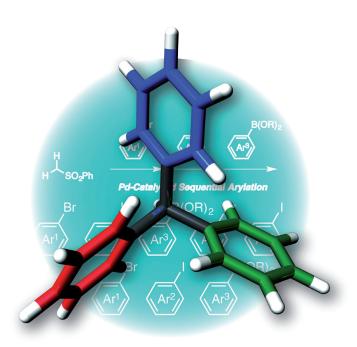
# Triarylmethanes were prepared ...





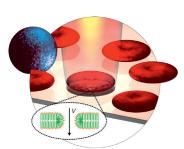
... in three steps from phenyl methyl sulfone, as described by M. Nambo and C. M. Crudden in their Communication on page 742 ff. After two selective C–H arylation reactions, the third aromatic ring was introduced through a novel arylative desulfonation. This sequence permits the synthesis of a wide variety of unsymmetric triarylmethanes from a simple, readily available starting material.

#### X...H Hydrogen Bonds

Unconventional CH···X hydrogen bonds are strong enough to drive supramolecular polymerization and gelation processes, as described by G. Fernández et al. in their Communication on page 700 ff.

The molecular arrangement is maintained in the crystalline state.



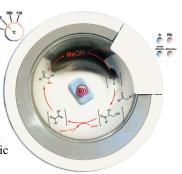


## Shape-Dependent Lysis

In their Communication on page 842 ff., J. M. Cooper et al. describe the selective lysis of red blood cells by an electric field. The selectivity results from the shape of the blood cells.

#### Ketone Alkylation

T. J. Donohoe et al. describe in their Communication on page 761 ff. the use of methanol as an alkylating reagent in a rhodium-catalyzed reaction to generate branched alkyl products from aromatic and aliphatic ketones under mild conditions.



#### How to contact us:

#### Editorial Office:

E-mail: angewandte@wiley-vch.de Fax: (+49) 62 01–606-331 Telephone: (+49) 62 01–606-315

## Reprints, E-Prints, Posters, Calendars:

Carmen Leitner

E-mail: chem-reprints@wiley-vch.de
Fax: (+49) 62 01-606-331
Telephone: (+49) 62 01-606-327

#### Copyright Permission:

Bettina Loycke

E-mail: rights-and-licences@wiley-vch.de

Fax: (+49) 62 01–606-332 Telephone: (+49) 62 01–606-280

#### Online Open:

Margitta Schmitt, Carmen Leitner

E-mail: angewandte@wiley-vch.de

Fax: (+49) 62 01–606-331

Telephone: (+49) 62 01–606-315

#### Subscriptions:

www.wileycustomerhelp.com Fax: (+49) 62 01–606-184

Telephone: 0800 1800536 (Germany only) +44(0) 1865476721 (all other countries)

#### Advertising:

Marion Schulz

E-mail: mschulz@wiley-vch.de

<u>ispiess@wiley-vch.de</u> (+49) 62 01–606-550

Fax: (+49) 62 01–606-550 Telephone: (+49) 62 01–606-565

#### Courier Services:

Boschstrasse 12, 69469 Weinheim

#### Regular Mail:

Postfach 101161, 69451 Weinheim

Angewandte Chemie International Edition is a journal of the Gesellschaft Deutscher Chemiker (GDCh), the largest chemistry-related scientific society in continental Europe. Information on the various activities and services of the GDCh, for example, cheaper subscription to Angewandte Chemie International Edition, as well as applications for membership can be found at www.gdch.de or can be requested from GDCh, Postfach 900440, D-60444 Frankfurt am Main, Germany.











# Enjoy Easy Browsing and a New Reading Experience on the iPad

- Keep up to date with the latest articles in Early View.
- Download new weekly issues automatically when they are published.
- Read new or favorite articles anytime, anywhere.





"... The declared goals of the International Year of Crystallography 2014 are to disseminate the role of crystallography for the development of the different branches of science: chemistry, mineralogy, physics, biology, medicine, materials and geosciences, and to emphasize the role of crystallographic research in everyday life. Many activities have been planned across the world, including this special issue of Angewandte Chemie ..." Read more in the Editorial by Gautum R. Desiraju.

# **Editorial**

G. R. Desiraju\* \_ 604 - 605

Crystallography and Chemistry: An Ongoing Engagement

# Service

Spotlight on Angewandte's Sister Journals

622 - 624



"My favorite quote is: "imagination is more important than knowledge" (Einstein).

If I could be any age I would be I would be same age, but young at heart. ..."

This and more about Weihong Tan can be found on page 626.

# **Author Profile**

Weihong Tan \_ 626

607



# News







C. Hardacre



G. R. Desiraju







New Members of the Royal Irish

P. J. Guiry and C. Hardacre \_\_\_ 627 - 628

Honorary Doctorate:

G. R. Desiraju \_\_\_\_ \_\_ 627 - 628

RUSNANOPRIZE:

O. Farokhzad and R. S. Langer 627 - 628

Prelog Medal and Lectureship:

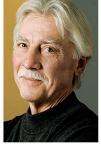
P. Wender \_\_\_\_ 627 - 628

Nature Award for Mentoring in Science:

Eucor Medal: J.-M. Lehn \_\_\_\_\_ 627 - 628



R. S. Langer



P. Wender



V. Balzani



J.-M. Lehn

# **Books**

Cross Coupling and Heck-Type Reactions

Gary A. Molander, John P. Wolfe, Mats Larhed

reviewed by H. Doucet \_

# Highlights

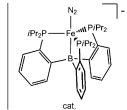
# Nitrogen Fixation

H. Broda, F. Tuczek\* \_\_\_\_\_ 632-634

Catalytic Ammonia Synthesis in Homogeneous Solution—Biomimetic at Last?

Excess HBAr<sup>F</sup><sub>4</sub> · 2 Et<sub>2</sub>O   
+ 
$$\mathbf{N}_2$$
  $\xrightarrow{\text{Cat.}}$   $\rightarrow$  NH<sub>3</sub>

Excess KC<sub>8</sub>  $\xrightarrow{\text{Et}_2\text{O}}$   $\xrightarrow{\text{-78 °C}}$ 



New iron dinitrogen complexes are crucial to a catalytic ammonia synthesis in homogeneous solution and establish new structural motifs related to the ironmolybdenum cofactor of the enzyme nitrogenase (see scheme; BAr<sup>F</sup>=

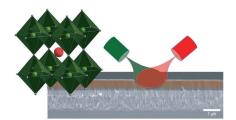
 $B[3,5-(CF_3)_2C_6H_3]_4$ ). These findings are put into the context of 50 years of synthetic nitrogen fixation and latest developments regarding the crystal structure and the molecular mechanism of nitrogenase.

#### For the USA and Canada:

ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. US POST-MASTER: send address changes to Angewandte Chemie, Journal Customer Services, John Wiley & Sons Inc., 350 Main St., Malden, MA 02148-5020. Annual subscription price for institutions: US\$ 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.





All in one: Perovskites are currently undergoing a renaissance as "allrounder" materials for solar cells. For a special type of methylammonium lead halide perovskites, a unique combination of properties, including high charge-carrier mobilities, exciton lifetimes, and panchromatic absorption, was observed, which renders this class of hybrid perovskites one of the most promising absorber and ambipolar charge-transport materials for all-solid-state solar cells.

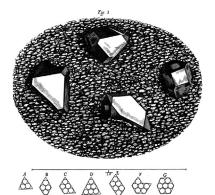
#### **Photovoltaics**

B. V. Lotsch\* \_\_\_\_\_\_ 635 – 637

New Light on an Old Story: Perovskites Go Solar

# 2012/2013 mark the 100th anniversary of

von Laue's diffraction of X-rays from single crystals of copper sulfate, the postulation of Bragg's law, and the solution of the first X-ray structure. However, even before 1912, the study of crystals was an integral part of chemistry and it played a major role in development of modern chemical science, including key concepts such as atoms, molecules, isomerism, and chirality.

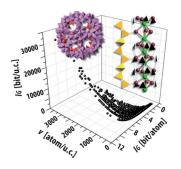


# Essays

#### History of Science

K. Molčanov, \* V. Stilinović \* \_\_ 638 - 652

Chemical Crystallography before X-ray Diffraction



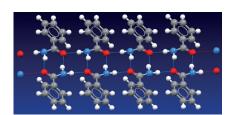
Cause and complexity: Analysis of inorganic crystal structures using information-based complexity measures indicates that structural complexity is generated by the assembly of nanoscale building blocks, modularity induced by complex chemical compositions, and the formation of superlattices as a result of local atomic ordering or displacive phase transitions.

# **Minireviews**

# Inorganic Crystal Structures

S. V. Krivovichev\* \_\_\_\_\_ 654 - 661

Which Inorganic Structures are the Most Complex?



Crystal-clear data: The Cambridge Crystallographic Data Centre (CCDC) was established in 1965; its core product, the Cambridge Structural Database (CSD), stores numerical, chemical, and bibliographic data for nearly 700 000 crystal structures. As X-ray crystallography celebrates its centenary, the CCDC nears its own 50th anniversary. The origins of the CCDC and development of the CSD system is presented. The CCDC's funding model in relation to open access paradigms is also considered.

#### Structural Databases

C. R. Groom,\* F. H. Allen\* \_\_\_ 662-671

The Cambridge Structural Database in Retrospect and Prospect

# Highly attractive 2014 Rates\*

# for members of ChemPubSoc Europe societies

\*(without local VAT)





IF 2012: 5.831



IF 2012: 3.344



IF 2012: 3.120



NEW to the family



Open-Access Journal



IF 2012: 3.740



IF 2012: 2.835



IF 2012: 7.475



IF 2012: 5.181



IF 2012: 3.349

CHEMELECTROCHEM

# **Online ordering:**

Simply visit the journal's homepage at

www.onlinelibrary.wiley.com

Choose Subscribe / Renew

on the left-hand menu and complete your order.







New! Starting 2014



Online: € 98









www.chempubsoc.eu





Twisted crystals: Crystals of many substances, including hippuric acid (see picture), will bend or twist as they grow under some conditions. These deviations are often activated by particular additives. How and why so many materials choose dramatic non-crystallographic distortions is analyzed for molecular crystals, high polymers, minerals, elements, and salts.

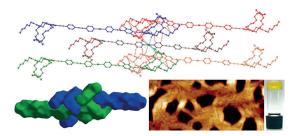


# Reviews

# Crystal Growth

A. G. Shtukenberg,\* Y. O. Punin, A. Gujral, B. Kahr\* \_\_\_\_\_\_ **672 – 699** 

Growth Actuated Bending and Twisting of Single Crystals



Growing hand in hand! Multiple unconventional C-H···X (X=O, Cl) hydrogenbonding interactions, assisted by  $\pi$ - $\pi$  interactions, are strong enough to drive the cooperative formation of supra-

molecular polymers and gels in polar and aqueous media. The aggregates consolidate themselves in the crystals, as shown by combined studies in solution and crystalline state.

# **Communications**

#### Weak Interactions

Colf According to the dealers of

Self-Assembly and (Hydro)gelation Triggered by Cooperative  $\pi$ – $\pi$  and Unconventional C—H···X Hydrogen Bonding Interactions



Frontispiece







A scanning laser ablation technique with a femtosecond laser was used to deposit highly luminescent thin films of the dense framework <code>[EuIm2]</code>. The polycrystalline films can be switched between transparent with visible light and nontransparent upon excitation with UV light due to the intrinsic luminescence of the hybrid material. This new PLD method is a suitable new approach for the preparation of coatings consisting of framework compounds and coordination polymers.

# Luminescent Thin Films

D. Fischer, L. V. Meyer, M. Jansen,\*
K. Müller-Buschbaum\* \_\_\_\_\_ 706-710

Highly Luminescent Thin Films of the Dense Framework [EuIm2] with Switchable Transparency Formed by Scanning Femtosecond-Pulse Laser Deposition



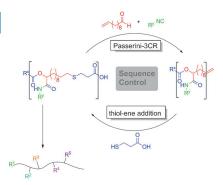


#### Sequence-Controlled Polymers

S. C. Solleder, M. A. R. Meier\* 711-714



Sequence Control in Polymer Chemistry through the Passerini Three-Component Reaction



The iterative application of the Passerini three-component reaction and the thiolene addition reaction provides sequence-defined macromolecules without the utilization of any protecting group.



#### Atmospheric Chemistry

J. Ahrens, P. T. M. Carlsson, N. Hertl, M. Olzmann, M. Pfeifle, J. L. Wolf, T. Zeuch\* \_\_\_\_\_\_ 715 – 719



Infrared Detection of Criegee Intermediates Formed during the Ozonolysis of  $\beta$ -Pinene and Their Reactivity towards Sulfur Dioxide



# Inside Cover

How is sulfuric acid formed in the troposphere? One route is the oxidation of SO<sub>2</sub> by hydroxyl radicals. Now, the relevance of an alternative path, oxidation of SO<sub>2</sub> by reaction with large, biogenic Criegee

an alternative path, oxidation of  $SO_2$  by reaction with large, biogenic Criegee intermediates, has been proven. Criegee intermediates are formed along with a carbonyl compound in the ozonolysis of alkenes. This study was conducted with  $\beta$ -pinene and its possible Criegee intermediates are shown.





#### Silicon-Stereogenic Aminomethoxysilanes

J. O. Bauer, C. Strohmann\* \_\_\_ 720-724



Stereoselective Synthesis of Silicon-Stereogenic Aminomethoxysilanes: Easy Access to Highly Enantiomerically Enriched Siloxanes



**Broad access** to silicon-stereogenic N,O-functionalized organosilanes in optically pure form is provided by a highly chemo-and diastereoselective substitution on aminodimethoxysilanes. The novel com-

pounds could be further transformed stereoselectively with alcohols and a silanol and are predestined as building blocks for a controlled development of chiral siloxane units.

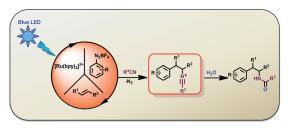
#### Photo Meerwein Addition

D. Prasad Hari, T. Hering,

B. König\* \_\_\_\_\_\_ 725 – 728



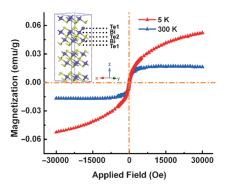
The Photoredox-Catalyzed Meerwein Addition Reaction: Intermolecular Amino-Arylation of Alkenes



From elimination to addition: A variety of amides are efficiently accessible under mild conditions by intermolecular aminoarylation using a photo Meerwein addition with visible light. The reaction has a broad

substrate scope, tolerates a large range of functional groups, and was applied to the synthesis of 3-aryl-3,4-dihydroisoquinoline.





Research with BiTe: Intriguing room-temperature ferromagnetism can be observed in a nanostructured topological insulator, Bi<sub>2</sub>Te<sub>3</sub>, without introducing any exotic magnetic dopants. These findings may pave the way for developing Bi<sub>2</sub>Te<sub>3</sub>-based dissipationless spintronics and fault-tolerant quantum computing.

#### Ferromagnetism

Unexpected Room-Temperature Ferromagnetism in Nanostructured Bi<sub>2</sub>Te<sub>3</sub>



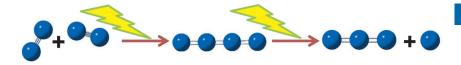
Weaker is better! Phenylacetic acids and benzoic acids are suitable substrates for a palladium-catalyzed *ortho*-selective C—H deuteration of arenes with deuterated acetic acid (see scheme; R = H, alkyl, CF<sub>3</sub>, OMe, NO<sub>2</sub>, Cl, F). This reaction demonstrates the superior reactivity of weakly coordinated palladacycle intermediates in C—H functionalization reactions.

#### C-H Activation

S. Ma, G. Villa, P. S. Thuy-Boun, A. Homs, J.-Q. Yu\* \_\_\_\_\_\_\_ 734-737

Palladium-Catalyzed *ortho*-Selective C—H Deuteration of Arenes: Evidence for Superior Reactivity of Weakly Coordinated Palladacycles





**Now on solid ground:** Irradiation of pure solid nitrogen at 3 K with vacuum-ultraviolet light generated product *I*-N<sub>3</sub>. This

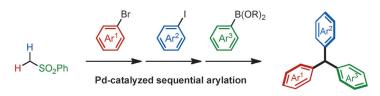
formation possibly occurs through an activated complex I- $N_4$  upon photoexcitation.

## Solid-State Nitrogen

S.-L. Chou, J.-l. Lo, M.-Y. Lin, Y.-C. Peng, H.-C. Lu, B.-M. Cheng\* \_\_\_\_\_\_ 738 – 741

Production of N₃ upon Photolysis of Solid Nitrogen at 3 K with Synchrotron Radiation





**Unsymmetric triarylmethanes** have been synthesized starting from methyl phenyl sulfone as an inexpensive and readily available template. The three aryl groups

were installed through two sequential palladium-catalyzed C-H arylation reactions, followed by an arylative desulfonation.

#### Palladium Catalysis

M. Nambo,\* C. M. Crudden\* \_ 742 - 746

Modular Synthesis of Triarylmethanes through Palladium-Catalyzed Sequential Arylation of Methyl Phenyl Sulfone



Front Cover



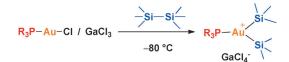


#### **Gold Complexes**

M. Joost, P. Gualco, Y. Coppel, K. Miqueu, C. E. Kefalidis, L. Maron,\* A. Amgoune,\* D. Bourissou\* \_\_\_\_\_\_\_ 747 – 751



Direct Evidence for Intermolecular Oxidative Addition of  $\sigma(\text{Si-Si})$  Bonds to Gold



Oxidative addition is the most elusive elementary step in reactions with gold. Now, evidence for the intermolecular oxidative addition of  $\sigma(Si-Si)$  bonds is reported. Phosphine gold chlorides readily reacted with disilanes at low temperature

in the presence of GaCl<sub>3</sub>. The ensuing bis(silyl) gold(III) complexes were characterized by <sup>31</sup>P and <sup>29</sup>Si NMR spectroscopy, and their structures were analyzed by DFT calculations.

# Alcohol Deoxygenation

H. Dang, N. Cox, G. Lalic\* \_\_\_\_ 752-756



Copper-Catalyzed Reduction of Alkyl Triflates and Iodides: An Efficient Method for the Deoxygenation of Primary and Secondary Alcohols

**Primarily reduced**: The copper-catalyzed reduction of 1° alkyl sulfonates, and 1° and 2° iodides, which is effective in the presence of a wide range of functional groups, provides a means for the effective

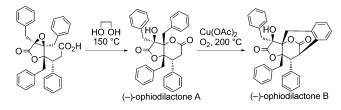
deoxygenation of alcohols. A preliminary study of the reaction mechanism suggests that the reduction does not involve free-radical intermediates.

#### **Natural Product Synthesis**

T. Matsubara, K. Takahashi, J. Ishihara, S. Hatakeyama\* \_\_\_\_\_\_ 757 – 760



Total Synthesis of (—)-Ophiodilactone A and (—)-Ophiodilactone B



**Bioinspired synthesis**: The first total synthesis of the title compounds has been accomplished in a highly stereocontrolled manner. Key features of the synthesis include an asymmetric epoxidation, a dia-

stereoselective iodolactonization, an intramolecular epoxide opening with a carboxylic acid, and a biomimetic radical cyclization of ophiodilactone A to ophiodilactone B.



#### Ketone Alkylation



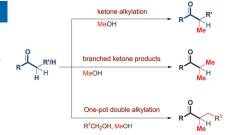
L. K. M. Chan, D. L. Poole, D. Shen, M. P. Healy, T. J. Donohoe\* \_\_\_\_ **761 – 765** 



Rhodium-Catalyzed Ketone Methylation Using Methanol Under Mild Conditions: Formation of  $\alpha$ -Branched Products



**Back Cover** 



Uniquely effective for making branched alkyl products from ketones (see scheme): The scope of the presented reaction includes aromatic and aliphatic ketones and consecutive one-pot double alkylation reactions to provide a convenient route to branched ketones from simple methyl ketones. A brief study into the mechanism of the reaction has given evidence for an aldol-based reaction pathway.



preexisting all-carbon quaternary centers

Smashing the mirror: The symmetry breaking of meso primary diols was employed to control all-carbon quaternary stereocenters using catalytic asymmetric acyl transfer. The planar chiral Fu DMAP

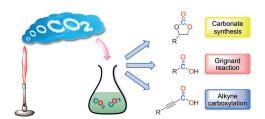
catalyst was used to reach a high degree of enantioselectivity (up to 97:3 e.r.) through a synergic effect, combining a desymmetrization step and a kinetic resolution.

#### Organocatalysis

C. Roux, M. Candy, J.-M. Pons, O. Chuzel,\* C. Bressy\* \_\_\_ \_\_\_ 766 – 770

Stereocontrol of All-Carbon Quaternary Centers through Enantioselective Desymmetrization of Meso Primary Diols by Organocatalyzed Acyl Transfer





Exhaust gas is good enough! Carbon dioxide captured directly from exhaust gas was used for organic syntheses (see picture) as efficiently as hyper-pure CO2 gas from a commercial source, even for

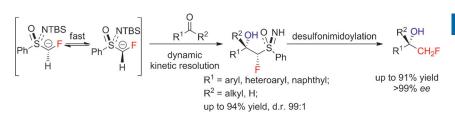
highly air- and moisture-sensitive reactions. The CO2 capturing aqueous ethanolamine solution could be recycled continuously without any diminished reaction efficiency.

## Sustainable Chemistry

S. H. Kim, K. H. Kim, S. H. Hong\* \_

Carbon Dioxide Capture and Use: Organic Synthesis Using Carbon Dioxide from Exhaust Gas





Fluoromethyl fix: An efficient and easy-tohandle protocol for the stereoselective synthesis of optically pure monofluoromethyl tertiary alcohols was developed, which showed higher facial selectivity than the corresponding difluoromethylation

and proceeded via a different type of transition state. Stereoselective control at the fluorinated carbon chiral center is believed to be facilitated by the dynamic kinetic resolution of the chiral  $\alpha$ -fluoro carbanions.

## Fluoroalkylation

X. Shen, W. Miao, C. Ni, J. Hu\* 775 - 779

Stereoselective Nucleophilic Fluoromethylation of Aryl Ketones: Dynamic Kinetic Resolution of Chiral α-Fluoro Carbanions



CF<sub>3</sub>CO<sub>2</sub>H (0.1% v/v) 70% MeCN/H<sub>2</sub>O 24 °C, 1.5 h Me Me Pectenotoxin-2b (PTX2b) Pectenotoxin-2 (PTX2) Pectenotoxin-2c (PTX2c) selectively obtained

A shellfish toxin: Non-anomeric spiroacetal pectenotoxin-2 was synthesized by the acidic isomerization of anomeric spiroacetal pectenotoxin-2b. In the isomerization step, [6,6]-spiroacetal

pectenotoxin-2c was the major product at equilibrium. However, the early termination of a dynamic transition process to equilibrium in the step produced pectenotoxin-2 selectively.

#### Natural Product Synthesis

K. Fujiwara,\* Y. Suzuki, N. Koseki, Y. Aki, Y. Kikuchi, S. Murata, F. Yamamoto, M. Kawamura, T. Norikura, H. Matsue, A. Murai, R. Katoono, H. Kawai, T. Suzuki \_\_ \_\_ 780 - 784

Total Synthesis of Pectenotoxin-2



615



#### Heterocycles

C. Jones, Q. Nguyen, T. G. Driver\* \_\_\_\_\_\_\_ **785 – 788** 



Dirhodium(II) Carboxylate Catalyzed Formation of 1,2,3-Trisubstituted Indoles from Styryl Azides

Selective migration of acyl groups in trisubstituted styryl azides leads to the formation of 1,2,3-trisubstituted indoles. The styryl azides are readily available in

three steps from cyclobutanone and 2-iodoaniline.  $esp = \alpha, \alpha, \alpha', \alpha'$ -tetramethyl-1,3-benzenedipropionic acid.

#### Homogeneous Catalysis

F. A. LeBlanc, W. E. Piers,\*
M. Parvez \_\_\_\_\_\_\_ **789-792** 



Selective Hydrosilation of CO<sub>2</sub> to a Bis(silylacetal) Using an Anilido Bipyridyl-Ligated Organoscandium Catalyst



**Lewis acid shuffle**: Selective hydrosilation of  $CO_2$  to a bis (silylacetal) is mediated by a scandium-based catalyst activated by  $B(C_6F_5)_3$ . The selectivity derives from the ability of the scandium complex to moderate the propensity of borane to further hydrosilate the  $Et_3SiOCH_2OSiEt_3$  product by limiting the amount of free  $B(C_6F_5)_3$  present in solution.

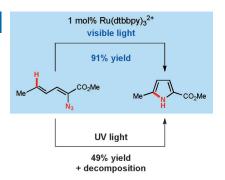
# VIP

#### **Photocatalysis**

E. P. Farney, T. P. Yoon\* \_\_\_\_\_ 793 - 797



Visible-Light Sensitization of Vinyl Azides by Transition-Metal Photocatalysis



Rock and pyrrole: Irradiation of vinyl and aryl azides with visible light in the presence of Ru photocatalysts results in the formation of reactive nitrenes, which can undergo a variety of C—N bond-forming reactions. The ability to use low-energy visible light instead of UV in the photochemical activation of azides (see picture) avoids competitive photodecomposition processes.



# C-H Oxidation

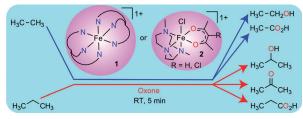
C.-W. Tse, T. W.-S. Chow, Z. Guo, H. K. Lee, J.-S. Huang, C.-M. Che\* \_\_\_\_\_\_ **798 – 803** 



Nonheme Iron Mediated Oxidation of Light Alkanes with Oxone: Characterization of Reactive Oxoiron(IV) Ligand Cation Radical Intermediates by Spectroscopic Studies and DFT Calculations



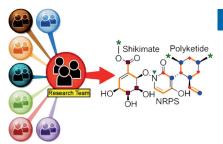
Highly reactive {Fe=O} intermediates, such as [Fe(Tp)<sub>2</sub>(O)]<sup>+</sup> or complex I (see Scheme), are likely to be involved in the oxidation of propane and ethane with oxone that is either mediated by



[Fe<sup>III</sup>(Tp)<sub>2</sub>]<sup>+</sup> (1) or catalyzed by iron complex 2. The cationic intermediate I features an {Fe=O} moiety and is stabilized by a combination of tridentate and bidentate ligands.



A fungus among us: A new *Tolypocladium* sp. was obtained through a crowdsourcing initiative. The expression of a silent biosynthetic pathway in this fungus was triggered through chemical epigenetics, culture medium manipulation, and coculture to yield the unique polyketideshikimate-NRPS-hybrid compound, maximiscin, which demonstrated in vivo antitumor activity. NRPS = non-ribosomal peptide synthetase.



#### Natural Products Discovery



L. Du, A. J. Robles, J. B. King, D. R. Powell, A. N. Miller, S. L. Mooberry,\*

R. H. Cichewicz\* \_\_\_\_\_\_ 804 – 809

Crowdsourcing Natural Products Discovery to Access Uncharted Dimensions of Fungal Metabolite Diversity



With a spoonful of sugar... Glycan-coated quantum dots were used to probe the effect of glycan presentation in intracellular localization in HeLa and SV40 epithelial cells. Glycan density was found to

mostly impact cell toxicity, whereas glycan type affects cell uptake and intracellular localization. Also, lactose was found to help the intracellular delivery of other non-internalizable glycan moieties.

#### Intracellular Localization



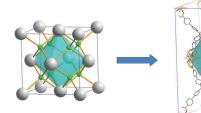
D. Benito-Alifonso, S. Tremel, B. Hou, H. Lockyear, J. Mantell, D. J. Fermin,

P. Verkade, M. Berry,\*

M. C. Galan\* \_\_\_\_\_\_ 810-814

Lactose as a "Trojan Horse" for Quantum Dot Cell Transport





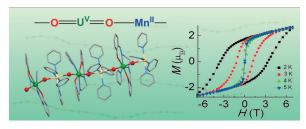
Meet me at the symmetry gates: Using a symmetry-guided design strategy, two stable, non-interpenetrated MOFs, were synthesized by augmenting the fluorite topology with tetrahedral linkers, thus expanding the cavity size (see scheme) and giving the largest pore size of any MOF with tetrahedral ligands.

#### Metal-Organic Frameworks

M. Zhang, Y.-P. Chen, M. Bosch,
T. Gentle, III, K. Wang, D. Feng,
Z. U. Wang, H.-C. Zhou\* \_\_\_\_\_ 815 - 818

Symmetry-Guided Synthesis of Highly Porous Metal-Organic Frameworks with Fluorite Topology





**Uranium in chains**: 5 f–3d heterometallic 1D chains are assembled from the reaction of pentavalent uranyl and Cd<sup>II</sup> or Mn<sup>II</sup>. The Mn-UO<sub>2</sub>-Mn coordination polymer exhibits slow relaxation of magnetization

with a high relaxation barrier, and shows an open hysteresis cycle, thus affording the first example of an actinide-based single-chain magnet.

# Molecular Magnets

V. Mougel, L. Chatelain, J. Hermle, R. Caciuffo, E. Colineau, F. Tuna, N. Magnani, A. de Geyer, J. Pécaut, M. Mazzanti\*

A Uranium-Based UO<sub>2</sub>+-Mn<sup>2+</sup> Single-Chain Magnet Assembled trough Cation-Cation Interactions



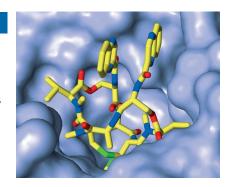


#### Natural Product Biosynthesis

K. Hotta, R. M. Keegan, S. Ranganathan, M. Fang, J. Bibby, M. D. Winn, M. Sato, M. Lian, K. Watanabe, D. J. Rigden, C.-Y. Kim\* \_\_\_\_\_\_\_ 824 – 828



Conversion of a Disulfide Bond into a Thioacetal Group during Echinomycin Biosynthesis

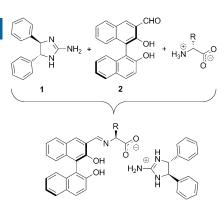


Disulfide to thioacetal: The S-adenosyl-L-methionine (SAM)-dependent methyl-transferase Ecm18 converts the disulfide bond of triostin A into a thioacetal linkage to form echinomycin. The 1.50 Å crystal structure of Ecm18 in complex with its reaction products S-adenosyl-L-homocysteine (SAH) and echinomycin provides insight into how Ecm18 catalyzes this unusual transformation.

#### Molecular Recognition



Highly Stereoselective Recognition and Deracemization of Amino Acids by Supramolecular Self-Assembly



A communal effort: A chiral guanidine derivative 1 and a chiral aldehyde 2 underwent self-assembly with amino acids to promote inversion of the stereogenic center of the guest (see scheme). The supramolecular self-assembly exhibited high stereoselectivity for amino acid recognition and was found to be useful for the separation of racemic mixtures of amino acids as well as for their deracemization.

#### Heterogeneous Catalysis

J. Yi, J. T. Miller, D. Y. Zemlyanov, R. Zhang, P. J. Dietrich, F. H. Ribeiro, S. Suslov, M. M. Abu-Omar\* \_ 833 – 836



A Reusable Unsupported Rhenium Nanocrystalline Catalyst for Acceptorless Dehydrogenation of Alcohols through  $\gamma\text{-C-H}$  Activation



Active particles: A rhenium nanoparticle (Re NP) catalyst is generated from NH<sub>4</sub>ReO<sub>4</sub> under mild solution conditions in neat 3-octanol at 180°C. The resulting

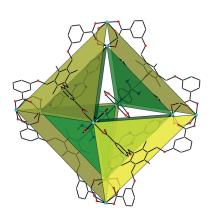
Re NPs catalyze acceptorless dehydrogenation of alcohols through a novel C-H activation pathway, and are fully recyclable.

## Metal-Organic Frameworks

D. Tian, Q. Chen, Y. Li, Y. H. Zhang, Z. Chang, X. H. Bu\* \_\_\_\_\_\_ 837 – 841

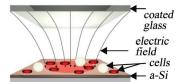


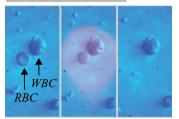
A Mixed Molecular Building Block Strategy for the Design of Nested Polyhedron Metal-Organic Frameworks MOF in a MOF: The integration of two size-matching  $C_3$ -symmetric ligands with different rigidities leads to two porous metal—organic frameworks built from unprecedented double-walled metal—organic octahedra. A new and reliable mixed molecular building block strategy for the synthesis of cage-within-cage materials is provided.





Selective lysis of specific cells in a mixture of different cell types is based upon the shape of the cells, a phenomenon that is explained by the electrical "shadow" that is cast by the cells. The technique is implemented on an optoelectronic platform, where light, focused onto a semiconductor surface by a projector, creates a reconfigurable pattern of electrodes over large areas. RBCs and WBCs are red and white blood cells, respectively, and a-Si is amorphous silicon.





#### Cell lysis



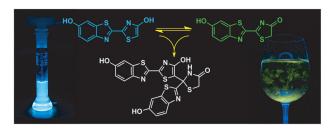
C. Kremer, C. Witte, S. L. Neale, J. Reboud, M. P. Barrett, J. M. Cooper\* — **842–846** 

Shape-Dependent Optoelectronic Cell Lysis



Inside Back Cover





Light into the darkness: Firefly oxyluciferin, the emitter of firefly bioluminescence, is notoriously difficult to handle. The cause behind its chemical lability is now ascribed to autodimerization of the coexisting enol (showing blue fluorescence in DMSO) and keto forms (contributing to the green fluorescence in water) in a Mannich reaction.

#### Bioluminescence

O. V. Maltsev, N. K. Nath, P. Naumov,\*
L. Hintermann\* \_\_\_\_\_\_\_ 847 - 850

Why is Firefly Oxyluciferin a Notoriously Labile Substance?





In the fast lane: The title reaction is described for the synthesis of peptides. Various carboxylic acids including easily epimerizable amino acids were rapidly converted into highly electrophilic spe-

cies, and then reacted with various amines, including less nucleophilic *N*-methyl amino acids, to afford the desired peptides in high yields without significant epimerization.

#### Peptides

S. Fuse,\* Y. Mifune,
T. Takahashi \_\_\_\_\_\_\_ **851 – 855** 

Efficient Amide Bond Formation through a Rapid and Strong Activation of Carboxylic Acids in a Microflow Reactor



Salting away: The title membranes having different PAA graft ratios were fabricated by using a salt-induced phase-inversion process. The membrane can separate both surfactant-free and surfactant-stabilized oil-in-water emulsions under either a small applied pressure (0.1 bar) or gravity, with a high separation efficiency and high flux. CA = contact angle.



#### Surface Chemistry

W. Zhang, Y. Zhu, X. Liu, D. Wang, J. Li, L. Jiang, J. Jin\* \_\_\_\_\_\_\_ **856-860** 

Salt-Induced Fabrication of Superhydrophilic and Underwater Superoleophobic PAA-g-PVDF Membranes for Effective Separation of Oil-in-Water Emulsions





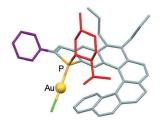
#### Asymmetric Gold Catalysis

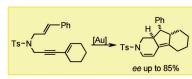
K. Yavari, P. Aillard, Y. Zhang, F. Nuter, P. Retailleau, A. Voituriez,\*

A. Marinetti\* \_\_\_\_\_\_ 861 - 865



Helicenes with Embedded Phosphole Units in Enantioselective Gold Catalysis





A twist of gold: Phosphahelicenes were for the first time used as chiral ligands in transition-metal catalysis. Unlike all helical phosphines used so far in catalysis, the phosphorus atom of phosphahelicenes is embedded within the helical

structure (see scheme). Structural design allowed both high catalytic activity and good *ee* values to be attained in gold-promoted cycloisomerizations of N-tethered 1,6-enynes and dienynes.

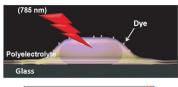
#### Plasmon-Enhanced Fluorescence

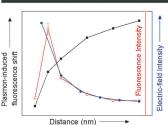
N. Gandra, C. Portz, L. Tian, R. Tang, B. Xu, S. Achilefu,\*

S. Singamaneni\* \_\_\_\_\_\_ 866 - 870



Probing Distance-Dependent Plasmon-Enhanced Near-Infrared Fluorescence Using Polyelectrolyte Multilayers as Dielectric Spacers





A simple and effective approach to probe distance-dependent plasmon-enhanced fluorescence is developed using polyelectrolyte multilayers to design ultrabright flurophores for near-infrared imaging (see picture). By carefully choosing the plasmonic nanostructures and chromophores with the corresponding maximum spectral overlap, a variety of ultrabright fluorescence probes can be designed.

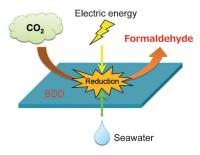
#### CO<sub>2</sub> Reduction

K. Nakata,\* T. Ozaki, C. Terashima,A. Fujishima, Y. Einaga\* \_\_\_\_\_\_ 871 – 874



High-Yield Electrochemical Production of Formaldehyde from CO<sub>2</sub> and Seawater

Boron is a diamond's best friend: A borondoped diamond (BDD) electrode exhibited very high Faradaic efficiency (74%) for the production of formaldehyde using either methanol, aqueous NaCl, or seawater as the electrolyte at room temperature and ambient pressure.



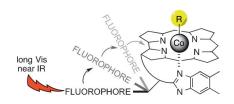


## Photoactivatable Agents

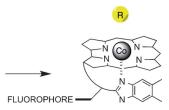
T. A. Shell,\* J. R. Shell, Z. L. Rodgers,
D. S. Lawrence\* \_\_\_\_\_\_ 875 – 878



Tunable Visible and Near-IR Photoactivation of Light-Responsive Compounds by Using Fluorophores as Light-Capturing Antennas

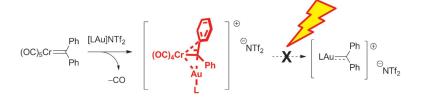


See it split: A palette of photoresponsive agents is described in which the desired activating wavelength is encoded with readily available fluorophores. Photomanipulation is feasible throughout the visible range into the near IR, and in a manner



that provides orthogonal control over multiple species. This technology has been used to trigger 1) interorganelle trafficking, 2) disassembly of stress fibers, and 3) light-dose-dependent cell death.





I do not want to be free! Whereas prototype Fischer-type chromium carbene complexes transfer their organic ligand to gold with exceptional ease, chromium complexes devoid of the heteroelement substituent do not want to release unstabilized gold carbenoids of the type that is often invoked in mechanistic discussions of  $\pi$ -acid catalysis. Instead, unusual bimetallic arrays are formed in which charge density gets delocalized over several positions.

## Carbophilic Catalysts



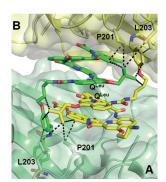
G. Seidel, B. Gabor, R. Goddard,

B. Heggen, W. Thiel,

A. Fürstner\* \_\_\_\_\_\_ 879 - 882

Gold Carbenoids: Lessons Learnt from a Transmetalation Approach





To design a foldamer that binds to a protein surface, a strategy is proposed that uses a known protein ligand to tether the foldamer to the protein surface. Candidates are first screened for induced circular dichroism in presence of the protein. Then, structural information about foldamer—protein interactions is collected before strong binding is established. The crystal structure of human carbonic anhydrase (A, B chains) with helical aromatic amide foldamers (stick models) is shown.

#### Foldamer-Protein Interactions

J. Buratto, C. Colombo, M. Stupfel,

S. J. Dawson, C. Dolain,

B. Langlois d'Estaintot, L. Fischer,

T. Granier, M. Laguerre, B. Gallois,\*

I. Huc\* \_\_\_\_\_\_ 883 - 887

Structure of a Complex Formed by a Protein and a Helical Aromatic Oligoamide Foldamer at 2.1 Å Resolution





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



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



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



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



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



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

The structural drawings in this Communication for anthracimycin (1) and its corresponding dichloro derivative 3 should be revised to illustrate the correct configuration at C-16. The structures should be drawn as shown below.

Anthracimycin, a Potent Anthrax Antibiotic from a Marine-Derived Actinomycete

Angew. Chem. Int. Ed. 2013, 52

DOI: 10.1002/anie.201302749