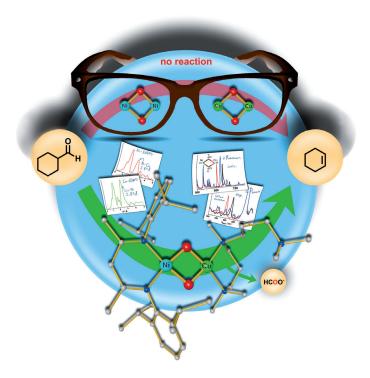
Unlike typical homodinuclear ...

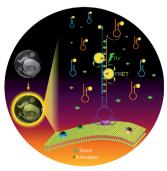




... high-valent $[M_2(\mu\text{-O})_2]^{n+}$ cores, a rare heterobimetallic high-valent CuNi bis(μ -oxo) complex behaves as a nucleophile. In their Communication on page 5622 ff., K. Ray, M. Driess, C. Limberg et al. show that this complex can initiate deformylation of aldehydes, indicating that mixed-metal bis(μ -oxo) cores are viable intermediates in the deformylation of fatty aldehydes by cyanobacterial aldehyde decarbonylase, for which a similar cofactor has been suggested, but not isolated.

Fluorescence

W. Tan and co-workers report fluorescent DNA nanodevices that undergo fluorescence resonance energy transfer (FRET) and can be anchored on living cell surfaces in their Communication on page 5490 ff.



рро Сно

Directed Evolution

In their Communication on page 5571 ff., F. H. Arnold and co-workers describe a synthetic substrate that can be used in a colorimetric screen for terpene synthase cyclization activity, thereby facilitating the optimization of these enzymes.

Micromotors

S. Sanchez et al. show in their Communication on page 5552 ff. that self-propelled micromotors in a solution change their trajectory when hydrogen peroxide is added. This response resembles the chemotactic behavior of some living organisms.



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Spotlight on Angewandte's Sister Journals

5428 - 5431

5435



"My worst nightmare is transcontinental travel for more than 36 hours.

My favorite piece of research is CO_2 activation ..." This and more about Licheng Sun can be found on page 5434.

Author Profile

Licheng Sun ______ **5434**

Books

Applications of Transition Metal Catalysis Matth in Drug Discovery and Development

Matthew L. Crawley, Barry M. Trost

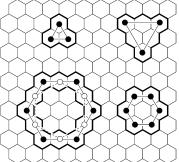
reviewed by J. Medlock, W. Bonrath

Highlights

All things graphene: Within the graph of graphene one finds subgraphs for

a myriad of novel aromatic hydrocarbons. For example, defining the vertices of a C3 subgraph within graphene evokes higher-order structures simply by changing the length of the ring fusion links.

Analogously, the C6 transformation yields coronene and kekulene (see scheme).



Nanostructures

K. K. Baldridge, J. S. Siegel* 5436 - 5438

Of Graphs and Graphenes: Molecular Design and Chemical Studies of Aromatic Compounds



Promiscuous Biocatalysis

G.-D. Roiban, M. T. Reetz* _ 5439 - 5440

Enzyme Promiscuity: Using a P450 Enzyme as a Carbene Transfer Catalyst

How about this for a change: The promiscuous enzyme cytochrome P450-BM3 catalyzes the cyclopropanation of olefins, sometimes with high stereoselectivity

(see scheme). The highlighted paper demonstrates that it is possible to design unusual enzyme promiscuity.

Correspondence

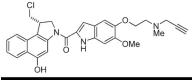
Antitumor Agents (1)

M. Tercel,* S. P. McManaway, E. Leung, H. D. S. Liyanage, G.-L. Lu,

F. B. Pruijn* _____ **5442 – 5446**



The Cytotoxicity of Duocarmycin Analogues is Mediated through Alkylation of DNA, not Aldehyde Dehydrogenase 1: A Comment The answer lies in the DNA: Recent claims that the alkylation of a particular protein contributes to the cytotoxicity of the duocarmycins could not be substantiated. The evidence, like the fluorescent signal derived from a clickable analogue, points instead to a reaction occurring in the nucleus.





Antitumor Agents (2)

L. F. Tietze,* S. A. Sieber* _ 5447 - 5449

Duocarmycin Analogues without a DNA-Binding Indole Unit Associate with Aldehyde Dehydrogenase 1A1 and not DNA: A Reply An open question: Activity-based protein profiling using seco-CBI derivative 1, containing a DNA-binding indole unit, showed that besides binding to DNA, compound 1 also interacts with aldehyde dehydrogenase 1. However, for CBI compounds without an indole unit, the origin of their cytotoxicity has not been identified, yet.

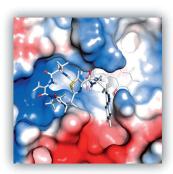
Reviews

Proteasome Inhibitors

A. Rentsch, D. Landsberg, T. Brodmann, L. Bülow, A.-K. Girbig,

M. Kalesse* _____ **5450 – 5488**

Synthesis and Pharmacology of Proteasome Inhibitors



The ubiquitin-proteasome system

controls fundamental processes such as cell cycle regulation, DNA repair, apoptosis, and immune and inflammatory responses, as well as hereditary disorders such as cystic fibrosis. This Review covers the synthesis of the most important proteasome inhibitors as well as their mode of action and clinical development.

For the USA and Canada:

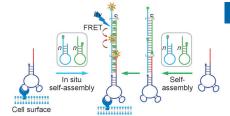
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. US POST-MASTER: send 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.



Communications

DNA nanotrain: Anchoring of preformed fluorescent DNA nanodevices (NDs; see picture) and in situ self-assembly of fluorescent DNA NDs on target living cell surfaces are reported. The in situ self-assembly of the nanodevice was further shown on surfaces of living cells in cell mixtures. These DNA NDs exhibited fluorescence emission and underwent fluorescence resonance energy transfer (FRET) on living cell surfaces.



Fluorescence

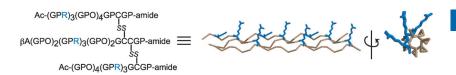
G. Zhu, S. Zhang, E. Song, J. Zheng,R. Hu, X. Fang, W. Tan* _____ 5490 – 5496

Building Fluorescent DNA Nanodevices on Target Living Cell Surfaces









Arginine-rich heterotrimeric collagen-like peptides were prepared, and their cellular uptake efficiency was evaluated. The spatial arrangement of the Arg residues (blue in picture) on the triple-helix surface

significantly affected the efficacy of the cellular uptake. The collagen-like triple-helical conformation provides these cell-penetrating peptides with a high resistance to proteases. O = L-4-hydroxyproline.

Protein Transduction

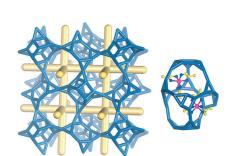
C. M. Yamazaki, I. Nakase, H. Endo,

S. Kishimoto, Y. Mashiyama, R. Masuda,

S. Futaki, T. Koide* _____ **5497 – 5500**



Collagen-like Cell-Penetrating Peptides



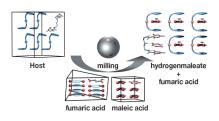
Ring the change: The gallogermanate zeolite $|(Ni(C_3H_{10}N_2)_3)_{36}Ni_{4.7}|$ $[Ga_{81.4}Ge_{206.6}O_{576}]$, which has three-dimensional intersecting 11-memberedring channels (see picture, left), was synthesized. It has the lowest framework density of all known oxide zeolites and features pairs of chiral $[3^{12}.4^3.6^2.11^6]$ cavities, induced by chiral $[Ni(1,2-PDA)_3]^{2+}$ cations formed in situ (see picture, right). 1,2-PDA = 1,2-diaminopropane.

Zeolite Analogues

Y. Xu, Y. Li, Y. Han, X. Song,

A Gallogermanate Zeolite with Eleven-Membered-Ring Channels





Flexible even if constrained: A polyamine host recognizes dicarboxylic acids in solution and in the solid state, with the highest selectivity towards maleic acid, binding it from mixtures with up to five other dicarboxylic acids, including fumaric acid (see picture). Recognition using mechanochemistry is a dynamic process involving intermediate phases, resulting in the same selectivity as achieved by crystallization from solution.

Molecular Recognition

K. Užarević,* I. Halasz, I. Đilović,

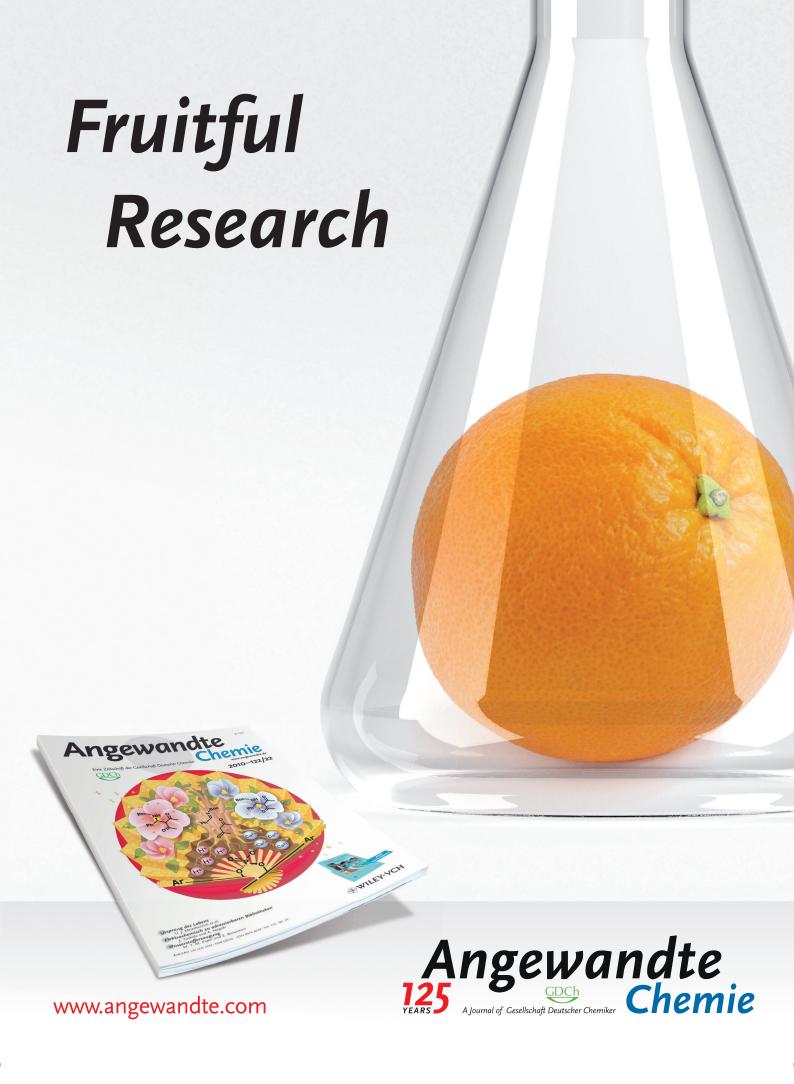
N. Bregović, M. Rubčić,

D. Matković-Čalogović,

V. Tomišić ______ **5504 – 5508**

Dynamic Molecular Recognition in Solid State for Separating Mixtures of Isomeric Dicarboxylic Acids









streptavidin trisbiotinylated oligonucleotide



"Monovalent streptavidin"



complement oligonucleotide

Only one place available: Monovalent streptavidin is prepared in a one-step process based on a trisbiotinylated oligonucleotide that blocks three of streptavidin's four biotin-binding sites. The complex is highly sensitive to single-base

differences: perfectly matched oligonucleotides trigger dissociation of the biotin-streptavidin interaction at higher rates than strands with single-base mismatches.

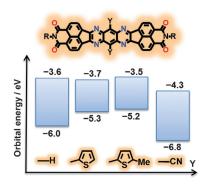
Biosensors

S. K. Taylor,* J. Wang, N. Kostic, M. N. Stojanovic __ _ 5509-5512

Monovalent Streptavidin that Senses Oligonucleotides



11-Ring heterocyclic diimides were synthesized and found to be planar and to exhibit a slipped face-to-face π stacking. Variation of the substituents tunes the electronic structure and properties. In n-channel organic field-effect transistors, the new organic semiconductors have a high electron mobility. When they were used as acceptor material in polymer solar cells, a power conversion efficiency of 1.8% was obtained.



Organic Semiconductors

H. Li, F. S. Kim, G. Ren, E. C. Hollenbeck, S. Subramaniyan,

S. A. Jenekhe* _ _ 5513 - 5517

Tetraazabenzodifluoranthene Diimides: Building Blocks for Solution-Processable n-Type Organic Semiconductors



The active state of a catalyst: A highpressure scanning tunneling microscope (STM) was used to bridge the pressure gap for the Ag-catalyzed ethylene epoxidation. An active oxygen species on an Ag(111) single crystal was characterized under ultrahigh vacuum conditions. The same species was identified with STM in an ethylene/oxygen mixture (see picture). In the STM cell the formation of ethylene oxide was detected.



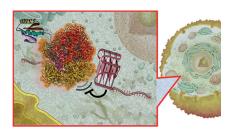
Heterogeneous Catalysis

S. Böcklein, S. Günther,

J. Wintterlin* _____ _ 5518 - 5521

High-Pressure Scanning Tunneling Microscopy of a Silver Surface during Catalytic Formation of Ethylene Oxide





Suppressing the urge to translate:

Sequences with the potential to form G-quadruplexes were identified in the open reading frames of E. coli genes. These sequences were found to form parallel G-quadruplexes and to suppress translation (see picture) of the mRNAs into proteins both in vitro and in cells.

Protein Translation

T. Endoh, Y. Kawasaki, N. Sugimoto* ____ 5522 - 5526

Suppression of Gene Expression by G-Quadruplexes in Open Reading Frames Depends on G-Quadruplex Stability



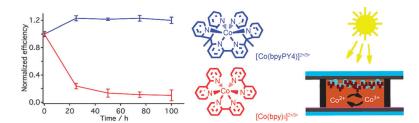


Dye-Sensitized Solar Cells

M. K. Kashif, M. Nippe, N. W. Duffy, C. M. Forsyth, C. J. Chang,* J. R. Long,* L. Spiccia,* U. Bach* ______ **5527 – 5531**



Stable Dye-Sensitized Solar Cell Electrolytes Based on Cobalt(II)/(III) Complexes of a Hexadentate Pyridyl Ligand



Energy conversion: A cobalt redox mediator, [Co(bpyPY4)]^{2+/3+}, based on a hexadentate polypyridyl ligand, was developed. Dye-sensitized solar cells (DSCs) made with this redox mediator showed improved stability and slightly higher

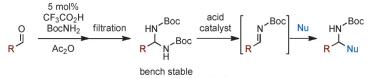
efficiencies compared to [Co(bpy)₃]^{2+/3+}-based devices. Long-term stability evaluation of DSCs based on [Co(bpyPY4)]^{2+/3+} revealed excellent stability under full irradiation conditions (see picture).

Imine Generation

T. Kano, T. Yurino, D. Asakawa, K. Maruoka* ______ **5532-5534**



Acid-Catalyzed In Situ Generation of Less Accessible or Unprecedented *N*-Boc Imines from *N*-Boc Aminals



R = alkyl, **alkenyl**, **alkynyl**, aryl

Crafty aminals: The in situ generation of hitherto unattainable alkynyl-substituted *N*-Boc-protected imines was realized by the acid-catalyzed elimination of *tert*-butyl carbamate from *N*-Boc aminals. A wide

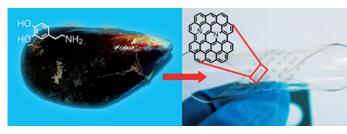
variety of *N*-Boc imines can be generated, which can then be utilized for subsequent carbon–carbon bond-forming reactions, such as Mannich-type reactions.

Carbon Electrodes

R. Li, K. Parvez, F. Hinkel, X. Feng,*
K. Müllen* ______ 5535 – 5538



Bioinspired Wafer-Scale Production of Highly Stretchable Carbon Films for Transparent Conductive Electrodes



Carbon-based films: Dopamine was used as the precursor for the facile yet controllable production of a highly stretchable transparent conductive film (see picture).

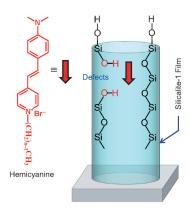
The film synthesized is transparent and can reversibly withstand mechanical deformations (such as being stretched to 20% for 100 cycles).

Mesoporous Materials

T. C. T. Pham, H. S. Kim, K. B. Yoon* ______ **5539 – 5543**

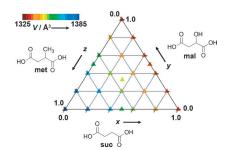


Large Increase in the Second-Order Nonlinear Optical Activity of a Hemicyanine-Incorporating Zeolite Film



Nonlinear optics: A hemicyanine-incorporating silicalite-1 film with second-order nonlinear optical properties supported on a glass plate was prepared. For the nonlinear optical properties of this material the number of hemicyanine dye moleclues included in the zeolite channels is important. Defects arising from Si deficiency along the channels prohibit the diffusion of the dyes into the interior of the zeolite film (see picture).





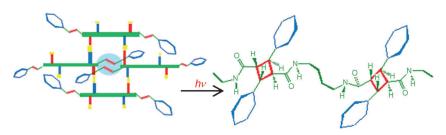
Grounded in fact: Inorganic-organic frameworks with 3D Li-O-Li connectivity can form solid solutions through mechanochemical synthesis. High-resolution synchrotron powder X-ray diffraction and cross-polarization solid-state NMR spectroscopy demonstrate complete ligand mixing in the resulting binary and ternary systems (see picture for trends in unit cell volume (V) of the ternary system $\{Li_2(suc)_x(mal)_y(met)_z\}_n$.

Hybrid Materials

H. H.-M. Yeung, W. Li, P. J. Saines, T. K. J. Köster, C. P. Grey, A. K. Cheetham* ____ 5544 - 5547

Ligand-Directed Control over Crystal Structures of Inorganic-Organic Frameworks and Formation of Solid Solutions





Film review: Two amide-containing bisolefin monomers undergo solid-state polymerization (see example) through a [2+2] reaction in a single-crystal-tosingle-crystal fashion. The transformation was favored by the self-templating and

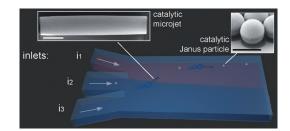
shock-absorbing nature of hydrogenbonding layers. The pyridine-containing polymers were soluble and useful for making plastic films with considerable tensile strengths.

Solid-State Photopolymerization

M. Garai, R. Santra, K. Biradha* _ 5548 - 5551

Tunable Plastic Films of a Crystalline Polymer by Single-Crystal-to-Single-Crystal Photopolymerization of a Diene: Self-Templating and Shock-Absorbing Two-Dimensional Hydrogen-Bonding Layers





Chemotaxis in practice: Two different artificial catalytic micromotors (tubular and spherical, see scheme) show chemotactic behavior in microfluidic channels

demonstrating that catalytic micromotors can sense the gradient of chemical fuel in their environment and be directed towards desired locations.

Micromotors

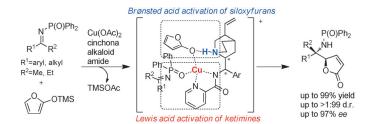
L. Baraban, S. M. Harazim, S. Sanchez,* O. G. Schmidt ______ 5552 - 5556

Chemotactic Behavior of Catalytic Motors in Microfluidic Channels



Back Cover





Managing the Mannich: The first enantioselective vinylogous Mannich reaction of siloxyfurans with ketimines derived from unactivated ketones has been developed. Excellent yields and enantioselectivities were obtained using a new class of readily accessible cinchona alkaloid amide/Cu(OAc)₂ catalysts on a range of substrates.

Asymmetric Synthesis

M. Hayashi, M. Sano, Y. Funahashi, S. Nakamura* ___ _ 5557 - 5560

Cinchona Alkaloid Amide/Copper(II) Catalyzed Diastereo- and Enantioselective Vinylogous Mannich Reaction of Ketimines with Siloxyfurans





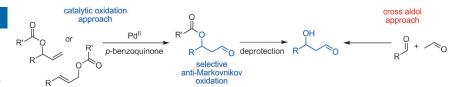
Synthetic Methods

J. J. Dong, M. Fañanás-Mastral, P. L. Alsters, W. R. Browne,*

B. L. Feringa* _ 5561 - 5565



Palladium-Catalyzed Selective Anti-Markovnikov Oxidation of Allylic Esters



An aldol alternative: The palladium(II)catalyzed anti-Markovnikov oxidation of allylic esters to aldehydes at room temperature provides a viable alternative to valuable cross aldol products. High regioselectivity towards the aldehyde

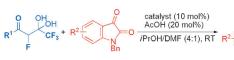
product was achieved using the ester protecting group for the allylic alcohol. Rapid isomerization and the much higher rate of oxidation of the branched isomer result in the same product forming from both linear and branched allylic esters.

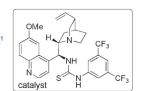
Organocatalysis

I. Saidalimu, X. Fang,* X.-P. He, J. Liang, _____ 5566 – 5570 X. Yang, F. Wu* ____



Highly Enantioselective Construction of 3-Hydroxy Oxindoles through a Decarboxylative Aldol Addition of Trifluoromethyl α -Fluorinated gem-Diols to N-Benzyl Isatins





An organocatalytic asymmetric direct aldol addition reaction that involves cleavage of a carbon-carbon bond through the release of trifluoroacetate was developed. The protocol is wide in scope,

generating the desired oxindoles of biological interest in nearly quantitative yields (up to 99%) with excellent enantioselectivities (up to 98% ee) and diastereoselectivities (up to 99:1 d.r.).

Directed Evolution

R. Lauchli, K. S. Rabe, K. Z. Kalbarczyk, A. Tata, T. Heel, R. Z. Kitto,

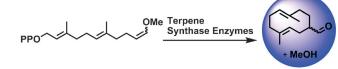
F. H. Arnold* _____ 5571 – 5574



High-Throughput Screening for Terpene-Synthase-Cyclization Activity and Directed Evolution of a Terpene Synthase



Inside Back Cover



An easy assay: A synthetic substrate enables a colorimetric screen for terpene synthase cyclization activity, thereby facilitating the engineering of these enzymes. By using directed evolution, the thermostability of a sesquiterpene synthase was

increased without the loss of other properties. The technique also enabled rapid optimization of conditions for expression and stabilization in lysate of another terpene synthase. PPO = diphosphate.

Heterocycle Synthesis

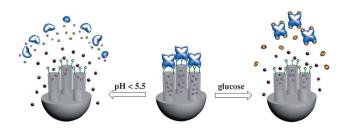
H. Kawai, Z. Yuan, T. Kitayama, E. Tokunaga, N. Shibata* __ 5575 - 5579



Efficient Access to Trifluoromethyl Diarylpyrrolines and their N-Oxides through Enantioselective Conjugate Addition of Nitromethane to β,β-Disubstituted Enones

The cupreidinium salt 1 catalyzes the highly enantioselective conjugate addition of nitromethane to β -aryl- β -trifluoromethyl aryl enones (2). The biologically important chiral pyrrolines 4 and N-oxide 5, having a trifluoromethylated all-carbon quaternary chiral center, were easily synthesized from the key intermediate (R)-3 in high to excellent yields. M.S. = molecular sieves.





Learning to let go: Controlled release of cargo (purple cubes) from lectin (blue squares)-gated nanopores was achieved using mannose (green loops)-functionalized mesoporous silica (see scheme). The

protein nanogates could be opened either by decreasing the pH of the buffer or by adding competing glucose (yellow rings) to release the cargo from the pores.

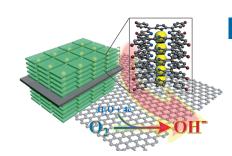
Drug Delivery

S. Wu, X. Huang, X. Du* ___ 5580-5584

Glucose- and pH-Responsive Controlled Release of Cargo from Protein-Gated Carbohydrate-Functionalized Mesoporous Silica Nanocontainers



ORR inspiring: Multilayers of Co²⁺ and porphyrin, fabricated on the surface of reduced graphene oxide sheets (see picture) by a layer-by-layer assembly technique, are potentially cost-effective and high-efficient oxygen reduction reaction (ORR) catalysts. The multilayers have comparable electrocatalytic activity to commercial C/Pt catalysts, but much better methanol tolerance and long-term stability toward ORR.

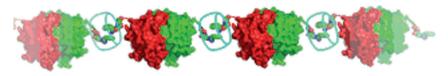


Metal-Free Electrocatalysts

H. Tang, H. Yin, J. Wang, N. Yang, D. Wang,* Z. Tang* ______ **5585 – 5589**

Molecular Architecture of Cobalt Porphyrin Multilayers on Reduced Graphene Oxide Sheets for High-Performance Oxygen Reduction Reaction





Getting your proteins in a row: Self-assembled protein nanowires were designed by utilizing highly specific supramolecular interactions of cucurbit[8]uril (CB[8]) and a tripeptide FGG-tag attached on the N-termini of dimeric glutathione S-transferase (GST). With the

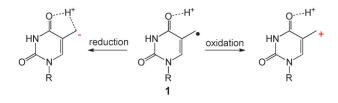
aid of enzyme simulation, model protein GST was converted into a selenoenzyme glutathione peroxidase mimic, and the CB[8]-induced Se-FGG-GST(Y6C) nanowires demonstrated excellent antioxidative capacity.

Protein Nanowires

C. X. Hou, J. X. Li, L. L. Zhao, W. Zhang, Q. Luo, Z. Y. Dong, J. Y. Xu, J. Q. Liu* ______ **5590 – 5593**

Construction of Protein Nanowires through Cucurbit[8]uril-based Highly Specific Host-Guest Interactions: An Approach to the Assembly of Functional Proteins





Sleeping beauty: The 5-(2'-Deoxyuridinyl) methyl radical 1 is a key intermediate in the thymine oxidative reaction mediated by reactive oxygen species. Evidence is presented that 1 is prone to both oxidation and reduction reactions at the

absence of O₂. These results question the current paradigm and suggest that the redox chemistry of 1, which has been largely overlooked in the past, may play a major role in determining the fate of 1.

Biological Radicals

G. Lin, L. Li* _____ **5594-5598**

Oxidation and Reduction of the 5-(2'-Deoxyuridinyl) methyl Radical





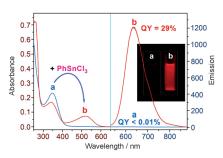
Fluorescence

Y. Niu, F. Han, Q. Zhang, T. Xie, L. Lu,S. Li,* H. Xia* _______ 5599 – 5603



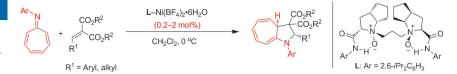
Off/On Fluorescent Chemosensors for Organotin Halides Based on Binuclear Ruthenium Complexes

Fluorescent organotin sensing: Molecular recognition driven by halogen-bonding interactions and the phenomenon of aggregation-induced emission were combined to construct fluorescent chemosensors. Binuclear ruthenium complexes containing multiple isocyanide ligands were synthesized as nonluminescent receptors that emit red fluorescence upon interacting with organotin halides (see picture; QY = quantum yield).



Asymmetric Catalysis

M. S. Xie, X. H. Liu, X. X. Wu, Y. F. Cai, L. L. Lin, X. M. Feng* ______ **5604 – 5607**



Catalytic Asymmetric [8+2] Cycloaddition: Synthesis of Cycloheptatriene-Fused Pyrrole Derivatives

Add a ring: A catalytic asymmetric [8+2] cycloaddition reaction of azaheptafulvenes with alkylidene malonates was developed. When employing catalytic amounts of a chiral *N,N'*-dioxide L–Ni^{II} complex, the reaction afforded function-

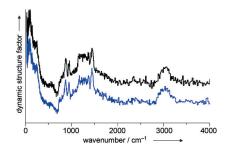
alized cycloheptatriene-fused pyrrole derivatives in excellent yields (up to 99%), diastereoselectivities (>95:5 d.r.), and enantioselectivities (91–97% *ee*) under mild conditions.

Heterogeneous Catalysis

N. G. Hamilton, I. P. Silverwood, R. Warringham, J. Kapitán, L. Hecht, P. B. Webb,* R. P. Tooze, S. F. Parker, D. Lennon*



Vibrational Analysis of an Industrial Fe-Based Fischer–Tropsch Catalyst Employing Inelastic Neutron Scattering Inelastic neutron scattering (INS) has been used to obtain the vibrational spectrum of a technical-grade iron-based Fischer—Tropsch catalyst that has been taken from an industrial large-scale unit operation. Whereas previous reports on iron Fischer—Tropsch catalysts highlight the presence of retained carbonaceous species, the INS spectra reveal the additional presence of partially hydrogenated aromatic molecules (see picture).



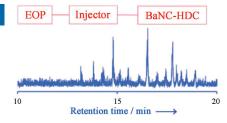
DNA Separation

Z. Zhu, H. Chen, W. Wang, A. Morgan, C. Gu, C. He,* J. J. Lu,

S. Liu* ______ **5612 – 5616**

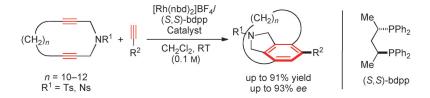


Integrated Bare Narrow Capillary— Hydrodynamic Chromatographic System for Free-Solution DNA Separation at the Single-Molecule Level



Turn the volume down: Coupling a highpressure electroosmotic pump (EOP) and a microfabricated chip-injector with a bare narrow capillary—hydrodynamic chromatographic system (BaNC-HDC), enables samples to be injected at low-picoliter volumes, analytes to be eluted at picoliters per minute, and a wide size range of DNA fragments to be resolved (see picture) rapidly in free solution at the singlemolecule level.





Just 'plane' chiral: The high-yielding and highly enantioselective synthesis of carba[10]–[12]paracyclophanes has been achieved with up to 91 % yield and 93 % *ee* by using the cationic rhodium(I)/(S,S)-

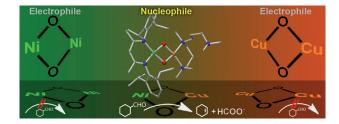
bdpp-catalyzed [2+2+2] cycloaddition of cyclic diynes with terminal monoynes under high substrate concentrations. nbd = 2,5-norbornadiene, Ns = p-nitrobenzenesulfonyl, Ts = 4-toluenesulfonyl.

Asymmetric Catalysis

T. Araki, K. Noguchi, K. Tanaka* ______ **5617 - 5621**

Enantioselective Synthesis of Planar-Chiral Carba-Paracyclophanes: Rhodium-Catalyzed [2+2+2] Cycloaddition of Cyclic Diynes with Terminal Monoynes





Cores and effect: Unlike homobimetallic analogues, the heterobimetallic CuNi bis-(μ-oxo) diamond core has nucleophilic oxo groups. A similar heterobimetallic core may, therefore, act as a viable intermediate during the deformylation of fatty aldehydes by cyanobacterial aldehyde decarbonylase.

Bioinorganic Chemistry



- S. Kundu, F. F. Pfaff, E. Miceli,
- I. Zaharieva, C. Herwig, S. Yao,
- E. R. Farquhar, U. Kuhlmann, E. Bill,
- P. Hildebrandt, H. Dau, M. Driess,*
- A High-Valent Heterobimetallic [Cu^{III}(μ-O)₂Ni^{III}]²⁺ Core with Nucleophilic

C. Limberg,* K. Ray* _____ **5622 – 5626**



Front Cover



$$R^{1}$$
 H + H-Si- R^{3} + 1/20₂ Au/OMS-2
 R^{1} R^{1} R^{2} R^{1} R^{2} R^{1} R^{2} R^{3} + H₂0
 R^{2} R^{3} R^{4} and alkyl alkovy
 R^{2} R^{3} R^{4} and alkyl alkovy

Cross-dehydrogenative coupling of various terminal alkynes and monohydrosilanes efficiently proceeded in the presence of gold supported on OMS-2 (Au/OMS-2) using O_2 as a terminal oxidant, affording the corresponding alkynylsilanes in mod-

erate to high yields (see picture). The observed catalysis was truly heterogeneous, and the catalyst could be reused at least ten times without a significant loss of its high catalytic performance.

Heterogeneous Catalysis

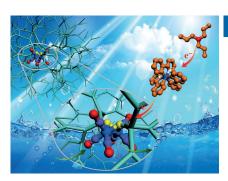
Oxo Groups

K. Yamaguchi, Y. Wang, T. Oishi, Y. Kuroda, N. Mizuno* _____ **5627 – 5630**

Heterogeneously Catalyzed Aerobic Cross-Dehydrogenative Coupling of Terminal Alkynes and Monohydrosilanes by Gold Supported on OMS-2



A three-component homogeneous catalyst system has been prepared with an Ir^{III} complex as the photosensitizer, artificial hydrogenases bearing a diiron core and dendritic frameworks as the proton reduction catalyst, and triethylamine as the sacrificial electron donor. An initial turnover frequency of over 7240 h⁻¹ and a quantum yield of up to 28% were determined for the photocatalytic evolution of hydrogen.



Energy Conversion

T. J. Yu, Y. Zeng,* J. P. Chen, Y. Y. Li, G. Q. Yang,* Y. Li* ______ **5631 – 5635**

Exceptional Dendrimer-Based Mimics of Diiron Hydrogenase for the Photochemical Production of Hydrogen







Cadmium Sulfide Nanoparticles

Y. Hu,* X. H. Gao, L. Yu, Y. R. Wang, J. Q. Ning, S. J. Xu, X. W. Lou* ______ **5636 – 5639**

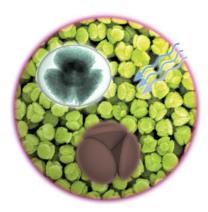


Carbon-Coated CdS Petalous Nanostructures with Enhanced Photostability and Photocatalytic Activity



Inside Cover

More than just skin deep: Carbon-coated CdS petalous particles have been synthesized through a one-pot solvothermal method. The carbon nanocoating serves multiple functions, including protection of the CdS surface, enhancement of visible light absorption, and facilitating the separation of photogenerated charges. As a result, this CdS-C nanohybrid photocatalyst exhibits significantly enhanced photostability and photocatalytic activity.

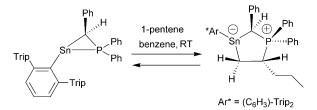


Main-Group Chemistry

S. Freitag, J. Henning, H. Schubert, L. Wesemann* ______ 5640 – 5643



Phosphastannirane: A Phosphorus/ Tin(II) Lewis Pair that Undergoes Alkyne and Alkene Addition



Bermuda triangle: The first molecule containing a cyclic three-membered Sn—C—P ring has been synthesized and characterized. This Sn^{II}—P Lewis pair reacts at room temperature with alkynes and pen-

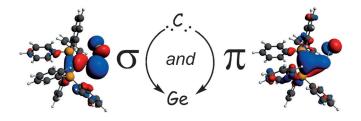
tene to give the five-membered cyclic addition products. In the case of pentene, this reaction is reversible at room temperature. Trip = 2.4,6-iPr₃C₆H₂.

Main-Group Elements

S. Khan, G. Gopakumar, W. Thiel, M. Alcarazo* ______ 5644 – 5647



Stabilization of a Two-Coordinate [GeCl]⁺ Cation by Simultaneous σ and π Donation from a Monodentate Carbodiphosphorane



Give me four: The synthesis, structure, and reactivity of [GeCl]+ and [SnCl]+ cations bearing a carbodiphosphorane as ancillary ligand are presented. In the Ge compound, simultaneous σ and π donation from the carbodiphosphorane to Ge

is observed (see HOMO (left) and HOMO-1 (right); C black, H white, P orange, Cl green, Ge purple (not visible)), whereas only the σ dative component is present in the Sn analogue.



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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Angewandte Corrigendum

By solving several crystal structures the authors of this Communication have found that the structure of compound 10 in Scheme 3 has been misassigned. It is not based on a β -lactame core as originally proposed but rather on the pyrrolidinedione scaffold 10' which has the same molecular weight and a similar NMR spectrum as the proposed β -lactame. Therefore it is proposed that the cyclization of the intermediate Ugi product under the basic reaction conditions proceeds via the isocyanide-derived amide NH group and the ester moiety.

This correction does not affect the results and conclusions of the other compounds described in the communication. The authors sincerely apologize for this mistake.

Efficient Assembly of Iminodicarboxamides by a "Truly" Four-Component Reaction

K. Khoury, M. K. Sinha,
T. Nagashima, E. Herdtweck,
A. Dömling* _______ 10280–10283

Angew. Chem. Int. Ed. 2012, 51

DOI: 10.1002/anie.201205366

Angewandte Corrigendum

The following sentence should be added to the acknowledgment section of this Communication:

"L.J.T. acknowledges support from NSF-REU program (Grant CHE-1003947)."

Synthesis of *ortho-*Acylphenols through the Palladium-Catalyzed Ketone-Directed Hydroxylation of Arenes

F. Mo, L. J. Trzepkowski, G. Dong* ______ 13075–13079

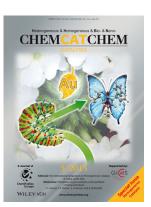
Angew. Chem. Int. Ed. 2012, 51

DOI: 10.1002/anie.201207479

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