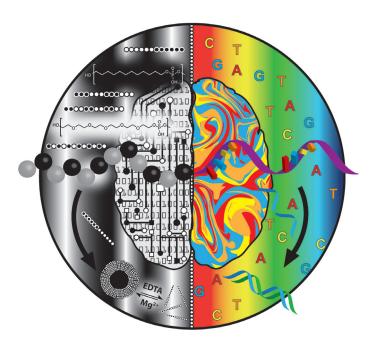
# Sequence-controlled polymers attached to DNA ...

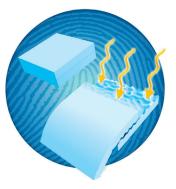




... can be prepared by solid-phase phosphoramidite coupling, as H. F. Sleiman, C. J. Serpell, and co-workers report in their Communication on page 4567 ff. Polymers with the same molecular composition but different monomer patterns exhibit different amphiphilic self-assembly. As the DNA component still retains base-pairing fidelity, these novel conjugates encode information in two distinct, and orthogonal, assembly languages.

## **Artificial Fingerprints**

D. Liu and D. J. Broer show in their Communication on page 4542 ff. that artificial fingerprints can be switched between a flat state and a protruding state. The resulting friction changes allow use in a robot-like gripper.

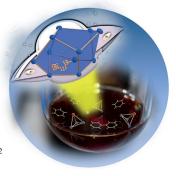


## **Bifunctional Nanopeapods**

In their Communication on page 4614 ff., J. B. Wiley et al. report the synthesis and characterization of both gold and gold–Fe<sub>3</sub>O<sub>4</sub> hexaniobate nanopeapods, which show variation in their optical and magnetic properties as a function of composition.

## **Bismuth Polyanions**

S. Dehnen and co-workers show in their Communication on page 4704 ff. that the  $[Bi_{11}]^{3-}$  ion, the first polycyclic bismuth polyanion, is formed in a surprisingly simple reaction of  $[K([2.2.2]\text{crypt})]_2$  (GaBi<sub>3</sub>) with the pyridine solvent.



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4514 - 4517



"If I were not a scientist, I would be a fiction writer. My favorite food is fruit salad ..." This and more about Dunwei Wang can be found on page 4518.

# **Author Profile**

Dunwei Wang \_ \_ 4518



H. Gröger



J. Strunk



K. C. Nicolaou



W. Dichtel

## News

Otto Roelen Medal: H. Gröger \_\_\_\_ 4519 Jochen Block Prize: J. Strunk \_\_\_\_\_ 4519 Rolf Sammet Guest Professorship: K. C. Nicolaou \_\_\_\_ Polymer International-IUPAC Award: W. Dichtel \_\_\_\_\_\_ 4519

Orbital Interactions in Chemistry

Thomas A. Albright, Jeremy K. Burdett, Myung Hwan Whangbo

Books

reviewed by S. Alvarez \_\_\_\_\_ 4520

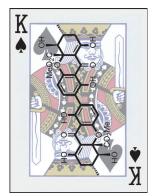


# Highlights

## **Dimeric Natural Products**

T. Wezeman, K.-S. Masters,\*
S. Bräse\* \_\_\_\_\_\_ 4524 – 4526

Double Trouble—The Art of Synthesis of Chiral Dimeric Natural Products



Double or nothing! Recently the total synthesis of secalonic acids A and D was reported. This work and other natural product syntheses with a dimerization step as a common feature are featured in this Highlight. The significant biological activity of the secalonic acids and the fact that their synthesis has fascinated synthetic chemists for the past forty years make this work a milestone in natural product synthesis.

## Hydrogen Storage

M. Beller,\*

U. T. Bornscheuer\* \_\_\_\_\_ 4527 - 4528

CO<sub>2</sub> Fixation through Hydrogenation by Chemical or Enzymatic Methods

Two birds with one stone: The simulaneous fixation of the greenhouse gas carbon dioxide and storage of the alternative fuel hydrogen can be accomplished with the formation of formic acid. In principle, this is now possible either with an enzymatic system based on a newly discovered bacterial hydrogen-dependent carbon dioxide reductase or by using organometallic catalysts at room temperature and ambient pressure.

# Reviews

## Metal-Organic Frameworks

O. Karagiaridi, W. Bury, J. E. Mondloch, J. T. Hupp,\* O. K. Farha\* \_\_\_\_ **4530 – 4540** 



Solvent-Assisted Linker Exchange: An Alternative to the De Novo Synthesis of Unattainable Metal-Organic Frameworks



Changing pillars: Solvent-assisted linker exchange (SALE) has gained a lot of attention as a novel synthetic pathway toward metal-organic frameworks (MOFs) that are challenging to access de novo. This Review analyzes the recent

advances in the application of SALE and provides a critical assessment of the studies that have facilitated our understanding of this invaluable tool for the development of new MOFs.

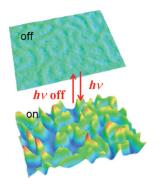
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electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.





Science friction: Artificial fingerprints are switched between a flat "off" state and a protruding "on" state. The switching principle is based on a modulated change of liquid-crystal chiral-nematic order, thus creating geometric changes. When illuminated with UV light, the 3D fingerprints are activated by azobenzene and appear in the coating. The surface friction decreases when the fingerprints form and increases when they are switched off.

# **Communications**

#### Smart Materials

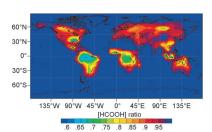
D. Liu, D. J. Broer\* \_\_\_\_\_ 4542 – 4546

Self-assembled Dynamic 3D Fingerprints in Liquid-Crystal Coatings Towards Controllable Friction and Adhesion



**Frontispiece** 





Gas-phase reactions: Direct measurements reveal that rate coefficients for reactions of Criegee intermediates with carboxylic acids are substantially larger than previously assumed. Using these new values, modeling suggests that these reactions can be major sinks both for Criegee intermediates and carboxylic acids in the atmosphere.

## Tropospheric Chemistry



O. Welz, A. J. Eskola, L. Sheps,
B. Rotavera, J. D. Savee, A. M. Scheer,
D. L. Osborn, D. Lowe, A. Murray Booth,
P. Xiao, M. Anwar H. Khan, C. J. Percival,\*
D. E. Shallcross,\*

C. A. Taatjes\* \_\_\_\_\_ 4547 – 4550

Rate Coefficients of C1 and C2 Criegee Intermediate Reactions with Formic and Acetic Acid Near the Collision Limit: Direct Kinetics Measurements and Atmospheric Implications



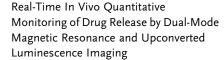
NIR-triggered drug release

LRET on DOX
High  $T_1$ Low  $T_1 \rightarrow R_1/(T_1^{-1})$ 

Lighting up drug delivery: Multifunctional Gd core/hollow mesoporous silica shell nanoparticles were synthesized. With doxorubicin (DOX) fully loaded inside the nanoparticles, the upconverted luminescence (UCL) signals are quenched through luminescence resonance energy transfer (LRET), and the longitudinal

relaxation time magnetic resonance ( $T_1$ -MR) signals are almost undetectable. Upon drug release, both the UCL and  $T_1$ -MR signals are restored. As a result, drug release can be detected by the designed dual-mode nanosensor (see figure;  $R_1$ : longitudinal relaxivity).

#### Biosensing







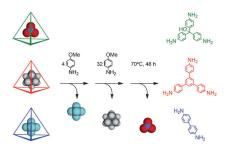
## Systems Chemistry

A. Jiménez, R. A. Bilbeisi, T. K. Ronson, S. Zarra, C. Woodhead,





Selective Encapsulation and Sequential Release of Guests Within a Self-Sorting Mixture of Three Tetrahedral Cages Well sorted: Three discrete metal-organic cages were prepared through the one-pot reaction of five subcomponents, that is, three amines, 2-formylpyridine, and a Zn<sup>II</sup> salt. Each cage selectively accommodates a single guest within a mixture of three guests, and each guest can be sequentially released following the addition of a chemical stimulus.

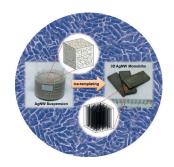


## Flexible Conducting Materials

H. L. Gao, L. Xu, F. Long, Z. Pan, Y. X. Du, Y. Lu, J. Ge, S. H. Yu\* \_\_\_\_\_\_ **4561 – 4566** 



Macroscopic Free-Standing Hierarchical 3D Architectures Assembled from Silver Nanowires by Ice Templating Silver lining: Macroscopic free-standing hierarchical 3D architectures can be directly built from monodispersed silver nanowires (AgNW) through a general, versatile ice-template assembly technique without using any extra functionalization agents or crosslinking agents. The 3D nanowire monoliths have a binary-network microstructure which provides them with a high electrical conductivity, and, when impregnated with PDMS, great mechanical flexibility.



# VIP

## Sequence-Defined Polymers

T. G. W. Edwardson, K. M. M. Carneiro, C. J. Serpell,\*

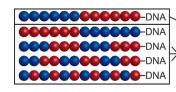
H. F. Sleiman\* \_\_\_\_\_ 4567 – 4571



An Efficient and Modular Route to Sequence-Defined Polymers Appended to DNA



Front Cover



**Bilingual**: A stepwise solid-phase synthesis approach provides easy access to sequence-controlled polymers attached to DNA. Polymers with the same molecular composition but different monomer pat-

terns exhibit different amphiphilic selfassembly. The DNA component still retains base-pairing fidelity, and thus one molecule "speaks" two orthogonal and programmable assembly languages.

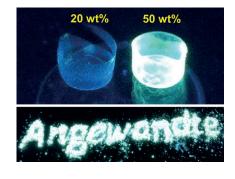
# White-Light Emission

Q. Y. Yang, J. M. Lehn\* \_\_\_\_ 4572 - 4577

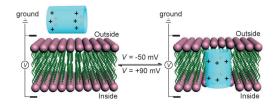


Bright White-Light Emission from a Single Organic Compound in the Solid Sate

A bright idea: Remarkably simple organic molecules, based on two 4-pyridone head groups located at the termini of a polymethylene chain, emit bright white light in the solid state. The emission band, which results from excited monomer molecules and stacked excimers, is almost flat over the visible range. Incorporation into a polymeric material gives white-light-emitting films, a feature of potential applied interest.







Controlling transport: A voltage can drive positively charged channel molecules to insert into or leave from a lipid bilayer (see picture), thus switching on and off the

transmembrane transport of K+ ions. The insertion and leaving processes can be tuned by adjusting the direction and strength of the voltage.

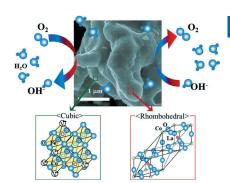
## Transmembrane Channels

W. Si, Z.-T. Li, J.-L. Hou\* \_\_\_ 4578-4581

Voltage-Driven Reversible Insertion into and Leaving from a Lipid Bilayer: Tuning Transmembrane Transport of Artificial Channels



The perovskite La<sub>0.3</sub>(Ba<sub>0.5</sub>Sr<sub>0.5</sub>)<sub>0.7</sub>Co<sub>0.8</sub>- $Fe_{0.2}O_{3-\delta}$  (La<sub>0.3</sub>-5582) is introduced as a bifunctional catalyst to compete with precious-metal-based catalysts. The newly introduced perovskite bears rhombohedral phase  $LaCoO_{3-\delta}$  particles on the surface of the grains.

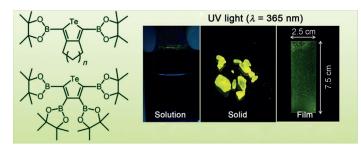


## Perovskite Catalysts

J. Jung, H. Jeong, J. Lee, M. Kim,\* **4582 – 4586** J. Cho\* -

A Bifunctional Perovskite Catalyst for Oxygen Reduction and Evolution





Light at the end of the tunnel: By incorporating pinacolboronate side groups, the first examples of tellurophenes that are phosphorescent in the solid state were

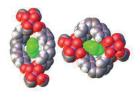
isolated. These tellurophenes readily form phosphorescent films from solution, making them amenable to device fabrication methods.

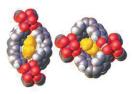
## Emissive Tellurophenes

G. He, W. Torres Delgado, D. J. Schatz, C. Merten, A. Mohammadpour, L. Mayr, M. J. Ferguson, R. McDonald, A. Brown, K. Shankar,\* E. Rivard\* \_\_\_\_ 4587 - 4591

Coaxing Solid-State Phosphorescence from Tellurophenes







Nobody's perfect: The metal-organic framework Ce(HTCPB) is structurally mismatched to both the para and meta isomers of xylene. It restructures synergically around the para isomer to give a high-quality structural and functional fit, but rearrangement around the meta isomer requires larger host distortions and gives a poorer fit than in the para case. This "off-target" host thus has high selectivity for the sorption of para- over meta-xylene.

# Selective Sorption

J. E. Warren, C. G. Perkins, K. E. Jelfs, P. Boldrin, P. A. Chater, G. J. Miller, T. D. Manning, M. E. Briggs, K. C. Stylianou, J. B. Claridge, M. J. Rosseinsky\* \_\_\_\_\_ 4592 - 4596

Shape Selectivity by Guest-Driven Restructuring of a Porous Material



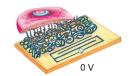


## **Electroactive Platforms**

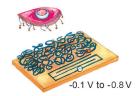
S. Jeon, J. Moon, E. Lee, Y. Kim, Y. Cho\* \_\_\_\_\_\_\_ **4597 – 4602** 



An Electroactive Biotin-Doped Polypyrrole Substrate That Immobilizes and Releases EpCAM-Positive Cancer Cells







An electroactive anti-EpCAM-immobilized, biotin-doped polypyrrole (Ppy) has been developed as a unique platform for the efficient capture and release of target cancer cells. Biotin-doped Ppy is ideal for

damage-free selective cell release using weak electric stimulation. This approach is promising for use in both basic and clinical cancer-related applications.

# Photochromism

W. Li, C. Jiao, X. Li, Y. Xie, K. Nakatani, H. Tian, W. Zhu\* \_\_\_\_\_ 4603 – 4607



Separation of Photoactive Conformers Based on Hindered Diarylethenes: Efficient Modulation in Photocyclization Quantum Yields



Large hindrance, high efficiency: A novel benzobis(thiadiazole)-bridged diarylethene system shows excellent thermal bistability and extremely high, solventindependent photocyclization quantum

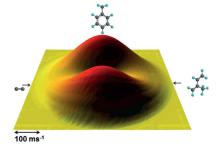
yields ( $\Phi_{\text{o-c}}$ , up to 90.6%). It is characterized by a complete separation of the anti-parallel conformer and the suppression of intramolecular charge transfer (ICT). EWG = electron-withdrawing group.

## **Reaction Dynamics**

B. B. Dangi, D. S. N. Parker, T. Yang, R. I. Kaiser, A. M. Mebel\* **4608-4613** 



Gas-Phase Synthesis of the Benzyl Radical  $(C_6H_5CH_2)$ 



**Do cross the streams!** Ab initio electronic structure calculations and crossed molecular beam experiments on the reaction of dicarbon with isoprene are presented. The picture shows a flux contour map of the reaction of dicarbon with isoprene that forms the benzyl radical and atomic hydrogen at a collision energy of 43 kJ mol<sup>-1</sup>.



## **Bifunctional Nanopeapods**

S. Adireddy, C. E. Carbo, T. Rostamzadeh, J. M. Vargas, L. Spinu,

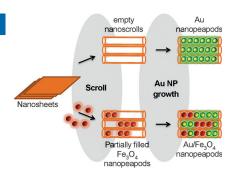
J. B. Wiley\* \_\_\_\_\_ 4614 – 4617



Peapod-Type Nanocomposites through the In Situ Growth of Gold Nanoparticles within Preformed Hexaniobate Nanoscrolls

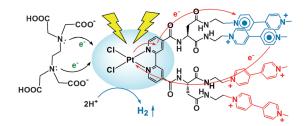


Inside Back Cover



Like peas in a pod: A facile in situ method for Au nanoparticle (NP) growth in nanoscrolls is applied to the formation of plasmonic Au@hexaniobate and bifunctional plasmonic-magnetic Au-Fe $_3$ O $_4$ @-hexaniobate nanopeapods (NPPs). Using a solvothermal treatment, rigid multiwalled hexaniobate nanoscrolls and partially filled Fe $_3$ O $_4$ @hexaniobate NPPs were formed and used as templates for the Au NPs.





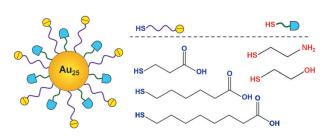
Electron harvesting: Photo-hydrogenevolving molecular devices showing substantially improved turnover numbers have been developed by introducing multiviologen tethers into a [PtCl<sub>2</sub>(2,2'-bipyridine)]-based moiety serving as a lightharvesting and  $H_2$ -evolving center (see scheme). The improved photocatalytic performance is attributed to the rapidly regenerating character of the pigment due to intramolecular electron transfer from the pigment to the electron reservoirs.

## **Photocatalysis**

K. Kitamoto, K. Sakai\* \_\_\_\_\_ 4618 - 4622

Pigment-Acceptor-Catalyst Triads for Photochemical Hydrogen Evolution





One, two ... many: A novel NaOH-mediated NaBH<sub>4</sub> reduction method was developed for the synthesis of mono-, bi-,

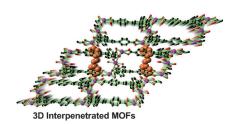
and tri-thiolate-protected  $Au_{25}$  nanoclusters. Both the Au core and thiolate ligand surface can be precisely controlled.

## **Protected Noble Metal Clusters**

X. Yuan, B. Zhang, Z. Luo, Q. Yao,D. T. Leong, N. Yan,\* J. Xie\* 4623 – 4627

Balancing the Rate of Cluster Growth and Etching for Gram-Scale Synthesis of Thiolate-Protected Au<sub>25</sub> Nanoclusters with Atomic Precision





All stitched up: Dipyridyl ligands were found to diffuse into the channels in the crystal lattice of a two-dimensional polymeric complex. The absorbed dipyridyls thread through the pores of one layer and substitute the surface solvent molecules on the neighboring layers to stitch alternate layers to form flexible interpenetrated metal—organic frameworks (see picture).

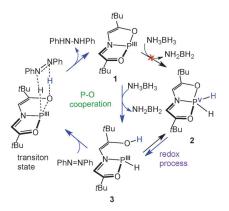
## Metal-Organic Frameworks

Z. X. Zhang, N. N. Ding, W. H. Zhang,\* J. X. Chen,\* D. J. Young,\*

T. S. A. Hor\* \_\_\_\_\_\_ 4628 – 4632

Stitching 2D Polymeric Layers into Flexible Interpenetrated Metal-Organic Frameworks within Single Crystals





Team work: The title reaction of azobenzene with ammonia—borane using 1 occurs through a P-O cooperation mechanism, where the active species is 3. This mechanism is new for main-group-element compounds, and resembles the metal-ligand cooperation observed in transition-metal complexes. When azobenzene is absent, the PIII/PV redox process occurs during the isomerization of 3 into 2, but it is not involved in the catalytic transfer hydrogenation.

## Main-Group Elements

G. Zeng, S. Maeda, T. Taketsugu,S. Sakaki\* \_\_\_\_\_\_ 4633 – 4637

Catalytic Transfer Hydrogenation by a Trivalent Phosphorus Compound: Phosphorus-Ligand Cooperation Pathway or P<sup>III</sup>/P<sup>V</sup> Redox Pathway?





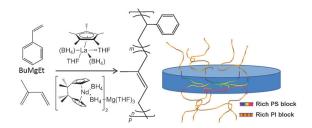
## **Block Copolymerization**

A. Valente, G. Stoclet, F. Bonnet, A. Mortreux, M. Visseaux,

P. Zinck\* \_\_\_\_\_ 4638 - 4641



Isoprene–Styrene Chain Shuttling Copolymerization Mediated by a Lanthanide Half-Sandwich Complex and a Lanthanidocene: Straightforward Access to a New Type of Thermoplastic Elastomers



Chain shuttling copolymerization of isoprene and styrene using a borohydrido lanthane half-sandwich complex, a borohydrido ansa-neodymocene, and a magnesium dialkyl affords direct access to new

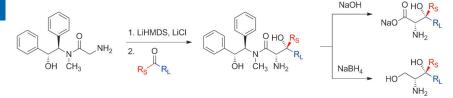
amorphous thermoplastic elastomers. The resulting multiblock microstructure of soft and hard statistical copolymeric segments self-assembles at the nanoscale.

## Synthetic Methods

I. B. Seiple, J. A. M. Mercer, R. J. Sussman,
 Z. Zhang, A. G. Myers\* \_\_\_\_\_\_ 4642 – 4647



Stereocontrolled Synthesis of syn-β-Hydroxy-α-Amino Acids by Direct Aldolization of Pseudoephenamine Glycinamide



**On aldol**: Enolization of (*R*,*R*)- or (*S*,*S*)-pseudoephenamine glycinamide with lithium hexamethyldisilazide (LiHMDS) in the presence of LiCl followed by addition of either an aldehyde or ketone substrate affords aldol addition products which are stereochemically homologous

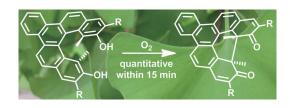
with L- or D-threonine, respectively. These products can be obtained in stereoisomerically pure form in yields of 55–98%, and are readily transformed into  $\beta$ -hydroxy- $\alpha$ -amino acids by mild hydrolysis or into 2-amino-1,3-diols by reduction.

## Synthetic Methods

Y. Shen, H.-Y. Lu, C.-F. Chen\* \_\_\_\_\_\_ 4648 – 4651



Dioxygen-Triggered Transannular Dearomatization of Benzo[5]helicene Diols: Highly Efficient Synthesis of Chiral  $\pi$ -Extended Diones



A bigger slice of  $\pi$ : In the title reaction, the helicity was successfully transferred into two quaternary all-carbon stereocenters of the  $\pi$ -extended diones. The optical reso-

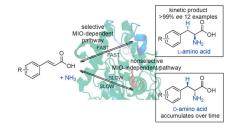
lution was easily achieved by column chromatography, and the absolute configurations were determined by X-ray analysis.

## Reaction Mechanisms

S. L. Lovelock, R. C. Lloyd, N. J. Turner\* \_\_\_\_\_\_ 4652 – 4656



Phenylalanine Ammonia Lyase Catalyzed Synthesis of Amino Acids by an MIO-Cofactor Independent Pathway All manner of things: A competing MIO-independent (MIO = 4-methylideneimid-azole-5-one) reaction pathway has been identified for phenylalanine ammonia lyases (PALs), which proceeds in a non-stereoselective manner, resulting in the generation of D-phenylalanine derivatives. The mechanism of D-amino acid formation is explored through isotopic-labeling studies and mutagenesis of key active-site residues.





Less basic, less hindered: The gold-catalyzed intermolecular Markovnikov addition of sulfinic acids to terminal alkynes has been achieved through the use of a bimetallic gold/gallium catalyst system. Various  $\alpha$ -substituted vinyl sulfones were efficiently synthesized. A one-pot synthesis that starts from the bench-stable sodium sulfinates was also developed (DCE = 1,2-dichloroethane).

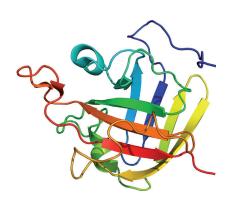
#### C-S Bond Formation



Y. Xi, B. Dong, E. J. McClain, Q. Wang, T. L. Gregg, N. G. Akhmedov, J. L. Petersen, X. Shi\* \_\_\_\_\_ 4657 - 4661

Gold-Catalyzed Intermolecular C-S Bond Formation: Efficient Synthesis of α-Substituted Vinyl Sulfones





Just like the original: A fully convergent total synthesis of the enzyme sortase A from four unprotected peptide segments was established by using modern chemical ligation methods. The synthetic protein was of high purity, had correct mass, and had full enzymatic activity in a typical transpeptidation assay.

## **Chemical Protein Synthesis**



F. K. Deng, L. Zhang, Y. T. Wang, O. Schneewind, S. B. H. Kent\* . 4662 - 4666

Total Chemical Synthesis of the Enzyme Sortase A<sub>AN59</sub> with Full Catalytic Activity

$$Ar - H \qquad \qquad Zn(tmp)_2 \text{ or } (tmp)ZnCl \bullet LiCl \\ BzONR^1R^2, \text{ cat. } Cu(OAc)_2 \\ room \text{ temperature} \qquad Ar - NR^1R^2 \qquad 44 \text{ examples} \\ 60-97\% \text{ yield} \\ 60-97\% \text{ yield} \\ R^1R^2 \qquad NR^1R^2 \qquad NR^1R^2 \\ X = CH_2, N; Y = O, S, NMe \qquad Z = O, S \qquad Br \qquad F_n$$

Direct amination of heteroarenes and arenes has been achieved in a one-pot zincation/Cu(OAc)2-catalyzed amination sequence using O-acylhydroxylamines. The method provides a rapid and efficient approach to a range of aromatic and heteroaromatic amines, including those which were previously inaccessible by using C-H amination methods. tmp= 2,2,6,6-tetramethylpiperidide.

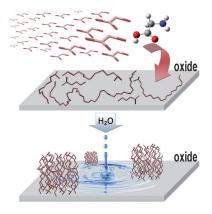
#### Synthetic Methods

S. L. McDonald, C. E. Hendrick, Q. Wang\* \_\_\_\_\_ 4667 - 4670

Copper-Catalyzed Electrophilic Amination of Heteroarenes and Arenes by C-H Zincation



Prebiotic peptides: The catalytic formation from unactivated glycine vapor of poly-Gly up to 16 units long on a surface of SiO<sub>2</sub> or TiO<sub>2</sub> and the subsequent selfassembly of the polypeptides into closely packed aggregates upon contact with water has been observed. Both aspects can provide useful insights into the general problem of the surface reactivity of amino acids, and in particular, the prebiotic formation of biopolymers and their subsequent self-organization.



# Amino Acid Chemistry

Acids on Oxide Surfaces



G. Martra,\* C. Deiana, Y. Sakhno, I. Barberis, M. Fabbiani, M. Pazzi, M. Vincenti \_\_\_\_\_\_ 4671 - 4674

The Formation and Self-Assembly of Long Prebiotic Oligomers Produced by the Condensation of Unactivated Amino



Inside Cove



4509



#### Synthetic Methods

K. Takenaka, S. C. Mohanta,
H. Sasai\* \_\_\_\_\_\_ 4675 – 4679



Palladium Enolate Umpolung: Cyclative Diacetoxylation of Alkynyl Cyclohexadienones Promoted by a Pd/SPRIX Catalyst



In a SPRIX: A new palladium-catalyzed reaction involving an unusual nucleophilic attack on a palladium enolate was developed using the SPRIX ligand. Treatment of alkynyl cyclohexadienone substrates with

Pd/SPRIX in acetic acid under an oxygen atmosphere furnished diacetoxylated benzofuranone derivatives in good yields and with high enantioselectivity.

## Asymmetric Catalysis

M.-C. Tong, X. Chen, J. Li, R. Huang, H. Tao, C.-J. Wang\* \_\_\_\_\_\_ 4680 – 4684



Catalytic Asymmetric Synthesis of [2,3]-Fused Indoline Heterocycles through Inverse-Electron-Demand Aza-Diels-Alder Reaction of Indoles with Azoalkenes

In(verse) demand: The unprecedented catalytic asymmetric inverse-electron-demand aza-Diels—Alder reaction of indoles with in situ formed azoalkenes is reported. A diverse set of [2,3]-fused

indoline heterocycles were produced in generally good yields with high regioselectivity and diastereoselectivity, and with excellent enantioselectivity.

up to 97% yield

up to 99% ee, >20:1 d.r.

 $(S,S_p)$ -L

tBu-Phosferrox

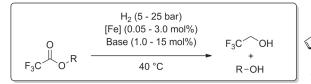
## Iron Catalysis

T. Zell, Y. Ben-David,

D. Milstein\* \_\_\_\_\_ 4685 - 4689



Unprecedented Iron-Catalyzed Ester Hydrogenation. Mild, Selective, and Efficient Hydrogenation of Trifluoroacetic Esters to Alcohols Catalyzed by an Iron Pincer Complex



The replacement of precious-metal catalysts by an iron complex was accomplished for the synthetically important, environmentally benign hydrogenation of esters to alcohols under mild conditions.

The iron pincer complex (see scheme) selectively and efficiently catalyzes the hydrogenation of trifluoroacetates under remarkably mild conditions (5–25 bar and 40 °C).

## C-H Activation

S. D. Halperin, H. Fan, S. Chang,

R. E. Martin, R. Britton\* \_\_\_\_ 4690 - 4693



A Convenient Photocatalytic Fluorination of Unactivated C—H Bonds

The direct fluorination of unactivated C(sp³)—H bonds is catalyzed by the inexpensive photocatalyst tetrabutylammonium decatungstate (TBADT). This convenient reaction provides direct access to

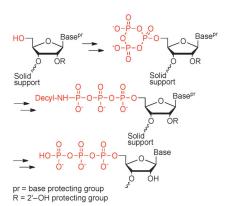


15 examples tolerates ketones, esters, lactones, ammonium salts

58% ( $\alpha$ : $\beta$  = 4:1)

a wide range of fluorinated organic molecules, including structurally complex natural products, acyl fluorides, and fluorinated amino acids.





Simple and straightforward: A strategy for the solid-phase synthesis and purification of 5'-triphosphate oligonucleotides through lipophilic tagging of the triphosphate moiety is reported. This method enables the efficient synthesis of 5'-triphosphorylated RNA derivatives and their gamma-phosphate-substituted analogues and will facilitate the advancement of therapeutic approaches that make use of 5'-triphosphate oligonucleotides as activators of the immune sensor RIG-I.

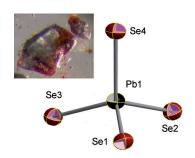
## Oligonucleotides

M. Goldeck, T. Tuschl, G. Hartmann, J. Ludwig\* \_\_\_\_\_\_ 4694 – 4698

Efficient Solid-Phase Synthesis of pppRNA by Using Product-Specific Labeling



**Against all odds**: The first inorganic lead (IV) compound without oxygen, nitrogen, or halogen ligands attached to the lead atom was obtained upon solvothermal reaction of a phase with the nominal composition " $K_2PbSe_2$ " in ethane-1,2-diamine (en). It contains the *ortho*-selenidoplumbate (IV) anion  $[Pb^{IV}Se_4]^{4-}$ , which, for reasons of relativistic effects on lead, is not intuitive; until now, tetrahedral  $[TE_4]^{4-}$  units (E=S, Se, Te) were only known for the lighter homologues T=Si, Ge, Sn.

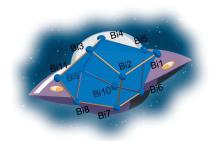


## Inorganic Lead(IV) Compound

G. Thiele, T. Krüger, S. Dehnen\* \_\_\_\_\_\_ **4699 – 4703** 

K<sub>4</sub>[PbSe<sub>4</sub>]·en·NH<sub>3</sub>: A Non-Oxide, Non-Halide Inorganic Lead(IV) Compound





A bismuth "ufosan" sighted: Upon activation of  $[K([2.2.2] \text{crypt})]_2(\text{GaBi}_3) \cdot \text{en}$  by the solvent pyridine,  $[K([2.2.2] \text{crypt})]_3 \cdot (\text{Bi}_{11}) \cdot 2$  py·tol was obtained as the first structurally characterized homoatomic, polycyclic bismuth polyanion. It has the  $[P_{11}]^{3-}$  "ufosan" structure. Spectroscopy, spectrometry, and DFT studies were employed to understand the unprecedented reaction and its (by-) products.

# Polycyclic Bismuth Polyanion

B. Weinert, A. R. Eulenstein, R. Ababei,

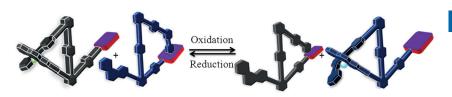
S. Dehnen\* \_\_\_\_\_ 4704 – 4708

Formation of [Bi<sub>11</sub>]<sup>3-</sup>, A Homoatomic, Polycyclic Bismuth Polyanion, by Pyridine-Assisted Decomposition of [GaBi<sub>3</sub>]<sup>2-</sup>



Back Cover





Life depends critically on information transfer, because ON-OFF regulation of biological machines requires error-free procedures for intra- and intercellular data exchange. Bidirectional molecular com-

Angew. Chem. Int. Ed. 2014, 53, 4501-4512

munication for the first time leads to a two-way information exchange between two nanomechanical switches within few minutes.

## Nanoswitches

S. Pramanik, S. De,

M. Schmittel\* \_\_\_\_\_ 4709 – 4713

Bidirectional Chemical Communication between Nanomechanical Switches





#### Titanium Dioxide

M. Setvin, X. Hao, B. Daniel, J. Pavelec,

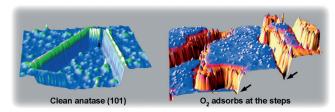
Z. Novotny, G. S. Parkinson, M. Schmid,

G. Kresse, C. Franchini,

U. Diebold\* -4714-4716



Charge Trapping at the Step Edges of TiO<sub>2</sub> Anatase (101)



In step: Step edges on the TiO2 anatase (101) surface act as exclusive charge trapping centers. While the electron trapping is not favorable at (101) terraces, it is

possible at the steps. It results in a higher reactivity of the steps towards some adsorbates, as illustrated for the example of O<sub>2</sub> adsorption.

## Protein-Protein Interactions

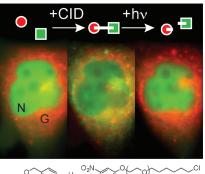
M. Zimmermann, R. Cal, E. Janett, V. Hoffmann, C. G. Bochet, E. Constable, F. Beaufils.\*

M. P. Wymann\* \_ 4717 - 4720



Cell-Permeant and Photocleavable Chemical Inducer of Dimerization

Effective transportation: The photocleavable chemical inducer of dimerization (CID) MeNV-HaXS allows the dynamic control of protein localization with high spatiotemporal and subcellular precision. MeNV-HaXS covalently links HaloTagand SNAP-tag fusion proteins, making it possible to target selected intracellular organelles. Subsequent illumination cleaves MeNV-HaXS to liberate target proteins. Subcellular enzyme activities can be manipulated in this way.

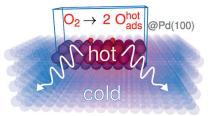


## QM/MM for Metals

J. Meyer,\* K. Reuter \_\_\_



Modeling Heat Dissipation at the Nanoscale: An Embedding Approach for Chemical Reaction Dynamics on Metal Surfaces



Hot or not: An embedding technique for metallic systems makes it possible to model energy dissipation into substrate phonons during surface chemical reactions from first principles. Application to O2 dissociation at Pd(100) predicts translationally "hot" oxygen adsorbates as a consequence of the released adsorption energy (ca. 2.6 eV). This calls into question the instant thermalization of reaction enthalpies generally assumed in heterogeneous catalysis modeling.



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).



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