Genetic information embedded ...

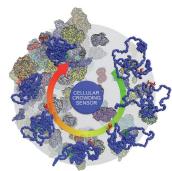




... in our bones may endure for thousands of years, while data written on hard drives will barely survive 50 years. In their Communication on page 2552 ff., R. N. Grass and co-workers show how artificially fossilized DNA (DNA encapsulated in silica) and modern data encoding techniques can be utilized to safely store, for example, the text of the Archimedes Palimpsest for future millennia. The error-correcting codes correct storage-related errors and allow for perfect recovery of the information.

Hydrogen Oxidation

In their Communication on page 2340 ff., G. A. Somorjai, J. Y. Park et al. report the effects of Pt nanoparticle size on hot electron flow during hydrogen oxidation. 1.7 nm nanoparticles show a higher catalytic activity than 4.5 nm nanoparticles.

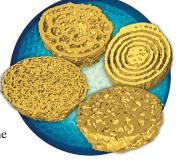


Macromolecule Biophysics

S. Ebbinghaus et. al. studied the macromolecular crowding in living cells by using a polymer-based probe. In their Communication on page 2548 ff., they report the effects of osmotic stress on the environment within the cell.

Supramolecular Chemistry

In their Communication on page 2457 ff., S. J. Holder, N. A. J. M. Sommerdijk et al. report on the internal morphology of complex polymeric nanospheres and show that the internal structure can be controlled by changing the overall molecular weight and relative hydrophilic content of the composite polymer.



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Service

Spotlight on Angewandte's Sister Journals

2314-2316



Norio Shibata ______ 2318 - 2319



"If I had one year of paid leave I would work for a Buddhist temple on a mountain whilst studying to become a priest. In a spare hour, I listen to 'new wave' music ..."

This and more about Norio Shibata can be found on page 2318.



A. O'Mullane



B. J. Smith



M. G. Banwell



R. J. Payne

News

Swiss Chemical Society Awards:

G. Gasser and N. Banerji _____ 2321



D. M. D'Alessandro



C. Wentrup



G. Gasser



N. Banerji



Obituaries



Paul von Ragué Schleyer, Graham Perdue Professor at the University of Georgia passed away on November 21, 2014. Schleyer was an eminent and prolific physical organic chemist, whose pioneering contributions included the application of computational chemistry to broad fields of physical organic, inorganic, organometallic, and mechanistic chemistry concepts.

Paul von Ragué Schleyer (1930–2014)

G. A. Olah,

G. K. S. Prakash* _____ 2322 - 2323

Books

Ligand Design in Medicinal Inorganic Chemistry

Tim Storr

reviewed by C. Hartinger _____ 2324

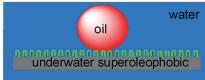
Reviews

Oil/Water Separation

Z. Chu, Y. Feng, S. Seeger* 2328 – 2338

Oil/Water Separation with Selective Superantiwetting/Superwetting Surface Materials Stringent segregation: Superhydrophobic/superoleophilic surfaces and underwater superoleophobic surfaces have been successfully designed, fabricated, and employed in the separation of oil/water-free mixtures and emulsions on the basis of their selective superantiwetting/superwetting properties towards water and oil. Progress, remaining problems, and future challenges in this field are discussed in this Review.





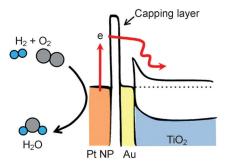
Communications

Hydrogen Oxidation

H. Lee, I. I. Nedrygailov, C. Lee, G. A. Somorjai,* J. Y. Park* **2340 – 2344**



Chemical-Reaction-Induced Hot Electron Flows on Platinum Colloid Nanoparticles under Hydrogen Oxidation: Impact of Nanoparticle Size Catalytic nanodiodes: Chemically induced hot electron flows on Pt nanoparticles were measured using Au/TiO₂ nanodiodes (see picture) and showed the correlation of chemicurrent with catalytic activity. The catalytic nanodiodes with smaller Pt nanoparticles lead to higher chemicurrent, and the temperature dependence is similar to that of the turnover frequency.



Frontispiece

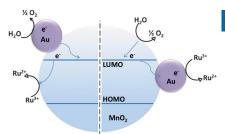
For the USA and Canada:

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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.

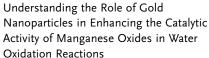


Just a pinch: A small amount of dopant gold nanoparticles (<5%) increased the catalytic activity of α -MnO₂ in water oxidation reactions with the established [Ru(bpy)₃]²⁺–S₂O₈²⁻ system (bpy=2,2'-bipyridine) by up to 8.2-fold in the photochemical and sixfold in the electrochemical system. The nanoparticle dopant is thought to mediate the electron-transfer steps in the mechanism as shown.



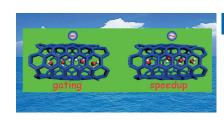
Water Oxidation Reaction

C.-H. Kuo, W. Li, L. Pahalagedara, A. M. El-Sawy, D. Kriz, N. Genz, C. Guild, T. Ressler, S. L. Suib, * J. He* 2345 – 2350





A vibrational charge outside a nanochannel can promote water flux within the channel. A decrease in the distance between the charge and the nanochannel causes an increase in the water net flux, which is contrary to that of the fixed-charge system. This electromanipulating transport phenomenon provides an important new mechanism of water transport confined in nanochannels.



Nanochannels

Electromanipulating Water Flow in Nanochannels



$$\begin{array}{c} R^1 \\ R^2 \\ R^2 \\ R^1 = \text{alkyl, allyl, benzyl} \\ R^2 = \text{H, alkyl, allyl, benzyl, aryl, halide} \end{array} \begin{array}{c} CO_2R' \\ (1 \text{ or } 5 \text{ mol}\%) \\ R^3 \\ \text{up to } 98\% \text{ yield} \\ \text{up to } 98\% \text{ ee} \end{array}$$

Asymmetric Catalysis

J. Nan, J. Liu, H. Zheng, Z. Zuo, L. Hou,
 H. Hu, Y. Wang, X. Luan* __ 2356 - 2360

Direct Asymmetric Dearomatization of 2-Naphthols by Scandium-Catalyzed Electrophilic Amination



Asymmetric aminative dearomatization:

The title reaction was successfully implemented with electrophilic azodicarboxylates under the catalysis of chiral Sc^{III}/pybox complexes. This reaction represents a hitherto unknown enantioselective

C-N bond-forming process through direct dearomatization of phenolic compounds to generate chiral nitrogen-containing quaternary carbon stereocenters. Tf=trifluoromethanesulfonyl.





 α,α -Difluoroketones are useful building blocks for the synthesis of therapeutics and probes for chemical biology. To access this substructure, complementary palladium-catalyzed decarboxylative ally-

lation reactions were developed to provide linear and branched α -allyl- α , α -difluoroketones. The regioselectivity was enabled by the fluorine substituents of the substrate and controlled by the ligand.

Fluorine

M.-H. Yang, D. L. Orsi, R. A. Altman* ______ 2361 – 2365

Ligand-Controlled Regiodivergent Palladium-Catalyzed Decarboxylative Allylation Reaction to Access α . α -Difluoroketones



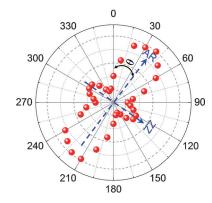


Black Phosphorus

J. Wu, N. Mao, L. Xie, H. Xu,*
J. Zhang* ______ 2366-2369



Identifying the Crystalline Orientation of Black Phosphorus Using Angle-Resolved Polarized Raman Spectroscopy



A compass to precisely identify the zigzag and armchair directions of black phosporus (BP) sheets is provided by angleresolved polarized Raman spectroscopy. The Raman modes of BP show periodic variation (90° or 180°) with the sample rotation angle. Under parallel polarization, the A_g^2 mode intensity achieves the larger (or smaller) local maximum when the armchair (or zigzag) direction is along the polarization direction of scattered light.

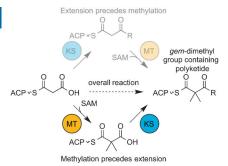
Biosynthesis

S. Poust, R. M. Phelan, K. Deng, L. Katz, C. J. Petzold,*

J. D. Keasling* ______ 2370 - 2373



Divergent Mechanistic Routes for the Formation of *gem*-Dimethyl Groups in the Biosynthesis of Complex Polyketides



Order of events: In order to elucidate the mechanism of *gem*-dimethyl group formation in polyketides, the *gem*-dimethyl group producing polyketide synthase (PKS) modules of yersiniabactin and epothilone were characterized using mass spectrometry. The study demonstrated, contrary to the canonical understanding of reaction order in PKSs, that methylation can precede condensation in PKS modules that produce *gem*-dimethyl groups.

Synthetic Methods

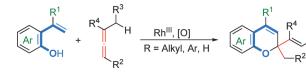
N. Casanova, A. Seoane,

J. L. Mascareñas,*

M. Gulías* ______ 2374-2377



Rhodium-Catalyzed (5+1) Annulations Between 2-Alkenylphenols and Allenes: A Practical Entry to 2,2-Disubstituted 2*H*-Chromenes



Skeleton crew: The synthesis of 2*H*-chromene skeletons was achieved by means of a rhodium(III)-catalyzed oxidative annulation of 2-alkenylphenols and allenes. This unconventional (5+1) process

involves the cleavage of the terminal C-H bond of the alkenyl moiety and the participation of the allene as a one-carbon cycloaddition component.



Natural Product Synthesis

S. A. Ruider, T. Sandmeier,

E. M. Carreira* ______ 2378 - 2382

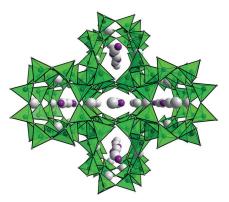


Total Synthesis of (\pm) -Hippolachnin A

Brevity makes sweetness! The first total synthesis of the marine polyketide (\pm) -hippolachnin A is realized in nine steps and an overall yield of 9%. The synthesis

relies on the strategic application of an ene cyclization, which provides rapid access to the oxacyclobutapentalene core skeleton.





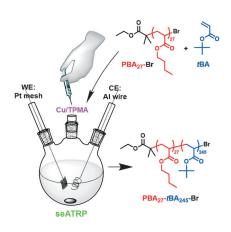
Under pressure: A nitridophosphate zeolite Ba₃P₅N₁₀Br was synthesized by a highpressure/high-temperature reaction at pressures between 1 and 5 GPa and 1000°C and investigated by single-crystal X-ray diffraction (see picture; Br = purple, $Ba = gray, PN_4 tetrahedra = green). Doped$ with Eu2+ ions, it exhibits natural-whitelight luminescence as a single emitter upon excitation by near-UV light.

Zeolite Synthesis

A. Marchuk, W. Schnick* ___ 2383 - 2387

Ba₃P₅N₁₀Br:Eu²⁺: A Natural-White-Light Single Emitter with a Zeolite Structure





Take it easy: Simplification of electrochemically mediated atom transfer radical polymerization was achieved by using an aluminum wire sacrificial anode (seATRP) under potentiostatic or galvanostatic conditions. Homopolymerization and diblock copolymerization show good control of reaction kinetics, providing polymers with molecular-weight evolution close to theoretical values and with narrow molecular-weight distributions.

Electrochemical Polymerization

S. Park, P. Chmielarz, A. Gennaro, K. Matyjaszewski* _____ 2388 – 2392

Simplified Electrochemically Mediated Atom Transfer Radical Polymerization using a Sacrificial Anode



$$R^{2} = \frac{1}{N} + H_{2} = \frac{[Ir] - Josiphos catalyst}{and Yb(OTf)_{3}} + \frac{R_{2}^{2}}{NH} + \frac{R^{1}}{NH} = \frac{Pt_{2}P}{Me} + \frac{Pt_{3}Pt_{4}Pt_{5}}{Me} + \frac{Pt_{4}Pt_{5}Pt_{5}}{Me} + \frac{Pt_{5}Pt_{5}Pt_{5}}{Me} + \frac{Pt_{5}Pt_{5}Pt_{5}}{Me} + \frac{Pt_{5}Pt_{5}Pt_{5}Pt_{5}}{Me} + \frac{Pt_{5}Pt_{5}Pt_{5}}{Me} + \frac{Pt_{5}Pt_{5}}{Me} + \frac{Pt_{5}Pt_{$$

A chiral catalyst combining iridium and a lanthanide salt promotes the hydrogenation of pyrimidines to form 1,4,5,6tetrahydropyrimidines. The reaction of 4substituted pyrimidines proceeded with high enantioselectivity (up to 99% ee) by using a chiral Josiphos ligand (see scheme) for the Ir catalyst.

Asymmetric Catalysis

R. Kuwano,* Y. Hashiguchi, R. Ikeda, K. Ishizuka _ _____ 2393 – 2396

Catalytic Asymmetric Hydrogenation of **Pyrimidines**





A composite aerogel consisting of resorcinol/formaldehyde and graphene oxide (GO) could be synthesized on large scale by using GO sheets as template skeletons and metal ions (Co2+, Ni2+, or Ca2+) as catalysts and linkers. These compressible aerogels can tolerate a strain as high as 80% and quickly recover their original shapes.

Aerogels

X. Wang, L. L. Lu, Z. L. Yu, X. W. Xu, Y. R. Zheng, S. H. Yu* _____ 2397 - 2401

Scalable Template Synthesis of Resorcinol-Formaldehyde/Graphene Oxide Composite Aerogels with Tunable Densities and Mechanical Properties



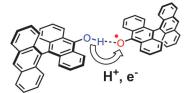


Stable Organic Radicals

Y. Hirao,* T. Saito, H. Kurata,
T. Kubo* ______ **2402 - 2405**



Isolation of a Hydrogen-Bonded Complex Based on the Anthranol/Anthroxyl Pair: Formation of a Hydrogen-Atom Self-Exchange System



Self-exchange PCET: The stable anthroxyl radical was synthesized, and a hydrogen-bonded complex with anthranol was isolated in crystalline form. X-ray analysis at 200 K revealed the activation of the self-exchange proton-coupled electron transfer (PCET) reaction at the hydrogen bond. A strong intermolecular magnetic interaction between radicals causes a phase transition at 125 K that inactivates this reaction.

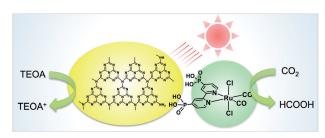


Carbon Dioxide Fixation

R. Kuriki, K. Sekizawa, O. Ishitani,
K. Maeda* ______ 2406 - 2409



Visible-Light-Driven CO₂ Reduction with Carbon Nitride: Enhancing the Activity of Ruthenium Catalysts



A heterogeneous photocatalyst that is based on a carbon nitride material modified by a ruthenium complex enables the reduction of CO_2 into formic acid with a high turnover number (>1000) and a good apparent quantum yield (5.7% at

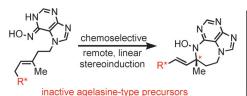
400 nm). These are the highest values that have been reported for CO_2 reduction by heterogeneous photocatalysts under visible-light irradiation to date (TEOA = triethanolamine).

Alkaloids

K. K. Wan, K. Iwasaki, J. C. Umotoy,D. W. Wolan,* R. A. Shenvi* 2410 – 2415



Nitrosopurines En Route to Potently Cytotoxic Asmarines



to cytotoxic asmarines

Me" Me Me

asmarine A (IC_{50} = 1.2 μ M)

Unnatural product: A nitrosopurine ene reaction easily assembles the asmarine pharmacophore and transmits remote stereochemistry to the diazepine-purine heterocycle. This reaction generates

potent cytotoxins which exceed the potency of asmarine A and supersede the metabolites as useful leads for biological discovery.

Dendrimer Synthesis

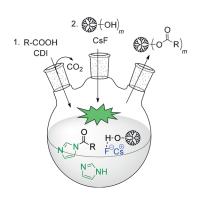
S. García-Gallego, D. Hult, J. V. Olsson, M. Malkoch* ______ 2416 – 2419



Fluoride-Promoted Esterification with Imidazolide-Activated Compounds: A Modular and Sustainable Approach to Dendrimers



Inside Cover



Esterifications with 1,1'-carbonyldiimidazole (CDI) were significantly improved by the use of cesium fluoride as the catalyst, which drives these reactions to completion. Structurally flawless and highly functional polyester dendrimers were obtained through a divergent growth approach featuring the fluoride-promoted esterification of hydroxy-functionalized scaffolds with imidazolide-activated monomers.





The acyclic pincer ligand bis (pyridine)-carbodicarbene was synthesized, isolated, and characterized. It features a C-C-C angle of 143°, which is larger than that in

the monodentate framework. Palladium complexes supported by this ligand are active catalysts in Heck-Mizoroki and Suzuki-Miyaura coupling reactions.

Carbodicarbenes

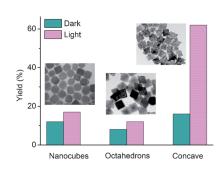
Y. Hsu, J. Shen, B. Lin, W. Chen, Y. Chan, W. Ching, G. Yap, C. Hsu,*

T. Ong* _____ 2420 - 2424

Synthesis and Isolation of an Acyclic Tridentate Bis(pyridine)carbodicarbene and Studies on Its Structural Implications and Reactivities



Taking shape: A Ru³+-mediated synthesis has been developed for unique Pd concave nanostructures which can directly harvest UV-to-visible light for styrene hydrogenation (see figure). The catalytic efficiency under full-spectrum irradiation at room temperature turns out to be comparable to that of the thermally (70°C) driven reaction. The yields are higher than those obtained using Pd nanocrystals such as nanocubes and octahedrons.



Heterogeneous Catalysis

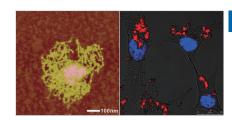
R. Long, Z. Rao, K. Mao, Y. Li, C. Zhang, Q. Liu, C. Wang Z.-Y. Li, X. Wu, Y. Xiong* — **2425 – 2430**

2.-1. Li, X. Wu, 1. Xiong^ ___ **2423 – 243**0

Efficient Coupling of Solar Energy to Catalytic Hydrogenation by Using Well-Designed Palladium Nanostructures



A novel 3D gold-DNA superstructure based on DNA growing and origami folding on gold nanoparticles had been fabricated. The new 3D superstructures exhibit great potential for high-efficiency molecule transport for use in cellular imaging and drug delivery.



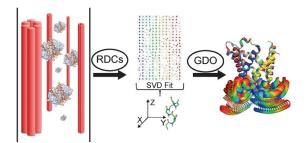
3D Superstructures

J. Yan, C. Hu, P. Wang, B. Zhao, X. Ouyang, J. Zhou, R. Liu, D. He,* C. Fan,

S. Song* _____ 2431 – 2435

Growth and Origami Folding of DNA on Nanoparticles for High-Efficiency Molecular Transport in Cellular Imaging and Drug Delivery





Flexing domains: Liquid-state NMR spectroscopy has been used to study conformational heterogeneity of mitochondrial GTP/GDP transporter. The data reveal that the carrier is intrinsically

plastic. Despite the threefold pseudosymmetry of the carrier, the plasticity is asymmetrically distributed among the domains. GDO = generalized degree of order, RDC = residual dipolar coupling.

Membranes

R. Sounier, G. Bellot,

J. J. Chou* _____ 2436 – 2441

Mapping Conformational Heterogeneity of Mitochondrial Nucleotide Transporter in Uninhibited States



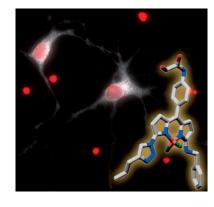


Neuron Imaging

J. C. Er, C. Leong, C. L. Teoh, Q. Yuan, P. Merchant, M. Dunn, D. Sulzer, D. Sames, A. Bhinge, D. Kim, S.-M. Kim, M.-H. Yoon, L. W. Stanton, S. H. Je, S.-W. Yun,* Y.-T. Chang* _____ 2442-2446



NeuO: a Fluorescent Chemical Probe for Live Neuron Labeling



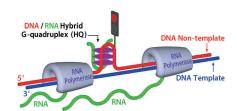
Selective labeling of live neurons over other brain cells was achieved with a novel fluorescent probe, NeuO. It enables stable, live neuron imaging in vivo and in vitro across species, thus setting the stage for various neuronal targeting applications including the study of neuron development and degeneration.

G-Quadruplexes

R.-y. Wu, K.-w. Zheng, J.-y. Zhang, Y.-h. Hao, Z. Tan* ______ **2447 – 2451**



Formation of DNA:RNA Hybrid G-Quadruplex in Bacterial Cells and Its Dominance over the Intramolecular DNA G-Quadruplex in Mediating Transcription Termination A transcription check-point: Transcription through guanine-rich regions produces DNA:RNA hybrid G-quadruplexes. In turn, these regulate transcription by mediating premature termination of transcription.

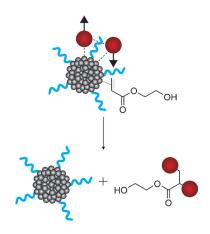


Nuclear-Spin Polarization

S. Glöggler, A. M. Grunfeld, Y. N. Ertas,
J. McCormick, S. Wagner,
P. P. M. Schleker,
L.-S. Bouchard* _______ 2452 – 2456



A Nanoparticle Catalyst for Heterogeneous Phase Para-Hydrogen-Induced Polarization in Water Hyperpolarization of molecules utilizing para-hydrogen (red spheres; see picture) and Pt nanoparticles (gray spheres) in water is described. The nanoparticles (diameter \approx 2 nm) are capped with glutathione ligands (blue lines) to allow for the pairwise addition of para-hydrogen and create observable magnetization. As the solvent is biocompatible, the generation of new molecular imaging contrast agents can be envisioned.



Supramolecular Chemistry

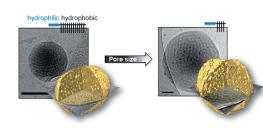
B. E. McKenzie, H. Friedrich,
M. J. M. Wirix, J. F. de Visser,
O. R. Monaghan, P. H. H. Bomans,
F. Nudelman, S. J. Holder,*
N. A. J. M. Sommerdijk* ____ 2457 – 2461



Controlling Internal Pore Sizes in Bicontinuous Polymeric Nanospheres



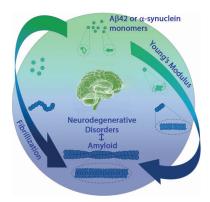
Back Cover



Tailoring polymer nanospheres: The relative hydrophilic–hydrophobic content in amphiphilic comb-like block copolymers can be tailored in solution to produce polymeric nanospheres with complex

internal morphology. The size and internal pore diameter of the resulting bicontinuous nanospheres can be tuned, showing promise for the formation of nanoporous hybrid materials.





Inflexibility that comes with age: During amyloid fibrillization, which is associated with neurodegenerative disorders, initially formed oligomeric and protofibrillar species aggregate to form fibrils with a core cross- β -sheet structure (see picture). AFM peak force quantitative nanomechanical measurements revealed an increase in the Young's modulus during the fibrillization process in conjunction with an increase in the amyloid β -sheet content.

Biomaterials

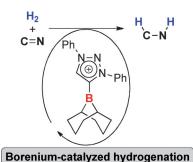
F. S. Ruggeri, J. Adamcik, J. S. Jeong,

H. A. Lashuel, R. Mezzenga,*

G. Dietler* _____ 2462 - 2466

Influence of the β -Sheet Content on the Mechanical Properties of Aggregates during Amyloid Fibrillization





Size does matter after all: Tunable, comparatively robust mesoionic borenium ions catalyze the mild hydrogenation of N-containing unsaturated organic functionalities at ambient temperature and ambient pressure. These reactions proceed through a mechanism reminiscent of frustrated Lewis pair chemistry.

Hydrogenation Reactions

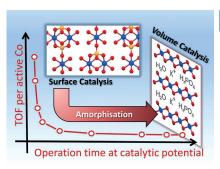
P. Eisenberger,* B. P. Bestvater,

E. C. Keske, C. M. Crudden* 2467 - 2471

Hydrogenations at Room Temperature and Atmospheric Pressure with Mesoionic Carbene-Stabilized Borenium Catalysts



The complete transformation during catalytic operation of crystalline and surface-active $\text{Co}_3(\text{PO}_4)_2\cdot 8\,\text{H}_2\text{O}$ into amorphous and volume-active cobalt oxide reveals basic features of heterogeneous water oxidation catalysis, which is discussed as a convolution of three phenomena: surface catalysis, volume catalysis, and restructuring of the material under operation.



Heterogeneous Catalysis

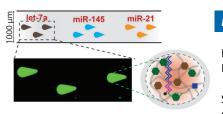


- D. González-Flores, I. Sánchez,
- I. Zaharieva, K. Klingan, J. Heidkamp,
- P. Chernev, P. W. Menezes, M. Driess,
- H. Dau,* M. L. Montero* __ 2472 2476

Heterogeneous Water Oxidation: Surface Activity versus Amorphization Activation in Cobalt Phosphate Catalysts



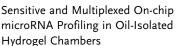
miRNA profiling: A versatile hydrogel-based microfluidic approach and novel amplification scheme were used for entirely on-chip, sensitive, and highly specific miRNA detection (let-7a, miR-145, and miR-21; see picture) without the risk of sequence bias. The approach uses photopolymerized hydrogel microposts for miRNA capture and labeling with a universal sequence. Fluorescence products are concentrated into the completely isolated gel posts.



Diagnostics



H. Lee, R. L. Srinivas, A. Gupta, P. S. Doyle* ______ **2477 - 2481**







Cluster Binding

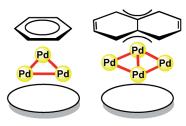
Y. Ishikawa, S. Kimura, K. Takase, K. Yamamoto, Y. Kurashige, T. Yanai,

_ 2482 - 2486 T. Murahashi* -



Modulation of Benzene or Naphthalene Binding to Palladium Cluster Sites by the Backside-Ligand Effect

The backside-ligand modulation strategy is used to enhance the substrate binding property of Pd clusters. The benzene or naphthalene binding ability of Pd3 or Pd4 clusters is enhanced significantly by the backside cyclooctatetraene ligand (see ovals in scheme), leading to the first isolable μ₃-benzene Pd₃ clusters or μ₄naphthalene Pd₄ clusters.



Radical Cascade Reactions

W. Kong, N. Fuentes,

A. García-Domínguez, E. Merino,

C. Nevado* __ _____ 2487 – 2491



Stereoselective Synthesis of Highly Functionalized Indanes and Dibenzocycloheptadienes through Complex Radical Cascade Reactions



Densely functionalized indanes and dibenzocycloheptadienes were produced through highly stereoselective radicalmediated reactions from ortho-vinyl- and ortho-vinylaryl-substituted N-(arylsulfonyl)acrylamides, respectively. The

chemoselective addition of in situ generated radicals (X*) onto the styrene moieties initiates a reaction cascade that results in the 5- and 7-membered ring carbocyclic products in a highly efficient manner.

Biocatalysis

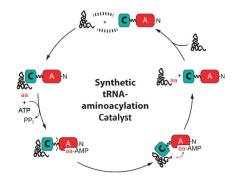
T. W. Giessen,* F. Altegoer, A. J. Nebel, R. M. Steinbach, G. Bange,*

M. A. Marahiel* _ _ 2492 – 2496



A Synthetic Adenylation-Domain-Based tRNA-Aminoacylation Catalyst

Best of both worlds: By fusing a eukaryotic tRNA-recruiting domain (C) to a prokaryotic adenylation domain (A) a new synthetic tRNA-aminoacylation catalyst was created. This catalyst was functionally characterized and was able to load proteinogenic and non-proteinogenic amino acids onto various tRNAs.



C-H Amination

D. Zhu, G. Yang, J. He, L. Chu, G. Chen, W. Gong, K. Chen, M. D. Eastgate,

J.-Q. Yu* ___ __ 2497 - 2500



Ligand-Promoted ortho-C-H Amination with Pd Catalysts

Trimethoxylpyridine is an efficient ligand for promoting Pd-catalyzed ortho-C-H amination of both benzamides and triflylprotected benzylamines. This finding provides guidance for the development of ligands that can improve or enable Pd"catalyzed C_{sp^2} —H activation reactions directed by weakly coordinating functional groups.



Benzo[e]indazole derivatives are obtained by a sequential triple C—H activation directed by a pyrazole and an amide group. This cascade reaction demonstrates that the often problematic competing C—H activation pathways in the

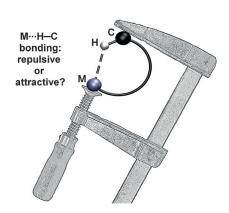
presence of multiple directing groups can be utilized to improve step economy in synthesis. Pyrazole as a relatively weak coordinating group is shown to direct C_{so^3} —H activation.

Cascade C-H Activation

W. Yang, S. Ye, D. Fanning, T. Coon, Y. Schmidt, P. Krenitsky, D. Stamos,*
J.-Q. Yu* ______ 2501 – 2504

Orchestrated Triple C-H Activation Reactions Using Two Directing Groups: Rapid Assembly of Complex Pyrazoles





Weakly attractive 3c–2e M···H—C agostic interactions can be established in square-planar d⁸-ML₄ complexes. A new characterization method is used to probe these interactions under pressure by combined high-pressure IR and X-ray diffraction studies. The use of the sign of ¹H NMR shifts as major criterion to classify M···H—C interactions as attractive (agostic) or repulsive (anagostic) is called into question.

Agostic Interactions

W. Scherer,* A. C. Dunbar,
J. E. Barquera-Lozada, D. Schmitz,
G. Eickerling, D. Kratzert, D. Stalke,
A. Lanza, P. Macchi,* N. P. M. Casati,
J. Ebad-Allah, C. Kuntscher 2505 – 2509

Anagostic Interactions under Pressure: Attractive or Repulsive?



... and BOB's your uncle: A fluorescent probe of mitochondrial polarity, termed BOB, showed a linear ratiometric fluorescence response to solution polarity. Various mitochondria of normal cells and cancer cells were examined, and it was found that mitochondrial polarity tends to be lower in cancer cells than in normal cells. The detection of mitochondrial polarity could thus be used as a method to distinguish cancer cells from normal cells.



Cellular Imaging

N. Jiang, J. Fan,* F. Xu, X. Peng, H. Mu, J. Wang, X. Xiong _______ 2510-2514

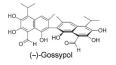
Ratiometric Fluorescence Imaging of Cellular Polarity: Decrease in Mitochondrial Polarity in Cancer Cells



PARP1 BRCT

inhibitor of DARRI





Array and break: By establishing a highthroughput microplate-based assay for screening potential inhibitors of protein– protein interactions of the PARP1 BRCT domain, (—)-gossypol was found to possess novel PARP1 inhibitory activity both in vitro and in cancer cells, presumably by acting as a chemical dimerizer of the PARP1 BRCT domain, which causes disruption of protein-protein interactions and leads to inhibition of the enzymatic activity.

Protein-Protein Interactions



Z. Na, B. Peng, S. Ng, S. Pan, J.-S. Lee, H.-M. Shen, S. Q. Yao* _____ **2515 – 2519**

A Small-Molecule Protein-Protein Interaction Inhibitor of PARP1 That Targets Its BRCT Domain





Asymmetric Cyclization

W. Fu, M. Nie, A. Wang, Z. Cao, W. Tang* ______ 2520 – 2524



Highly Enantioselective Nickel-Catalyzed Intramolecular Reductive Cyclization of Alkynones









A P-chiral monophosphine is used as the ligand in the first asymmetric nickel-catalyzed intramolecular reductive cyclization of alkynones. This transformation enabled the formation of a series of

tertiary allylic alcohols bearing furan/ pyran rings in excellent yields and enantioselectivities and the efficient synthesis of dehydroxycubebin and the chiral dibenzocyclooctadiene skeleton.

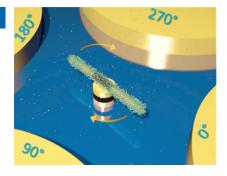


Nanorobotics

X. Xu, K. Kim, D. L. Fan* ___ 2525 - 2529



Tunable Release of Multiplex Biochemicals by Plasmonically Active Rotary Nanomotors



Motorized nanomotor sensors are used to tune the release rate of biochemicals and allow their real-time detection. The nanomotor sensors are assembled from designed nanoentities and can be rotated controllably. Both single and multiple biochemicals can be released from the rotating nanomotor sensors in a tunable fashion.



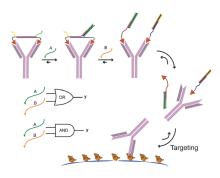
DNA Nanotechnology

B. M. G. Janssen, M. van Rosmalen, L. van Beek, M. Merkx* _____ 2530 – 2533



Antibody Activation using DNA-Based Logic Gates

Logic antibody locks: Bivalent peptide—DNA conjugates are presented as generic, noncovalent, and easily applicable molecular locks that allow the control of antibody activity using toehold-mediated strand displacement. By connecting antibody-based molecular recognition and DNA-based computing, this new approach allows the introduction of autonomous signal-processing in antibody-based targeting.



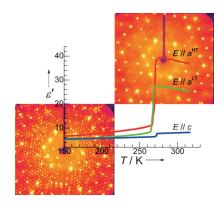
MOF Phase Transitions

R. Shang, Z.-M. Wang,* S. Gao*

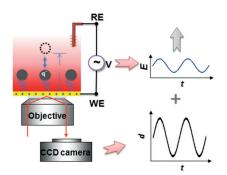
__ 2534-2537



A 36-Fold Multiple Unit Cell and Switchable Anisotropic Dielectric Responses in an Ammonium Magnesium Formate Framework Multiply the unit cell: An ammonium Mg formate framework has a rare three-dimensional binodal framework with long cavities accommodating 1,3-propane-diammonium and water. The framework displays a phase transition at 275 K to give a 36-fold multiple unit cell and anisotropic switchable dielectric responses.







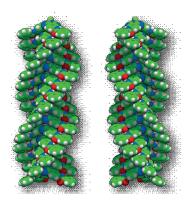
The phosphorylation kinetics of a few peptide molecules could be monitored in real time with self-assembled nano-oscillators. Each oscillator consists of a gold nanoparticle tethered to a gold chip with a molecular linker.

Charge-Based Detection

Y. Fang, S. Chen, W. Wang, * X. Shan, * 2538 - 2542

Real-Time Monitoring of Phosphorylation Kinetics with Self-Assembled Nanooscillators





Piling up rigid tetrahedral-shaped subphthalocyanine dye molecules in a convexto-concave fashion results in the formation of unconventional homochiral noncentrosymmetric columnar assemblies (see picture). Assembly occurs through a cooperative supramolecular polymerization process driven by a combination of noncovalent interactions (C green, N blue, O red, H white).

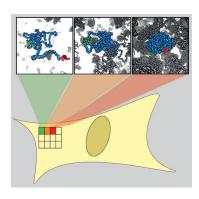
Supramolecular Chemistry

J. Guilleme, M. J. Mayoral, J. Calbo, J. Aragó, P. M. Viruela, E. Ortí,* T. Torres,* D. González-Rodríguez* ___ 2543 - 2547

Non-Centrosymmetric Homochiral Supramolecular Polymers of Tetrahedral Subphthalocyanine Molecules



Crowding in cells: A FRET-labeled homopolymer serves as a sensor to study macromolecular crowding in single living cells. Contrary to expectations, the cellular environment does not lead to a compression of the sensor. The sensor is further utilized to probe sub-cellular heterogeneities and crowding changes upon osmotic stress.



Macromolecule Biophysics



D. Gnutt, M. Gao, O. Brylski, M. Heyden, S. Ebbinghaus* _____ 2548 – 2551



Excluded-Volume Effects in Living Cells



Inside Back Cove





Committing to memory: Digital information can endure thousands of years of storage when translated into ACGT nucleotide coding and encapsulated as

DNA in silica glass spheres. This method was demonstrated with the digitalized Archimedes Palimpsest.

Long-Term Memory

R. N. Grass,* R. Heckel, M. Puddu, D. Paunescu, W. J. Stark ____ 2552-2555

Robust Chemical Preservation of Digital Information on DNA in Silica with Error-Correcting Codes



Front Cover





Mechanophores

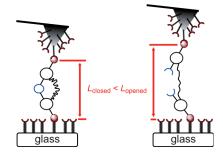
D. Schütze, K. Holz, J. Müller, M. K. Beyer,* U. Lüning,*

B. Hartke* 2556 - 2559



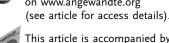
Pinpointing Mechanochemical Bond Rupture by Embedding the Mechanophore into a Macrocycle

Caught in the act: A 1,4-diaryl-1,2,3-triazole was embedded in a poly(ethylene glycol) chain and additionally bridged by an aliphatic chain. Single polymer molecules were then stretched in an atomic force microscope. Mechanochemical bond rupture in the macrocycle leads to a defined length increase of the polymer of more than 1 nm, which is large enough to be measured directly for a single molecule.





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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