient and Patterned Polymer Brushes

Front Cover

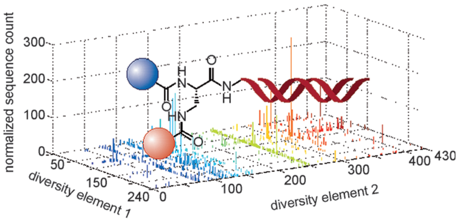
A potential gradient generated on a bipolar electrode allowed the formation of a concentration gradient of a Cu^{I} polymerization catalyst through the one-electron reduction of Cu^{II}, resulting in the gradient growth of polymer brushes from an initiator-modified substrate surface set close to a bipolar electrode. These polymer brushes could be fabricated in three-dimensional gradient shapes with control over thickness, steepness, and modified area.



Encoded Libraries

R. M. Franzini, T. Ekblad, N. Zhong, M. Wichert, W. Decurtins, A. Nauer, M. Zimmermann, F. Samain, J. Scheuermann, P. J. Brown, J. Hall, S. Gräslund, H. Schüler, D. Neri* ______________ **3927 – 3931**

Identification of Structure–Activity Relationships from Screening a Structurally Compact DNA-Encoded Chemical Library



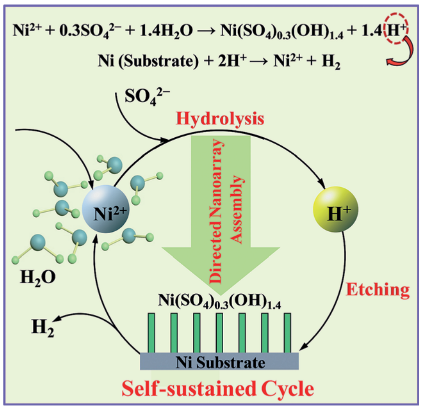
Panning for protein binders: A novel DNA-encoded chemical library enabled the rapid discovery of structurally compact hit compounds for varied proteins. Library screening provided nanomolar small-molecule ligands for several target proteins and information on structural features important for binding.

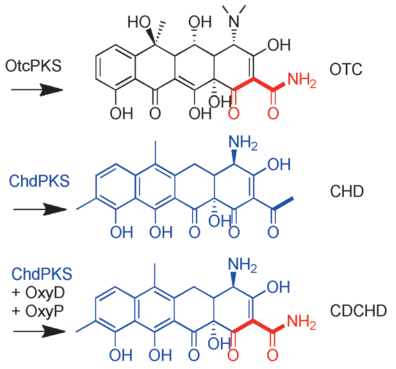
Lithium-Ion Batteries

Y. M. Zhang, W. X. Zhang,* Z. H. Yang, H. Y. Gu, Q. Zhu, S. H. Yang,* M. Li ______________ **3932 – 3936**

Self-Sustained Cycle of Hydrolysis and Etching at Solution/Solid Interfaces: A General Strategy To Prepare Metal Oxide Micro-/Nanostructured Arrays for High-Performance Electrodes

Electrode materials: A general self-sustained cycle of hydrolysis and etching (SCHE) has been exploited to synthesize an extensive series of metal oxide arrays on a wide range of metal substrates. The SCHE strategy offers a systematic approach to design metal oxide micro-/nanostructured arrays on metal substrates, which are valuable not only for lithium-ion batteries but also for other energy conversion and storage systems.



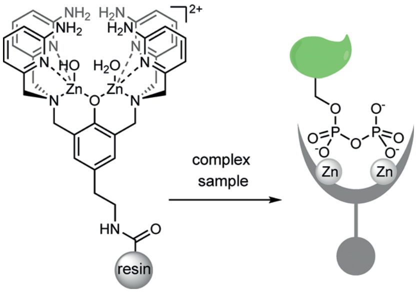


Mix and match: The carboxamido moiety of tetracyclines is important for their bioactivity. Through rational biosynthetic engineering, biosynthesis genes (OxyD, OxyP) from the oxytetracycline (OTC) polyketide synthase (PKS) from *Streptomyces rimosus* were expressed in *Amycolatopsis sulphurea*, a producer of the atypical tetracycline chelocardin (CHD). The resulting CHD analogue (CDCHD) was produced in high yield and exibits greatly improved antibacterial activity.

Combinatorial Biosynthesis

U. Lešnik, T. Lukežič, A. Podgoršek, J. Horvat, T. Polak, M. Šala, B. Jenko, K. Harmrolfs, A. Ocampo-Sosa, L. Martínez-Martínez, P. R. Herron, Š. Fujs, G. Kosec, I. S. Hunter, R. Müller,* H. Petković* ———— **3937 – 3940**

Construction of a New Class of Tetracycline Lead Structures with Potent Antibacterial Activity through Biosynthetic Engineering



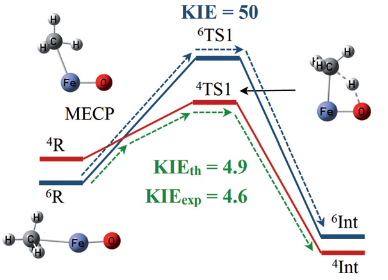
It's a trap: A resin-bound dinuclear zinc(II) complex for the selective capture of pyrophosphopeptides (green) is reported. The metal complex binds diphosphate esters over other anionic groups with high specificity. This results in an affinity reagent capable of binding and retaining nanomolar quantities of pyrophosphopeptide from cell lysates.

Proteomics

J. H. Conway, D. Fiedler* —— **3941 – 3945**

An Affinity Reagent for the Recognition of Pyrophosphorylated Peptides

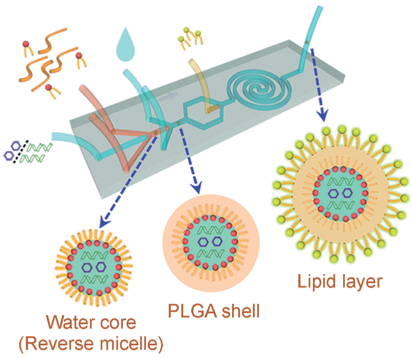
A direct dynamics approach was used to generate potential energy surfaces of the sextet and quartet H-transfers for transition-metal–oxo reagents. Variational transition-state-theory rate constants and kinetic isotope effects including multidimensional tunneling revealed that the reaction proceeds from the sextet reactant to quartet transition state with a spin crossover along the intrinsic reaction paths.



Spin Crossover

B. K. Mai, Y. Kim* ———— **3946 – 3951**

The Kinetic Isotope Effect as a Probe of Spin Crossover in the C–H Activation of Methane by the FeO^+ Cation



Nanocarriers made easy: A multistage microfluidic chip is adopted for the one-step synthesis of water core/PLGA shell/lipid layer rigid nanovesicles (RNVs) and effective entrapment of various kinds of hydrophilic reagents. An enhanced antitumor effect is observed by co-delivering siMDR1 and Dox using RNVs in both in vitro and in vivo experiments.

Nanocarriers

L. Zhang, Q. Feng, J. Wang, J. Sun,* X. Shi, X. Jiang* ———— **3952 – 3956**

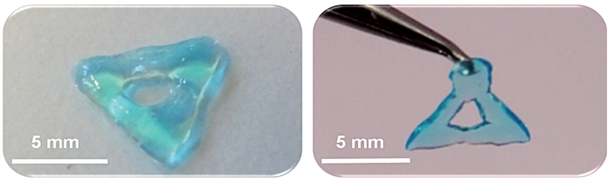
Microfluidic Synthesis of Rigid Nanovesicles for Hydrophilic Reagents Delivery

Inside Cover

Biofabrication

C. Li, A. Faulkner-Jones, A. R. Dun, J. Jin, P. Chen, Y. Xing, Z. Yang, Z. Li, W. Shu,* D. Liu,* R. R. Duncan ______ **3957 – 3961**

Rapid Formation of a Supramolecular Polypeptide–DNA Hydrogel for In Situ Three-Dimensional Multilayer Bioprinting

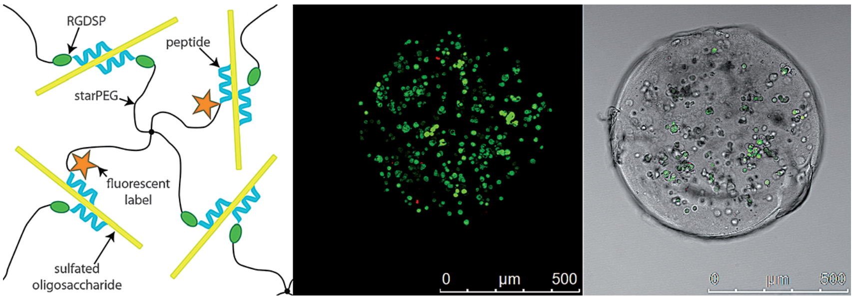


Printed DNA hydrogel: The rapid formation of a supramolecular polypeptide–DNA hydrogel with self-healing properties and a high mechanical strength is described. The hydrogel was used for in situ multilayer three-dimensional bioprinting and cell printing, which produced structures that contain living cells with normal cellular functions, and is fully biodegradable by proteases or nucleases.

Cell Encapsulation

R. Wieduwild, S. Krishnan, K. Chwalek, A. Boden, M. Nowak, D. Drechsel, C. Werner,* Y. Zhang* ______ **3962 – 3966**

Noncovalent Hydrogel Beads as Microcarriers for Cell Culture

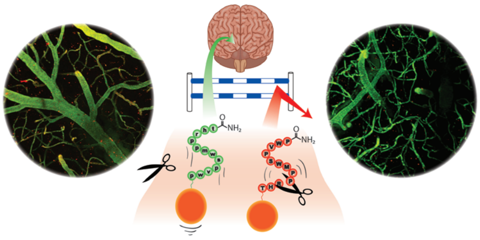


Cells in beads: Monodisperse noncovalent hydrogel beads are obtained from peptide–poly(ethylene glycol) conjugates and oligosaccharides under very mild and cell-compatible conditions. Cells can be encapsulated in the beads with high survival rate. They can be attached onto the beads surface specifically depending on the peptide sequence and function as a protein production system.

Peptides

R. Prades, B. Oller-Salvia, S. M. Schwarzmaier, J. Selva, M. Moros, M. Balbi, V. Grazú, J. M. de La Fuente, G. Egea, N. Plesnila, M. Teixidó,* E. Giralt* ______ **3967 – 3972**

Applying the Retro-Enantio Approach To Obtain a Peptide Capable of Overcoming the Blood–Brain Barrier

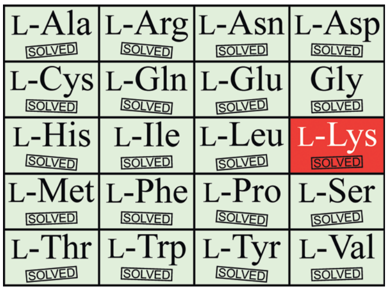


Jumping hurdles: The retro-enantio approach has been applied to a peptide that targets the transferrin receptor. The stability and permeability of the peptide across the blood–brain barrier (BBB) were notably increased. This new protease-resistant peptide was tested as a BBB shuttle, and it does facilitate the transport of cargo across the BBB, both in vitro and in vivo, as demonstrated by intravital microscopy in living mice.

Structure Determination

P. A. Williams, C. E. Hughes, K. D. M. Harris* ______ **3973 – 3977**

L-Lysine: Exploiting Powder X-ray Diffraction to Complete the Set of Crystal Structures of the 20 Directly Encoded Proteinogenic Amino Acids



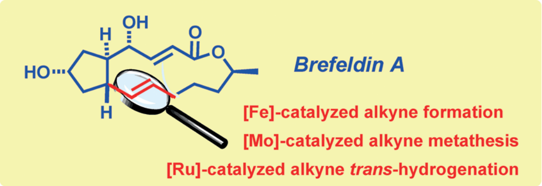
L-Ala SOLVED	L-Arg SOLVED	L-Asn SOLVED	L-Asp SOLVED
L-Cys SOLVED	L-Gln SOLVED	L-Glu SOLVED	Gly SOLVED
L-His SOLVED	L-Ile SOLVED	L-Leu SOLVED	L-Lys SOLVED
L-Met SOLVED	L-Phe SOLVED	L-Pro SOLVED	L-Ser SOLVED
L-Thr SOLVED	L-Trp SOLVED	L-Tyr SOLVED	L-Val SOLVED

Completing the set: L-lysine is the final member of the set of 20 directly encoded proteinogenic amino acids to have its crystal structure determined, 75 years after glycine became the first member of this set to have a crystal structure reported. With good-quality single crystals of L-lysine unavailable, modern powder X-ray diffraction methods were exploited for the structure determination.

Total Synthesis

M. Fuchs, A. Fürstner* ____ 3978 – 3982

trans-Hydrogenation: Application to a Concise and Scalable Synthesis of Brefeldin A



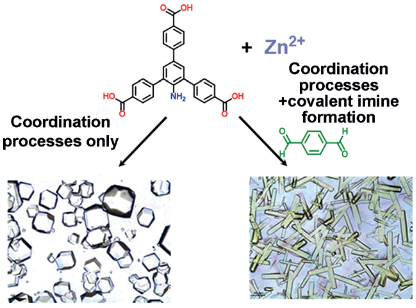
The focal point: The recently disclosed ruthenium-catalyzed *trans*-hydrogenation of internal alkynes to *E*-alkenes is noteworthy for its unorthodox stereochemical course, as well as its compatibility with other reducible or sensitive sites. This favorable profile allowed this emerging methodology to be implemented in a concise total synthesis of brefeldin A at a stage at which a conventional Birch-type *trans*-reduction would no longer be applicable.

Microporous Materials

A. Dutta, K. Koh, A. G. Wong-Foy, A. J. Matzger* ____ 3983 – 3987

Porous Solids Arising from Synergistic and Competing Modes of Assembly: Combining Coordination Chemistry and Covalent Bond Formation

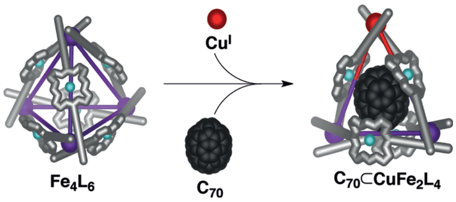
Teamwork saves the day when coordination chemistry and covalent bond formation can both occur in a single material. A balance between the incubation time of the organic components and solvent decomposition/base formation governs the competition between the two processes and determines the phase outcome. Even the temporary formation of reversible connections between components can be leveraged to make new phases.



Supramolecular Chemistry

D. M. Wood, W. Meng, T. K. Ronson, A. R. Stefankiewicz, J. K. M. Sanders, J. R. Nitschke* ____ 3988 – 3992

Guest-Induced Transformation of a Porphyrin-Edged $Fe^{II}_4L_6$ Capsule into a $Cu^IFe^{II}_2L_4$ Fullerene Receptor



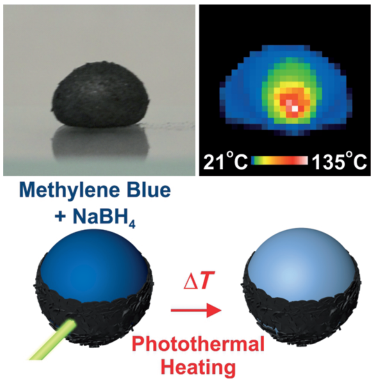
An accommodating host: The combination of a bent nickel(II) porphyrin containing bis-bidentate ligand and Fe^{II} yielded an $Fe^{II}_4L_6$ cage that undergoes a structural transformation in the presence of different fullerenes. The new product is an $Fe^{II}_3L_4$ cone-shaped assembly with a fullerene bound inside its central cavity. The simultaneous addition of Cu^I and fullerene leads to the formation of an unprecedented $Cu^IFe^{II}_2L_4$ heterometallic host–guest complex.

Photothermal Reactions

W. Gao, H. K. Lee, J. Hobley, T. Liu,* I. Y. Phang,* X. Y. Ling* ____ 3993 – 3996

Graphene Liquid Marbles as Photothermal Miniature Reactors for Reaction Kinetics Modulation

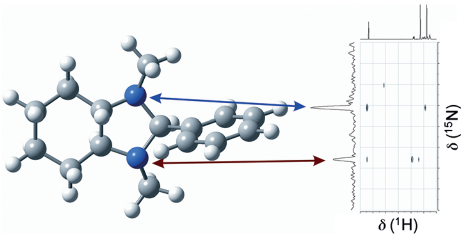
The fabrication of graphene liquid marbles as photothermal miniature reactors with high mechanical robustness is demonstrated. The reaction temperature can be precisely controlled between 21 and 135 °C by tuning the laser power applied. This allows their application for the modulation and acceleration of reaction kinetics and overcomes the lack of a heating mechanism in conventional liquid marble reactors.



Analytical Methods

I. Alkorta, C. Dardonville,*
J. Elguero ______ 3997 – 4000

Observation of Diastereotopic Signals in ^{15}N NMR Spectroscopy

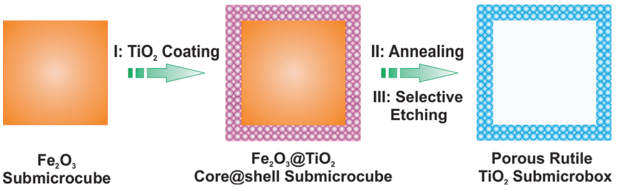


Different strokes: The first example of a compound showing anisochronous ^{15}N atoms resulting from diastereotopicity is described. Racemic 1,3-dimethyl-2-phenyloctahydro-1*H*-benzimidazole was prepared and studied by ^{1}H, ^{13}C, and ^{15}N NMR spectroscopy. If convenient conditions were used (monitored by theoretical calculations of $^{2}J_{N-H}$ spin–spin coupling constants), two ^{15}N NMR signals were observed and corresponded to the diastereotopic atoms.

Lithium Storage Materials

X. Y. Yu, H. B. Wu, L. Yu, F. X. Ma,
X. W. Lou* ______ 4001 – 4004

Rutile TiO_2 Submicroboxes with Superior Lithium Storage Properties



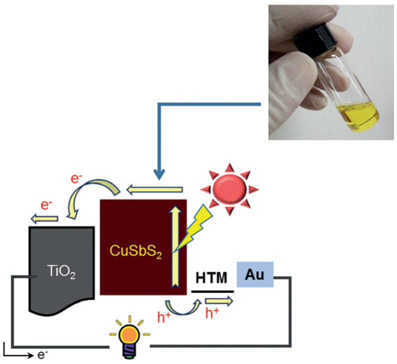
Rutile TiO_2 submicroboxes were synthesized by a facile templating strategy. A solvothermal method was developed to first deposit a uniform TiO_2 layer on Fe_2O_3 submicrocube templates. Unexpectedly, the rutile TiO_2 phase is formed after annealing in air. Compared to other rutile TiO_2 materials, these submicroboxes have unprecedented lithium storage properties in terms of specific capacity, long-term cycling stability, and rate capability.

Solar Cells

Y. C. Choi, E. J. Yeom, T. K. Ahn,
S. I. Seok* ______ 4005 – 4009

$CuSbS_2$-Sensitized Inorganic–Organic Heterojunction Solar Cells Fabricated Using a Metal–Thiourea Complex Solution

Ternary $CuSbS_2$-sensitized inorganic–organic heterojunction solar cells can be assembled with an efficiency of 3.12%. The $CuSbS_2$ is simply deposited on a F-doped SnO_2 substrate/TiO_2 blocking layer/mesoporous TiO_2/$CuSbS_2$/hole-transporting material (HTM)/Au electrode by processing with a Cu–Sb–thiourea complex (yellow solution in picture). The highest photocurrent is 21.5 mA cm^{-2} under standard AM 1.5 G conditions.

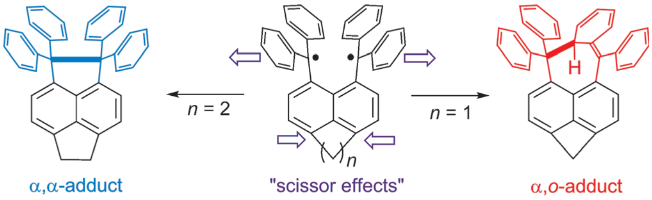


Radicals

Y. Uchimura, T. Takeda, R. Katoono,
K. Fujiwara, T. Suzuki* ______ 4010 – 4013

New Insights into the Hexaphenylethane Riddle: Formation of an α,*o*-Dimer

Inside Back Cover

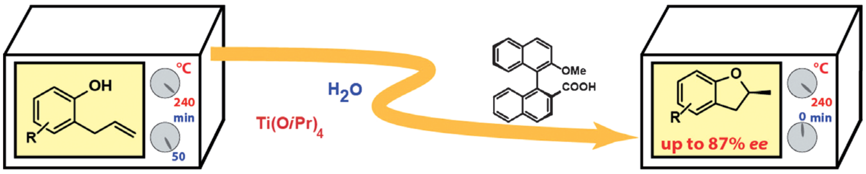


Beyond the ultralong C–C bond: Whereas an acenaphthene-5,6-diyl ($n=2$) undergoes smooth conversion into the corresponding tetraarylpyracene (the α,α-adduct) with an ultralong C–C bond, enhanced "scissor effects" in the cyclobutanaphthalene-4,5-diyl diradical ($n=1$) place the two C_α atoms so far apart that C_α–C_α bond formation is prevented. Instead, the α,*o*-adduct is formed.

Asymmetric Catalysis

J. Schlüter, M. Blazejak, F. Boeck,
L. Hintermann* ______ **4014 – 4017**

Asymmetric Hydroalkoxylation of Non-Activated Alkenes: Titanium-Catalyzed Cycloisomerization of Allylphenols at High Temperatures

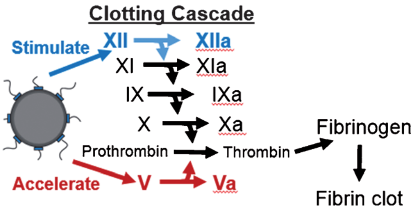


Best served hot and fast: The metal-catalyzed asymmetric hydroalkoxylation of non-activated alkenes was catalyzed by a chiral titanium–carboxylate complex that requires co-catalytic amounts of water to reach full activity. This homogeneous thermal catalysis (HOT-CAT) proceeds at remarkably high temperatures (above 220 °C, typically 240 °C) and produces 2-methylcoumarans from 2-allylphenols in up to 90% yield and 87% *ee*.

Medicinal Chemistry

D. Kudela,* S. A. Smith, A. May-Masnou,
G. B. Braun, A. Pallaoro, C. K. Nguyen,
T. T. Chuong, S. Nownes, R. Allen,
N. R. Parker, H. H. Rashidi,
J. H. Morrissey,*
G. D. Stucky* ______ **4018 – 4022**

Clotting Activity of Polyphosphate-Functionalized Silica Nanoparticles

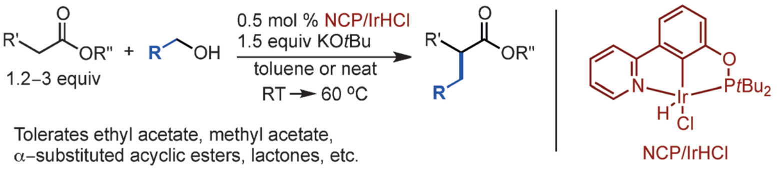


Stemming the flow: Current hemorrhage treatments are designed to clot upon exposure to blood. Safety concerns over the spread of therapeutics to healthy vessels limit their use. Agents such as polyphosphate that accelerate rather than initiate clotting (see picture) have the potential to retain efficacy while minimizing safety concerns in the treatment of haemorrhage.

Homogeneous Catalysis

L. Guo, X. Ma, H. Fang, X. Jia,
Z. Huang* ______ **4023 – 4027**

A General and Mild Catalytic α-Alkylation of Unactivated Esters Using Alcohols

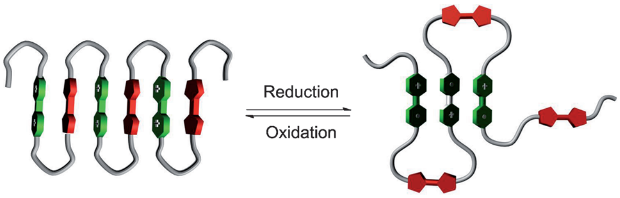


In a pinch: An NCP pincer/iridium catalyst is highly efficient for the α-alkylation of unactivated esters using alcohol under mild reaction conditions. The reaction is simple, clean, and scalable (1–10 mmol), and the scope with respect to the ester is wide.

Polymer Folding

L. Chen, H. Wang, D.-W. Zhang,*
Y. Zhou,* Z.-T. Li* ______ **4028 – 4031**

Quadruple Switching of Pleated Foldamers of Tetrathiafulvalene–Bipyridinium Alternating Dynamic Covalent Polymers

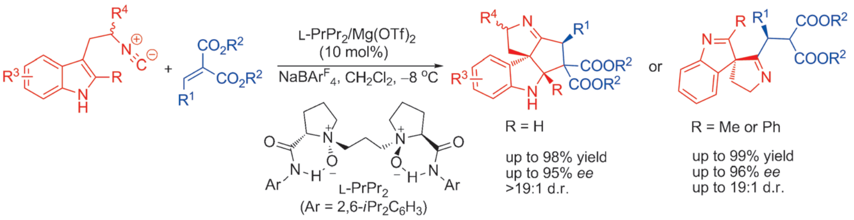


Dancing to four different tunes: Tetrathiafulvalene and bipyridinium can be oxidized and reduced, respectively, to radical cations. Depending on their redox state, a donor–acceptor interaction or a radical-cation dimerization can occur. These noncovalent forces have been used to induce two tetrathiafulvalene–bipyridinium alternating dynamic covalent polymers to fold (see picture) and unfold reversibly in four ways.

Heterocycle Synthesis

X. H. Zhao, X. H. Liu,* H. J. Mei, J. Guo, L. L. Lin, X. M. Feng* ______ 4032–4035

Asymmetric Dearomatization of Indoles through a Michael/Friedel–Crafts-Type Cascade To Construct Polycyclic Spiroindolines

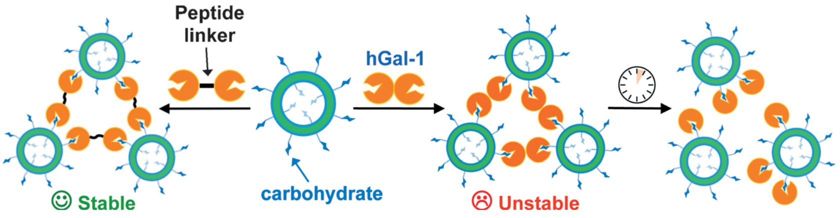


De-aromatically: A highly efficient dearomatization of 2-isocyanoethylindole derivatives with alkylidene malonates by the title reaction has been developed. With easily available chiral *N*,*N*′-dioxide/Mg^{II} complex catalysts, fused polycyclic indolines and spiroindolines were afforded in moderate to excellent yield, excellent diastereo- and enantioselectivity. Tf = trifluoromethanesulfonyl.

Supramolecular Chemistry

S. Zhang, R.-O. Moussodia, C. Murzeau, H.-J. Sun, M. L. Klein, S. Vértesy, S. André, R. Roy, H.-J. Gabius, V. Percec* ______ 4036–4040

Dissecting Molecular Aspects of Cell Interactions Using Glycodendrimersomes with Programmable Glycan Presentation and Engineered Human Lectins



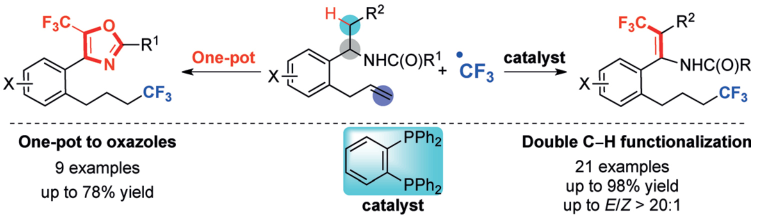
A combination of supramolecular glycodendrimersomes with programmed glycan presentation and engineering of human galectin-1 provides answers to fundamental questions on structure–activity relationships in cell interactions and guidelines for the design of new tools for biomedical applications.

Radical Chemistry

P. Yu, S.-C. Zheng, N.-Y. Yang, B. Tan,* X.-Y. Liu* ______ 4041–4045

Phosphine-Catalyzed Remote β-C–H Functionalization of Amines Triggered by Trifluoromethylation of Alkenes: One-Pot Synthesis of Bistrifluoromethylated Enamides and Oxazoles

Back Cover



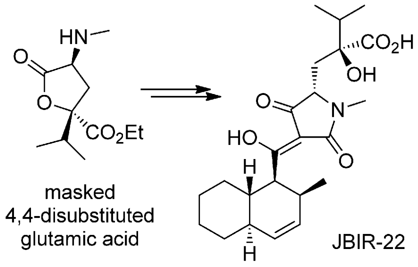
The radical tandem functionalization of unactivated alkenes and the remote β-C_{sp^3}–H bond of amine derivatives is achieved by phosphine catalysis. The one-pot protocol provides facile access to bistrifluoromethylated enamides as well as trisubstituted 5-(trifluoromethyl)oxazoles.

Total Synthesis

A. R. Healy, M. Izumikawa, A. M. Z. Slawin, K. Shin-ya, N. J. Westwood* ______ 4046–4050

Stereochemical Assignment of the Protein–Protein Interaction Inhibitor JBIR-22 by Total Synthesis

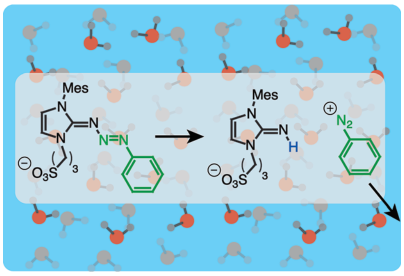
Members of the tetramic acid class of natural products that contain an unnatural amino acid unit have not yet been synthesized, despite their exciting biological activities. Rapid access to the shown masked 4,4-disubstituted glutamic acid derivative enabled the highly efficient total synthesis of JBIR-22, the relative and absolute stereochemistry of which was consequently assigned.



Diazonium Salts

F. W. Kimani, J. C. Jewett* **4051 – 4054**

Water-Soluble Triazabutadienes that Release Diazonium Species upon Protonation under Physiologically Relevant Conditions

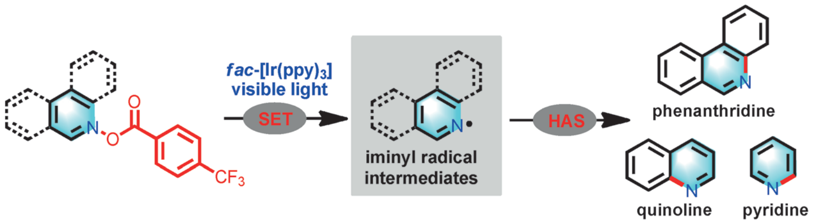


Just add water: Triazabutadienes readily release diazonium species in a pH-dependent manner in a series of buffer solutions with pH ranges similar to those found in living systems. These compounds offer one of the mildest ways of generating diazonium species in aqueous solutions.

Photochemistry

H. Jiang, X. An, K. Tong, T. Zheng, Y. Zhang,* S. Yu* **4055 – 4059**

Visible-Light-Promoted Iminyl-Radical Formation from Acyl Oximes: A Unified Approach to Pyridines, Quinolines, and Phenanthridines

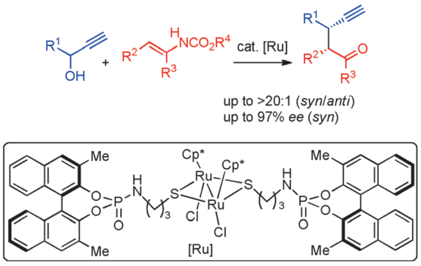


See the light: A unified strategy involving visible-light-induced iminyl-radical formation followed by intramolecular homolytic aromatic substitution (HAS) has been established for the efficient construction of heteroarenes with a N-containing six-membered ring (see scheme; ppy = 2-phenylpyridine, SET = single-electron transfer). This strategy was applied to a five-step concise synthesis of benzo[*c*]phenanthridine alkaloids.

Synthetic Methods

Y. Senda, K. Nakajima, Y. Nishibayashi* **4060 – 4064**

Cooperative Catalysis: Enantioselective Propargylic Alkylation of Propargylic Alcohols with Enecarbamates Using Ruthenium/Phosphoramide Hybrid Catalysts

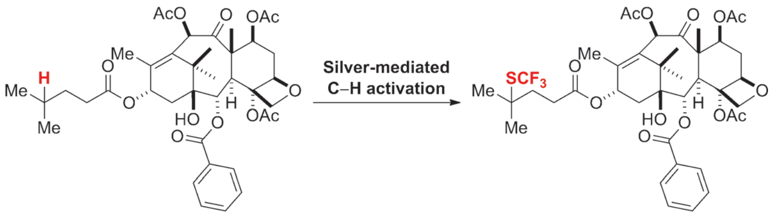


A productive pair: The diastereo- and enantioselective propargylic alkylation of propargylic alcohols with *E*-enecarbamates in the presence of a thiolate-bridged diruthenium complex bearing an optically active phosphoramide moiety as a catalyst gives the corresponding propargylic alkylated products. The use of the hybrid catalyst achieves the catalytic reactions with high diastereo- and enantioselectivities. Cp* = η^5-C_5Me_5.

Trifluoromethylthiolation

S. Guo, X. Zhang, P. Tang* **4065 – 4069**

Silver-Mediated Oxidative Aliphatic C–H Trifluoromethylthiolation

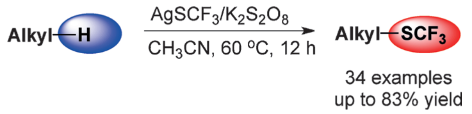


The silver-mediated trifluoromethylthiolation of unactivated aliphatic C–H bonds is reported. The reaction is operationally simple, amenable to gram-scale synthesis, and can be employed for the late-stage trifluoromethylthiolation of complex small molecules.

C–H Activation

H. Wu, Z. Xiao, J. Wu, Y. Guo, J.-C. Xiao, C. Liu,* Q.-Y. Chen* ——— **4070 – 4074**

Direct Trifluoromethylthiolation of Unactivated C(sp^3)–H Using Silver(I) Trifluoromethanethiolate and Potassium Persulfate

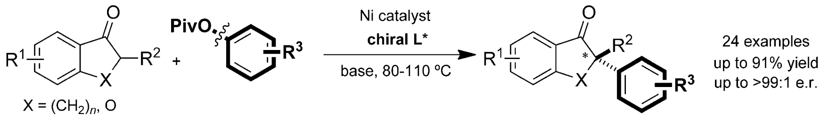


Direct and mild: A variety of alkyl-trifluoromethylthioethers were efficiently synthesized by direct trifluoromethylthiolation of unactivated C(sp^3)–H bonds under mild reaction conditions. The reagent system comprises AgSCF$_3$ and K$_2$S$_2$O$_8$, the latter of which both activates the C(sp^3)–H bond and oxidizes AgSCF$_3$. The reaction has a broad substrate scope with good functional-group tolerance and good selectivity.

Synthetic Methods

J. Cornella, E. P. Jackson, R. Martin* ——— **4075 – 4078**

Nickel-Catalyzed Enantioselective C–C Bond Formation through C$_{sp^2}$–O Cleavage in Aryl Esters



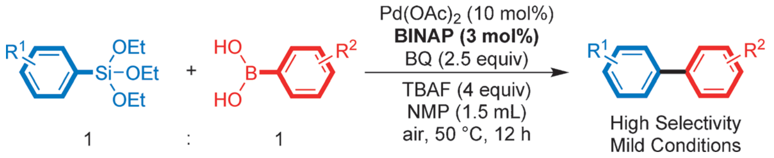
Aryl ester electrophiles are used in an enantioselective C–C bond formation through C–O bond cleavage. This reaction proceeds under nickel catalysis by means of an axially chiral bidentate ligand, allowing the formation of enantioenriched quaternary stereocenters. This procedure is characterized by its high asymmetric induction and remarkable wide scope.

VIP

Cross-Coupling

J. Yu, J. Liu, G. Shi, C. Shao, Y. Zhang* ——— **4079 – 4082**

Ligand-Promoted Oxidative Cross-Coupling of Aryl Boronic Acids and Aryl Silanes by Palladium Catalysis

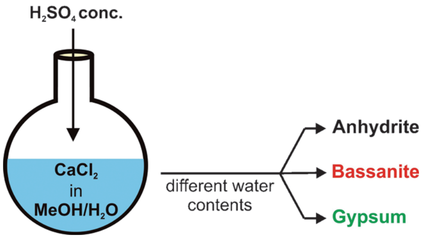


Two nucleophiles: The first cross-coupling reaction between aryl silanes and aryl boronic acids is one of the very few examples of coupling reactions between two nucleophilic organometallic reagents and provides access to biaryl compounds. With the commercially available ligand BINAP, the formation of the homocoupling products was suppressed, and the reaction yielded the cross-coupling products with high selectivity.

Materials Chemistry

U. Tritschler, A. E. S. Van Driessche, A. Kempter, M. Kellermeier,* H. Cölfen* ——— **4083 – 4086**

Controlling the Selective Formation of Calcium Sulfate Polymorphs at Room Temperature

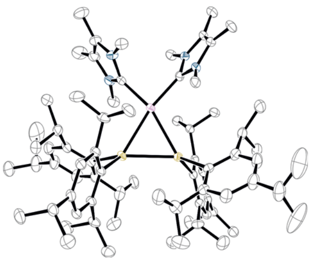


Pick a polymorph: Precipitation of calcium sulfate from methanolic solutions containing very low amounts of water leads to the formation of phase-pure anhydrite at ambient conditions. By changing the water content, all three polymorphs of CaSO$_4$ (anhydrite, bassanite, or gypsum) can be obtained selectively, as well as binary mixtures of the different phases.

Tin Ligands

C. P. Sindlinger, S. Weiß, H. Schubert, L. Wesemann* ——— **4087 – 4091**

Nickel-Triad Complexes of a Side-on Coordinating Distannene

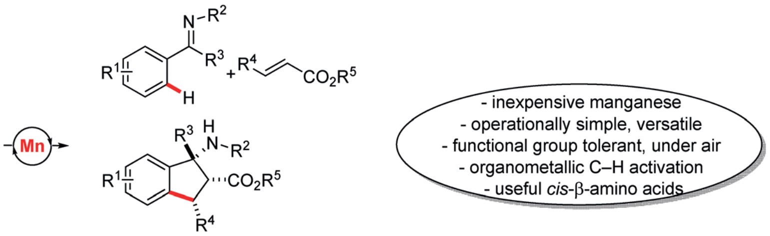


Differing analogues: On reacting the carbene adduct of the stannylene [Trip$_2$Sn] (Trip = 2,4,6-triisopropylphenyl) with zero-valent Group 10 complexes, symmetrically coordinating complexes of the distannene [Sn$_2$Trip$_4$] to Ni, Pd, and Pt have been obtained. Their structural and spectroscopic properties are presented and discussed.

C–H Activation

W. Liu, D. Zell, M. John,
L. Ackermann* ________ **4092 – 4096**

Manganese-Catalyzed Synthesis of *cis*-β-Amino Acid Esters through Organometallic C–H Activation of Ketimines

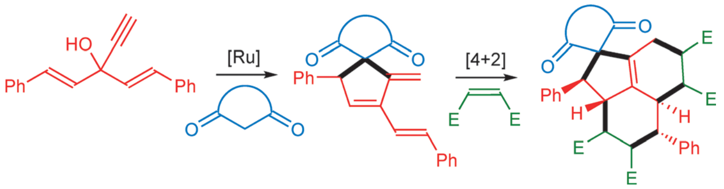


An operationally simple manganese-catalyzed C–H functionalization of ketimines provides access to β-amino acid esters. The mechanism of this transformation was studied, and its utility proven by further modifications of the synthetically useful β-amino acid esters into attractive compounds.

Cascade Reactions

N. Thies, E. Haak* ________ **4097 – 4101**

Ruthenium-Catalyzed Synthesis of 2,3-Cyclo[3]dendralenes and Complex Polycycles from Propargyl Alcohols

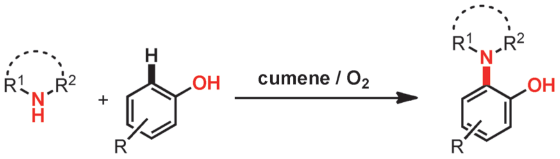


Molecular complexity: Ruthenium-catalyzed multicomponent cascade transformations for the construction of complex polycyclic compounds from readily available propargyl alcohols are presented. The atom-economic reaction sequence proceeds via 2,3-cyclo[3]dendralenes and generates six new bonds and up to nine stereocenters.

Metal-Free Synthesis

M.-L. Louillat-Habermeyer, R. Jin,
F. W. Patureau* ________ **4102 – 4104**

O_2-mediated dehydrogenative amination of phenols

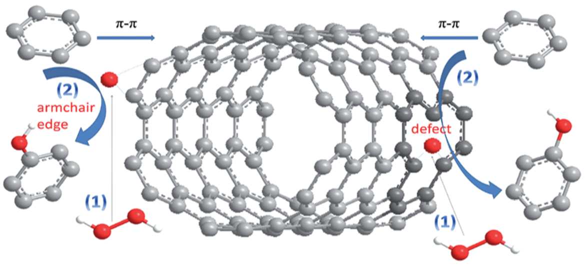


O_2 will do: A dehydrogenative amination coupling of amines with phenols is described, which operates without halides or metal salts and utilizes O_2 as sole oxidant. The reaction is atom-economical and tolerates a range of functional groups.

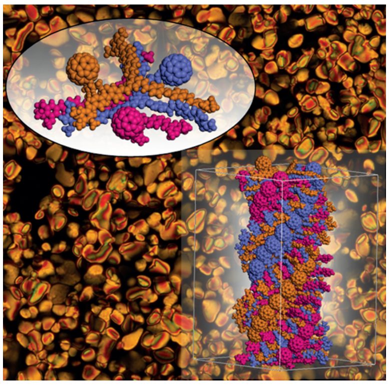
Heterogeneous Catalysis

G. D. Wen, S. C. Wu, B. Li, C. L. Dai,
D. S. Su* ________ **4105 – 4109**

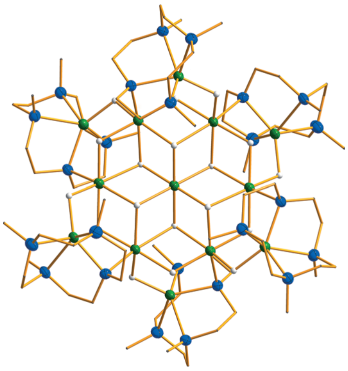
Active Sites and Mechanisms for Direct Oxidation of Benzene to Phenol over Carbon Catalysts



Watching the defectives: Combining model catalysts with Raman spectra, secondary ion mass spectra, and quasi in situ ATR-IR and UV spectra gives an insight into the mechanism of direct oxidation of benzene over carbon materials, such as carbon nanotubes. The defects in the armchair configuration (see picture) are capable of forming active oxygen species, and are the active sites.



Come into my arms: Stilbenoid star-shaped mesogens pack densely, in helical structures that have a short correlation length, in columnar liquid-crystal phases. Attaching a fullerene guest to the interior of the star fills the void space between the arms and considerably increases the mesophase stability by approximately 70 °C. The stabilization is the result of the formation of a fullerene triple helix.



A light giant: A large cationic magnesium hydride cluster with a $[Mg_{13}H_{18}]$ core was stabilized by an NNNN-type macrocycle ligand (Mg green, N blue, H white). The structure of the central $[Mg_7H_{12}]^{2+}$ fragment is formally derived from $Mg(OH)_2$ (Brucite) and thus differs significantly from that of the salt-like MgH_2.

DOI: 10.1002/anie.201581314

Flashback: 50 Years Ago …

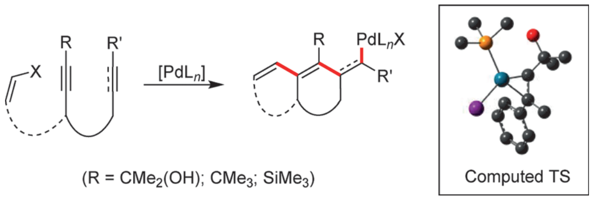
2015 sees the 150th anniversary of BASF, and Issue 11/2015 of *Angewandte Chemie* was dedicated to this jubilee. For the 100th anniversary in 1965, *Angewandte Chemie* also published a series of Reviews dedicated to the company, then called the Badische Anilin- & Soda-Fabrik. These included contributions by Siegfried Hünig et al. on the chemistry of diimine (N_2H_2), and by Ralph G. Pearson and Mary M. Anderson on the exchange rates of ligands in complex ions. Pearson is best known for his work on hard and soft acids and bases, which he first published in 1963. Contributions from BASF included Reviews on cotton dyes (H. R. Hensel and G. Lützel), metal chelates as polymerization initiators (E.-G. Kastning et al.), the catalytic oligomerization of butene (H. Müller et al.), fungicidal compounds (K.-H. König et al.), catalysts for the synthesis of ammonia (R. Krabetz and C. Peters), and the latest technological developments in "mechanizing" the storage of chemical documentation (E. Meyer).

Emanuel Vogel et al. reported on the synthesis of the bicyclo[5.4.1.]dodecapentaenylium ion. Reaction of 1,6-methanocyclodecapentaene with diazomethane and treatment of the resulting olefin with triphenylmethyl fluoroborate resulted in the target product, which is an arenium ion with 10 π electrons.

K. Pilgram and F. Korte reported on the synthesis of the highly explosive bis(1,2,3,4-thiatriazol)thio compounds from sodium 1,2,3,4-thiatriazol-5-thiolate. These compounds were found to be stable at room temperature but exploded with a loud bang upon striking.

Read more in Issue 4/1965.

Reaction Mechanisms



Reduced options: Diyne and enyne systems are designed that lead exclusively to formal *anti*-carbopalladation reactions. A prerequisite is the absence of β-hydrogen atoms that could offer other reaction channels. The mechanism is demonstrated by means of experiments as well as DFT calculations.

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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This article is accompanied by a cover picture (front or back cover, and inside or outside).

The Very Important Papers, marked VIP, have been rated unanimously as very important by the referees.

The Hot Papers are articles that the Editors have chosen on the basis of the referee reports to be of particular importance for an intensely studied area of research.

Angewandte Corrigendum

Recyclable Mitsunobu Reagents: Catalytic Mitsunobu Reactions with an Iron Catalyst and Atmospheric Oxygen

D. Hirose, T. Taniguchi,* H. Ishibashi ——— 4613–4617

In the reference section of this Communication, on page 4616, the journal name for reference [2a] is incorrect. The correct reference should be "O. Mitsunobu, *Synthesis* **1981**, 1–28".

In the Supporting Information, on page S3, for ^{1}H NMR data of ethyl 2-(3,4-dichlorophenyl)azocarboxylate, "7.64 (d, $J = 8.6$ Hz, 3 H)" should be "7.64 (d, $J = 8.6$ Hz, 1 H)".

Angew. Chem. Int. Ed. **2013**, *52*

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