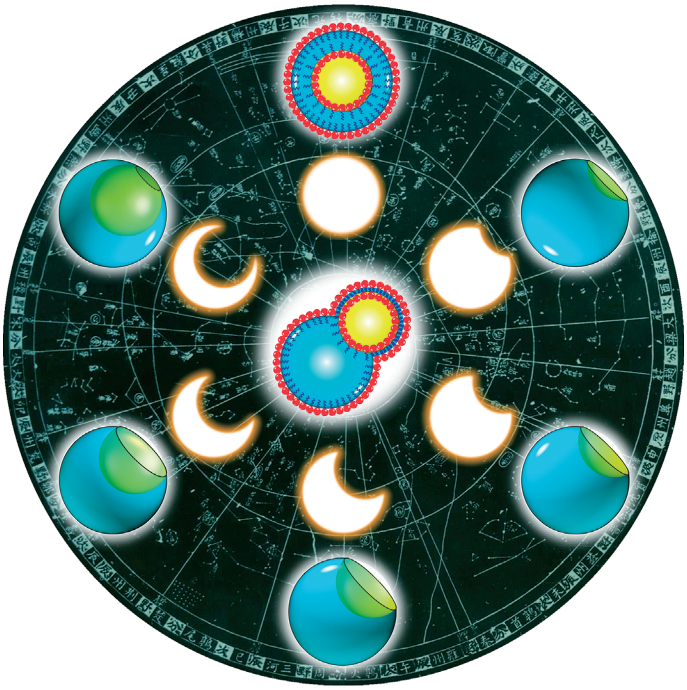
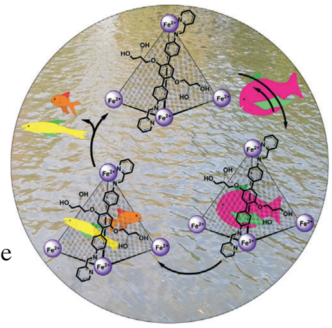
# Hole–shell microparticles …

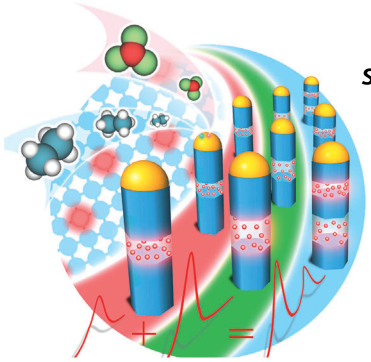


… with controllable structures and flexible internal surfaces have been fabricated from controllably evolved water/oil/water emulsions, as described by L.-Y. Chu et al. in their Communication on page 8084 ff. These microparticles could be used as microcontainers for controlled capture/release and as microreactors for confined reactions.

### Host–Guest Catalysis

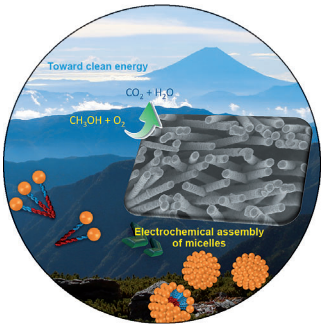
A water-soluble [$Fe_4L_6$] capsule catalyzes the hydrolysis of the neurotoxic organophosphate dichlorvos. J. R. Nitschke and co-workers show in their Communication on page 7958 ff. that dichlorvos is hydrolyzed in the capsule and the water soluble products released from it.





### Surface Plasmon Resonances

In their Communication on page 8079 ff., M. A Filler and L.-W. Chou report the synthesis of silicon nanowires containing multiple, axially registered, doped regions, which are investigated by infrared spectroscopy.



### Electrocatalysis

In their Communication on page 8050 ff. Y. Yamauchi et al. report self-supported platinum nanorods that are prepared by electrochemical assembly of platinum-containing micelles in the pores of a polycarbonate membrane.

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## Service

## Author Profile

*"When I was eighteen I wanted to be a football player for Real Madrid.*
*If I could be described as an animal it would be a fighting bull ..."*
This and more about Tomás Torres can be found on page 7914.

## News

T. Baumgartner

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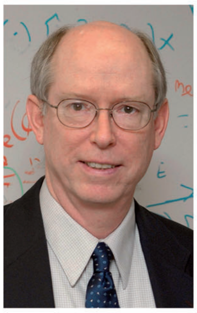


J. C. Tully

Z. Zhong

## Books

Life's Ratchet Peter M. Hoffmann *reviewed by F. Zerbetto* **7917**

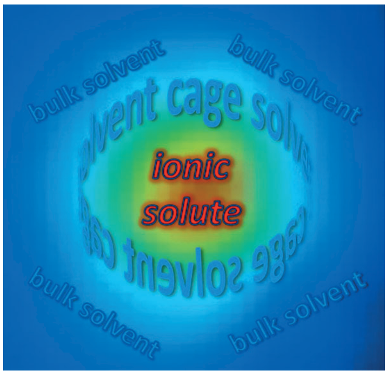
## Correspondence

### *Microwaves in Synthesis*

G. B. Dudley,* A. E. Stiegman,
M. R. Rosana **7918 – 7923**

Correspondence on Microwave Effects in Organic Synthesis

**They're real.** Microwave effects in organic synthesis remain controversial, but there is no longer any room for doubt that they exist. The question of whether the organic synthesis community should try to harness microwave effects strategically is the focus of this Correspondence.



### *Microwaves in Synthesis*

C. O. Kappe* **7924 – 7928**

Reply to the Correspondence on Microwave Effects in Organic Synthesis

**Selective heating or superheating?** The enhancement effects seen by Dudley and co-workers in the microwave-heated Friedel–Crafts alkylation (see graphic) are due to superheating of the bulk reaction mixture and not selective reactant heating. This argument forms the basis of this Correspondence.

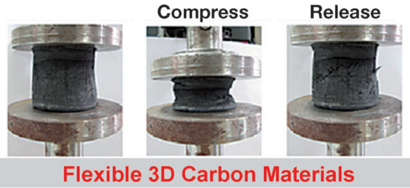
## Highlights

### *Flexible Carbon Materials*

A.-H. Lu,* G.-P. Hao,
Q. Sun **7930 – 7932**

Design of Three-Dimensional Porous Carbon Materials: From Static to Dynamic Skeletons

**A new generation** of three-dimensional carbon nanostructures is evolving. These flexible carbon systems based on carbon nanotubes and nanofibers and graphene sheets are capable of substantial shape deformation and thus have exciting applications in flexible electronics, sensors, and complex mechanical structures.



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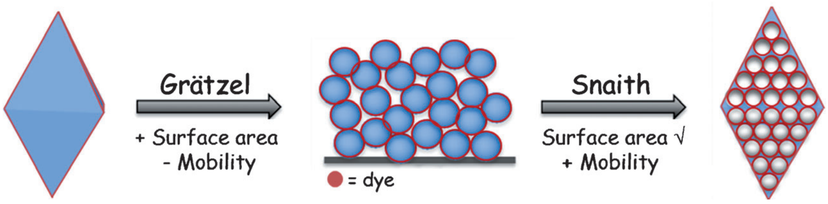
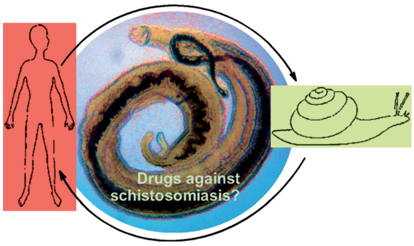


**A remarkable approach** to the production of large mesoporous anatase single crystals was reported recently by Snaith et al. These crystals display two properties—high surface area and high electron mobility—that fundamentally affect the performance of any $TiO_2$-based photoelectrochemical device, such as Grätzel-type dye-sensitized solar cells.

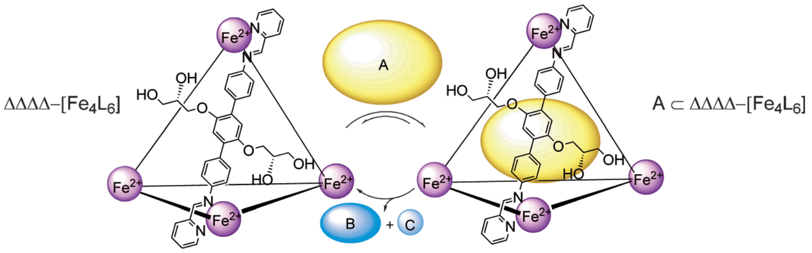
## Reviews



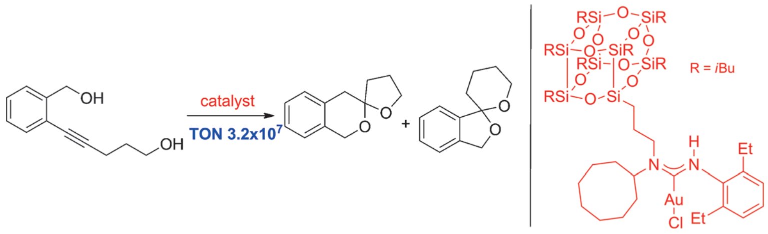
**Bilharziasis** (schistosomiasis) is the second most prevalent parasitic disease in Africa after malaria. The therapeutic arsenal against this disease is currently limited to a single drug, praziquantel, which has been used for 35 years. It is thus urgent to develop new antischistosomal drugs for efficient bi- or tri-therapies in combination with praziquantel.

## Communications

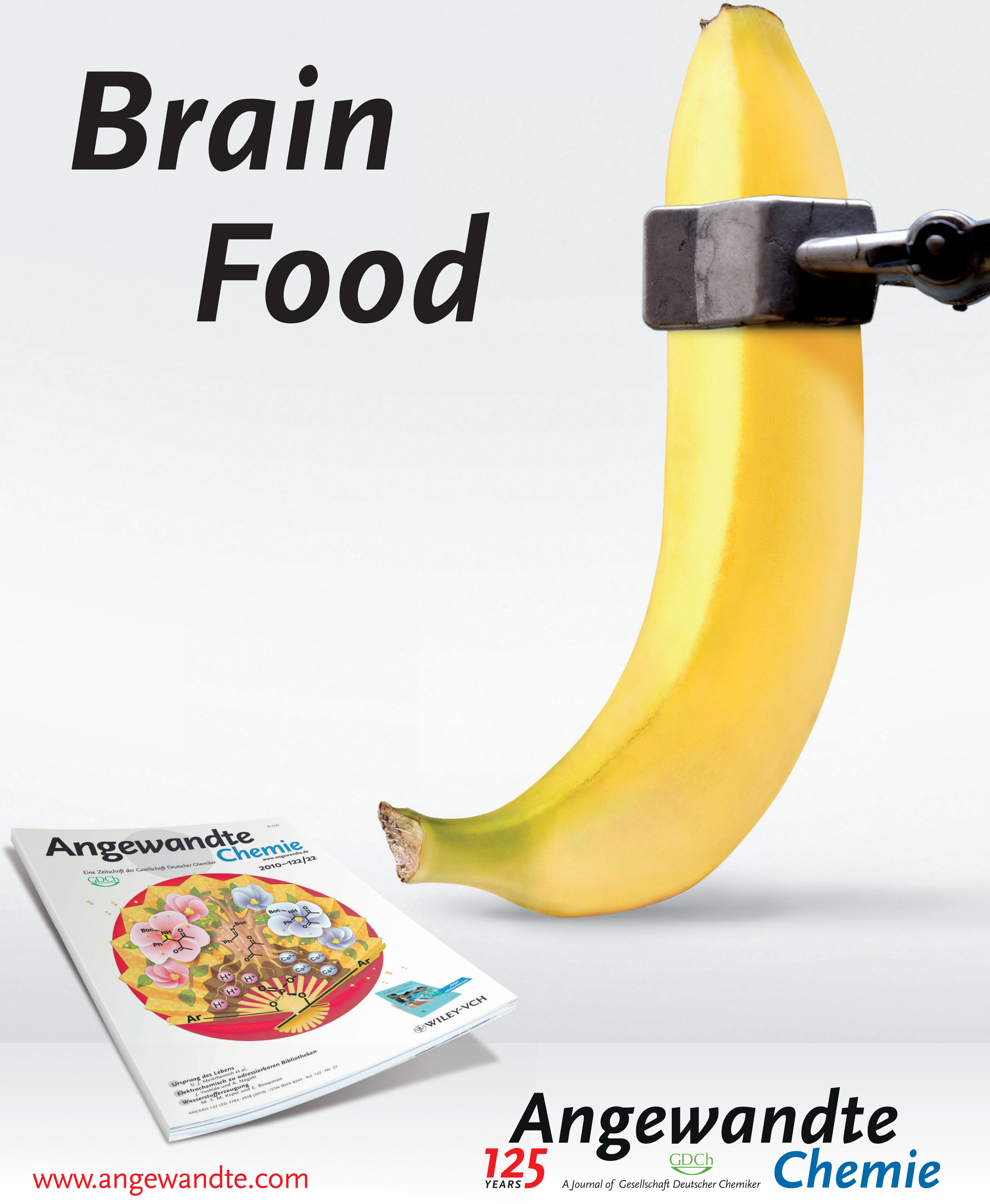
**Frontispiece**



**Inside information**: The new enantiopure cage molecule ΔΔΔΔ-$Fe_4L_6$ (and its enantiomer, ΛΛΛΛ-$Fe_4L_6$) was prepared by subcomponent self-assembly. It binds a range of organic guests (**A**, see scheme) in its cavity and distinguishes between the enantiomers of a chiral organic guest. Host ΔΔΔΔ-$Fe_4L_6$ is also a catalyst for the hydrolysis (giving **B** and **C**) of the neurotoxic organophosphate dichlorvos.



**One gold is enough**: Mononuclear, homogeneous gold catalysts displayed excellent catalytic activity on the order of that previously reported for gold nanoparticle catalysts and surface-bound gold complexes. In the model synthesis of spiro compounds (see picture) extremely high turnover numbers were achieved with only 0.000001 mol% of a silsesquioxane-substituted catalyst.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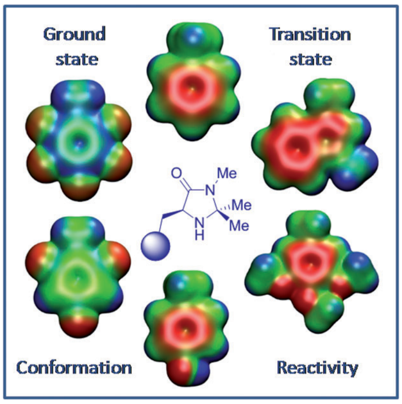

**Intriguing imidazolidinones!** Inspired by noncovalent interactions in proteins, a series of electronically distinct MacMillan catalysts were designed. The effect of electronic modulation on ground state conformation, reactivity, and performance was studied in a catalytic setting with intriguing outcomes.

## *Catalyst Design*

M. C. Holland, S. Paul, W. B. Schweizer,
K. Bergander, C. Mück-Lichtenfeld,
S. Lakhdar,* H. Mayr,
R. Gilmour* ———— **7967 – 7971**

Noncovalent Interactions in Organocatalysis: Modulating Conformational Diversity and Reactivity in the MacMillan Catalyst

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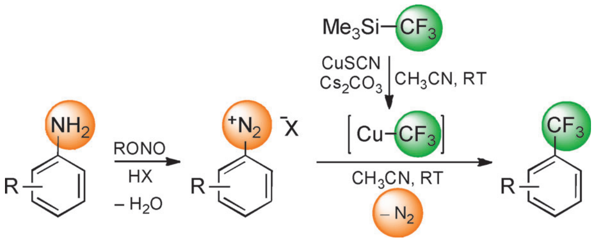

**Copper capabilities**: Diazonium salts are converted into the corresponding trifluoromethyl derivatives in the presence of a trifluoromethyl–copper complex generated in situ from CuSCN and the inexpensive, easy-to-use trifluoromethylating reagent $Me_3Si\text{-}CF_3$ (see scheme). This Sandmeyer-type reaction allows the straightforward synthesis of trifluoromethylated arenes and heteroarenes from the corresponding amines.

## *Trifluoromethylation*

G. Danoun, B. Bayarmagnai,
M. F. Grünberg,
L. J. Gooßen* ———— **7972 – 7975**

Sandmeyer Trifluoromethylation of Arenediazonium Tetrafluoroborates

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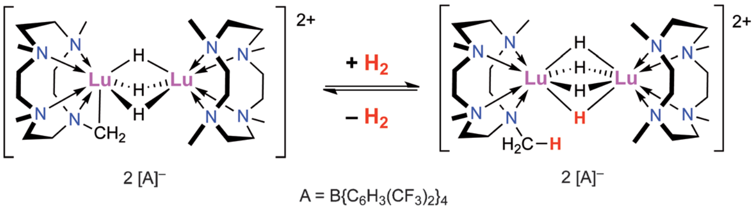

**In or out?** A quadruply hydride-bridged dilutetium complex releases dihydrogen under C–H bond activation of one of the methyl groups of the ligand. The resulting trihydrido complex readily takes up dihydrogen (see scheme).

## *Reversible $H_2$ Activation*

W. Fegler, A. Venugopal, T. P. Spaniol,
L. Maron, J. Okuda* ———— **7976 – 7980**

Reversible Dihydrogen Activation in Cationic Rare-Earth-Metal Polyhydride Complexes

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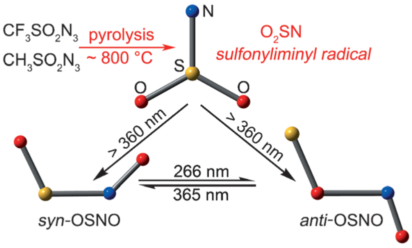


**The novel iminyl radical $O_2SN$**, a $SO_3$ analogue, was produced by flash vacuum pyrolysis of gaseous alkyl sulfonyl azides $RSO_2N_3$ ($R = CF_3$, $CH_3$) mixed with argon. Photoisomerization ($\lambda > 360$ nm) of $O_2SN$ into planar *syn*-OSNO and *anti*-OSNO (see picture) was observed in solid noble-gas matrices.

## *Small Molecules*

X.-Q. Zeng,* H. Beckers,*
H. Willner ———— **7981 – 7984**

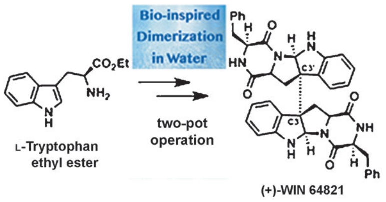
The Iminyl Radical $O_2SN$

### C–H Functionalization

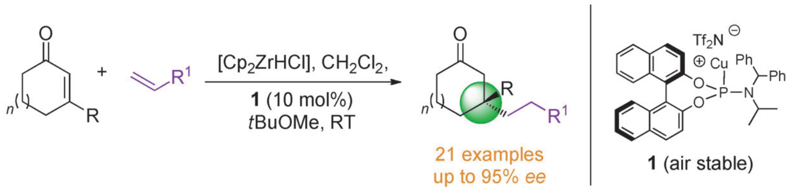
**A novel method** for the oxidative radical azidation of alkenes relies on an azide in combination with a hypervalent iodine reagent. A cascade of C–N and C–C bond-forming reactions yields 2-oxindoles under metal-free conditions with high reaction rates at ambient temperature and provides access to complex products (see scheme; TMS = trimethylsilyl).

### Alkaloid Synthesis

**Doubling up**: The direct bio-inspired dimerization of commercially available amine-free tryptophan derivatives in aqueous acidic media provides $C_2$-symmetrical and nonsymmetrical dimeric compounds. Further processing completes the concise syntheses of naturally occurring dimeric diketopiperazine alkaloids such as (+)-WIN 64821 (see picture) in overall yields of up to 20%.

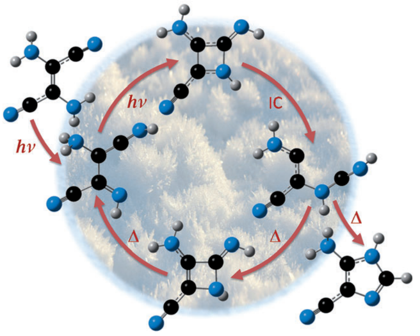


### Asymmetric Catalysis

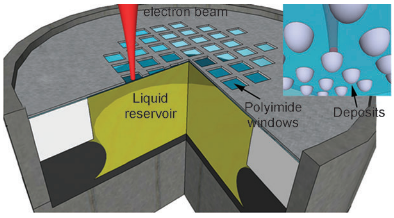


**Pure and simple**: Alkylzirconocenes generated in situ from simple alkenes are used in highly enantioselective copper-catalyzed 1,4-addition reactions to trisubstituted cyclic enones to generate quaternary centers. These reactions operate at room temperature under a range of conditions and tolerate many functional groups. Cp = cyclopentadienyl, Tf = trifluoromethanesulfonyl.

### Prebiotic Photochemistry



**So much excitement**: The mechanism for the photoconversion of the HCN tetramer into a precursor of purine nucleobases and nucleotides has been revealed by computational methods. Dissipation of the photoenergy in less than 2 ps eliminates the possibility of hot-ground-state reactions. Instead, a series of photoexcitations followed by internal conversion (IC) drives the reaction via an excited azetene (see picture).

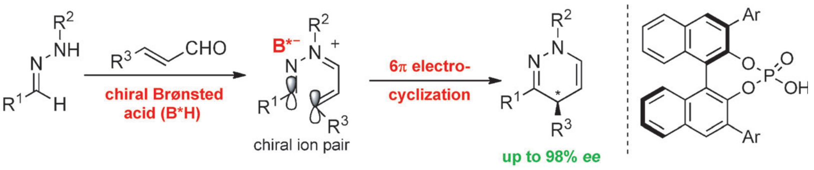


**Bimetallic deposits**: Liquid-phase electron-beam-induced deposition is shown to result in bimetallic deposits with predictable final compositions. The compositions were predicted by the first-order rates of the reaction between solvated electrons and metal ionic complexes. AuAg and AuPt nanoparticles are shown with diameters typically less than 100 nm and high purity.

## Nanoparticles

M. Bresin, A. Chamberlain, E. U. Donev,
C. B. Samantaray, G. S. Schardien,
J. T. Hastings* **8004 – 8007**

Electron-Beam-Induced Deposition of Bimetallic Nanostructures from Bulk Liquids

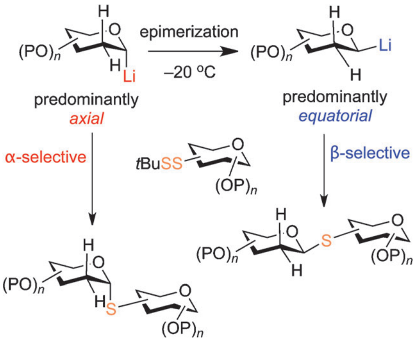


**Electric slide**: Described is a general, operationally simple, highly enantioselective Brønsted acid catalyzed condensation/6π-electrocyclization reaction between hydrazones and α,β-unsaturated aldehydes that yields valuable 1,4-dihydropyridazines. The reaction exhibits high tolerance towards functional groups and affords products with up to 98 % *ee*.

## Asymmetric Catalysis

A. Das, C. M. R. Volla, I. Atodiresei,
W. Bettray, M. Rueping* **8008 – 8011**

Asymmetric Ion Pair Catalysis of 6π Electrocyclizations: Brønsted Acid Catalyzed Enantioselective Synthesis of Optically Active 1,4-Dihydropyridazines

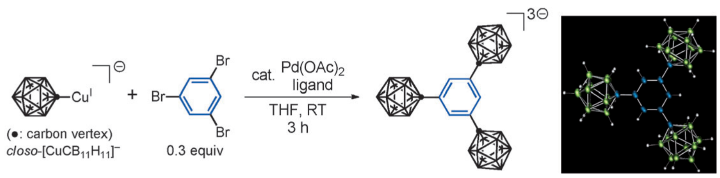


**Take control!** An unprecedented sulfenylation of stereochemically defined 2-deoxyglycosyl lithium species with asymmetric sugar-derived disulfide acceptors enabled the stereoselective synthesis of both α- and β-S-linked 2-deoxyoligosaccharides. Reductive lithiation of 2-deoxyglycosyl phenylsulfides at −78 °C provides predominantly axial glycosyl lithium species, which upon warming isomerize to predominantly equatorial lithium species (see scheme).

## Thioglycoside Synthesis

K. N. Baryal, D. Zhu, X. Li,
J. Zhu* **8012 – 8016**

Umpolung Reactivity in the Stereoselective Synthesis of S-Linked 2-Deoxyglycosides



**New couple**: A cross-coupling reaction at the carbon vertex of a monocarba-*closo*-dodecaborate has been developed to allow efficient introduction of various aryl groups and other sp$^2$/sp-hybridized carbon centers. A copper(I) complex facilitated the coupling process with a wide range of electrophiles at room temperature. The reaction was used to prepare a series of *C*-arylated carborane anion derivatives (see picture; B green, C blue), some of which showed androgen-receptor binding activity and also mesogenic properties.

## Carborate Anions

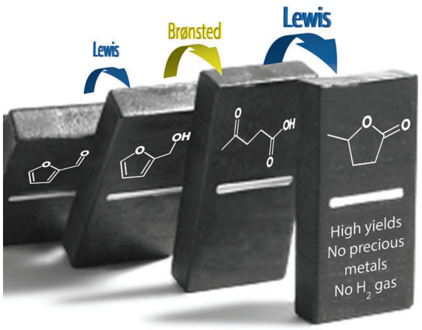
J. Kanazawa, R. Takita,* A. Jankowiak,
S. Fujii, H. Kagechika, D. Hashizume,
K. Shudo, P. Kaszyński,
M. Uchiyama* **8017 – 8021**

Copper-Mediated C–C Cross-Coupling Reaction of Monocarba-*closo*-dodecaborate Anion for the Synthesis of Functional Molecules

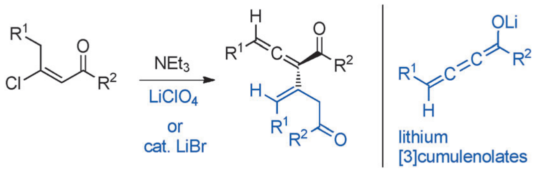
## Biomass Conversion

**Inside Cover**

**Take the straight path**: Furfural was converted into γ-valerolactone (GVL) through sequential transfer-hydrogenation and hydrolysis reactions catalyzed by zeolites with Lewis and Brønsted acid sites (see picture). Together, Zr-Beta and Al-MFI nanosheets generated GVL in 78 % yield without the use of precious metals or molecular $H_2$. This system offers an attractive streamlined strategy for the production of GVL from biomass-derived molecules.

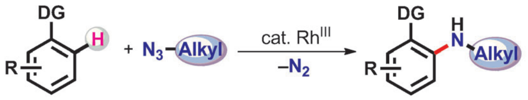


## Cumulenes



**Soft spot**: The soft vinyl enolization of (*E*)-β-chlorovinyl ketones results in the in situ generation of electrophilic lithium [3]cumulenolates, which react with nucleophiles such as another lithium [3]cumulenolate to stereoselectively form vinyl allenones. They can also react with ketimine esters to give 3-methylenepyrrolidines.

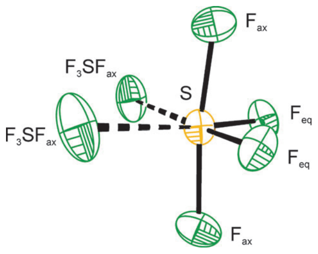
## Catalytic Amination



**New horizons in the utility of azides**: The rhodium-catalyzed intermolecular direct C–H amination of arenes with alkyl azides provides a convenient route to *N*-alkyl anilines (see scheme; DG = directing group). Alkyl azides with a wide range of functional groups reacted readily with various substrates, including benzamides, aromatic ketones, and flavones.

## Sulfur Tetrafluoride

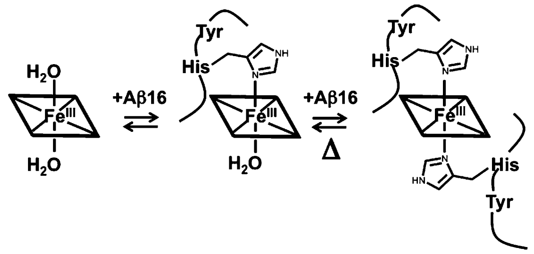
**Solved at last**: The crystal structure of solid $SF_4$, which has a melting point of −121 °C, has been obtained. It exhibits weak intermolecular S···F interactions. A similar structural motif was observed within a layer of $SF_4$ in $[HNC_5H_3(CH_3)_2{}^+]_2F^-\cdots SF_4[SF_5{}^-]\cdot 3\,SF_4$. The latter structure contains a range of bonding modes between S and F, namely $SF_5{}^-$, $F_4S\cdots F^-$, $F_4S\cdots FSF_4{}^-$, and $F_4S\cdots FSF_3$.



## Neurochemistry

G. Thiabaud, S. Pizzocaro,
R. Garcia-Serres, J.-M. Latour, E. Monzani,
L. Casella* ——— **8041 – 8044**

Heme Binding Induces Dimerization and Nitration of Truncated β-Amyloid Peptide Aβ16 Under Oxidative Stress



**Stressful situation**: Ferric heme binds to Aβ16 giving a mixture of five-coordinate [hemin(Aβ16)] and six-coordinate [hemin(Aβ16)$_2$] species, the equilibrium of which depends on the Aβ16/hemin ratio and on temperature. Under oxidative and nitrative stress conditions the heme–Aβ16 complexes promote peroxidase-like reactions causing oxidation and nitration of the Aβ Tyr10 residue. Both dityrosine formation and tyrosine nitration strongly enhance Aβ aggregation.

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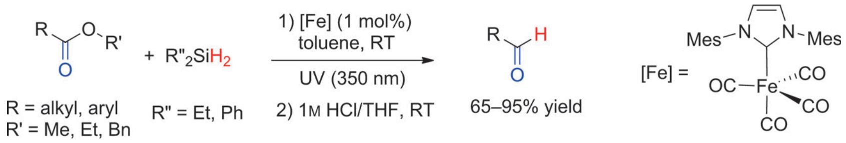
## Iron-Catalyzed Reduction

H. Li, L. C. Misal Castro, J. Zheng,
T. Roisnel, V. Dorcet, J.-B. Sortais,*
C. Darcel* ——— **8045 – 8049**

Selective Reduction of Esters to Aldehydes under the Catalysis of Well-Defined NHC–Iron Complexes



**On a direct course to the aldehyde**: Hydrosilylation catalyzed by a well-defined N-heterocyclic-carbene–iron complex under UV irradiation enabled the selective reduction of esters to aldehydes (see scheme; Bn = benzyl, Mes = mesityl). The low catalyst loading and very mild reaction conditions make this chemoselective transformation a promising alternative to the reduction of esters with diisobutylaluminum hydride.

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## Electrocatalysis

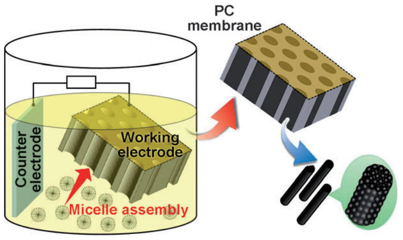
VIP

C. Li, T. Sato, Y. Yamauchi* **8050 – 8053**

Electrochemical Synthesis of One-Dimensional Mesoporous Pt Nanorods Using the Assembly of Surfactant Micelles in Confined Space

**Back Cover**

**Platinum nanorods**: A general way to synthesize novel self-supported one-dimensional mesoporous Pt nanorods with a high density of mesopores by electrochemical assembly of micelles in the pores of a polycarbonate (PC; see picture) membrane is reported. The obtained 1D motifs show high activity and tolerance towards CO in the methanol oxidation reaction and exhibit superior electrochemical activity in the oxygen reduction reaction.



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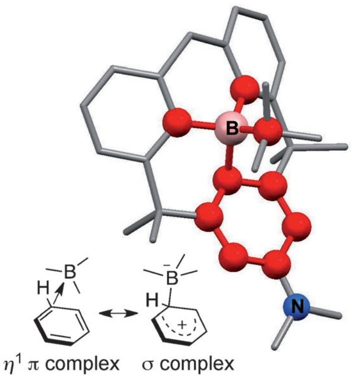
## Structure Elucidation

T. Kushida, S. Yamaguchi* — **8054 – 8058**

Boracyclophanes: Modulation of the σ/π Character in Boron–Benzene Interactions

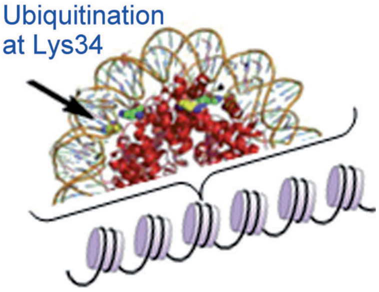


**Character sketch**: Boracyclophanes, in which the benzene ring coordinates to the boron atom, were synthesized. X-ray crystallographic analysis and theoretical calculations revealed the intrinsic character of the boron–benzene interaction. Its σ/π character can be modulated by changing the electron-donating character of the benzene ring.

## Ubiquitination

P. Siman, S. V. Karthikeyan, M. Nikolov, W. Fischle, A. Brik* ________ 8059 – 8063

### Convergent Chemical Synthesis of Histone H2B Protein for the Site-Specific Ubiquitination at Lys34

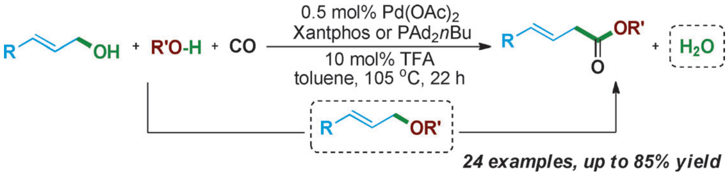


**As You Like It**: The convergent chemical synthesis of the histone H2B protein was achieved. This approach enabled the attachment of ubiquitin at Lys34 (see picture) and should make it possible to synthesize H2B with any other posttranslational modification in demand.

## Carbonylation

Q. Liu, L. Wu, H. Jiao, X. Fang, R. Jackstell, M. Beller* ________ 8064 – 8068

### Domino Catalysis: Palladium-Catalyzed Carbonylation of Allylic Alcohols to β,γ-Unsaturated Esters

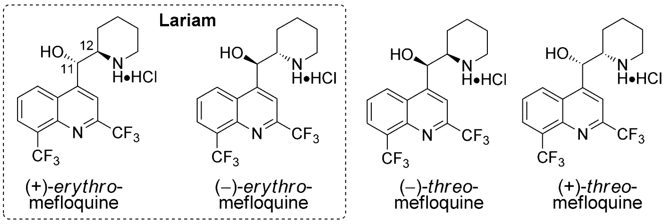


**Make it green**: The Pd-catalyzed carbonylation of allylic alcohols with aliphatic alcohols represents a cost-effective, salt-free, and atom-economic carbonylation process generating water as the sole by-product. Mechanistic studies uncovered a new domino C–O coupling/carbonylation reaction pathway.

## Drug Synthesis

J. Ding, D. G. Hall* ________ 8069 – 8073

### Concise Synthesis and Antimalarial Activity of All Four Mefloquine Stereoisomers Using a Highly Enantioselective Catalytic Borylative Alkene Isomerization



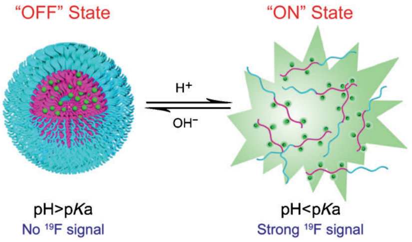
**The pluses and minuses of mefloquine**: A highly enantioselective catalytic borylative isomerization/aldehyde allylboration method for the stereoselective synthesis of the antimalarial drug mefloquine was optimized, thus leading to an efficient synthesis of all four mefloquine stereoisomers and analogues (see scheme). The absolute configuration of these potent compounds was determined for the first time by using chemical synthesis.

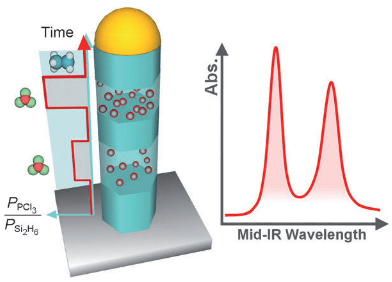
## Imaging Agents

X. Huang, G. Huang, S. Zhang, K. Sagiyama, O. Togao, X. Ma, Y. Wang, Y. Li, T. C. Soesbe, B. D. Sumer, M. Takahashi, A. D. Sherry, J. Gao* ________ 8074 – 8078

### Multi-Chromatic pH-Activatable $^{19}$F-MRI Nanoprobes with Binary ON/OFF pH Transitions and Chemical-Shift Barcodes

**Imaging all the people**: Using ionizable diblock copolymers a series of nanoprobes encoded with different $^{19}$F reporters for specific pH transitions is prepared for use in MRI. The pH response of the nanoprobes is extremely sharp ($\Delta pH_{ON/OFF} \approx 0.25$ pH), and results from the disassembly of polymer micelles (see scheme). A collection of three nanoprobes provides the proof of concept and allows for a qualitative measurement of environmental pH values.





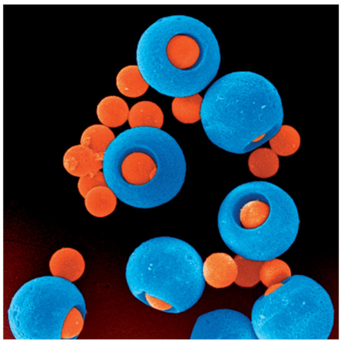
**Multimodal plasmonic resonances**: Silicon nanowires that contain multiple, dimensionally controlled, axially registered doped regions were synthesized and investigated by angle-dependent mid-infrared spectroscopy (see picture; $P=$ partial pressure). The wires support mid-infrared multimodal localized surface plasmon resonances.

## *Semiconductor Plasmonics*

L.-W. Chou, M. A. Filler* ____ **8079 – 8083**

Engineering Multimodal Localized Surface Plasmon Resonances in Silicon Nanowires

*Inside Back Cover*



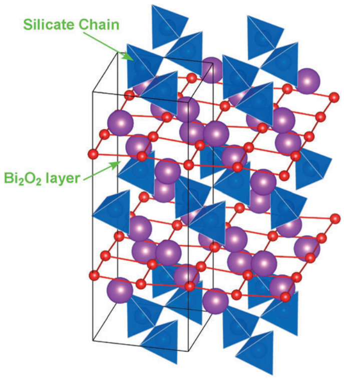
**Hole in one!** Hole–shell microparticles (blue, see picture) with controllable structures and flexible internal surfaces have been fabricated from W/O/W emulsions. These microparticles could be used as microcontainers for the controlled capture/release of molecules, microsphere classification/separation, confined cell culture, or as microreactors for catalysis.

## *Microfabrication*

W. Wang, M.-J. Zhang, R. Xie, X.-J. Ju, C. Yang, C.-L. Mou, D. A. Weitz, L.-Y. Chu* ____ **8084 – 8087**

Hole–Shell Microparticles from Controllably Evolved Double Emulsions

*Front Cover*

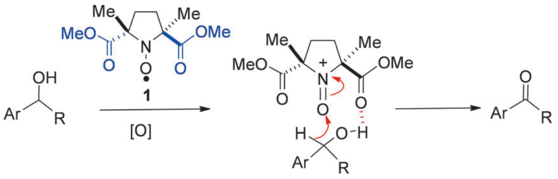


**A lead-free ferroelectric**: The occurrence of ferroelectricity is demonstrated in a silicate-based compound ($Bi_2SiO_5$, see picture), by direct observation of polarization switching. The mechanism of ferroelectricity in $Bi_2SiO_5$ has been studied by Raman scattering, transmission electron microscopy, X-ray powder diffraction, and first-principles calculations. The observed ferroelectricity stems from twisting of the one-dimensional $SiO_4$ tetrahedral chain.

## *Ferroelectricity*

H. Taniguchi,* A. Kuwabara, J. Kim, Y. Kim, H. Moriwake, S. Kim, T. Hoshiyama, T. Koyama, S. Mori, M. Takata, H. Hosono, Y. Inaguma, M. Itoh ____ **8088 – 8092**

Ferroelectricity Driven by Twisting of Silicate Tetrahedral Chains



**Electronic tuning:** Nitroxyl radical **1** is shown to be an efficient catalyst for the oxidation of secondary alcohols, and promotes oxidation through an oxoammonium species which is highly reactive because of the adjacent electron-withdrawing ester groups. Chemoselective oxidation of benzylic alcohols in the presence of aliphatic alcohols is observed and is proposed to proceed by a rate-determining hydride transfer.

## *Radical Reactions*

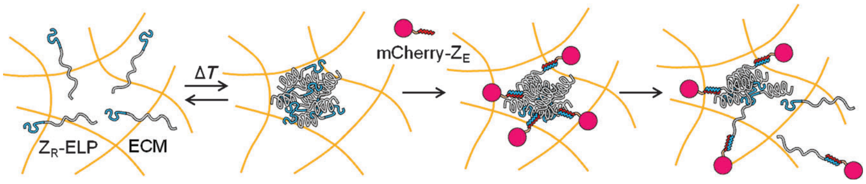
S. Hamada, T. Furuta, Y. Wada, T. Kawabata* ____ **8093 – 8097**

Chemoselective Oxidation by Electronically Tuned Nitroxyl Radical Catalysts

## Protein Delivery

W. M. Park, J. A. Champion* **8098 – 8101**

Two-Step Protein Self-Assembly in the Extracellular Matrix

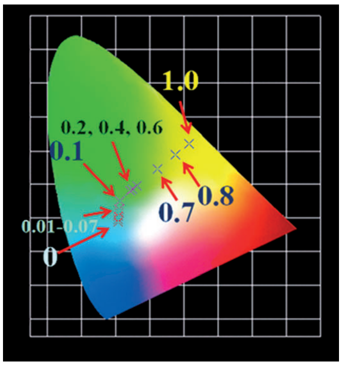


**Carrier-free protein delivery**: Protein self-assembly can be conducted in the extracellular matrix (ECM) where engineered protein components ($Z_R$-ELP) form particles that become entrapped, bind a model protein (mCherry-$Z_E$), and dissociate. Spontaneous diffusion–coacervation and high-affinity binding of proteins mediate in situ formation of the self-assembled particles that shrink and release the model protein in the ECM (see scheme).

## Phosphor Materials

W.-Y. Huang, F. Yoshimura, K. Ueda, Y. Shimomura, H.-S. Sheu, T. S. Chan, H. F. Greer, W. Zhou, S. F. Hu, R. S. Liu,* J. P. Attfield* **8102 – 8106**

Nanosegregation and Neighbor-Cation Control of Photoluminescence in Carbidonitridosilicate Phosphors



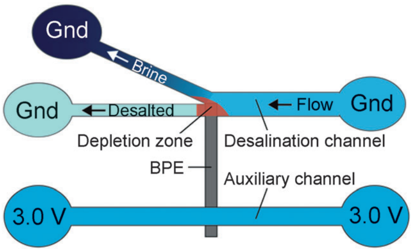
**Blue, green, and yellow** phosphors are obtained in the $Sr_{1-x}Y_{0.98+x}Ce_{0.02}Si_4N_{7-x}C_x$ system ($x = 0 \rightarrow 1$). Decreases in thermal quenching barrier height with $x$ result from a dominant neighboring-cation effect, through which the replacement of $Sr^{2+}$ by $Y^{3+}$ reduces the covalency of Ce–N bonding. Green emission is observed from a cation-segregated nanostructure of $SrYSi_4N_7$ and $Y_2Si_4N_6C$ domains in $x =$ 0.2–0.6 samples.

## Electrochemistry

K. N. Knust, D. Hlushkou, R. K. Anand, U. Tallarek,* R. M. Crooks* **8107 – 8110**

Electrochemically Mediated Seawater Desalination

**Membraneless desalination**: A simple power supply is used to apply a 3.0 V potential bias across a microelectrochemical cell comprising two microchannels spanned by a single bipolar electrode (BPE) to drive chloride oxidation and water electrolysis at the BPE poles. The resulting ion depletion zone and associated electric field gradient direct ions into a branching microchannel, consequently producing desalted water. Gnd = ground.

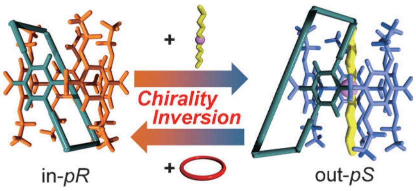


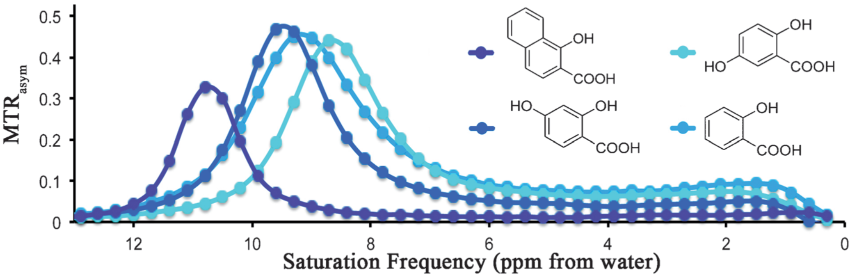
## Inversion of Chirality

T. Ogoshi,* T. Akutsu, D. Yamafuji, T. Aoki, T. Yamagishi **8111 – 8115**

Solvent- and Achiral-Guest-Triggered Chiral Inversion in a Planar Chiral *pseudo*[1]Catenane

**On the flipside**: A planar chiral *pseudo*-[1]catenane based on pillar[5]arene, in which an alkyl chain is connected to one pillar[5]arene unit, has been synthesized. Capture and release of achiral guests and solvents trigger the inclusion and dethreading of the alkyl chain, which causes the inversion of planar chirality.





**More than water**: Chemical exchange saturation transfer (CEST) contrast agents have used water bound to lanthanides as a source of highly shifted exchangeable proton frequencies. Compounds with the 2-hydroxybenzoic acid scaffold were investigated as a source of highly shifted protons for CEST MRI contrasting.

## MRI Contrast Agents

X. Yang, X. Song, Y. Li, G. Liu,
S. Ray Banerjee, M. G. Pomper,*
M. T. McMahon* ________ **8116–8119**

Salicylic Acid and Analogues as diaCEST MRI Contrast Agents with Highly Shifted Exchangeable Proton Frequencies

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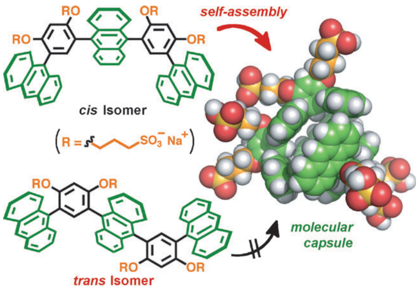
**Atroposelective formation**: Selective formation of a molecular capsule was demonstrated from an amphiphilic *cis*-atropisomer bearing three anthracene rings and four sulfonate groups through hydrophobic and aromatic–aromatic interactions. The dimeric capsule binds small guest molecules; the resultant host–guest complexes exhibit ground-state charge-transfer interactions accompanied by changes in host emission.



## Molecular Capsules

A. Suzuki, K. Kondo, M. Akita,
M. Yoshizawa* ________ **8120–8123**

Atroposelective Self-Assembly of a Molecular Capsule from Amphiphilic Anthracene Trimers

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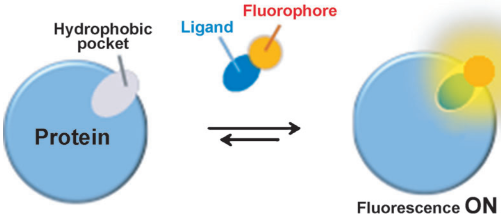

**Bind and shine**: An approach for the selective detection of both enzymes and non-enzymatic proteins using an environment-sensitive fluorescent turn-on probe is described (see scheme). This approach targets the hydrophobic ligand-binding domain of the target protein to trigger the fluorescence turn-on and was shown to be specific for the targeted protein.

## Fluorescent Probes

Y.-D. Zhuang, P.-Y. Chiang, C.-W. Wang,
K.-T. Tan* ________ **8124–8128**

Environment-Sensitive Fluorescent Turn-On Probes Targeting Hydrophobic Ligand-Binding Domains for Selective Protein Detection

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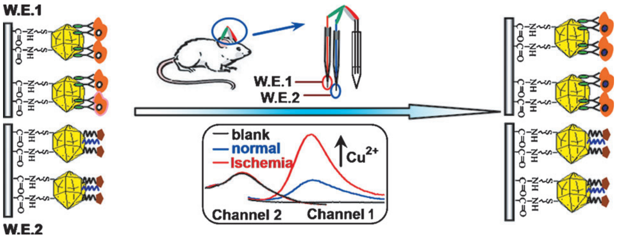


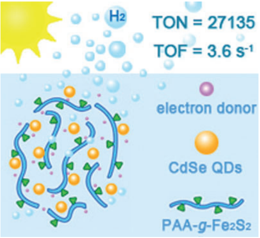
**Brain chemistry**: A biosensor has been developed for in vivo determination of copper ions in a rat brain by using gold truncated octahedral microcages. The significant analytical performance of the present biosensor, as well as the properties of a carbon fiber microelectrode have provided a direct and reliable approach for monitoring cerebral metal ions (W.E. = working electrode; see picture).

## Biosensors

X. Chai, X. Zhou, A. Zhu, L. Zhang, Y. Qin,
G. Shi, Y. Tian* ________ **8129–8133**

A Two-Channel Ratiometric Electrochemical Biosensor for In Vivo Monitoring of Copper Ions in a Rat Brain Using Gold Truncated Octahedral Microcages

## $H_2$ Production



**Light, polymer, action**: A set of water-soluble poly(acrylic acid) catalysts PAA-g-$Fe_2S_2$ containing {$Fe_2S_2$}, an [FeFe]-hydrogenase active-site mimic, is synthesized. This system, combined with CdSe quantum dots and ascorbic acid, has an exceptional turnover number and initial turnover frequency (27135 and 3.6 $s^{-1}$) for the photocatalytic production of $H_2$ in water, which is the highest efficiency to date for [FeFe]-hydrogenase mimics.

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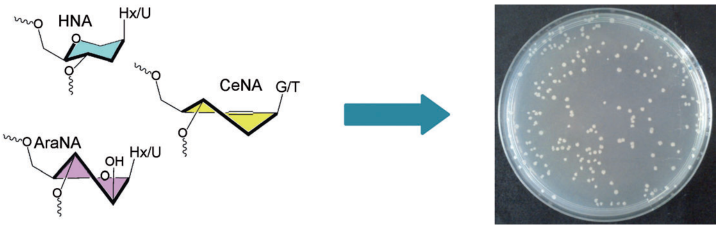
VIP

## Nucleic Acid Analogues



**Hereditary information**, coded in two bases, can be conveyed to DNA in vivo in the form of cyclohexenyl nucleic acid (CeNA), arabinofuranosyl nucleic acid (AraNA), and hexitol nucleic acid (HNA) messages. It was thus demonstrated that a binary genetic cassette can be used for the title process.

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DOI: 10.1002/anie.201305265

# 50 Years Ago . . .

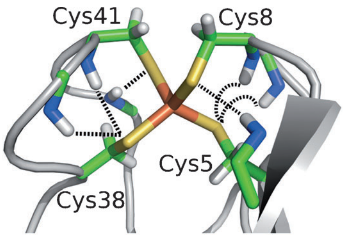
*Angewandte Chemie International Edition* was first published in 1962, the mother journal first in 1888. In this monthly flashback, we feature some of the articles that appeared 50 years ago. This look back can open our eyes, stimulate discussion, or even raise a smile.

"Mental Biochemistry and Control of the Mind" was the concluding section of a Review by J. W. Daly and B. Witkop on centrally active endogenous amines. This Review outlined the biosynthesis, storage, release, and metabolism of compounds such as dopamine and serotonin, as well as their use in treatment of conditions such as schizophrenia.

Horst Prinzbach (1931–2012) reported on the cycloisomerization of 1,3-cyclohexadienes. This diazomethane-sensitized intramolecular reaction results in the formation of bicyclo[2.2.0]hex-2-ene species, as well as hexatrienes and bicyclo[3.1.0]hex-2-ene derivatives. Prinzbach was regarded as one of the top German organic chemists in the second half of the 20th century, and the synthesis of the smallest unsaturated dodecahedrane $C_{20}$ was among his achievements (see *Angew. Chem. Int. Ed.* **2012**, *51*, 11936 for his Obituary).

The analysis of peptide sequences by mass spectrometry had already been established 50 years ago. F. Weygand et al. reported how the high vapor pressure of *N*-trifluoroacetyl peptide esters made them suitable for mass spectrometric analysis, and how mixtures of peptides could be separated by using gas chromatography and identified from the mass spectra of the characteristic fragment ions.

***Read more in Issue 8/1963.***

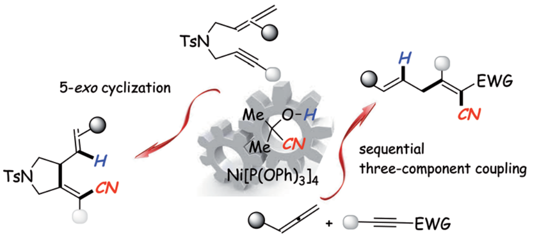


**Spin is the thing**: Iron–sulfur proteins of the rubredoxin family only have one Fe center coordinated by four cysteine residues (see picture, Fe orange). A multiscale modeling approach is used to see if Fe–S bond dissociation in these iron–sulfur clusters occurs by heterolytic fission or homolytic cleavage. As Fe complexes can have near-degenerate levels with different total spin, their spin states and spin crossovers must be characterized during the reaction.

## Bioinorganic Modeling

G. M. Arantes,* A. Bhattacharjee,
M. J. Field ———— **8144–8146**

Homolytic Cleavage of Fe–S Bonds in Rubredoxin under Mechanical Stress

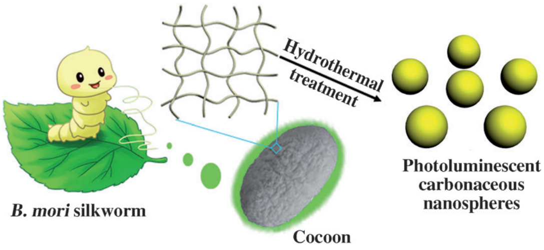


**Packed with functionality**: The key step in the title reactions with acetone cyanohydrin is a regioselective hydronickelation of allenes. Subsequent carbometalation of the alkyne followed by reductive elimination gave cyano-functionalized tetrasubstituted alkenes in a regio- and stereoselective manner (see scheme; EWG = electron-withdrawing group, Ts = *p*-toluenesulfonyl).

## Catalytic Cyanation

S. Arai,* Y. Amako, X. Yang,
A. Nishida ———— **8147–8150**

Hydrocyanative Cyclization and Three-Component Cross-Coupling Reaction between Allenes and Alkynes under Nickel Catalysis

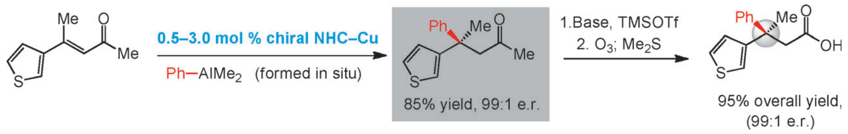


**From silk to spheres**: A large-scale synthesis of water-soluble nitrogen-doped polymer-like carbonaceous nanospheres with a uniform size of ca. 70 nm, through a simple and green hydrothermal process employing cocoon silk in water, has been developed. The resultant nanospheres show excellent photoluminescent properties, exhibit low toxicity, and are biocompatible for in vivo imaging.

## Carbon Nanospheres

W. Li, Z. H. Zhang, B. Kong, S. S. Feng,
J. X. Wang, L. Z. Wang, J. P. Yang,
F. Zhang, P. Y. Wu,*
D. Y. Zhao* ———— **8151–8155**

Simple and Green Synthesis of Nitrogen-Doped Photoluminescent Carbonaceous Nanospheres for Bioimaging



**Acyclic quaternary carbons by conjugate addition**: The first examples of catalytic enantioselective conjugate additions of aryl and alkyl units that generate acyclic all-carbon quaternary stereogenic centers have been developed (see scheme). The requisite organoaluminum reagents can either be prepared in situ from easily available organolithiums or purchased at low cost.

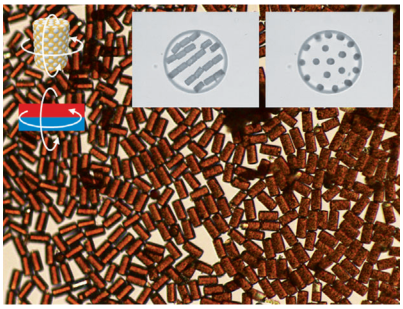
## Enantioselective Catalysis

J. A. Dabrowski, M. T. Villaume,
A. H. Hoveyda* ———— **8156–8159**

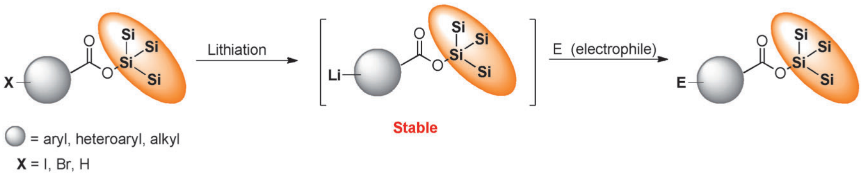
Enantioselective Synthesis of Quaternary Carbon Stereogenic Centers through Copper-Catalyzed Conjugate Additions of Aryl- and Alkylaluminum Reagents to Acyclic Trisubstituted Enones

## Magnetic Particles

**Molded magnets**: The co-assembly of silica colloids and iron oxide nanoparticles in a PDMS mold gives magnetic responsive microparticles. When dispersed in an aqueous solution (see picture), the microparticles could rotate and flip under the action of a magnetic field (1 kG). The particles could also be reversibly switched between aligned chain structures and a hexagonal array in both bulk solutions and in emulsion droplets.



## Synthetic Methods



**It's super-silyl-fragilithyl-ester-aryl-docious**: The super silyl group is a strong protecting group for carboxylic acids and provides a method for direct lithiation that is compatible with the ester moiety. Organolithium compounds bearing a super silyl ester react with a variety of electrophiles in high yields (see scheme). The reaction of lithiated super silyl chloroacetate with a boron compound gives α-functionalization of the ester moiety by Matteson rearrangement.

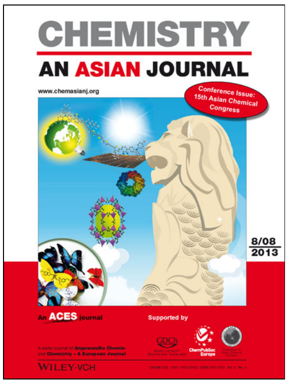
Supporting information is available on www.angewandte.org (see article for access details).

A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

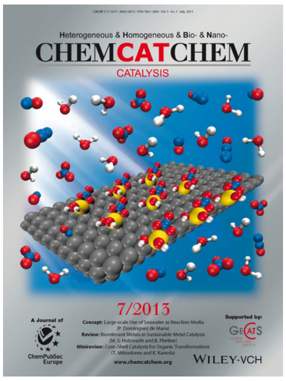
This article is available online free of charge (Open Access).

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

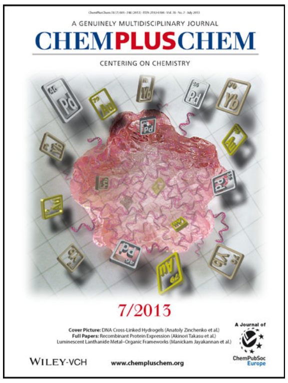
***Check out these journals:***



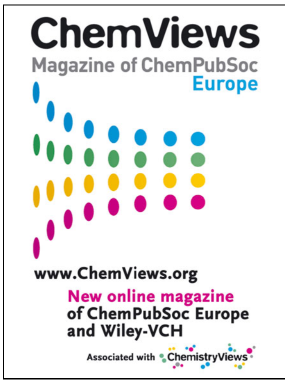
*www.chemasianj.org*



*www.chemcatchem.org*



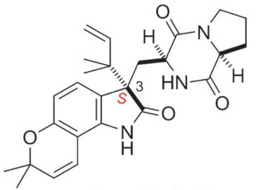
*www.chempluschem.org*



*www.chemviews.org*

# Angewandte Corrigendum

In Scheme 1 of this communication, the structure of notoamide C (**3**) should be corrected as shown below.



notoamide C (**3**)

The configuration at C3 of **3** was not determined by spectroscopic methods and the co-occurrence of notoamides A and B indicated the 3*R* configuration of **3** based on biogenetic considerations. Recently, the absolute configuration of notoamide C was corrected to be 3*S* based on the biochemical conversion of notoamide E into notoamide C by recombinant NotB.[1] This correction affects the structure that appeared in Figure S3 of the Supporting Information. Recently, the relative and absolute configuration of notoamide C was independently reported by Chen et al. on the basis of a single crystal X-ray analysis of notoamide C isolated from *Aspergillus* sp. XS-20090066.[2]

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[1] S. Li, J. M. Finefield, J. D. Sunderhaus, T. J. McAfoos, R. M. Williams, D. H. Sherman, *J. Am. Chem. Soc.* **2012**, *134*, 788 – 791.

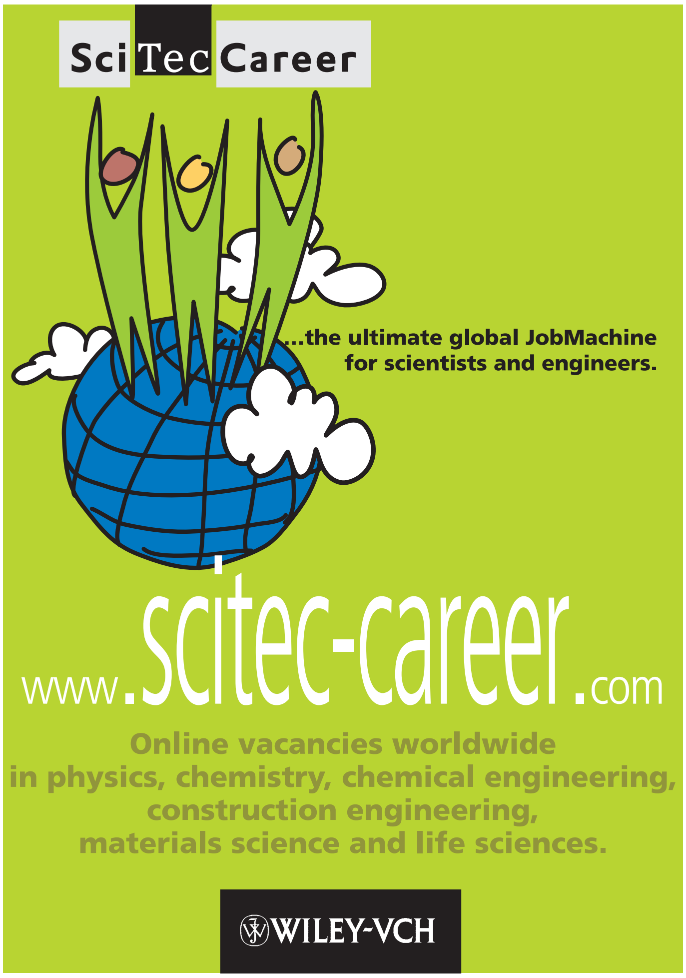
[2] M. Chen, C.-L. Shao, X.-M. Fu, R.-F. Xu, J.-J. Zheng, D.-L. Zhao, Z.-G. She, C.-Y. Wang, *J. Nat. Prod.* **2013**, *76*, 547 – 553.

Notoamides A–D: Prenylated Indole Alkaloids Isolated from a Marine-Derived Fungus, *Aspergillus* sp.

H. Kato, T. Yoshida, T. Tokue, Y. Nojiri,
H. Hirota, T. Ohta, R. M. Williams,
S. Tsukamoto* ______ **2254–2256**

*Angew. Chem. Int. Ed.* **2007**, *46*

DOI: 10.1002/anie.200604381



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**School II** - Department of Chemistry - BasCat, UniCat-BASF Joint Lab

**Reference Number:** II-221/13 (to be filled as soon as possible for 36 months/ closing date for applications 02.09.2013)

**Working field:** The Cluster of Excellence "Unifying Concepts in Catalysis" (UniCat) and the world´s leading chemical company BASF SE established the new joint lab BasCat at Technische Universität Berlin. BasCat is dedicated to the development of new catalytic processes for raw material change. The research program promotes the search for alternatives to petroleum, e.g. by using natural gas. The long term goal is to ensure the continued future availability of raw materials for the production of chemicals. We offer positions for these interdisciplinary approaches in heterogeneous catalysis in a stimulating international workplace with excellent new research facilities in the JointLab on campus of Technische Universität Berlin.

You will participate in research projects to discover and develop new heterogeneous catalysts and process technologies for oxidative conversions of alkanes. The focus of your scientific work will be either on synthesis and characterization of catalytic materials with advanced technologies or on investigation of reaction mechanisms and the state of active catalysts using state-of-the-art testing facilities and in-situ techniques.

**Requirements:** We are looking for candidates with a Master or Diplom with above-average grades in chemistry, chemical engineering or in physics. Experience in preparation of solid materials and/or in common solid state characterization techniques or in heterogeneous catalysis would be of advantage.

Applicants should send a cover letter, CV, copy of the Bachelor / Vordiplom certificate and copy of the Master / Diplom certificate including a summary of the Master thesis and a publication record **with the reference number** to Technische Universität Berlin - Der Präsident - , **Fakultät II, Institut für Chemie, BasCat, UniCat-BASF Joint Lab Office BEL 6, Marchstr. 6, 10587 Berlin** or **by email** to **contact@bascat.tu-berlin.de.**

To ensure equal opportunities between men and women, applications by women with the required qualifications are explicitly desired.

Handicapped applicants with equal qualifications will be favored.

Please send only copies and no originals of documents, as they will not be returned by mail.

The vacancy is also available on the internet at
**http://www.personalabteilung.tu-berlin.de/menue/jobs/**

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