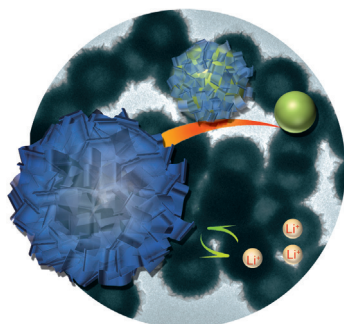
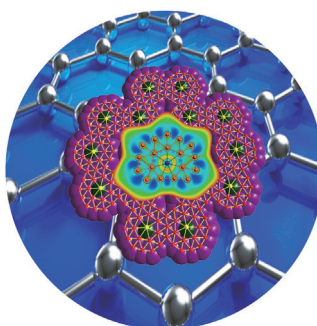


... as building blocks offers attractive synthetic pathways ranging from large-volume base chemicals to highly functionalized complex molecules. J. Klankermayer, W. Leitner et al. describe in their Review on page 7296 ff. how efficient catalysts are becoming available to master the bond breaking and bond formation events required for these processes like strategic moves on a molecular chess board.

Metalloborophenes

The CoB₁₈⁻ cluster is investigated by J. Li, L.-S. Wang et al. in their Communication on page 7358 ff. It is a highly stable and perfectly planar structure with the Co atom centered in a seven-membered ring.

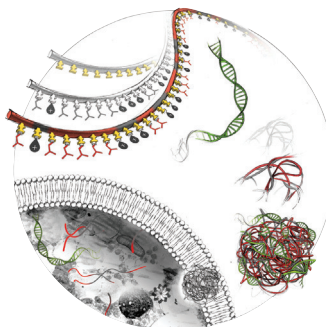


Hierarchical Nanomaterials

In their Communication on page 7423 ff. X. W. Lou et al. prepare hierarchical spherical MoS₂ structures that are formed from ultrathin subunits and have a hollow interior. They are promising anode materials for lithium-ion batteries.

siRNA Delivery

The post-polymerization functionalization of a polyhydrazide scaffold to produce amphiphilic vectors for polynucleotide delivery is reported by J. Montenegro, F. Fernandez-Trillo et al. in their Communication on page 7492 ff.



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

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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

E-mail: angewandte@wiley-vch.de

Fax: (+49) 62 01-606-331

Telephone: (+49) 62 01-606-315

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Spotlight on Angewandte's Sister Journals

7286 – 7289

Author Profile



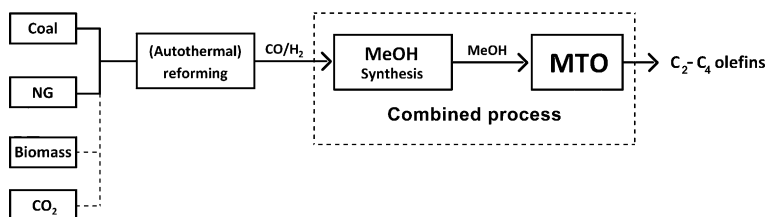
*"If I could be a piece of lab equipment, I would be a centrifuge.
The greatest scientific advance of the last decade was 3D printing ..."*
This and more about Zhiyong Tang can be found on page 7290.

Zhiyong Tang _____ 7290

Books

Cleavage of Carbon–Carbon Single Bonds by Transition Metals Masahiro Murakami, Naoto Chatani

reviewed by C. Aïssa* _____ 7291



All together now: Combination in a single reactor of the catalysts for converting syngas into methanol and methanol into

olefins was recently reported by Cheng et al. This approach considerably simplifies the catalytic conversion of natural gas.

Highlights

Heterogeneous Catalysis

U. Olsbye* _____ 7294 – 7295

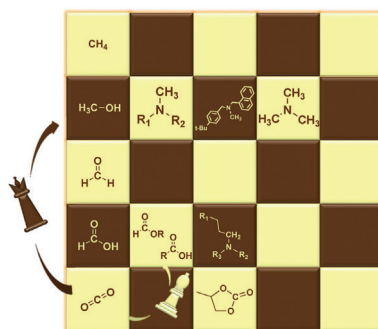
Single-Pass Catalytic Conversion of Syngas into Olefins via Methanol

Reviews

CO₂ Utilization

J. Klankermayer,* S. Wesselbaum,
K. Beydoun, W. Leitner* — 7296–7343

Selective Catalytic Synthesis Using the
Combination of Carbon Dioxide and
Hydrogen: Catalytic Chess at the Interface
of Energy and Chemistry



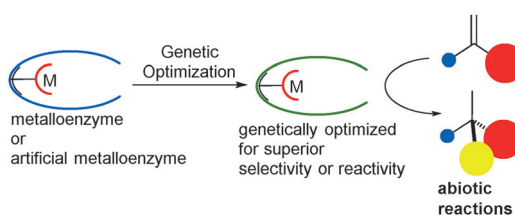
The catalytic gambit: The combined use of CO₂ and H₂ as building blocks in catalytic processes provides access to products ranging from large volume base chemicals to highly functionalized complex molecules. The current state-of-the-art is critically reviewed, highlighting pathways that are in line with “green chemistry” principles and offer the potential to harness renewable energy into the chemical value chain.

Front Cover

Artificial Metalloenzymes

T. K. Hyster,* T. R. Ward* — 7344–7357

Genetic Optimization of Metalloenzymes:
Enhancing Enzymes for Non-Natural
Reactions



The second row also matters: In contrast to traditional transition-metal catalysts, artificial metalloenzymes can modulate both the first and second coordination spheres, and thus result in novel reactiv-

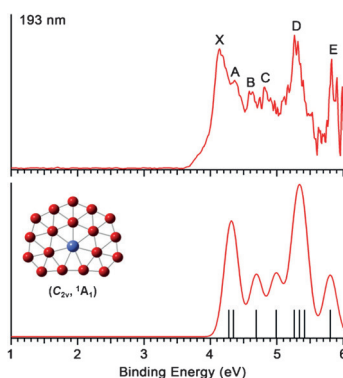
ities. This Review discusses attempts to modulate the second coordination sphere of artificial metalloenzymes through genetic modifications of the protein sequence.

Communications

Metallo-Borophene

W. L. Li, T. Jian, X. Chen, T. T. Chen,
G. V. Lopez, J. Li,*
L. S. Wang* — 7358–7363

The Planar CoB₁₈[−] Cluster as a Motif for
Metallo-Borophenes



No bending: The CoB₁₈[−] cluster was investigated experimentally and theoretically. It is found to be a highly stable and perfectly planar structure consisting of a monovalent Co atom centered in a seven-membered ring.

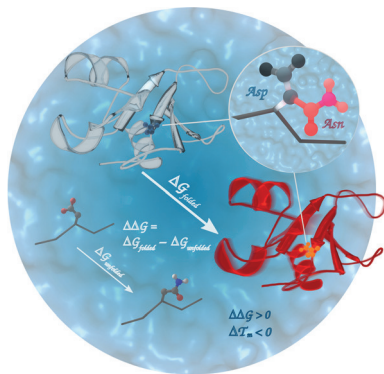
Frontispiece

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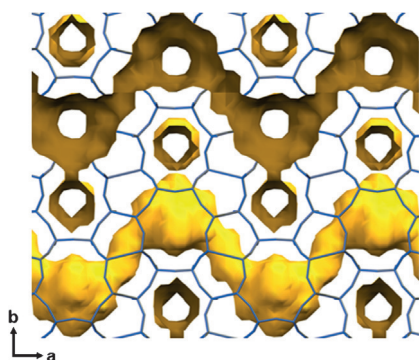


The computational prediction of the changes in protein thermostability upon an amino acid mutation greatly aids protein engineering and design. It is shown that such predictions can be rendered remarkably accurate by means of molecular-dynamics-based alchemical free-energy calculations.

Thermostability

V. Gapsys,* S. Michielssens, D. Seeliger, B. L. de Groot* ————— **7364–7368**

Accurate and Rigorous Prediction of the Changes in Protein Free Energies in a Large-Scale Mutation Scan



Structure elucidation: The structure of the small-pore zeolite EU-12, which has remained unknown during the past 30 years, was determined by synchrotron powder X-ray diffraction and Rietveld analyses (see picture). EU-12 shows a superior catalytic performance for the dehydration of ethanol.

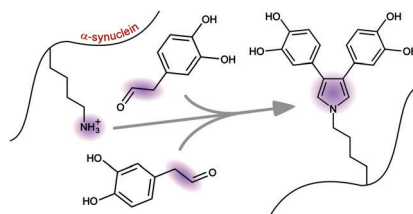
Microporous Materials

J. Bae, J. Cho, J. H. Lee, S. M. Seo, S. B. Hong* ————— **7369–7373**

EU-12: A Small-Pore, High-Silica Zeolite Containing Sinusoidal Eight-Ring Channels



Amyloid disease: The primary dopamine metabolite, 3,4-dihydroxyphenylacetaldehyde, reacts with α -synuclein Lys residues to form dicatechol pyrrole lysine adducts, which may act as the scaffold for the protein crosslinking observed in dopaminergic cells. The dicatechol pyrrole lysine adducts were characterized by NMR spectroscopy and mass spectrometry.



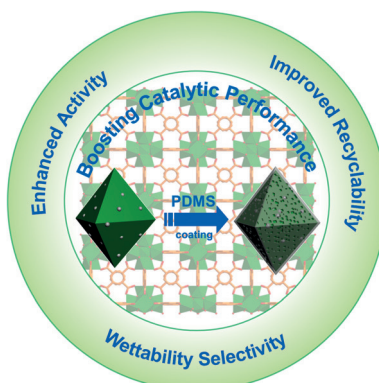
Protein Modification

J. W. Werner-Allen, J. F. DuMond, R. L. Levine,* A. Bax* ————— **7374–7378**

Toxic Dopamine Metabolite DOPAL Forms an Unexpected Dicatechol Pyrrole Adduct with Lysines of α -Synuclein



Hydrophobic visions: Surface hydrophobization of Pd/UiO-66, a composite of a metal–organic framework (MOF) and stabilized palladium nanoparticles, was realized using a simple polydimethylsiloxane (PDMS) coating. The resultant Pd/UiO-66@PDMS composite exhibits superior catalytic activity and recyclability compared to pristine Pd/UiO-66, and additional selectivity in sieving reactants with different wettability. This approach is extendable to various Pd-based catalysts.



Metal–Organic Framework Composites

G. Huang, Q. Yang, Q. Xu, S.-H. Yu, H.-L. Jiang* ————— **7379–7383**

Polydimethylsiloxane Coating for a Palladium/MOF Composite: Highly Improved Catalytic Performance by Surface Hydrophobization



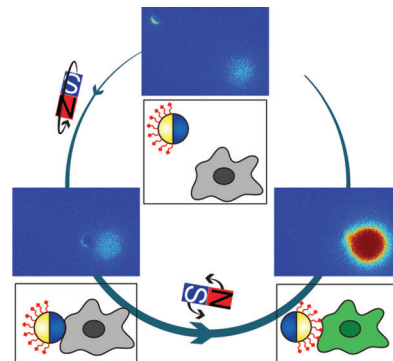
Janus Particles

K. Lee, Y. Yi, Y. Yu* — 7384 – 7387



Remote Control of T Cell Activation Using Magnetic Janus Particles

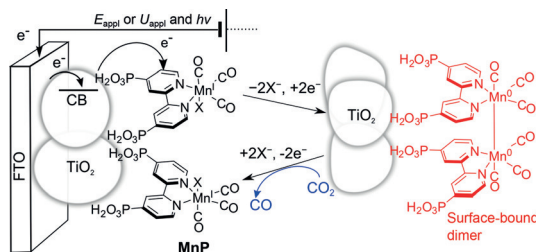
Janus particles were employed to control T cell activation. The particles were magnetically responsive on one side and displayed ligands for T cell stimulation on the other side. T cell activation was remotely controlled by simultaneously manipulating the rotation and locomotion of the magnetic Janus particles.

CO₂ Reduction

T. E. Rosser, C. D. Windle, E. Reisner* — 7388 – 7392



Electrocatalytic and Solar-Driven CO₂ Reduction to CO with a Molecular Manganese Catalyst Immobilized on Mesoporous TiO₂



One small step for Mn: A Mn catalyst immobilized on TiO₂ gave electrocatalytic CO₂ reduction with a turnover number of 112. The low overpotential of 420 mV is a result of dimerization of the catalyst on

the mesoporous electrode. The heterogeneous hybrid cathode was used in a photoelectrochemical cell enabling solar-driven CO production by a photo-unstable Mn catalyst for the first time.

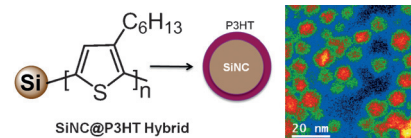
Hybrid Materials

M. A. Islam, T. K. Purkait, M. H. Mobarok, I. M. D. Hoehlein, R. Sinelnikov, M. Iqbal, D. Azulay, I. Balberg, O. Millo, B. Rieger, J. G. C. Veinot* — 7393 – 7397



Grafting Poly(3-hexylthiophene) from Silicon Nanocrystal Surfaces: Synthesis and Properties of a Functional Hybrid Material with Direct Interfacial Contact

Hybrid functional materials of silicon nanocrystals and poly(3-hexylthiophene) (SiNC@P3HT) consisting of a direct conjugate covalent bond between SiNC and P3HT were developed. Systematic characterization provides evidence of a core-shell structure, enhanced interfacial electron and/or energy transfer between the P3HT and SiNC components, as well as formation of a type-II heterostructure.

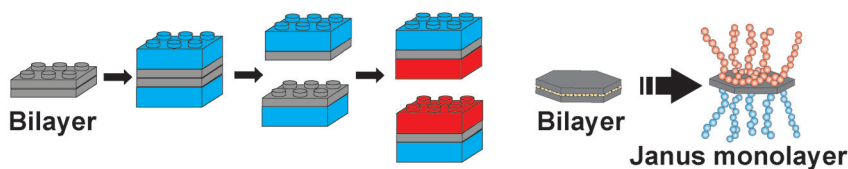


Hybrid Materials

M. Stöter, S. Gödrich, P. Feicht, S. Rosenfeldt, H. Thurn, J. W. Neubauer, M. Seuss, P. Lindner, H. Kalo, M. Möller, A. Fery, S. Förster, G. Papastavrou,* J. Breu* — 7398 – 7402

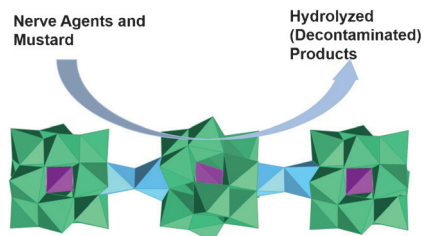


Controlled Exfoliation of Layered Silicate Heterostructures into Bilayers and Their Conversion into Giant Janus Platelets



Controlled exfoliation of layered silicate heterostructures into bilayers with unprecedented precision by osmotic swelling gives access to a general method for

asymmetrical modification of basal planes. Only two simple steps are needed to obtain Janus-type monolayers as bulk material.

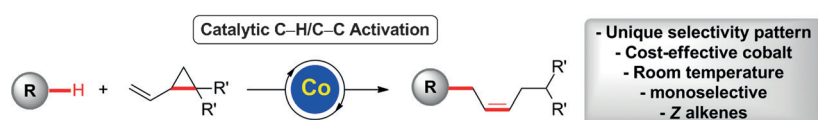


POM against CWAs: A new one-dimensional polymeric polyoniobate, $K_{12}[Ti_2O_2][GeNb_{12}O_{40}]$, removes a wide range of chemical warfare agents (CWAs) and their simulants. The transformations are catalytic and proceed effectively under very mild conditions and in the dark.

Decontamination

W. Guo, H. Lv, K. P. Sullivan, W. O. Gordon, A. Balboa, G. W. Wagner, D. G. Musaev, J. Bacsa, C. L. Hill* ————— **7403 – 7407**

Broad-Spectrum Liquid- and Gas-Phase Decontamination of Chemical Warfare Agents by One-Dimensional Heteropolyoniobates



Double activation: Challenging C–H/C–C functionalizations were achieved through the use of cobalt catalysis under exceedingly mild reaction conditions. This

method leads to the formation of Z alkenes with unique chemo- and diastereo-selectivity.

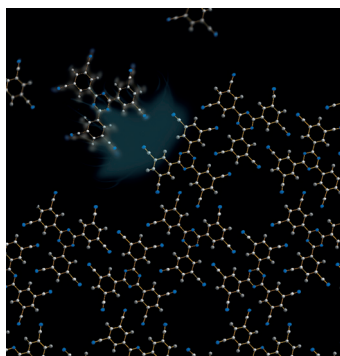
C–H/C–C Activation

D. Zell, Q. Bu, M. Feldt, L. Ackermann* ————— **7408 – 7412**

Mild C–H/C–C Activation by Z-Selective Cobalt Catalysis



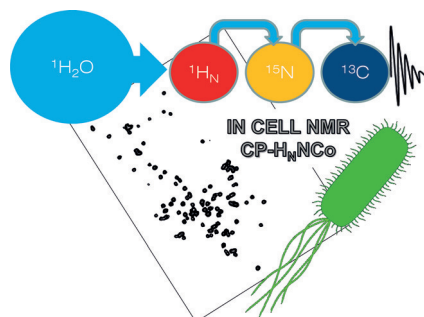
Sturdy crystals: The formation of organic-molecule-based superstructures was realized by solid-state conversion of an organic single-crystal. The resultant porous organic framework with 1-dimensional channels showed unusually high thermal stability tolerance to electron-beams.



Porous Crystals

S.-M. Jung, D. Kim, D. Shin, J. Mahmood, N. Park, M. S. Lah, H. Y. Jeong,* J.-B. Baek* ————— **7413 – 7417**

Unusually Stable Triazine-based Organic Superstructures



Keep your finger on the pulse: A new pulse sequence combining proton–nitrogen cross-polarization and carbonyl detection is proposed for recording high-resolution, high-sensitivity NMR spectra of IDPs under true physiological conditions. By this method, a high-quality N–CO correlation spectrum was acquired of α -synuclein in bacterial cells at 37°C.

In-Cell NMR Spectroscopy

J. Lopez,* R. Schneider, F.-X. Cantrelle, I. Huvent, G. Lippens* ————— **7418 – 7422**

Studying Intrinsically Disordered Proteins under True In Vivo Conditions by Combined Cross-Polarization and Carbonyl-Detection NMR Spectroscopy



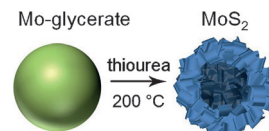
Nanospheres

Y. Wang, L. Yu,* X. W. Lou* 7423 – 7426



Synthesis of Highly Uniform Molybdenum–Glycerate Spheres and Their Conversion into Hierarchical MoS₂ Hollow Nanospheres for Lithium-Ion Batteries

Dr Mo: Hierarchical MoS₂ hollow nanospheres are synthesized with a self-templating method from highly uniform Mo–glycerate solid spheres. By sulfidation and annealing, these Mo–glycerate solid spheres can be converted into hierarchical MoS₂ hollow nanospheres. Owing to their unique structures, the hierarchical nanospheres show enhanced electrochemical properties as the anode material for lithium-ion batteries.



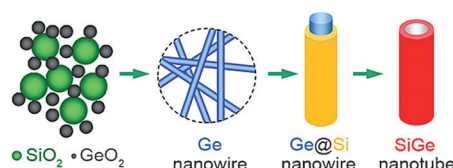
Inside Back Cover

Lithium Storage

W. Xiao, J. Zhou, L. Yu, D. H. Wang,*
X. W. Lou* 7427 – 7431



Electrolytic Formation of Crystalline Silicon/Germanium Alloy Nanotubes and Hollow Particles with Enhanced Lithium-Storage Properties



Li likes alloys: Crystalline SiGe alloy nanotubes and hollow particles are synthesized through a one-pot electrolytic process in molten salts. The solid-diffusion process, governed by the nanoscale Kirkendall effect, leads to the formation of

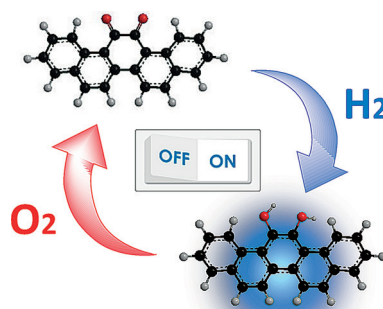
internal voids in the SiGe alloy particles. Owing to the unique structural features and desirable composition, the SiGe alloy nanotubes exhibit enhanced lithium-storage performance.

Photoluminescent Materials

K. Urakawa, M. Sumimoto, M. Arisawa,
M. Matsuda,* H. Ishikawa* 7432 – 7436



Redox Switching of Orthoquinone-Containing Aromatic Compounds with Hydrogen and Oxygen Gas



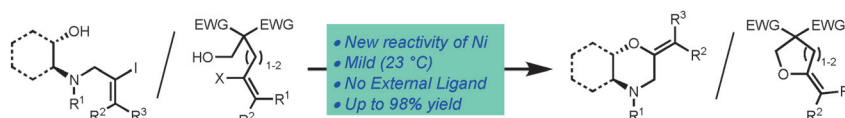
A tale with a twist: Unique redox switching of orthoquinone-containing pentacyclic aromatic compounds was observed upon exposure to H₂ and O₂ in the presence of a sulfur-modified gold-supported palladium nanoparticle catalyst (see picture). Switching between the orthoquinone and the corresponding hydroquinone led to a drastic change in the photoluminescence and color of the system owing to differences in the aromaticity and twist strain of the molecules.

Cross-Coupling

S.-J. Han, R. Doi,
B. M. Stoltz* 7437 – 7440



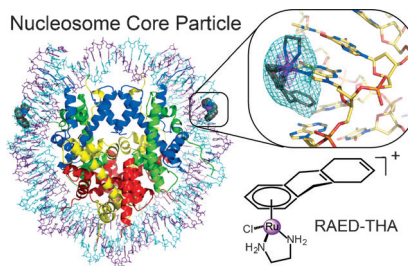
Nickel-Catalyzed Intramolecular C–O Bond Formation: Synthesis of Cyclic Enol Ethers



Nickel-O-C-eon: The title reaction between aliphatic hydroxy nucleophiles and tethered vinyl halides provides access to cyclic vinyl ethers in a single step and under exceptionally mild and operationally simple reaction conditions. The

exploration of this new reactivity of nickel catalysts can provide further insight into the unique properties and opportunities afforded by nickel catalysts. EWG = electron-withdrawing group.

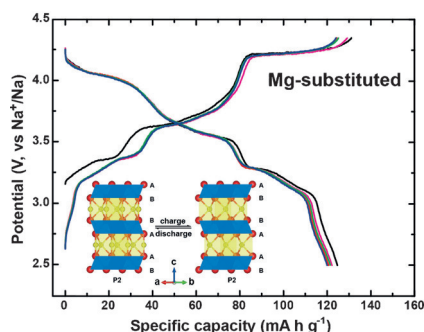
Binding preferences: Using crystallographic methods and molecular dynamics simulations it was shown that adducts formed by the anticancer agent $[(\eta^6-5,8,9,10\text{-tetrahydroanthracene})\text{Ru}(\text{ethylenediamine})\text{Cl}][\text{PF}_6]$ on a nucleosome comprise a novel one-stranded intercalation and DNA distortion mode. The adduct dimorphism and DNA topology dependence might contribute to the unusually high cytotoxicity of this anticancer agent.



Bioinorganic Chemistry

Z. Ma, G. Palermo, Z. Adhikarsan, B. S. Murray, T. von Erlach, P. J. Dyson, U. Rothlisberger,*
C. A. Davey* 7441–7444

An Organometallic Compound which Exhibits a DNA Topology-Dependent One-Stranded Intercalation Mode

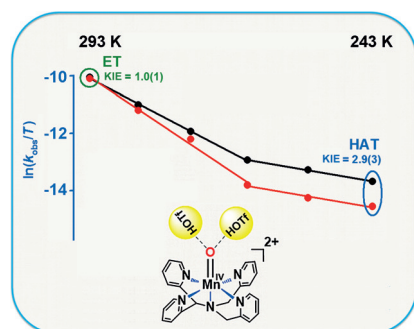


The P2–O2 phase transition in $\text{P2-Na}_{0.67}\text{Mn}_{0.67}\text{Ni}_{0.33-x}\text{Mg}_x\text{O}_2$ can be effectively suppressed by substituting some of the nickel ions with magnesium. Both the reversible capacity and the capacity retention of this cathode material were thus remarkably improved, and the various phases were characterized by scanning tunneling electron microscopy with atomic resolution.

Sodium-Ion Batteries

P.-F. Wang, Y. You, Y.-X. Yin, Y.-S. Wang, L.-J. Wan, L. Gu,*
Y.-G. Guo* 7445–7449

Suppressing the P2–O2 Phase Transition of $\text{Na}_{0.67}\text{Mn}_{0.67}\text{Ni}_{0.33}\text{O}_2$ by Magnesium Substitution for Improved Sodium-Ion Batteries



The switchover of the reaction mechanism from electron transfer (ET) to hydrogen-atom transfer (HAT) for a protonated nonheme manganese(IV)–oxo complex was investigated. The switchover occurs in the presence of triflic acid by changing only the reaction temperature in the boundary region between ET and HAT pathways. KIE = kinetic isotope effect; black = mesitylene, red = $[\text{D}_{12}]$ mesitylene.

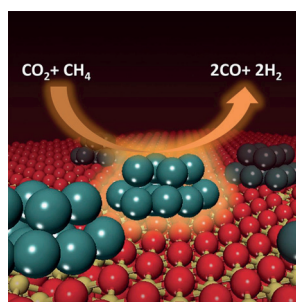
Bioinorganic Chemistry

J. Jung, S. Kim, Y.-M. Lee, W. Nam,*
S. Fukuzumi* 7450–7454

Switchover of the Mechanism between Electron Transfer and Hydrogen-Atom Transfer for a Protonated Manganese(IV)–Oxo Complex by Changing Only the Reaction Temperature



NiCe and dry: Ni–CeO₂ is shown to be highly efficient, stable, and non-expensive catalyst for methane dry reforming at relative low temperatures (700 K). The active phase of the catalyst consists of small nanoparticles of nickel dispersed on partially reduced ceria. Strong metal–support interactions activate Ni for the dissociation of methane.



Methane Reforming

Z. Liu, D. C. Grinter, P. G. Lustemberg, T.-D. Nguyen-Phan, Y. Zhou, S. Luo, I. Waluyo, E. J. Crumlin, D. J. Stacchiola, J. Zhou, J. Carrasco, H. F. Busnengo, M. V. Ganduglia-Pirovano,*
S. D. Senanayake,*
J. A. Rodriguez* 7455–7459

Dry Reforming of Methane on a Highly-Active Ni–CeO₂ Catalyst: Effects of Metal-Support Interactions on C–H Bond Breaking



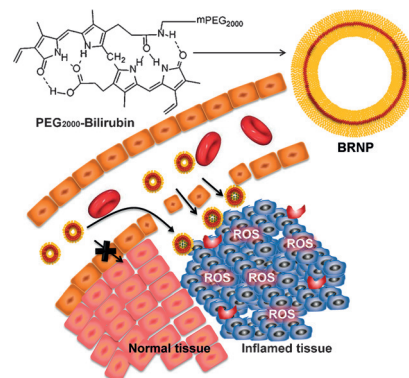
Nanomedicines

Y. Lee, H. Kim, S. Kang, J. Lee, J. Park,
S. Jon* ————— 7460 – 7463



Bilirubin Nanoparticles as a Nano-
medicine for Anti-inflammation Therapy

Bilirubin, a nanomedicine for inflamm-
atory diseases: Bilirubin, a highly potent
anti-inflammatory but extremely water
insoluble compound, is converted into
nanoparticles by simply introducing PEG.
The resultant bilirubin nanoparticles show
potential as a nanomedicine in anti-
inflammation therapy. ROS = reactive
oxygen species, BRNP = Bilirubin nano-
particle.



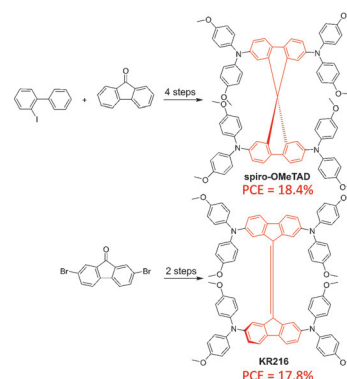
Solar Cells

K. Rakstys, M. Saliba, P. Gao, P. Gratia,
E. Kamarauskas, S. Paek, V. Jankauskas,
M. K. Nazeeruddin* ————— 7464 – 7468



Highly Efficient Perovskite Solar Cells
Employing an Easily Attainable
Bifluorenylidene-Based Hole-Transporting
Material

The hole-transporting material KR216
(4,4'-dimethoxydiphenylamine-substi-
tuted 9,9'-bifluorenylidene) reached
a photon-to-current efficiency (PCE) of
17.8% in perovskite-based solar cells. A
novel material was synthesized using
a straightforward two-step procedure
from commercially available and inex-
pensive starting reagents, mimicking the
9,9'-spirobifluorene moiety of the well-
studied spiro-OMeTAD.

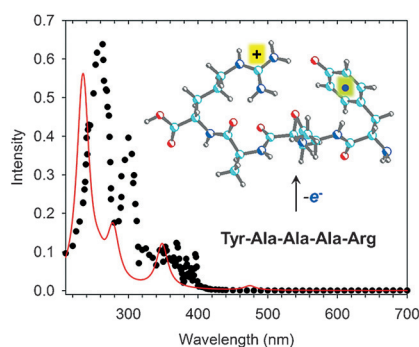


Gas-Phase Chemistry

E. Viglino, C. J. Shaffer,
F. Tureček* ————— 7469 – 7473



UV/Vis Action Spectroscopy and
Structures of Tyrosine Peptide Cation
Radicals in the Gas Phase



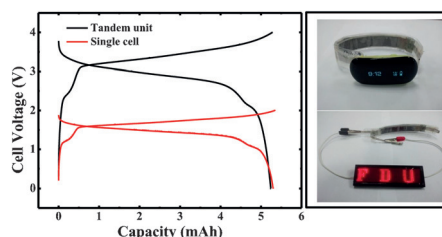
UV/Vis action spectrum: Tyrosine pep-
tides underwent different courses of oxi-
dation by copper(II) ions depending on
the position of the tyrosine residue in the
peptide sequence. Tyrosine peptide cation
radicals were produced by oxidative
intramolecular electron transfer in the
gas-phase copper complexes.

Lithium-Ion Batteries

X. L. Dong, L. Chen, X. L. Su, Y. G. Wang,*
Y. Y. Xia ————— 7474 – 7477

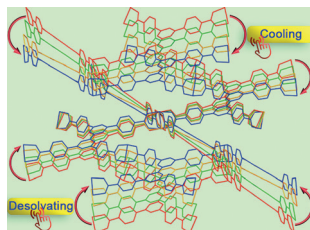


Flexible Aqueous Lithium-Ion Battery with
High Safety and Large Volumetric Energy
Density



Wearable electronic devices: A wearable
aqueous lithium-ion battery based on a
spinel $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$ cathode and a carbon-
coated $\text{LiTi}_2(\text{PO}_4)_3$ anode offered a high

safety standard and showed excellent
flexibility, and a large volumetric energy
density.



See the shrink: A record high uniaxial positive thermal expansion coefficient of $653.2 \times 10^{-6} \text{ K}^{-1}$ and large c -axial shrinkage of 32.4%, is found for metal-organic framework (MOF) temperature- and solvent-responsive soft crystals. The dynamic process can both be visualized by in situ single-crystal X-ray snapshot analyses. The stimuli-responsive mechanism results from rotations and deformations of the organic linkers.

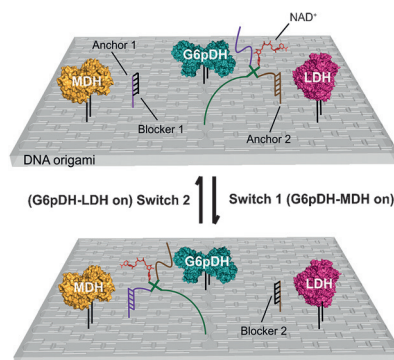
Responsive Materials

J. Pang, C. Liu, Y. Huang, M. Wu,* F. Jiang, D. Yuan,* F. Hu, K. Su, G. Liu, M. Hong ————— **7478 – 7482**

Visualizing the Dynamics of Temperature- and Solvent-Responsive Soft Crystals



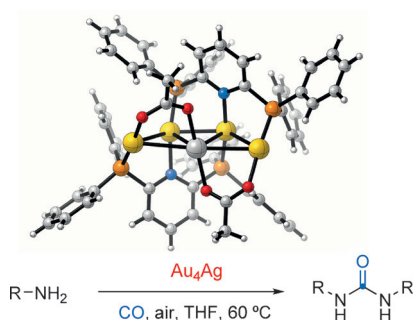
Artificial multi-enzyme systems with precise and directional control over the enzyme pathway activities are of great significance in bionanotechnology and synthetic biology. A DNA origami system for the directional regulation of the activities of two enzyme pathways (G6pDH–MDH and G6pDH–LDH) through the control of NAD^+ substrate channeling by specifically shifting NAD^+ between the two enzyme pairs is now reported.



Substrate Channeling

G. Ke, M. Liu, S. Jiang, X. Qi, Y. R. Yang, S. Wootten, F. Zhang, Z. Zhu, Y. Liu,* C. J. Yang,* H. Yan* ————— **7483 – 7486**

Directional Regulation of Enzyme Pathways through the Control of Substrate Channeling on a DNA Origami Scaffold

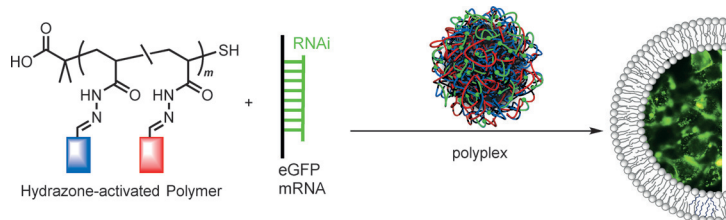


Gold aplenty: The synthesis of tetranuclear gold complexes, a structurally unprecedented octanuclear complex with a planar $[\text{Au}_8]$ core, and pentanuclear $[\text{Au}_4\text{M}]$ ($\text{M} = \text{Cu}, \text{Ag}$) complexes is presented. The linear $[\text{Au}_4]$ complex undergoes C–H functionalization of carbonyl compounds under mild reaction conditions. In addition, $[\text{Au}_4\text{Ag}]$ catalyzes the carbonylation of primary amines to form ureas under homogeneous conditions with efficiencies higher than those achieved by gold nanoparticles.

Heterometallic Complexes

E. S. Smirnova, J. M. Muñoz Molina, A. Johnson, N. A. G. Bandeira, C. Bo, A. M. Echavarren* ————— **7487 – 7491**

Polynuclear Gold $[\text{Au}]_4$, $[\text{Au}]_8$, and Bimetallic $[\text{Au}_4\text{Ag}]$ Complexes: C–H Functionalization of Carbonyl Compounds and Homogeneous Carbonylation of Amines



Signed, sealed, delivered: The chemical functionality of a polyhydrazone scaffold was modified by careful choice of cationic (blue box; see picture) and hydrophobic

(red) aldehydes to produce amphiphilic vectors for supramolecular polynucleotide delivery.

siRNA delivery

J. M. Priegue, D. N. Crisan, J. Martínez-Costas, J. R. Granja, F. Fernandez-Trillo,* J. Montenegro* ————— **7492 – 7495**

In Situ Functionalized Polymers for siRNA Delivery



Back Cover



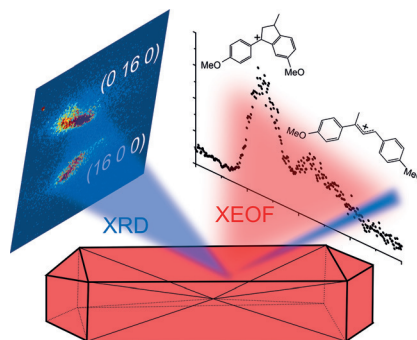
Chemical Imaging



Z. Ristanović, J. P. Hofmann,
M.-I. Richard, T. Jiang, G. A. Chahine,
T. U. Schüllli, F. Meirer,
B. M. Weckhuysen* 7496 – 7500



X-ray Excited Optical Fluorescence and
Diffraction Imaging of Reactivity and
Crystallinity in a Zeolite Crystal:
Crystallography and Molecular
Spectroscopy in One



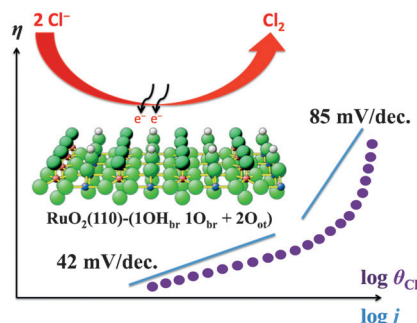
Two worlds in one X-ray shot: The local crystallinity and acid-catalyzed chemistry of a single zeolite crystal were determined by a combination of micro-X-ray diffraction (μ -XRD) and X-ray excited optical fluorescence (μ -XEOF), achieved by using one X-ray beam to excite fluorescent products formed in a zeolite. The inter-growth structure and Al zoning play a decisive role in the degree of dealumination and shape-selective product formation.

Electrocatalysis

K. S. Exner, J. Anton, T. Jacob,
H. Over* 7501 – 7504



Full Kinetics from First Principles of the
Chlorine Evolution Reaction over
a $\text{RuO}_2(110)$ Model Electrode



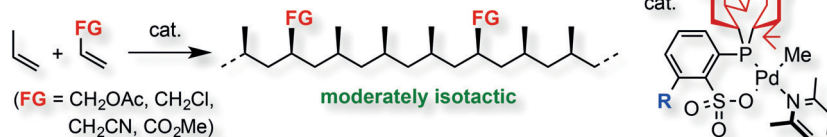
Beyond thermodynamics: An intimate interplay of thermodynamics and kinetics from first principles together with micro-kinetic modeling allows the microscopic processes of the chlorine evolution reaction over a $\text{RuO}_2(110)$ model electrode to be unraveled. This combined approach may provide a general roadmap on how electrocatalytic reactions can be studied to gain unprecedented molecular insight.

Polymerization

Y. Ota, S. Ito, M. Kobayashi, S. Kitade,
K. Sakata, T. Tayano,
K. Nozaki* 7505 – 7509



Crystalline Isotactic Polar Polypropylene
from the Palladium-Catalyzed
Copolymerization of Propylene and Polar
Monomers



Control center: High-molecular-weight polypropylenes can be obtained by using palladium catalysts bearing menthyl-substituted phosphine-sulfonate ligands for the isospecific homopolymerization of propylene or the copolymerization of

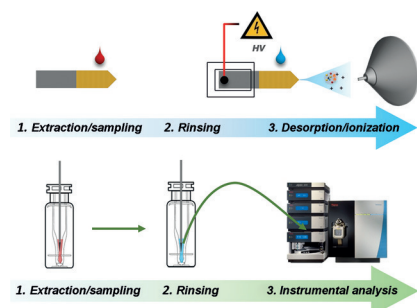
propylene with polar monomers. The introduction of substituents at the *ortho*-position relative to the sulfonate group favors enantiomeric site control over chain end control in the chain propagation step.

Sample Preparation

H. Piri-Moghadam, F. Ahmadi,
G. A. Gómez-Ríos, E. Boyaci,
N. Reyes-Garcés, A. Aghakhani, B. Bojko,
J. Pawliszyn* 7510 – 7514



Fast Quantitation of Target Analytes in
Small Volumes of Complex Samples by
Matrix-Compatible Solid-Phase
Microextraction Devices



Simple sampling: solid-phase microextraction (SPME) devices perform fast extraction/enrichment of target analytes in small sample volumes. Micro-sampling is performed with metal tips coated with a thin layer of polypyrrole (see picture, bottom) or by using thin-coated blade spray (CBS) devices (top). These devices can be coupled with liquid chromatography (LC), or directly to mass spectrometry (MS).



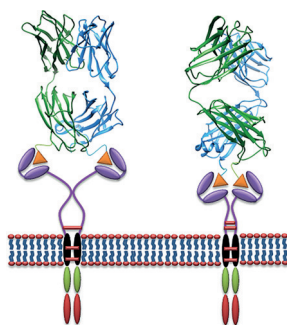
Chemically redesigned DNA, in which all four nucleobases are functionalized (denoted DZA), was used to transfer genetic information in living organisms.

Using a gene encoding resistance to the antibiotic trimethoprim, a fully morphed DNA was successfully replicated *in vitro* and served as a genetic template *in vivo*.

Nucleic Acids

E. Ereemeeva, M. Abramov,
L. Margamuljana, J. Rozenski, V. Pezo,
P. Marlière, P. Herdewijn* — 7515–7519

Chemical Morphing of DNA Containing Four Noncanonical Bases



CAR-T control: Chimeric antigen receptor T (CAR-T) cells were engineered to be controlled by exogenous switch molecules. Site-specific incorporation of the small molecule FITC or a short peptide neo-epitope in the anti-Her2 4D5 Fab allowed activation of corresponding switchable CAR-T cells towards Her2-expressing solid tumor cells, and displayed significant anti-cancer effects both *in vitro* and *in vivo*.

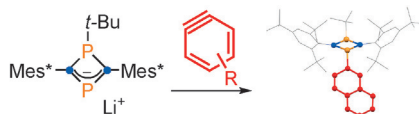
Cancer Immunotherapy

Y. Cao, D. T. Rodgers, J. Du, I. Ahmad,
E. N. Hampton, J. S. Y. Ma, M. Mazagova,
S. H. Choi, H. Y. Yun, H. Xiao, P. Yang,
X. Luo, R. K. V. Lim, H. M. Pugh, F. Wang,
S. A. Kazane, T. M. Wright, C. H. Kim,*
P. G. Schultz,* T. S. Young* — 7520–7524

Design of Switchable Chimeric Antigen Receptor T Cells Targeting Breast Cancer



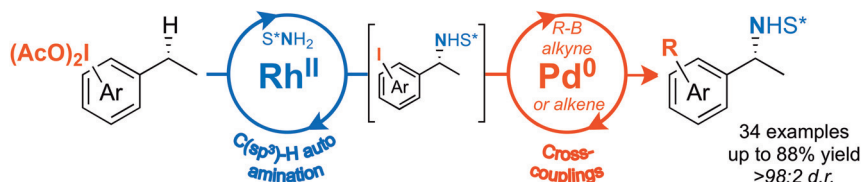
A Promising Constellation: The reaction of a sterically encumbered 1,3-diphosphacyclobuten-4-yl anion with *ortho*-silylated aryl triflates in the presence of fluoride under appropriate conditions afforded the corresponding 1-aryl-1,3-diphosphacyclobutane-2,4-diyls (see scheme). These air-stable open-shell singlet P-heterocycles exhibit considerable electron-donating character and can be used as detectors of hydrogen fluoride.



Phosphorus Heterocycles

Y. Ueta, K. Mikami, S. Ito* — 7525–7529

Access to Air-Stable 1,3-Diphosphacyclobutane-2,4-diyls by an Arylation Reaction with Arynes



Poly-valent iodine: The design of one-pot reactions involving a catalytic auto C-(sp³)-H amination followed by Pd-catalyzed couplings has led to polyfunctionalized enantiopure amines. An

iodine(III) reagent can thus be used both as an oxidant and a substrate, then as a coupling partner. The overall process reveals iodoarene-derived oxidants to be versatile building blocks in synthesis.

C–H Amination

J. Buendia, G. Grelier, B. Darses,
A. G. Jarvis, F. Taran,
P. Dauban* — 7530–7533

The Multiple Facets of Iodine(III) Compounds in an Unprecedented Catalytic Auto-amination for Chiral Amine Synthesis

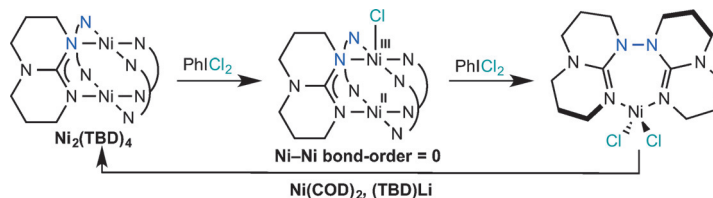


N–N Bond Formation

J. B. Diccianni, C. Hu,
T. Diao* 7534–7538



N–N Bond Forming Reductive Elimination via a Mixed-Valent Nickel(II)–Nickel(III) Intermediate



A “paddle-wheel” Ni complex undergoes N–N bond forming reductive elimination under oxidative conditions. The inter-

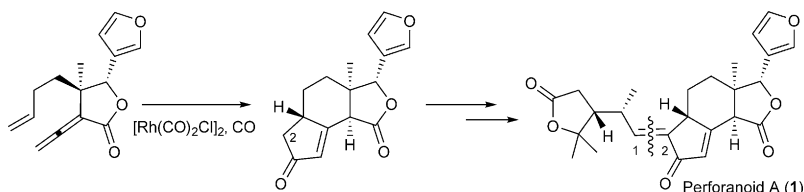
mediate is a mixed-valent Ni^{II}–Ni^{III} complex with a Ni–Ni bond order of zero.

Total Synthesis

C. Lv, X. Yan, Q. Tu, Y. Di, C. Yuan, X. Fang,
Y. Ben-David, L. Xia, J. Gong, Y. Shen,*
Z. Yang,* X. Hao* 7539–7543



Isolation and Asymmetric Total Synthesis of Perforanoid A



When life gives you limonoids: A novel limonoid, perforanoid A, was isolated, and an asymmetric total synthesis was achieved in 10 steps. The key steps are chiral tertiary aminonaphthol mediated enantioselective alkenylation of an alde-

hyde to an allylic alcohol, Pd-catalyzed coupling of the allylic alcohol with vinyl ether to form the γ -lactone ring, and cyclopentenone ring formation through a Rh-catalyzed Pauson–Khand reaction.

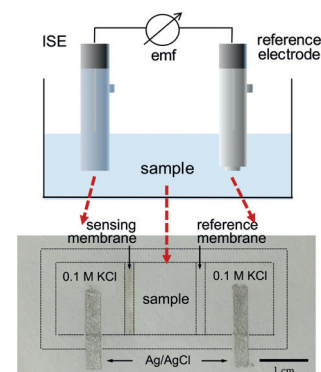
Analytical Methods

J. Hu, A. Stein,*
P. Bühlmann* 7544–7547



A Disposable Planar Paper-Based Potentiometric Ion-Sensing Platform

Paper-based sensors: Embedding a potentiometric cell into paper brings selective ion sensors into the reach of users with limited resources and training. The paper-based device is simple to use, does not need any pretreatment, and requires only a low sample volume of 20 μ L. It can be used to detect clinically relevant ions in biological samples with high sensitivity and reproducibility. ISE = ion-selective electrode.



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



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



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