



The following Communications have been judged by at least two referees to be “very important papers” and will be published online at [www.angewandte.org](http://www.angewandte.org) soon:

M. A. Newton,\* M. Di Michiel, A. Kubacka, A. Iglesias-Juez, M. Fernández-García\*

**Observing Oxygen Storage and Release at Work under Cycling Redox Conditions: Synergies between Noble Metal and Oxide Promoter**

P. Berrouard, A. Najari, A. Pron, D. Gendron, P.-O. Morin, J.-R. Pouliot, J. Veilleux, M. Leclerc\*

**Synthesis of 5-Alkyl[3,4-c]thienopyrrole-4,6-dione-Based Polymers through Direct Heteroarylation**

J. Zeng, C. Zhu, J. Tao, M. Jin, H. Zhang, Z.-Y. Li, Y. Zhu, Y. Xia\*  
**Controlling the Nucleation and Growth of Silver on Palladium Nanocubes by Manipulating the Reaction Kinetics**

C. A. DeForest, K. S. Anseth\*

**Photoreversible Patterning of Biomolecules within Click-Based Hydrogels**

T. A. Nigst, J. Ammer, H. Mayr\*

**Ambident Reactivities of Methylhydrazines**

M. Nazaré,\* H. Matter,\* D. W. Will, M. Wagner, M. Urmann, J. Czech, H. Schreuder, A. Bauer, K. Ritter, V. Wehner

**Fragment Deconstruction of Small, Potent Factor Xa Inhibitors: Exploring the Superadditivity Energetics of Fragment Linking in Protein–Ligand Complexes**

G. J. L. Bernardes, G. Casi, S. Trüssel, I. Hartmann, K. Schwager, J. Scheuermann, D. Neri\*

**A Traceless Vascular Targeting Antibody–Drug Conjugate for Cancer Therapy**

H. Chinen, K. Mawatari, Y. Pihosh, K. Morikawa, Y. Kazoe, T. Tsukahara, T. Kitamori\*

**Enhancement of Proton Mobility in Extended Nanospace Channels**

K. Mandal, B. L. Pentelute, D. Bang, Z. P. Gates, V. Y. Torbeev, S. B. H. Kent\*

**Design, Total Chemical Synthesis, and X-ray Structure of a Protein with a Novel Polypeptide Chain Topology**



*“The most significant scientific advance of the last 100 years has been quantum mechanics. The greatest scientific advance in the next decade will be the discovery of a wireless interface between our brains and the internet ...”*  
This and more about Bas de Bruin can be found on page 1102.

## Author Profile

Bas de Bruin \_\_\_\_\_ 1102



G. Wegner



D. Hilvert



J. M. Thomas

## News

Honorary Doctorate:  
G. Wegner \_\_\_\_\_ 1103

Credit Suisse Award:  
D. Hilvert \_\_\_\_\_ 1103

Kapitza Gold Medal and Jayne Prize Lectureship:  
J. M. Thomas \_\_\_\_\_ 1103

## Books

Periodic Tales

Hugh Aldersey-Williams

reviewed by M. Driess \_\_\_\_\_ 1104

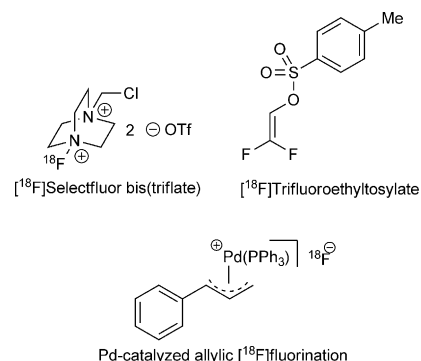
## Highlights

### Radiochemistry

R. Littich, P. J. H. Scott\* — 1106–1109

Novel Strategies for Fluorine-18  
Radiochemistry

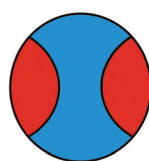
**Radiotracers:** The growing demand for novel radiopharmaceuticals can only be met through the development of new approaches to isotopic labeling. Effective strategies and reagents for nucleophilic and electrophilic  $^{18}\text{F}$ -radiolabeling are highlighted (see picture).



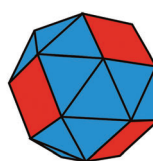
### Self-Assembly

L. R. MacGillivray\* — 1110–1112

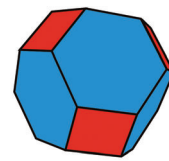
Design Rules: A Net and Archimedean  
Polyhedra Score Big for Self-Assembly



tennis ball



snub cube



truncated octahedron

**Caged:** Taking its origin in recent work by Ward and co-workers, an overview is given on the synthesis of Archimedean and

Platonic bodies (see picture) by different approaches, such as hydrogen-bonded self-assembly and coordination chemistry.

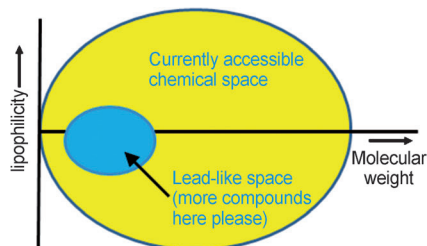
## Minireviews

### Synthetic Chemistry

A. Nadin, C. Hattotuwigama,  
I. Churcher\* — 1114–1122



Lead-Oriented Synthesis: A New  
Opportunity for Synthetic Chemistry



**Leading the way:** Lead-oriented synthesis (LOS) is a new but simple concept describing reactions that allow the efficient preparation of diverse sets of small, polar molecules to act as starting points for drug discovery. Much existing synthetic methodology cannot easily deliver this, and a huge opportunity exists for developers of new reactions to help the search for new medicines by developing more syntheses that are lead-oriented in nature.

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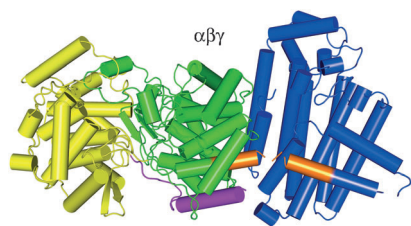
individuals who are personal members of a  
national chemical society prices are available  
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sales tax.

## Reviews

### Terpenes

E. Oldfield,\* F.-Y. Lin — 1124–1137

Terpene Biosynthesis: Modularity Rules



**Natural building blocks:** Recent progress has been achieved in determining the structure, function, and inhibition of the enzymes responsible for the formation of terpenes and isoprenoids. Most of these enzymes contain combinations of  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -,  $\epsilon$ -, and/or  $\zeta$ -domain structures that in many cases are fused to form modular proteins. Gene fusion, exon loss, and recombination are thought to play major roles in the genesis of these enzymes.

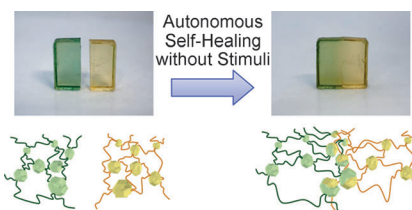
## Communications

### Self-Healing Materials

K. Imato, M. Nishihara, T. Kanehara, Y. Amamoto, A. Takahara,\* H. Otsuka\* — 1138–1142

Self-Healing of Chemical Gels Cross-Linked by Diarylbibenzofuranone-Based Trigger-Free Dynamic Covalent Bonds at Room Temperature

**Linked:** Polymers cross-linked with diarylbibenzofuranone units have been prepared by polyaddition. The exchange of bonds of the gels and their macroscopic self-healing were accomplished under air at room temperature in the dark. The macroscopic fusion of completely separated parts was successful (see picture).

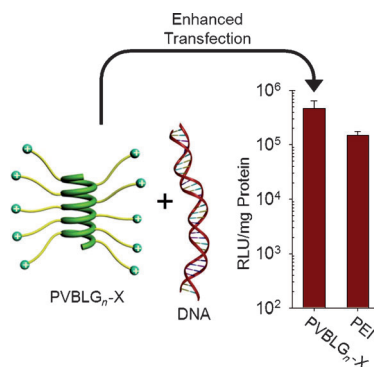


Frontispiece

### Gene Delivery

N. P. Gabrielson, H. Lu, L. Yin, D. Li, F. Wang,\* J. Cheng\* — 1143–1147

Reactive and Bioactive Cationic  $\alpha$ -Helical Polypeptide Template for Nonviral Gene Delivery

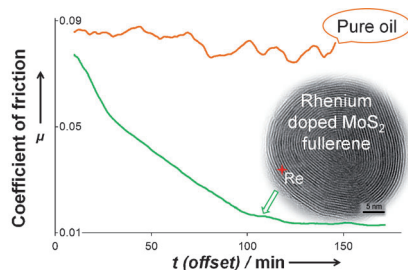


**At every turn:** Poly( $\gamma$ -(4-vinylbenzyl)-L-glutamate) (PVBLG) is a bioactive and reactive template for a library of cationic  $\alpha$ -helical polypeptides (PVBLG<sub>n</sub>-X) for gene delivery. The top-performing PVBLG<sub>n</sub>-X outperformed polyethyleneimine (PEI) by 12-fold. Preliminary data indicate that the helicity of the polypeptides is essential for their performance, and enhanced membrane disruption is a likely source of their transfection efficiency. RLU = relative light unit.

### Nanomaterials

L. Yadgarov, R. Rosentsveig, G. Leituss, A. Albu-Yaron, A. Moshkovich, V. Perfilov, R. Vasic, A. I. Frenkel, A. N. Enyashin, G. Seifert, L. Rapoport, R. Tenne\* — 1148–1151

Controlled Doping of MS<sub>2</sub> (M = W, Mo) Nanotubes and Fullerene-like Nanoparticles



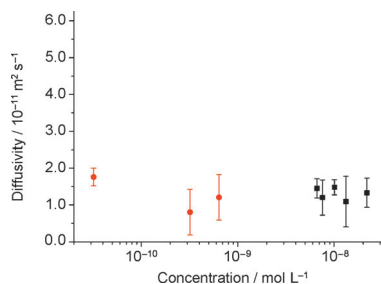
**Lubricating nanoparticles:** The effect of doping semiconductor hollow closed-fullerene-like nanoparticles of MoS<sub>2</sub> and WS<sub>2</sub> has been overlooked to date. Rhenium doping of these nanoparticles leads to a marked increase in the nanoparticle's conductivity, reduced agglomeration, and a great reduction in friction and wear (see picture) that approaches superlubricity.

### Single-Molecule Spectroscopy

F. Feil, S. Naumov, J. Michaelis,  
R. Valiullin, D. Enke, J. Kärger,\*  
C. Bräuchle\* — 1152–1155



Single-Particle and Ensemble  
Diffusivities—Test of Ergodicity



To prove the ergodic theorem experimentally the diffusivities of guest molecules inside a nanostructured porous glass were measured by using two conceptually different approaches under identical conditions. The data obtained through the direct observation of dye-molecule diffusion by single-molecule tracking experiments (red circles) was in perfect agreement with the ensemble value obtained in pulsed-field gradient NMR experiments (black squares).

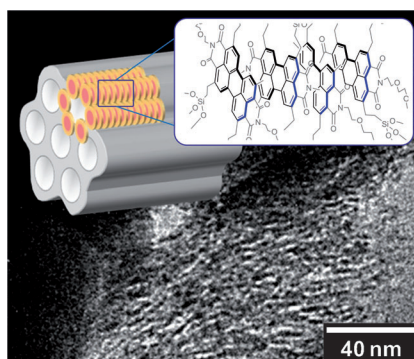
Back Cover

### Mesoporous Organosilica

N. Mizoshita,\* T. Tani, H. Shinokubo,  
S. Inagaki\* — 1156–1160



Mesoporous Organosilica Hybrids  
Consisting of Silica-Wrapped  $\pi$ - $\pi$   
Stacking Columns



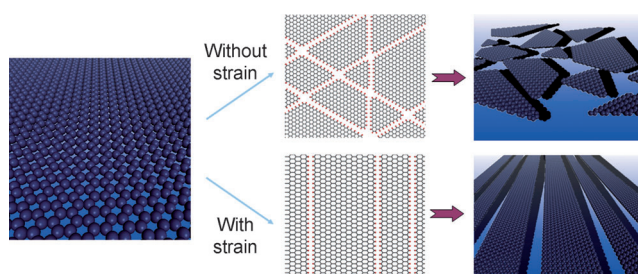
A new class of periodic mesoporous organosilica (PMO) materials with a columnar  $\pi$ -stacking arrangement of the framework organic groups has been prepared from disklike precursors with hydrophobic perylene bisimide (PBI) cores (see picture). The PBI-bridged PMOs exhibit exciton coupling and efficient formation of mobile radical spins by electron doping within the pore walls.

### Cutting Graphene

L. Ma, J. Wang,\* F. Ding\* — 1161–1164

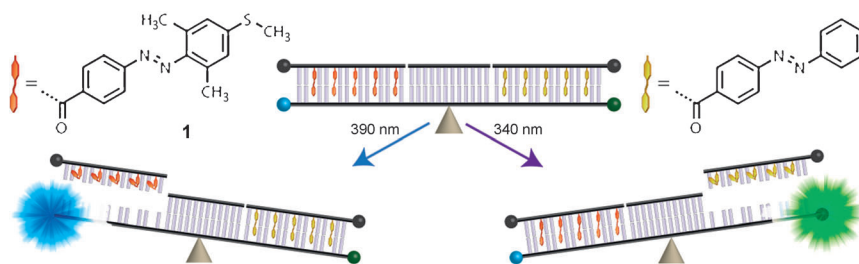


Strain-Induced Orientation-Selective  
Cutting of Graphene into Graphene  
Nanoribbons on Oxidation



**Cut to ribbons:** Making atomically well-controlled graphene nanoribbons (GNRs) is prerequisite for many graphene applications. Ab initio calculations reveal that, on applying a uniaxial external tensile strain, O atoms adsorbed on graphene

form parallel epoxy chains, and subsequent cutting by oxygen attack gives GNRs instead of the quantum dots that are obtained from unstrained graphene (see picture).



**DNA seesaw:** Photoswitchable azobenzene carboxylic acid **1** reversibly photoisomerizes between the *trans* form and the thermally stable *cis* form upon irradiation with visible light. A photon-fueled DNA nanodevice that moves like a seesaw in

response to irradiation with different wavelengths of light was made by modifying DNA oligonucleotides with a combination of **1** and a conventional azobenzene (see picture).

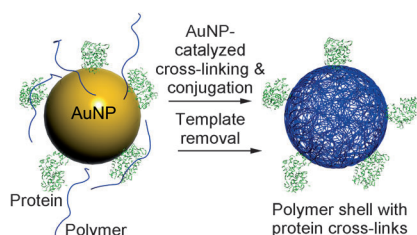
## Molecular Devices

H. Nishioka, X. Liang,\* T. Kato, H. Asanuma\* — 1165–1168

A Photon-Fueled DNA Nanodevice that Contains Two Different Photoswitches



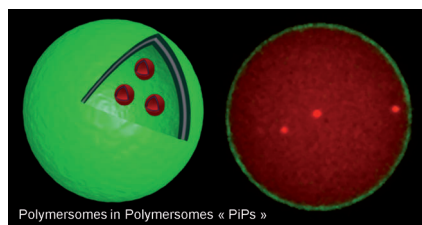
**Nanopods** functionalized with anti-HER2 antibodies (ImmunoPods, see scheme) have been synthesized by adsorbing the proteins onto gold nanoparticles and catalytically cross-linking them with a coadsorbed polymer through pendant propargyl ether groups. Upon dissolution of the gold template, the hollow polymer nanopod–protein conjugates remain. ImmunoPods are bioactive and can target cancer cells that express the HER2 antigen.



## Nanoconjugates

K. Zhang, D. Zheng, L. Hao, J. I. Cutler, E. Auyeung, C. A. Mirkin\* — 1169–1172

ImmunoPods: Polymer Shells with Native Antibody Cross-Links

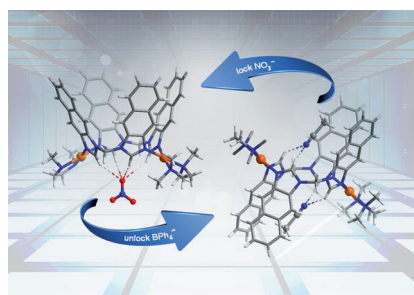


**Capsules in capsules:** An emulsion–centrifugation method allows polymersomes in polymersomes “PiPs” (see picture) or polymer vesosomes to be prepared. This simple approach to generate biomimetic compartmentalized structures offers a way to encapsulate several different and even mutually incompatible active substances, thereby opening avenues in combinatory drug release and providing exquisite control of permeation properties.

## Vesicles

M. Marguet, L. Edembe, S. Lecommandoux\* — 1173–1176

Polymersomes in Polymersomes: Multiple Loading and Permeability Control



**Anion switches:** A bistable self-assembled metal–organic macrocycle undergoes intramolecular conformational motion that is switched reversibly with anions by multiple hydrogen-bonding interactions (see picture; Pd orange, N blue, O red). The molecular bowl fixed with a nitrate anion could be freed to a partial chair by adding a tetraphenylborate anion.

## Molecular Devices

T.-Z. Xie, C. Guo, S.-Y. Yu,\* Y.-J. Pan\* — 1177–1181

Fine-Tuning Conformational Motion of a Self-Assembled Metal–Organic Macrocycle by Multiple C–H...Anion Hydrogen Bonds



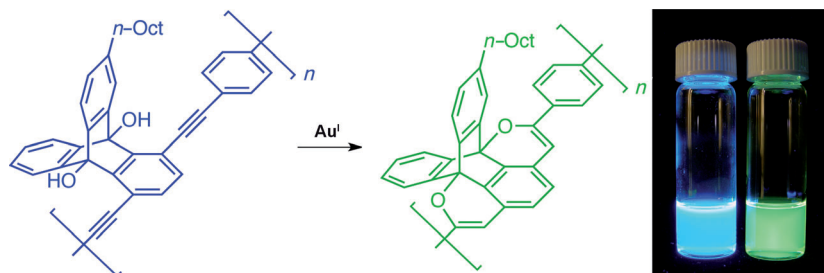


## Annulation

B. VanVeller, D. Robinson,  
T. M. Swager\* 1182–1186



Triptycene Diols: A Strategy for  
Synthesizing Planar  $\pi$  Systems through  
Catalytic Conversion of a  
Poly(*p*-phenylene ethynylene) into a  
Poly(*p*-phenylene vinylene)



**At level best:** A strategic synthesis of a new class of poly(*p*-phenylene vinylene)-bearing annulated alkene units from a parent poly(*p*-phenylene ethynylene) is described (see scheme). The gold-mediated cycloisomerization reaction of

alkynes with appended hydroxy-group reacting partners delivers products having a stark increase in chain rigidity and planarity, as evidenced by pronounced photophysical changes.

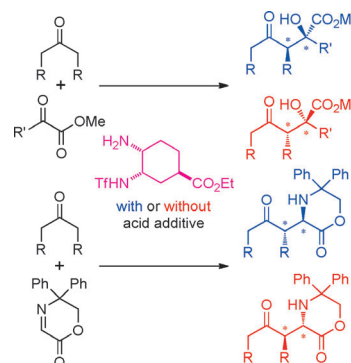
## Organocatalysis

S. A. Moteki, J. Han, S. Arimitsu,  
M. Akakura, K. Nakayama,  
K. Maruoka\* 1187–1190



An Achiral-Acid-Induced Switch in the  
Enantioselectivity of a Chiral *cis*-Diamine-  
Based Organocatalyst for Asymmetric  
Aldol and Mannich Reactions

**Pick and choose:** The asymmetric synthesis of two different enantiomeric products has been achieved through the use of a single organocatalyst with or without achiral organic acid additives (see scheme). These additives may assist in altering the substrate orientations at the catalytic center, leading to efficient enantiomeric inversions in both aldol and Mannich products.

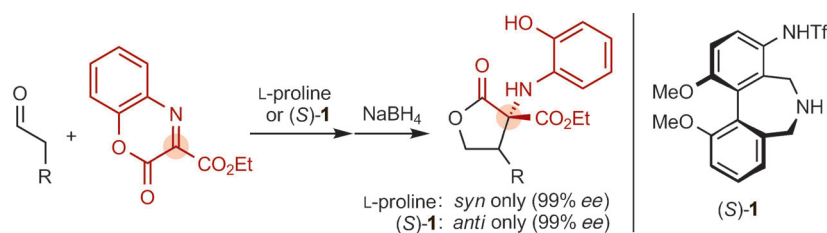


## Organocatalysis

T. Kano, S. Song, Y. Kubota,  
K. Maruoka\* 1191–1194

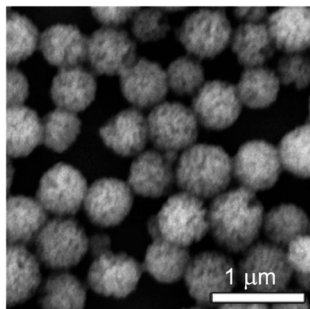


Highly Diastereo- and Enantioselective  
Mannich Reactions of Synthetically  
Flexible Ketimines with Secondary Amine  
Organocatalysts



**High selectivity:** A highly diastereo- and enantioselective Mannich reaction between a synthetically flexible ketimine and aldehydes has been developed. The *syn*- or *anti*-Mannich products contain tetrasubstituted chiral carbon centers and

were obtained with almost complete stereoselectivity by using either L-proline or an axially chiral aminosulfonamide, respectively, as the catalyst (see scheme, Tf = trifluoromethanesulfonyl).



**Simply smaller:** Sub-micrometer vaterite particles (see picture) were synthesized by modifying the crystal growth parameters. Their porous structure allows the loading and storage of various payloads. The recrystallization to calcite in aqueous solutions can be used as a release mechanism. The release can be controlled by the properties of the immersion medium, thereby creating a simple, cost-effective, and versatile system for drug-delivery applications.

### Nanocontainers

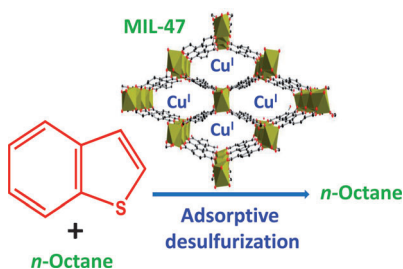
B. V. Parakhonskiy,\* A. Haase,  
R. Antolini — 1195 – 1197

Sub-Micrometer Vaterite Containers:  
Synthesis, Substance Loading, and  
Release



Inside Cover

**A molecular sieve:** A metal–organic framework (MOF) MIL-47 loaded with  $\text{CuCl}_2$  shows the highest adsorption capacity for benzothiophene because of the presence of  $\text{Cu}^I$  ions derived from  $\text{Cu}^{II}$  ions and porous MIL-47. The  $\text{Cu}^I$  ions were obtained by reduction of  $\text{Cu}^{II}$  with  $\text{V}^{III}$  ions in MIL-47. The modified MOF could be successfully used for the desulfurization of a liquid fuel (see picture).



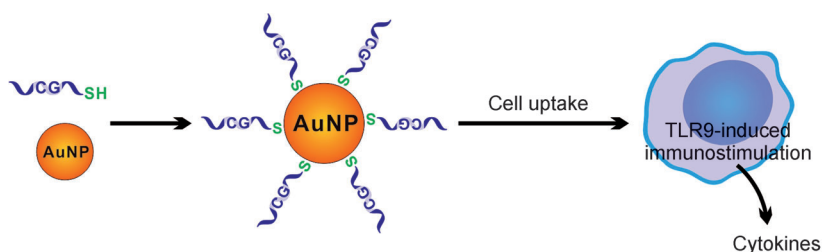
### Metal–Organic Frameworks

N. A. Khan, S. H. Jhung\* — 1198 – 1201

Remarkable Adsorption Capacity of  
 $\text{CuCl}_2$ -Loaded Porous Vanadium  
Benzenedicarboxylate for Benzothiophene



Inside Back Cover



**Delivery vehicles:** Gold nanoparticles (AuNPs) have been used as a nanocarrier to non-invasively deliver synthetic cytosine–phosphate–guanosine (CpG) oligodeoxynucleotides (ODNs) into cells. Compared to unconjugated single-

stranded CpG ODNs, self-assembled polyvalent CpG-AuNP conjugates enhance the efficiency of cellular uptake and stimulate secretion of cytokines (see picture).

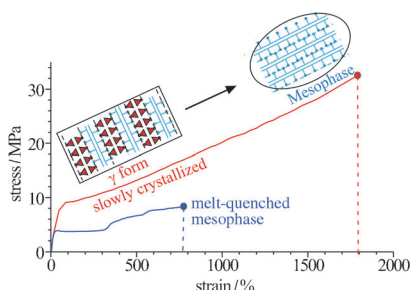
### Oligodeoxynucleotides

M. Wei, N. Chen, J. Li, M. Yin, L. Liang,  
Y. He, H. Song, C. Fan,\*  
Q. Huang\* — 1202 – 1206

Polyvalent Immunostimulatory  
Nanoagents with Self-Assembled CpG  
Oligonucleotide-Conjugated Gold  
Nanoparticles



**Crystals in polymers:** The  $\gamma$  form of isotactic polypropylene shows an unexpected better ductility than the mesophase because of the occurrence of a stress-induced transition from the  $\gamma$  form to the mesophase. This provides a mechanism of conversion of mechanical energy into latent heat of fusion that induces local melting of the crystals followed by recrystallization at high deformation in the mesophase (see picture).



### Homogeneous Catalysis

C. De Rosa,\* F. Auriemma — 1207 – 1211

The Deformability of Polymers: The Role  
of Disordered Mesomorphic Crystals and  
Stress-Induced Phase Transformations

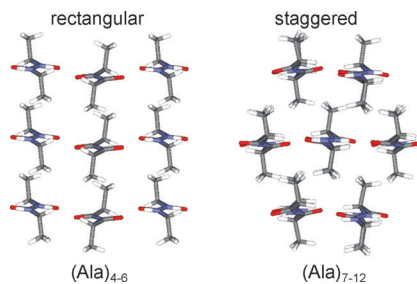


## Structure Elucidation

T. Asakura,\* M. Okonogi, K. Horiguchi,  
A. Aoki, H. Saitô, D. P. Knight,  
M. P. Williamson — 1212–1215



Two Different Packing Arrangements of  
Antiparallel Polyalanine



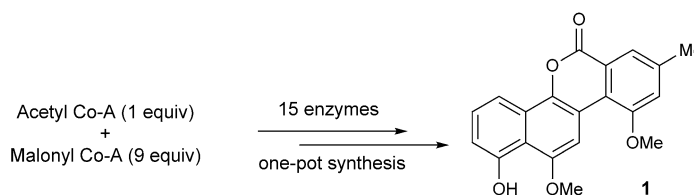
**Two  $\beta$ -sheet arrangements:** Polyalanines have been shown to adopt two different antiparallel crystal-packing arrangements, depending on the length of the polymers. Short polymers that contain six alanine residues or fewer adopt a rectangular packing arrangement, whereas longer polymers are packed in a staggered pattern (see scheme). The elucidation of these structures may help to explain the physical and biological properties of polyalanines.

## Biosynthesis

P. Pahari, M. K. Kharel, M. D. Shepherd,  
S. G. van Lanen, J. Rohr\* — 1216–1220



Enzymatic Total Synthesis of  
Defucogilvocarcin M and Its Implications  
for Gilvocarcin Biosynthesis



**Teamwork:** Defucogilvocarcin M (**1**, see scheme) was synthesized in a one-pot, enzymatic reaction from acetyl-CoA and malonyl-CoA by a combination of 15 enzymes obtained from *E. coli* as well as the gilvocarcin, jadomycin, and ravidomycin biosynthetic pathways. The mixture of enzymes was systematically reduced and varied to further delineate the sequence of reactions in the complex, post-polyketide steps of gilvocarcin biosynthesis.

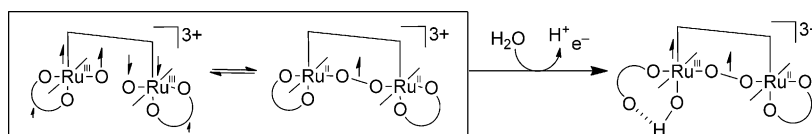
mycin biosynthetic pathways. The mixture of enzymes was systematically reduced and varied to further delineate the sequence of reactions in the complex, post-polyketide steps of gilvocarcin biosynthesis.

## Water Oxidation Catalysis

S. Ghosh, M.-H. Baik\* — 1221–1224



The Mechanism of O–O Bond Formation  
in Tanaka's Water Oxidation Catalyst



**Oh-oh!** The mechanism of water oxidation by Tanaka's catalyst (shown schematically in the picture) has been studied by using quantum chemical methods. The formation of the O–O bond between the two terminal oxo moieties of the catalyst lacks

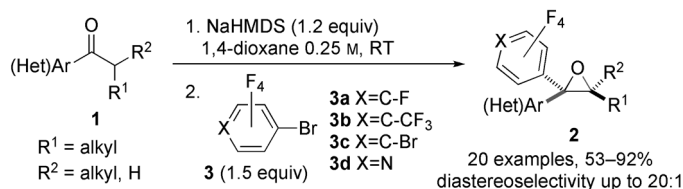
any thermodynamic driving force. The redox-active quinone ligand, however, assists in the addition of a water molecule to one of the Ru centers, thus facilitating the release of dioxygen.

## Cascade Reactions

Z. Li, V. Gevorgyan\* — 1225–1227



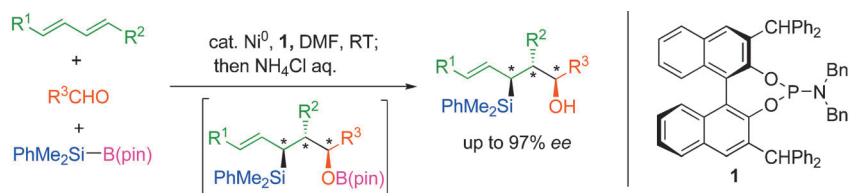
One-Pot Arylative Epoxidation of Ketones  
by Employing Amphoteric  
Bromoperfluoroarenes



**A one-pot cascade** synthesis of perfluoroaryl oxiranes **2** by the arylative epoxidation of enolizable ketones **1** with bromopentafluorobenzene (PFPBr) and derivatives (**3**) is reported. PFPBr is utilized as an

equivalent of Br<sup>+</sup> and PFP<sup>−</sup> in this highly efficient, easily scaled-up, diastereoselective epoxidation reaction, which produces synthetically useful polyfluoroaryl oxiranes.





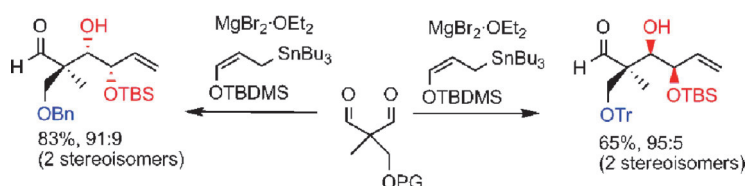
**Three-in-one:** The nickel-catalyzed asymmetric three-component coupling of 1,3-dienes, aldehydes, and a silylborane in the presence of a chiral phosphoroamidite ligand has been realized. The reaction

proceeds by  $\alpha$ -bond metathesis of an oxanickelacycle intermediate with the silylborane to afford the corresponding  $\alpha$ -chiral allylsilane derivative in a highly diastereo- and enantioselective manner.

### $\alpha$ -Chiral Allylsilanes

N. Saito,\* A. Kobayashi,  
Y. Sato\* — 1228–1231

Nickel-Catalyzed Enantio- and Diastereoselective Three-Component Coupling of 1,3-Dienes, Aldehydes, and a Silylborane Leading to  $\alpha$ -Chiral Allylsilanes



**Tamed by chelation:** The  $\text{MgBr}_2$  chelation of prochiral malonaldehydes allows diastereoselective monoaddition reactions with allyl stannane nucleophiles (see scheme; PG = protecting group, TBDMS = *tert*-butyldiphenylmethylsilyl,

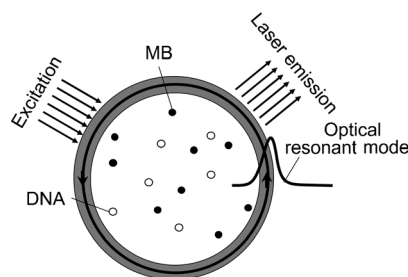
Tr = trityl). In the same pot, addition of a second nucleophile proceeds in high diastereoselectivity to generate nonsymmetric products with up to five contiguous stereogenic centers, including a chiral all-carbon quaternary center.

### Synthetic Methods

B. Linclau,\* E. Cini, C. S. Oakes, S. Josse,  
M. Light, V. Ironmonger — 1232–1235

Stereoarrays with an All-Carbon Quaternary Center: Diastereoselective Desymmetrization of Prochiral Malonaldehydes

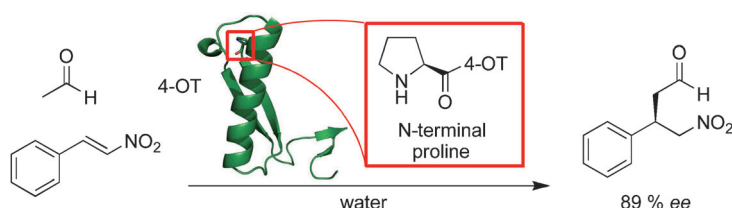
**Laser precision:** A highly sensitive technique based on laser emission for differentiating a target DNA strand from strands that contain single base mismatches has been developed. Laser emission is used to amplify the small difference in signals that are generated by the different strands after hybridization with a molecular beacon (MB, see picture) in a conversion that is similar to analog-to-digital.



### DNA Detection

Y. Sun, X. Fan\* — 1236–1239

Distinguishing DNA by Analog-to-Digital-like Conversion by Using Optofluidic Lasers



**Non-natural beauty:** The enzyme 4-oxalocrotonate tautomerase (4-OT) promiscuously (i.e., with non-natural activity) catalyzes the Michael-type addition of acetaldehyde to nitrostyrene. Catalysis likely proceeds via enamine formation of

the amino-terminal proline residue of 4-OT with acetaldehyde (see picture), reminiscent of organocatalysis. High stereoselectivity, low catalyst loading, and water as reaction medium characterize this methodology.

### Enzyme Catalysis

E. Zandvoort, E. M. Geertsema, B.-J. Baas,  
W. J. Quax,  
G. J. Poelarends\* — 1240–1243

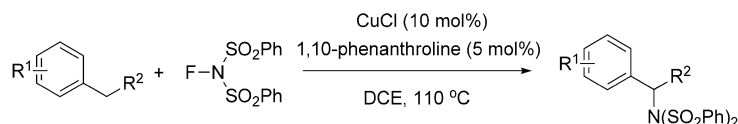
Bridging between Organocatalysis and Biocatalysis: Asymmetric Addition of Acetaldehyde to  $\beta$ -Nitrostyrenes Catalyzed by a Promiscuous Proline-Based Tautomerase

## Synthetic Methods

Z.-K. Ni, Q. Zhang,\* T. Xiong, Y.-Y. Zheng,  
Y. Li, H.-W. Zhang, J.-P. Zhang,\*  
Q. Liu\* ————— 1244–1247



Highly Regioselective Copper-Catalyzed  
Benzylic C–H Amination by  
N-Fluorobenzenesulfonimide



**Primary target:** A practical and effective copper-catalyzed amination strategy for synthesizing various benzylic amines from benzylic hydrocarbons is described (see scheme; DCE = 1,2-dichloroethane).

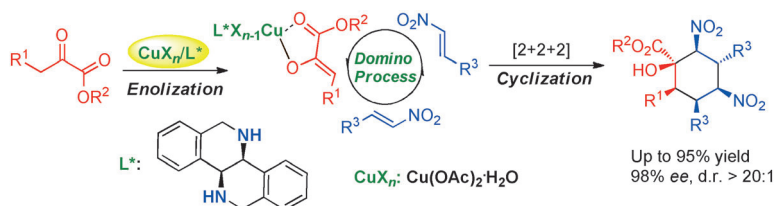
Xylene substrates can undergo diamination reactions using this method. The remarkable preference for primary over secondary benzylic C–H bonds has been observed for the first time.

## Asymmetric Catalysis

D. Shi, Y. Xie, H. Zhou, C. Xia,  
H. Huang\* ————— 1248–1251



A Highly Diastereo- and Enantioselective  
Reaction for Constructing Functionalized  
Cyclohexanes: Six Contiguous  
Stereocenters in One Step



**Just mix to get six:** Six contiguous stereocenters, including one quaternary stereocenter, and three C–C bonds are created by a new copper-catalyzed tandem reaction (see scheme). Rigid chiral di-

amine ligands enabled this asymmetric tandem reaction to proceed with excellent stereoselectivity (complete diastereoselectivity and high enantioselectivity) and high yield under mild reaction conditions.

DOI: 10.1002/anie.201108796

# 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.

The Nobel Prize in Chemistry 1961 was awarded to M. Calvin for his “research on the carbon dioxide assimilation in plants”. Issue 2/1962 contains Calvin’s Nobel Lecture, in which he describes how  $^{14}\text{C}$  radiolabeling was used to track carbon that enters a plant as carbon dioxide and is turned to carbohydrate in the photosynthetic carbon cycle. *Angewandte Chemie* has kept the tradition of publishing the Nobel Lectures to this very day.

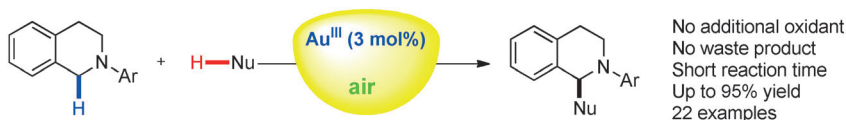
These days, the mercury ion is considered an environmental hazard and its sensing and extraction are frequently

reported. In former times however,  $\text{HgSO}_4 \cdot 2\text{HgO}$ , which was discovered in 1604, was even used medicinally! In 1962, A. Weiss reported on the structure of this salt, which was shown by X-ray studies to consist of polymeric  $(\text{Hg}_3\text{O}_2)^+$  cations in slightly undulating two-dimensional infinite layers.

The butterfly and the salamander are the sources of natural products that were discussed in two Communications. C. Schöpf outlined how the pigment erythropterin was synthesized by treatment of xanthoperin with oxalacetic acid at pH 4.2 and 80 °C. It was postulated that

xanthoperin was the primary product in the biosynthesis of pteridine butterfly pigments. G. Habermehl reported the elucidation of the structure of samandaridine, which was isolated along with a range of other alkaloids from the skin gland venom of the fire and alpine salamanders. The structure was deduced from an X-ray study of the hydrobromide salt, and the configuration was confirmed by the two-dimensional electron density projection—quite an achievement 50 years ago!

[Read more in Issue 2/1962](#)



### Gold Catalysis

J. Xie, H. Li, J. Zhou, Y. Cheng,  
C.-J. Zhu\* — 1252 – 1255

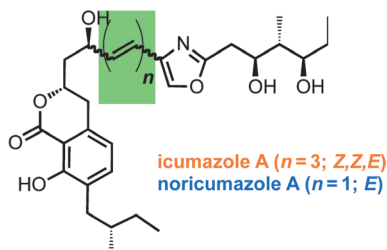
**A breath of fresh air:** The title reaction has been developed for the coupling of amines with nitroalkanes and different unmodified ketones using air as the sole oxidant under mild reaction conditions.

The safe, convenient, and environmentally benign process, as well as the low catalyst loading, short reaction time, and good yields make this protocol very practical (see scheme).

A Highly Efficient Gold-Catalyzed Oxidative C–C Coupling from C–H Bonds Using Air as Oxidant



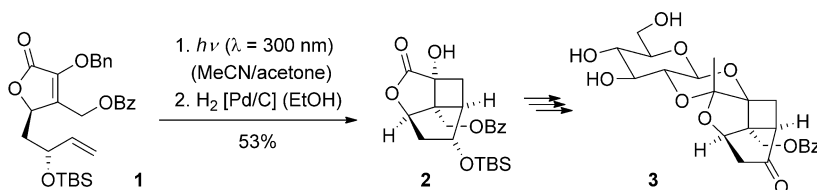
**Joint efforts:** The antifungal icumazole A, the potassium-ion-channel inhibitor noricumazole A, and their glycosylated derivatives are new, structurally related secondary metabolites isolated from *Sorangium cellulosum*. Their structures have been fully assigned by a joint strategy that relied on spectroscopy, derivatization, fragmentation, and finally the first total synthesis of noricumazole A.



### Natural Products

J. Barbier, R. Jansen, H. Irschik, S. Benson,  
K. Gerth, B. Böhlendorf, G. Höfle,  
H. Reichenbach, J. Wegner, C. Zeilinger,  
A. Kirschning,\* R. Müller\* — 1256 – 1260

Isolation and Total Synthesis of Icumazoles and Noricumazoles—Antifungal Antibiotics and Cation-Channel Blockers from *Sorangium cellulosum*



**Enlightning synthesis:** A light-induced intramolecular [2+2] photocycloaddition reaction (**1**→**2**) was the key step in the stereoselective synthesis of (+)-lactiflorin (**3**) and its triacetate. By comparison with

reported analytical data, it was possible to unambiguously elucidate the structure of this natural product, to which three different structures had been previously assigned.

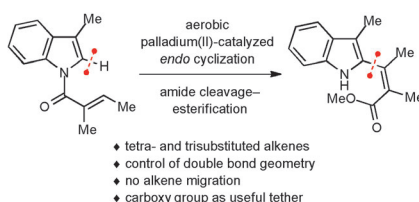
### Natural Product Synthesis

P. Lu, T. Bach\* — 1261 – 1264

Total Synthesis of (+)-Lactiflorin by an Intramolecular [2+2] Photocycloaddition



**The endo trick:** An *endo* ring closure onto the trigonal  $\beta$  carbon atom of  $\alpha,\beta$ -unsaturated acceptors that are tethered to the indole nitrogen atom followed by amide cleavage enables the diastereoselective C-2 alkenylation of indoles with fully substituted double bonds. The carboxy group functions as a synthetically useful temporary tether (see scheme).



### C–H Bond Functionalization

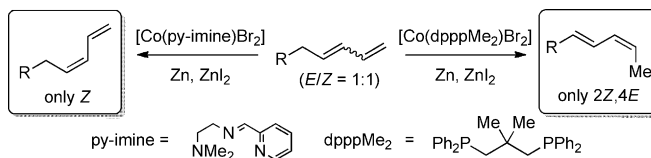
S. R. Kandukuri, J. A. Schiffner,  
M. Oestreich\* — 1265 – 1269

Aerobic Palladium(II)-Catalyzed 5-*endo-trig* Cyclization: An Entry into the Diastereoselective C-2 Alkenylation of Indoles with Tri- and Tetrasubstituted Double Bonds



## Synthetic Methods

F. Pünner, A. Schmidt,  
G. Hilt\* \_\_\_\_\_ 1270–1273



Up the Hill: Selective Double-Bond Isomerization of Terminal 1,3-Dienes towards Z-1,3-Dienes or 2Z,4E-Dienes

**Against all odds:** Two different cobalt catalyst systems led to the selective isomerization of 1,3-dienes. In the case of the [CoBr<sub>2</sub>(py-imine)]-catalyzed reaction, the Z-1,3-diene was formed in a highly

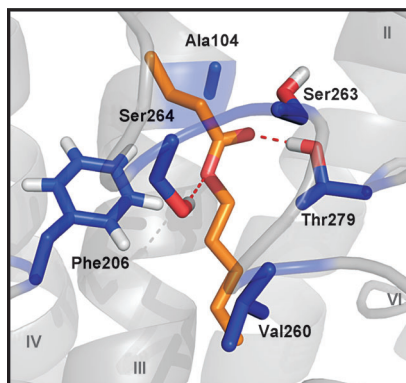
selective manner (see scheme). When the catalyst precursor [CoBr<sub>2</sub>(dpppMe<sub>2</sub>)] was applied, a double-bond migration and selective isomerization towards the 2Z,4E-configured 2,4-dienes were observed

## Structural Biology

L. Gelis, S. Wolf, H. Hatt, E. M. Neuhaus,  
K. Gerwert\* \_\_\_\_\_ 1274–1278



Prediction of a Ligand-Binding Niche within a Human Olfactory Receptor by Combining Site-Directed Mutagenesis with Dynamic Homology Modeling



**Reprogramming a smell receptor:** The ligand-binding niche within a three-dimensional model of a human olfactory receptor has been predicted by dynamic homology modeling and confirmed experimentally by functional studies of site-directed receptor mutants. Even a proposed reprogramming of the receptor's binding and activation properties was experimentally confirmed.

**Front Cover**



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