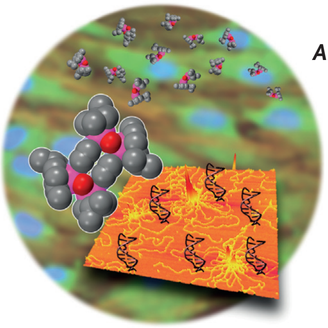
An Iridium-Catalyzed …

… asymmetric hydroalkynylation of enamides occur regioselectively at the β position of an enamide. In their Communication on page 9007 ff., B.-J. Li and co-workers report a method for the straightforward synthesis of chiral homopropargyl amides with a stereocenter β to the amide. As illustrated in the cover image, enamide and alkyne undergo rapid union to form a chiral product.

Photocatalysis

Using Cu_2O as a dark cathode, J. Gong and co-workers show in their Communication on page 8840 ff., that it can preferentially reduce CO_2 to fuels while suppressing the hydrogen evolution reaction.

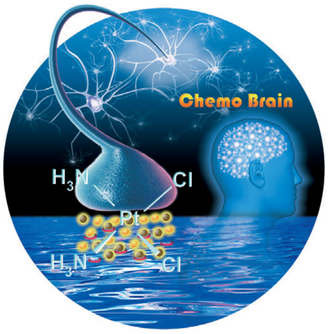


Anticancer Complexes

In their Communication on page 8909 ff., P. J. Sadler and co-workers describe two tetranuclear organometallic Os^{II} complexes that show significant differences in cytotoxicity against cancer cells and behavior towards DNA condensation.

Amperometry

Amperometry and intracellular electrochemical cytometry are used by A. G. Ewing et al. in their Communication on page 9041 ff., to show that low concentrations of cisplatin stimulate catecholamine release, whereas high concentrations inhibit it.



How to contact us:

Editorial Office:
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Fax: (+49) 6201–606-331
Telephone: (+49) 6201–606-315

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Spotlight on Angewandte's Sister Journals 8790 – 8793

Author Profile

*"When I was eighteen I wanted to be a professional cricketer.
My favorite drink is cup of tea (how very British!) ..."*
This and more about Russell Morris can be found on page 8794.

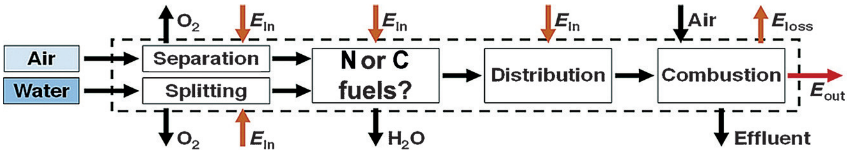
Russell Morris ______ 8794

Books

Organic Synthesis Using Biocatalysis Jon Stewart, Animesh Goswami *reviewed by N. J. Turner** ______ 8795

Essays

Alternative Fuels



What are the fuels of the future? Seven representative carbon- and nitrogen-based fuels are evaluated on an energy basis in a power-to-fuel-to-power analysis as possible future chemical hydrogen-storage media. It is intriguing to consider that a nitrogen economy, where hydrogen obtained from water splitting is chemically stored on abundant nitrogen in the form of a nontoxic and safe nitrogen-based alternative fuel, is energetically feasible.

A. Grinberg Dana, O. Elishav, A. Bardow, G. E. Shter, G. S. Grader* ___ 8798 – 8805

Nitrogen-Based Fuels: A Power-to-Fuel-to-Power Analysis

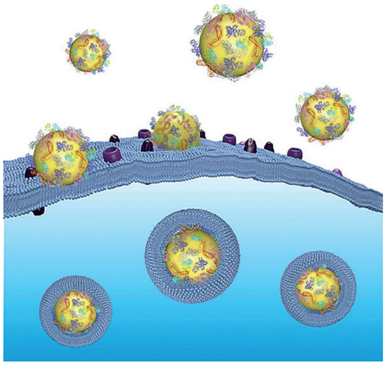
Minireviews

Drug Delivery

S. Schöttler, K. Landfester,*
V. Mailänder ______ 8806 – 8815

Controlling the Stealth Effect of Nanocarriers through Understanding the Protein Corona

Stealth shield: The use of nanocarriers in medical applications is complicated by the formation of a protein corona on the nanocarrier surface. This can influence interaction with cell membranes, and makes it difficult to predict cellular interactions, biodistribution, and toxicity. This Minireview provides an overview of what we know about the protein corona of nanocarriers, with a focus on surface functionalization to reduce unspecific uptake—termed the stealth effect.



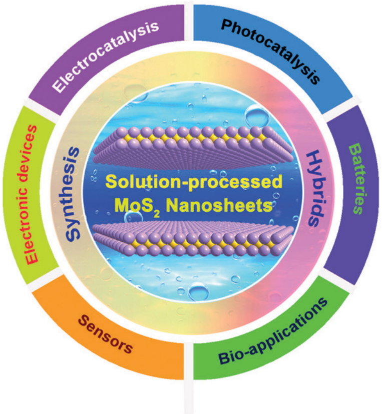
Reviews

2D Nanomaterials

X. Zhang, Z. C. Lai, C. L. Tan,
H. Zhang* ______ 8816 – 8838

Solution-Processed Two-Dimensional MoS_2 Nanosheets: Preparation, Hybridization, and Applications

Sheets ahead: Solution-based methods offer an effective route for the preparation of MoS_2 nanosheets. With the an emphasis on applications, the synthetic strategies and methods for functionalization and hybridization are discussed.



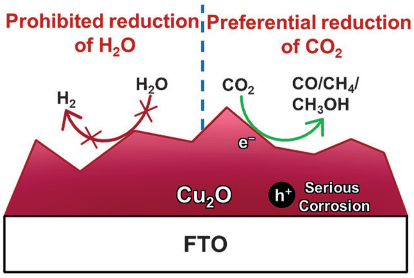
Communications

Photocatalysis

X. Chang, T. Wang, P. Zhang, Y. Wei,
J. Zhao, J. Gong* ______ 8840 – 8845

Stable Aqueous Photoelectrochemical CO_2 Reduction by a Cu_2O Dark Cathode with Improved Selectivity for Carbonaceous Products

Copper on the dark side: Cu_2O preferentially reduced CO_2 to fuels while suppressing hydrogen evolution. It was found that the photogenerated holes primarily account for the instability of Cu_2O. The Cu_2O was used as a dark cathode to minimize the adverse effects of holes, achieving excellent stability and a selectivity of 92.6% for carbonaceous products in CO_2 photoreduction.



Frontispiece

For the USA and Canada:
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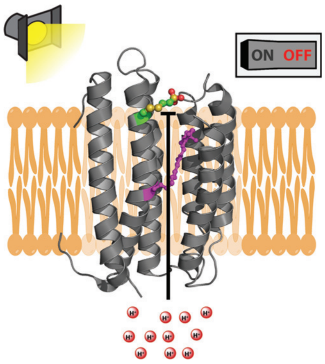
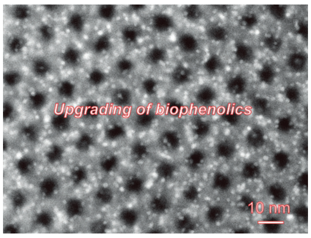
A chemical switch: Light-driven proton pumps like proteorhodopsin (PR; gray structure with retinal cofactor in magenta) are excellent candidates for efficient energy conversion. The versatility of PR was extended by means of an on/off switch based on reversible chemical modification of a site-specifically introduced cysteine residue. Chemical modification of this residue (green/yellow/red) blocks the channel and abolishes proton pumping under illumination.



Synthetic Biology

D. Harder, S. Hirschi, Z. Ucurum, R. Goers, W. Meier, D. J. Müller, D. Fotiadis* **8846 – 8849**

Engineering a Chemical Switch into the Light-driven Proton Pump Proteorhodopsin by Cysteine Mutagenesis and Thiol Modification

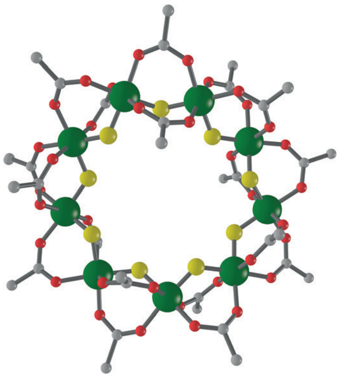


The phenol cut: A novel method allows the synthesis of bimetallic PtCo nanoparticles (ca.1.5 nm) which are highly dispersed in the framework of nitrogen-doped ordered mesoporous carbon (NOMC). The resulting PtCo-NOMC shows high catalytic activity for hydrodeoxygenation of phenolic compounds and "real-world" biomass-derived phenolic streams.

Heterogeneous Catalysis

G.-H. Wang, Z. Cao, D. Gu, N. Pfänder, A.-C. Swertz, B. Spliethoff, H.-J. Bongard, C. Weidenthaler, W. Schmidt, R. Rinaldi, F. Schüth* **8850 – 8855**

Nitrogen-Doped Ordered Mesoporous Carbon Supported Bimetallic PtCo Nanoparticles for Upgrading of Biophenolics

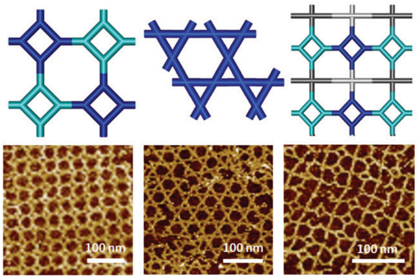


Spin frustration: The first homometallic wheel compound containing an odd number of metal centers and an odd number of electrons has been synthesized. The extent of spin frustration in the ring has been characterized spectroscopically, showing a near perfect frustrated ground state from a sterically undemanding chemical structure.

Molecular Magnetism

R. J. Woolfson, G. A. Timco, A. Chiesa, I. J. Vitorica-Yrezabal, F. Tuna, T. Guidi, E. Pavarini, P. Santini, S. Carretta, R. E. P. Winpenny* **8856 – 8859**

[CrF(O$_2$C^{t}Bu)$_2$]$_9$: Synthesis and Characterization of a Regular Homometallic Ring with an Odd Number of Metal Centers and Electrons



Tiny tiling: Two novel Archimedean tiling patterns, (4.8.8) and (3.6.3.6), and one pattern with higher-order structures beyond the complexity observed in Archimedean tiling were achieved through the self-assembly of DNA tiles. Such complicated DNA structures expand the complexity boundaries of DNA tile-based tessellation.

DNA Nanotechnology

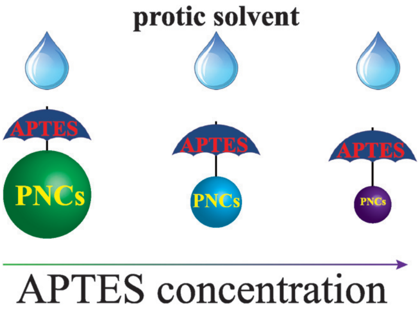
F. Zhang,* S. Jiang, W. Li, A. Hunt, Y. Liu,* H. Yan* **8860 – 8863**

Self-Assembly of Complex DNA Tessellations by Using Low-Symmetry Multi-arm DNA Tiles

Perovskite Stability

B. Luo, Y.-C. Pu, S. A. Lindley, Y. Yang,
L. Lu, Y. Li, X. Li,*
J. Z. Zhang* ____________ **8864 – 8868**

Organolead Halide Perovskite Nanocrystals: Branched Capping Ligands Control Crystal Size and Stability

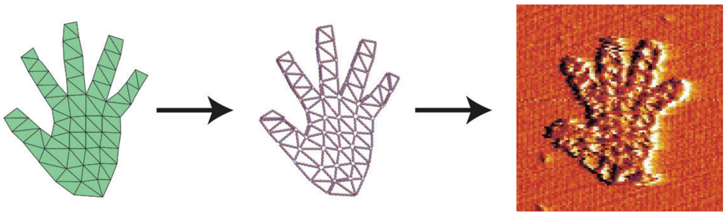


Perovskite nanocrystals: Variously sized perovskite nanocrystals (PNCs) with high photoluminescence quantum yield and uniformity have been synthesized using branched ligands (APTES). APTES-capped PNCs show high stability in protic solvents because the steric and hydrolysis properties of APTES prevent protic reactions with the core of PNCs.

DNA Nanotechnology

E. Benson, A. Mohammed, A. Bosco,
A. I. Teixeira, P. Orponen,
B. Högberg* ____________ **8869 – 8872**

Computer-Aided Production of Scaffolded DNA Nanostructures from Flat Sheet Meshes



Flat-sheet DNA nanostructures: Using algorithmic tools, DNA nanostructures were designed from 2D meshes with varying internal geometries. Using this method, structures with complex internal and external features were prepared that self-assemble under physiological salt concentrations and have larger surface areas compared to classic DNA origami flat-sheet designs.

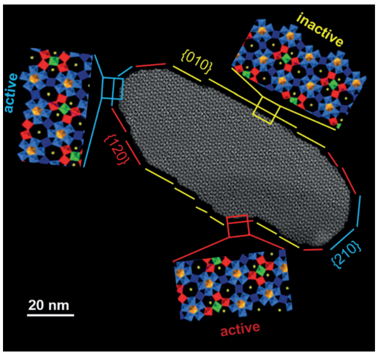
Heterogeneous Catalysis

D. Melzer, P. Xu, D. Hartmann, Y. Zhu,
N. D. Browning,* M. Sanchez-Sanchez,*
J. A. Lercher* ____________ **8873 – 8877**

Atomic-Scale Determination of Active Facets on the MoVTeNb Oxide M1 Phase and Their Intrinsic Catalytic Activity for Ethane Oxidative Dehydrogenation

Inside Cover

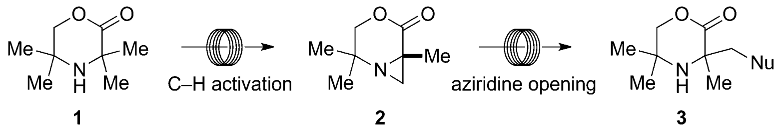
Surface structures: High-angle annular dark-field scanning transmission electron microscopy analysis provided an atomic level description of the termination of M1 phase crystals of MoVTeNbOx catalysts. The statistical analysis of electron microscopy images combined with reaction kinetics allowed identification of those crystalline facets active in ethane oxidative dehydrogenation.



Flow Reactions

J. Zakrzewski, A. P. Smalley,
M. A. Kabeshov, M. J. Gaunt,*
A. A. Lapkin* ____________ **8878 – 8883**

Continuous-Flow Synthesis and Derivatization of Aziridines through Palladium-Catalyzed C(sp^3)—H Activation



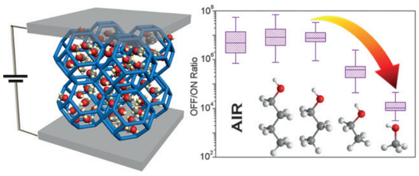
0.77 g per hour with a space–time yield of 0.46 kg L(reactor)$^{-1}$ h^{-1}

Keep up with the flow! A predictive mechanistic model was developed and used to design a flow process for C—H activation. The resulting continuous-flow synthesis of aziridines through palladium-catalyzed C(sp^3)—H activation was combined with ring opening of the aziridine in flow to give highly functionalized aliphatic amines in a consecutive process involving the capture and release of the aziridine intermediate (see scheme).

Molecular Devices

Y. Liu, H. Wang, W. Shi, W. Zhang, J. Yu, B. K. Chandran, C. Cui, B. Zhu, Z. Liu, B. Li, C. Xu, Z. Xu, S. Li, W. Huang, F. Huo,* X. Chen* ________ **8884 – 8888**

Alcohol-Mediated Resistance-Switching Behavior in Metal–Organic Framework-Based Electronic Devices

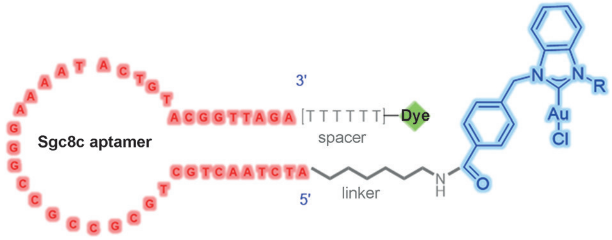


A MOF never forgets: Alcohol-mediated memory devices with reliable resistance-switching properties were realized in metal–organic framework (MOF) films. The memory behavior can be controlled by the intermolecular interactions among the guest molecules adsorbed in MOF crystals to achieve multilevel information storage.

Drug Bioconjugates

W. Niu, X. Chen, W. Tan, A. S. Veige* ________ **8889 – 8893**

N-Heterocyclic Carbene–Gold(I) Complexes Conjugated to a Leukemia-Specific DNA Aptamer for Targeted Drug Delivery

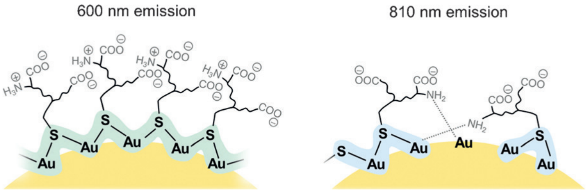


Apt to enter cancer cells: N-Heterocyclic carbene (NHC)–gold(I) complexes were conjugated to the CCRF-CEM leukemia-specific aptamer sgc8c as a strategy for the selective targeting of cancer cells. Cell-viability assays in combination with other techniques indicated that the NHC–Au^{I}–aptamer conjugate (see structure) was more cytotoxic than the NHC–gold complex alone and targeted CCRF-CEM leukemia cells selectively.

Nanoparticles

J. B. Liu, P. N. Duchesne, M. X. Yu, X. Y. Jiang, X. H. Ning, R. D. Vinluan, III, P. Zhang, J. Zheng* ________ **8894 – 8898**

Luminescent Gold Nanoparticles with Size-Independent Emission

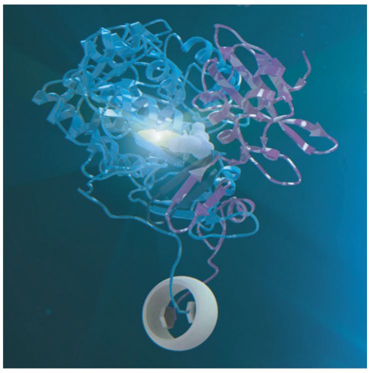


Size-independent emission has been widely observed for ultrasmall thiolated gold nanoparticles (AuNPs). Herein, the emission wavelength of thiolated AuNPs is found to depend on the surface coverage and local binding geometry of the thiolate ligands (glutathione) on the AuNP; AuNPs with different surface coverages emit at different wavelengths in spite of their identical size (ca. 2.5 nm).

Supramolecular Chemistry

R. P. G. Bosmans, J. M. Briels, L.-G. Milroy, T. F. A. de Greef, M. Merkx, L. Brunsveld* ________ **8899 – 8903**

Supramolecular Control over Split-Luciferase Complementation

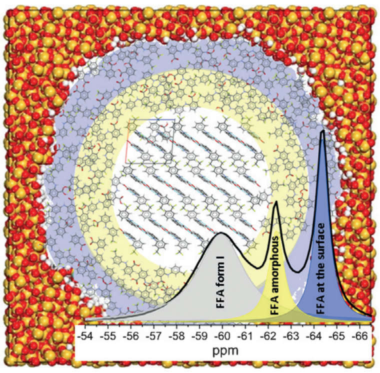


Cucurbit[8]uril-based supramolecular complementation of split-luciferase allows exact control over the level of enzyme activity with a maximum 20-fold activity enhancement. Competitive small-molecule cucurbit[8]uril binders allow the underlying binding characteristics to be elucidated and a system featuring switchable enzyme activity to be developed.

Solid-State NMR Spectroscopy

K. P. Nartowski, D. Malhotra,
L. E. Hawarden, J. Sibik, D. Iuga,
J. A. Zeitler, L. Fábián,
Y. Z. Khimyak* ____________ 8904 – 8908

^{19}F NMR Spectroscopy as a Highly Sensitive Method for the Direct Monitoring of Confined Crystallization within Nanoporous Materials



Detailed mechanistic insight into the crystallization of flufenamic acid (FFA) in the confined environment of mesoporous silica materials with different pore diameters (3.2–29 nm) was obtained by ^{19}F magic-angle-spinning NMR spectroscopy. This approach provided direct experimental evidence for the formation of a molecular-liquid-like layer besides crystalline confined FFA form I.

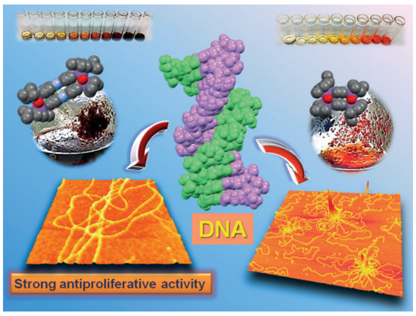
Anticancer Complexes

Y. Fu, M. J. Romero, L. Salassa, X. Cheng,
A. Habtemariam, G. J. Clarkson, I. Prokes,
A. Rodger, G. Costantini,
P. J. Sadler* ______________ 8909 – 8912

Os_2–Os_4 Switch Controls DNA Knotting and Anticancer Activity

Inside Back Cover

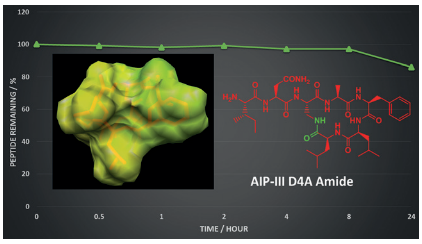
DNA and osmium tie the knot: Two Os^{II} tetranuclear metallacycle frameworks constructed by linking inactive dihydroxido arene dimers show significant differences in cytotoxicity against cancer cells and behavior toward DNA condensation.



Quorum Sensing

Y. Tal-Gan, M. Ivancic, G. Cornilescu,
T. Yang, H. E. Blackwell* ___ 8913 – 8917

Highly Stable, Amide-Bridged Autoinducing Peptide Analogues that Strongly Inhibit the AgrC Quorum Sensing Receptor in *Staphylococcus aureus*

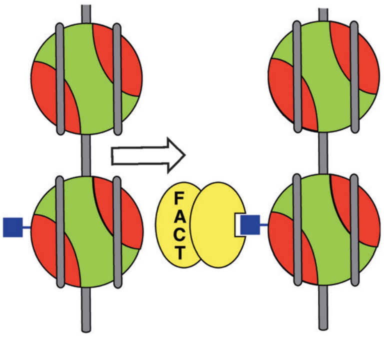


Strong words: Lactam analogues of peptidic quorum sensing inhibitors in *Staphylococcus aureus* have significantly enhanced physical properties, whilst maintaining their strong biological activities. Structural analyses reveal that they adopt conformations similar to their thioester precursors, and corroborate their activities in cell-based assays for AgrC-type receptor modulation.

Protein Modifications

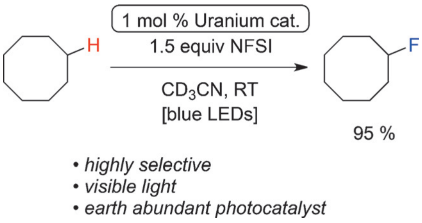
R. Raj, L. Lercher, S. Mohammed,
B. G. Davis* ______________ 8918 – 8922

Synthetic Nucleosomes Reveal that GlcNAcylation Modulates Direct Interaction with the FACT Complex



Tag and modify: Precise chemical synthesis of a histone glycoprotein and its use in the construction of an entire synthetic GlcNAcylated nucleosome as a fragment of model chromatin has allowed direct interaction with the central FACT complex to be detected. In the picture, the *O*-GlcNAc (*O*-linked β-*N*-acetylglucosamine) residue is shown as a blue square, and the nucleosome is shown as a red/green/gray unit.

U can do it: The uranyl cation (UO_2^{2+}) is able to effect the catalytic fluorination of unactivated C(sp^3)–H bonds under visible-light irradiation. Uranyl nitrate is highlighted as a convenient molecular C–H abstraction catalyst, which exhibits selectivity that is distinct from previously reported catalytic systems. NFSI: *N*-fluorobenzenesulfonimide.



C(sp^3)–H Fluorination

J. G. West, T. A. Bedell, E. J. Sorensen* —— **8923–8927**

The Uranyl Cation as a Visible-Light Photocatalyst for C(sp^3)–H Fluorination

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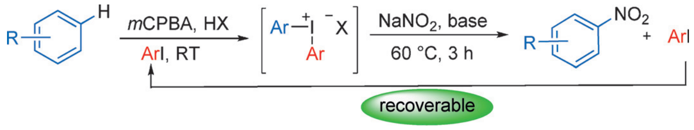

Without a trace: Nitroarenes are obtained in a sequential one-pot reaction from arenes via diaryliodonium intermediates. Aryl azides can also be synthesized with this novel approach, where iodine(III) reagents with two carbon ligands are formed in situ from iodine(I), and subsequently reacted with nucleophiles. The presented one-pot method is an important step towards catalytic reactions with these hypervalent iodine reagents. *m*CPBA = *m*-chloroperbenzoic acid.

Hypervalent Compounds

M. Reitti, P. Villo, B. Olofsson* —— **8928–8932**

One-Pot C–H Functionalization of Arenes by Diaryliodonium Salts

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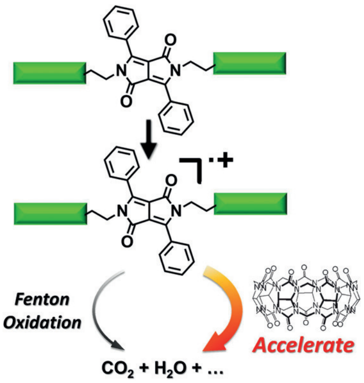


Acceleration to dye for: In the Fenton oxidation of a 1,4-diketopyrrolo[3,4-*c*]pyrrole dye (see scheme), the key electron-deficient radical-cation intermediate was activated by host–guest interactions with electrostatically negative cucurbit[7]uril. A drastic decrease in the apparent activation energy of the transformation, and thus a remarkable improvement in the reaction rate, was observed upon the formation of the supramolecular complex.

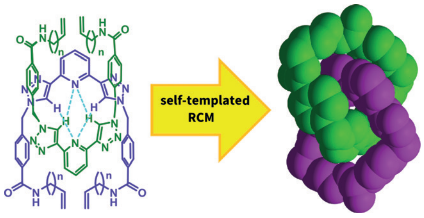
Radical Reactions

Y. Jiao, W.-L. Li, J.-F. Xu, G. Wang, J. Li, Z. Wang, X. Zhang* —— **8933–8937**

A Supramolecularly Activated Radical Cation for Accelerated Catalytic Oxidation

---

Captured and put in chains: Olefin-appended 2,6-bis(1,2,3-triazol-4-yl)pyridine compounds were able to self-template [2]catenane formation by ring-closing metathesis in up to 50% yield (see scheme). When screened against a range of ions, the [2]catenanes acted as selective hosts for the tetrahedral phosphate anion, which was bound through triazolyl hydrogen-bonding interactions.



Interlocked Molecules

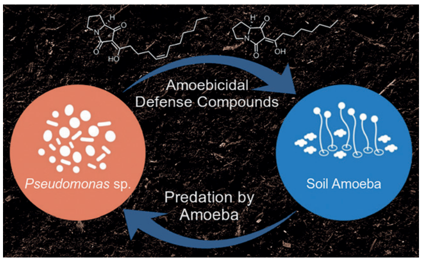
J. P. Byrne,* S. Blasco, A. B. Aletti, G. Hessman, T. Gunnlaugsson* —— **8938–8943**

Formation of Self-Templated 2,6-Bis(1,2,3-triazol-4-yl)pyridine [2]Catenanes by Triazolyl Hydrogen Bonding: Selective Anion Hosts for Phosphate

Natural Products

M. Klapper, S. Götze, R. Barnett, K. Willing, P. Stallforth* ____ 8944 – 8947

Bacterial Alkaloids Prevent Amoebal Predation



You eat me, I kill you: A set of bacterial pyrrolizidine alkaloids (pyreudiones A–D) were discovered that protect the producer, *Pseudomonas fluorescens* HKI0770, against amoebal predation. Isolation, structure elucidation, total synthesis, a proposed biosynthetic pathway for these structures, and gene-deletion experiments are presented.

Caged Biomolecules

M. A. H. Fichte, X. M. M. Weyel, S. Junek, F. Schäfer, C. Herbivo, M. Goeldner, A. Specht, J. Wachtveitl, A. Heckel* ____ 8948 – 8952

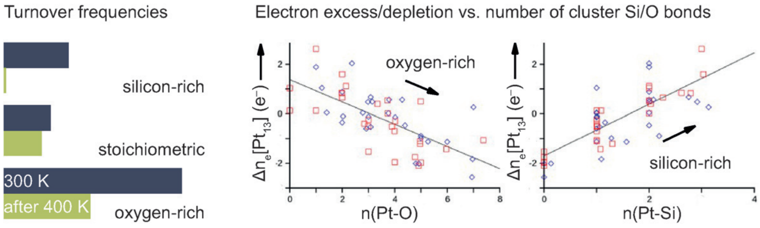
Three-Dimensional Control of DNA Hybridization by Orthogonal Two-Color Two-Photon Uncaging

Now also in 3D! Oligonucleotides with different sequences could be photoactivated with exact three-dimensional control when different two-photon-sensitive photolabile groups were introduced into the strands. Uncaging was visualized by fluorescence as a result of double-strand displacement. By using distinct irradiation conditions, either one of two sequences could be addressed selectively (see left-hand images, which are overlayed on the right).

Hydrogenation Catalysis

A. S. Crampton, M. D. Rötzer, F. F. Schweinberger, B. Yoon, U. Landman,* U. Heiz* ____ 8953 – 8957

Controlling Ethylene Hydrogenation Reactivity on Pt_{13} Clusters by Varying the Stoichiometry of the Amorphous Silica Support

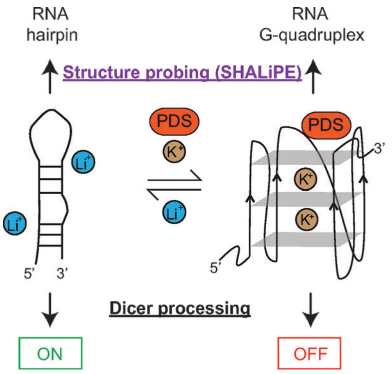


Precise control of thin-film stoichiometry, and application of such films as heterogeneous catalyst supports, enables the investigation of their effect on catalytic reactivity. With the application of a single cluster size as catalyst (Pt_{13}), the deconvolution of individual characteristics imparted by each stoichiometrically unique film is attainable through calculations, and the subsequent influence on a model hydrocarbon reaction is elucidated.

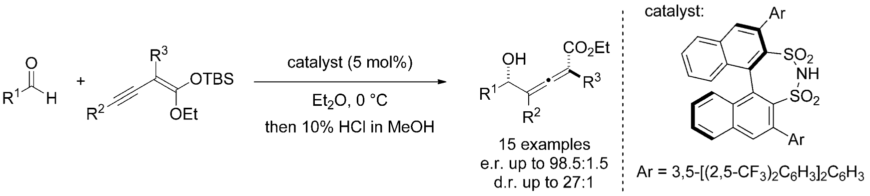
G-Quadruplexes

C. K. Kwok, A. B. Sahakyan, S. Balasubramanian* ____ 8958 – 8961

Structural Analysis using SHALiPE to Reveal RNA G-Quadruplex Formation in Human Precursor MicroRNA



Chemical probing of RNA G-quadruplexes: A novel strategy, SHALiPE, is used to structurally probe and characterize RNA G-quadruplexes (rG4s) at single-nucleotide resolution. Application of this new method on the human precursor microRNA (pre-miRNA) 149 under Li^+, K^+, and K^+ + pyridostatin (PDS) conditions reveals rG4 structure formation, which inhibits in vitro Dicer processing.

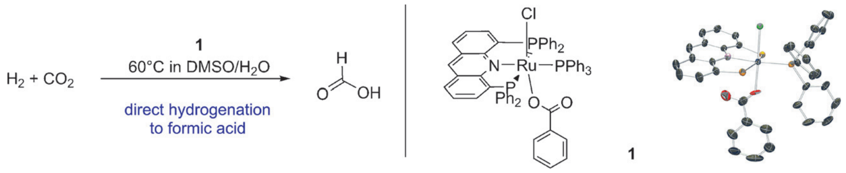


A lean machine: A chiral disulfonimide was designed as a catalyst for an alkynylogous Mukaiyama aldol reaction (see scheme). A broad range of aldehydes and diverse alkynyl-substituted ketene acetals underwent the transformation to deliver chiral allenoates in high yield with excellent regio-, diastereo-, and enantioselectivity. The products can be readily derivatized to furnish highly substituted enantiomerically enriched building blocks.

Organocatalysis

A. Tap, A. Blond, V. N. Wakchaure,
B. List* ______ 8962 – 8965

Chiral Allenes via Alkynylogous Mukaiyama Aldol Reaction



Stable environment: The direct hydrogenation of CO_2 into formic acid without the need for amine bases as a product stabilizer is described. Complex **1** shows high catalytic productivity and activity. The dimethylsulfoxide (DMSO)/H_2O medium is capable of stabilizing the reaction product thermodynamically, which was rationalized by DFT calculations.

Reduction

K. Rohmann, J. Kothe, M. W. Haenel,
U. Englert, M. Hölscher,
W. Leitner* ______ 8966 – 8969

Hydrogenation of CO_2 to Formic Acid with a Highly Active Ruthenium Acriphos Complex in DMSO and DMSO/Water

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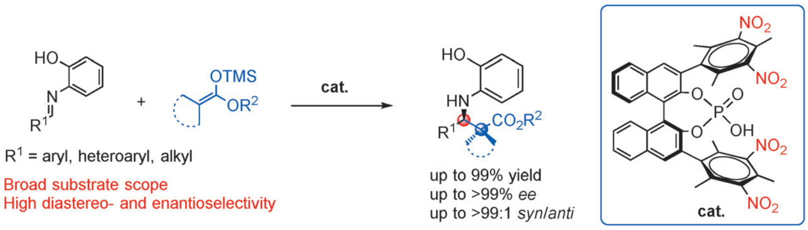

A selection of M&M's: 2,4,6-trimethyl-3,5-dinitrophenyl substituents were introduced into the 3,3′-positions of BINOL-derived chiral phosphoric acids. The resulting catalysts exhibit excellent enantioselectivity and good diastereoselectivity in asymmetric Mukaiyama–Mannich reactions of imines with a wide range of ketene silyl acetals.

Asymmetric Catalysis

F. Zhou,* H. Yamamoto* ______ 8970 – 8974

A Powerful Chiral Phosphoric Acid Catalyst for Enantioselective Mukaiyama–Mannich Reactions

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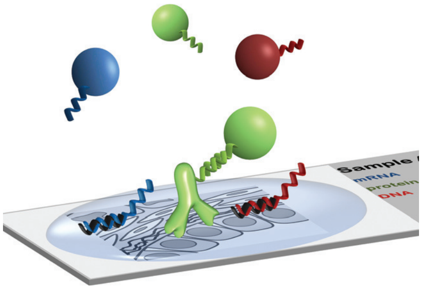
Now you see it: DNA encoding chemistry combined with multiplexed imaging enables simultaneous in situ interrogation of a panel of selected DNA, RNA, and/or protein markers (red, blue, and green probes, respectively) in single cells by bringing different target types onto the same detection platform. In a proof-of-concept study with multicolor quantum dot probes, DNA encoding was used to explore the spatial and temporal aspects of cell transfection and RNAi.



Imaging

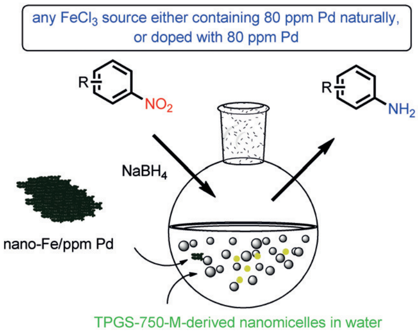
P. Zrazhevskiy, S. Akilesh, W. Tai,
K. Queitsch, L. D. True, J. Fromm, D. Wu,
P. Nelson, J. A. Stamatoyannopoulos,
X. Gao* ______ 8975 – 8978

Cross-Platform DNA Encoding for Single-Cell Imaging of Gene Expression

Green Chemistry

J. Feng, S. Handa,* F. Gallou,
B. H. Lipshutz* ______ **8979 – 8983**

Safe and Selective Nitro Group Reductions Catalyzed by Sustainable and Recyclable Fe/ppm Pd Nanoparticles in Water at Room Temperature

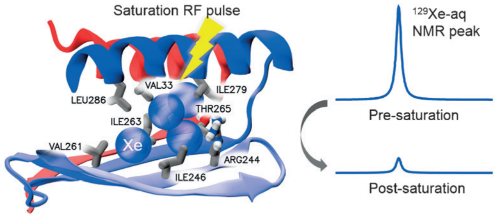


By design: As a result of a unique synergy between ligand-free Fe/ppm Pd nanoparticles and PEG-containing designer surfactants, a facile and selective reduction of nitro-containing (hetero)aromatics by $NaBH_4$ can be effected in water at room temperature. The process offers a general, environmentally responsible, and notably safe approach to highly valued reductions of nitro-containing compounds.

Molecular Imaging

Y. Wang, B. W. Roose, E. J. Palovcak,
V. Carnevale,
I. J. Dmochowski* ______ **8984 – 8987**

A Genetically Encoded β-Lactamase Reporter for Ultrasensitive ^{129}Xe NMR in Mammalian Cells

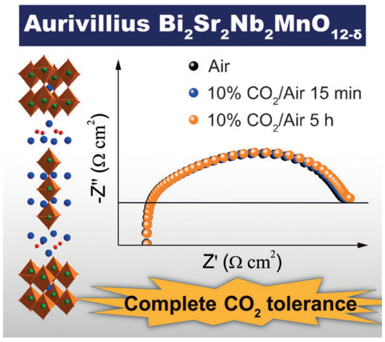


Xenon-assisted MRI: TEM-1 β-lactamase (bla) is a single-protein reporter for hyperpolarized ^{129}Xe NMR, with significant saturation contrast. Xenon chemical exchange saturation transfer interactions with an allosteric site in bla give rise to a unique saturation peak at 255 ppm, well removed from the ^{129}Xe-H_2O peak, and allowed bla to be detected in bacterial and mammalian cells.

Electrochemistry

Y. L. Zhu, W. Zhou,* Y. B. Chen,
Z. P. Shao* ______ **8988 – 8993**

An Aurivillius Oxide Based Cathode with Excellent CO_2 Tolerance for Intermediate-Temperature Solid Oxide Fuel Cells

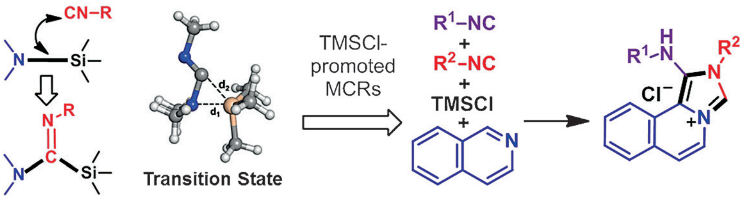


The Aurivillius oxide $Bi_2Sr_2Nb_2MnO_{12-\delta}$ is a highly promising cathode material with excellent CO_2 tolerance for intermediate-temperature solid oxide fuel cells. This cathode not only shows high activity in the oxygen reduction reaction, but also exhibits a very low thermal expansion coefficient, excellent structural stability, and good chemical compatibility with the electrolyte.

Multicomponent Reactions

K. G. Kishore, O. Ghashghaei,
C. Estarellas, M. M. Mestre, C. Monturiol,
N. Kielland, J. M. Kelly, A. F. Francisco,
S. Jayawardhana, D. Muñoz-Torrero,
B. Pérez, F. J. Luque,
R. Gámez-Montaño,*
R. Lavilla* ______ **8994 – 8998**

Insertion of Isocyanides into N–Si Bonds: Multicomponent Reactions with Azines Leading to Potent Antiparasitic Compounds



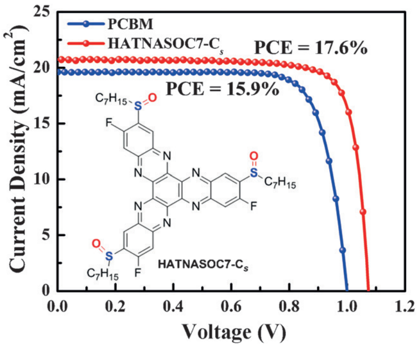
Insert here! Multicomponent reactions (MCRs) with isoquinolines and other azines that proceed through the insertion of an isocyanide into a N–Si bond are described. This novel activation mode enables a variety of transformations to take place with high selectivity under mild reaction conditions. Some of the products showed in vitro activity against the causative agents of trypanosomiasis. TMS = trimethylsilyl.

Perovskite Solar Cells

D. Zhao, Z. Zhu, M.-Y. Kuo, C.-C. Chueh, A. K.-Y. Jen* ____ 8999 – 9003

Hexaazatrinaphthylene Derivatives: Efficient Electron-Transporting Materials with Tunable Energy Levels for Inverted Perovskite Solar Cells

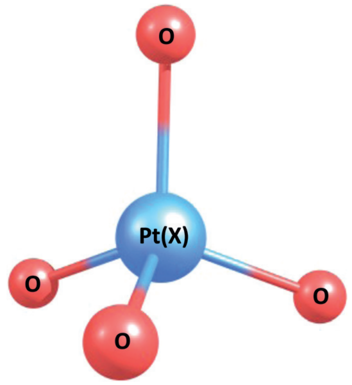
Only sulfur has the answer: Fine tuning of the energy levels and solution processability of hexaazatrinaphthylene (HATNA) derivatives is achieved by introducing alkylsulfanyl chains of various chain lengths and with different sulfur oxidation states. Perovskite solar cells employing these HATNA derivatives as electron-transporting materials exhibited excellent performances, with power conversion efficiencies (PCE) up to 17.6%.



Inorganic Chemistry

H. S. Yu, D. G. Truhlar* ____ 9004 – 9006

Oxidation State 10 Exists



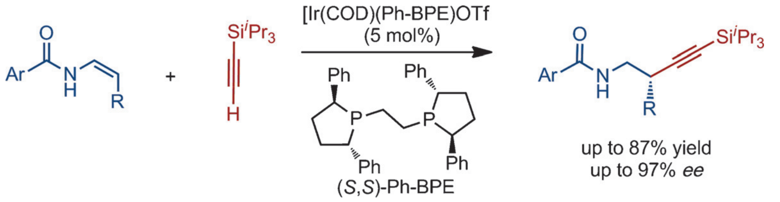
An existential conundrum: The stability of transition-metal compounds with a metal formal oxidation state of 10 was determined with Kohn–Sham density functional theory, and PtO_4^{2+} was found to be stable. PtO_4^{2+} reveals a similar electron density but a larger partial atomic charge on the metal when compared to IrO_4^+, for which the highest oxidation state of 9 was previously found.

Asymmetric Catalysis

X.-Y. Bai, Z.-X. Wang, B.-J. Li* ____ 9007 – 9011

Iridium-Catalyzed Enantioselective Hydroalkynylation of Enamides for the Synthesis of Homopropargyl Amides

Front Cover

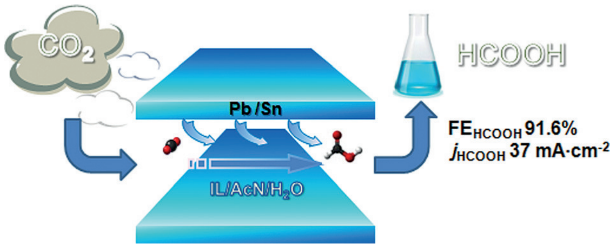


Jockeying into position: The title reaction proceeds regioselectively with reaction at the β-position of an enamide, thus delivering homopropargyl amides. Good to high enantioselectivities were observed with an iridium complex ligated by the Ph-BPE ligand. This method provides a straightforward route to the synthesis of chiral homopropargyl amides with a stereocenter β to the amide. cod = 1,5-cyclooctadiene, Tf = trifluoromethanesulfonyl.

Carbon Dioxide Reduction

Q. G. Zhu, J. Ma, X. C. Kang, X. F. Sun, H. Z. Liu, J. Y. Hu, Z. M. Liu, B. X. Han* ____ 9012 – 9016

Efficient Reduction of CO_2 into Formic Acid on a Lead or Tin Electrode using an Ionic Liquid Catholyte Mixture

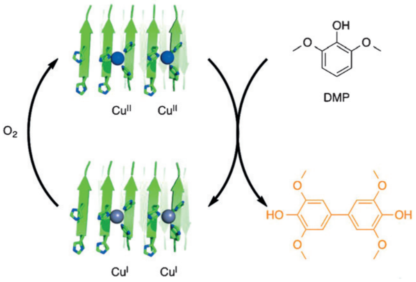


Just a splash: Addition of a small amount of water to an ionic liquid/acetonitrile electrolyte mixture enhanced the efficiency of the electrochemical reduction of CO_2 into formic acid significantly using a Pb or Sn electrode. The partial current density for HCOOH was as high as 37.6 mA cm^{-2} at a Faradaic efficiency of 91.6%.

Synthetic Biology

O. V. Makhlynets, P. M. Gosavi,
I. V. Korendovych* ________ 9017 – 9020

Short Self-Assembling Peptides Are Able to Bind to Copper and Activate Oxygen

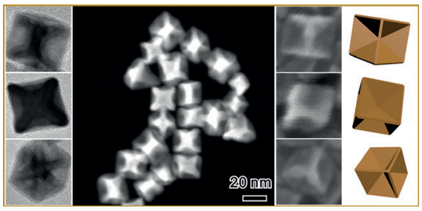


Let's get together: De novo designed peptides were developed that self-assemble in the presence of copper to create supramolecular assemblies that catalyze the oxidation of dimethoxyphenol in the presence of dioxygen. Formation of the supramolecular assembly, which is akin to a protein fold, is critical for productive catalysis since peptides possessing the same functional groups but lacking the ability to self-assemble do not catalyze substrate oxidation.

Nanocrystals

Q. Chen, Y. Yang, Z. Cao, Q. Kuang,*
G. Du, Y. Jiang, Z. Xie,*
L. Zheng ________ 9021 – 9025

Excavated Cubic Platinum–Tin Alloy Nanocrystals Constructed from Ultrathin Nanosheets with Enhanced Electrocatalytic Activity

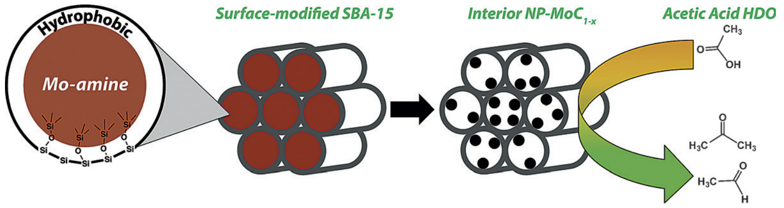


Excavated cubic Pt–Sn alloy nanocrystals with {110} facets were constructed by the assembly of ultrathin nanosheets by co-reduction in the presence of a surfactant. These nanocrystals have a very high surface area and displayed superior electrocatalytic activity towards methanol oxidation.

Nanocomposite Catalysts

F. G. Baddour, C. P. Nash, J. A. Schaidle,*
D. A. Ruddy* ________ 9026 – 9029

Synthesis of α-MoC_{1-x} Nanoparticles with a Surface-Modified SBA-15 Hard Template: Determination of Structure–Function Relationships in Acetic Acid Deoxygenation

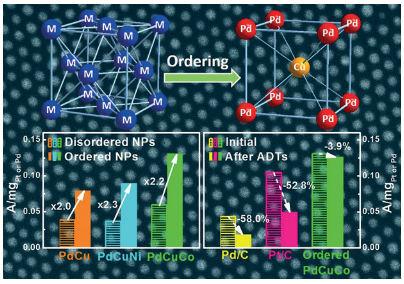


A molybdenum-carbide and SBA-15 silica nanocomposite catalyst: A synthetic route was developed for direct growth of isolated α-MoC_{1-x} nanoparticles in the pores of surface-modified SBA-15 silica. Compared to bulk carbides, the bifunctional nanocatalysts exhibit a greater acid-site:H-site ratio and a fraction of stronger acid sites, which influence catalytic selectivity during acetic acid hydrodeoxygenation.

Ordered Nanoparticles

K. Jiang, P. Wang, S. Guo,* X. Zhang,
X. Shen, G. Lu, D. Su,
X. Huang* ________ 9030 – 9035

Ordered PdCu-Based Nanoparticles as Bifunctional Oxygen-Reduction and Ethanol-Oxidation Electrocatalysts

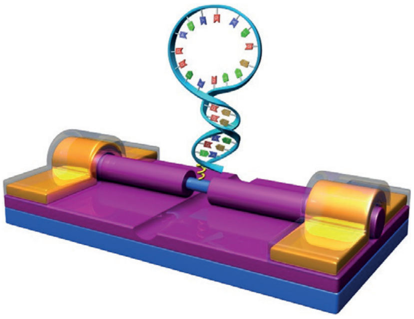


Non-platinum electrocatalysts for fuel-cell reactions, composed of ordered intermetallic PdCuM nanoparticles (NPs; M = Ni or Co), have been synthesized. These ordered PdCuM NPs are generally much more active and stable than the conventional disordered counterparts and also the commercial Pt/C and Pd/C catalysts, towards both the ethanol-oxidation and oxygen-reduction reactions (ADTs = accelerated durability tests).

Single-Molecule Detection

G. He, J. Li, H. Ci, C. Qi,*
X. Guo* ———— 9036 – 9040

Direct Measurement of Single-Molecule DNA Hybridization Dynamics with Single-Base Resolution



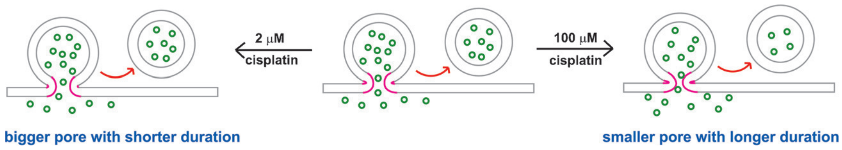
By using an electronic circuit on decorated silicon nanowires, the folding/unfolding process of individual hairpin DNAs were recorded. These measurements revealed current oscillations with strong temperature dependence, allowing determination of the thermodynamic and kinetic properties of hairpin DNA hybridization and the generation of a single-base pair kinetic zipper model for DNA hybridization.

Amperometry

X. Li, J. Dunevall,
A. G. Ewing* ———— 9041 – 9044

Using Single-Cell Amperometry To Reveal How Cisplatin Treatment Modulates the Release of Catecholamine Transmitters during Exocytosis

Back Cover

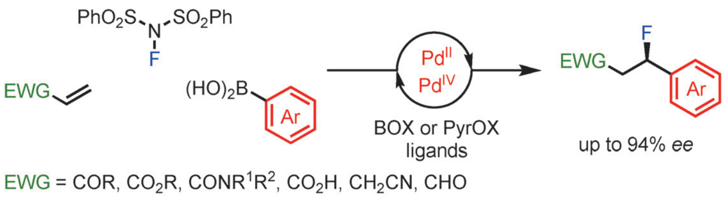


The pretreatment of PC12 cells with cisplatin influences the exocytotic ability of the cells in a dose-dependent manner. Single-cell amperometry experiments show that low concentrations of cisplatin stimulate catecholamine release whereas high concentrations inhibit this process.

Synthetic Methods

J. Miró, C. del Pozo,* F. D. Toste,*
S. Fustero* ———— 9045 – 9049

Enantioselective Palladium-Catalyzed Oxidative β,β-Fluoroarylation of α,β-Unsaturated Carbonyl Derivatives

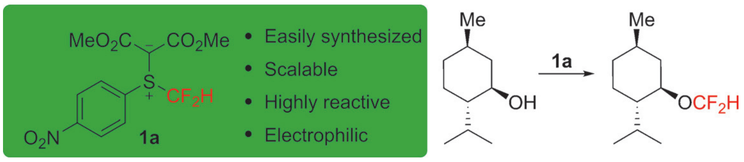


Box in: A modular and step-economical method for the direct β,β-fluoroarylation of conjugated carbonyl derivatives is reported. This approach provides access to a range of enantioenriched β-fluorinated carbonyl derivatives in good yields. BOX = bis(oxazoline), PyrOX = pyridine oxazoline.

Synthetic Methods

J. Zhu, Y. Liu, Q. Shen* ———— 9050 – 9054

Direct Difluoromethylation of Alcohols with an Electrophilic Difluoromethylated Sulfonium Ylide

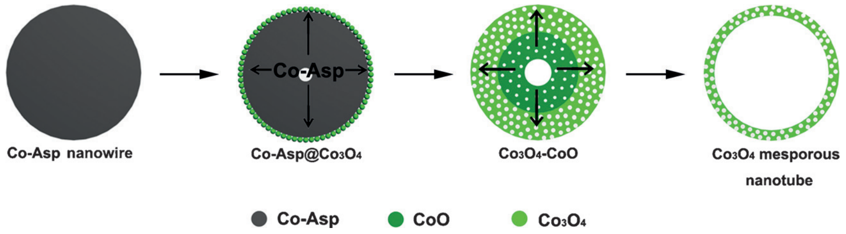


A general method for the formation alkyl difluoromethylethers from the reaction of an alcohol with an electrophilic difluoromethylating reagent (**1a**) is reported. The reaction conditions are mild and a variety of functional groups are compatible.

Inorganic Nanotubes

H. Wang, S. Zhuo, Y. Liang, X. Han, B. Zhang* **9055 – 9059**

General Self-Template Synthesis of Transition-Metal Oxide and Chalcogenide Mesoporous Nanotubes with Enhanced Electrochemical Performances

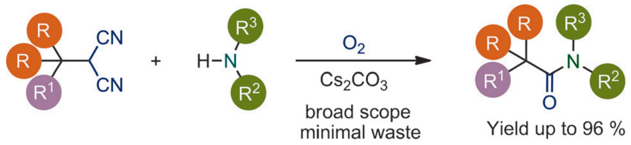


Down to the wire: A facile thermal oxidation-induced transformation using cheap metal–organic coordination nanowires as starting precursors is the basis of the synthesis of inorganic nanotubes with open-ended channels and mesoporous walls. The nanotubes exhibit excellent performances in the electrocatalytic oxygen evolution reaction and for rechargeable lithium-ion batteries.

Amides

J. Li, M. J. Lear,* Y. Hayashi* **9060 – 9064**

Sterically Demanding Oxidative Amidation of α-Substituted Malononitriles with Amines Using O_2

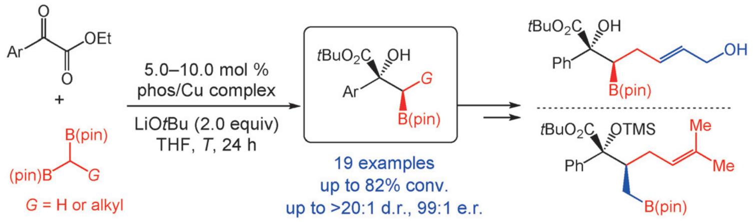


Mix and stir: With just O_2 and base, the direct coupling of readily available malononitriles and amines provides an efficient way to make sterically hindered amides. A radical mechanism involving dioxirane intermediates is proposed, and is supported by cyclopropane-based radical-clock experiments.

Enantioselectivity

S. A. Murray, J. C. Green, S. B. Tailor, S. J. Meek* **9065 – 9069**

Enantio- and Diastereoselective 1,2-Additions to α-Ketoesters with Diborylmethane and Substituted 1,1-Diborylalkanes

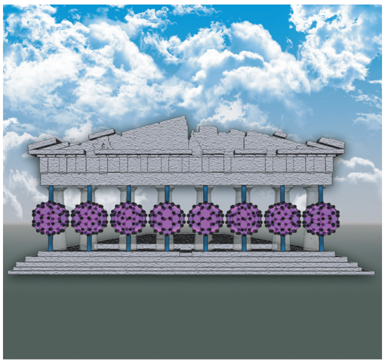


Catalytic enantioselective synthesis of boronate-substituted tertiary alcohols is possible through the title reaction. The reactions are catalyzed by chiral phosphine/copper(I) complexes and produce β-hydroxyboronates containing up to two contiguous stereogenic centers. The utility of the organoboron products is demonstrated through several chemoselective functionalizations. pin = pinacolato, TMS = trimethylsilyl.

Metal–Organic Frameworks

D. E. Williams, E. A. Dolgopolova, D. C. Godfrey, E. D. Ermolaeva, P. J. Pellechia, A. B. Greytak, M. D. Smith, S. M. Avdoshenko, A. A. Popov,* N. B. Shustova* **9070 – 9074**

Fulleretic Well-Defined Scaffolds: Donor–Fullerene Alignment Through Metal Coordination and Its Effect on Photophysics

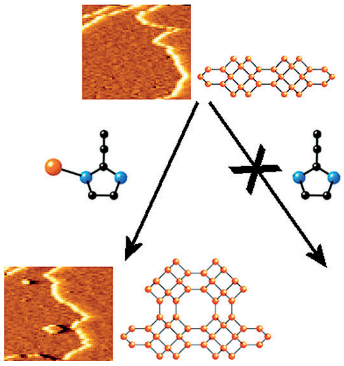


Photophysics: In a crystalline metal–donor–fullerene framework the donor–fullerene mutual orientation is controlled through metal coordination. Because of ultrafast energy and electron transfer, fulleretic materials will contribute not only to the basic science of fullerene chemistry, but also be used for developments in photovoltaics and molecular electronics.

Crystal Growth

R. Wagia, I. Strashnov, M. W. Anderson,
M. P. Attfield* ____ 9075 – 9079

Determination of the Preassembled Nucleating Units That Are Critical for the Crystal Growth of the Metal–Organic Framework CdIF-4

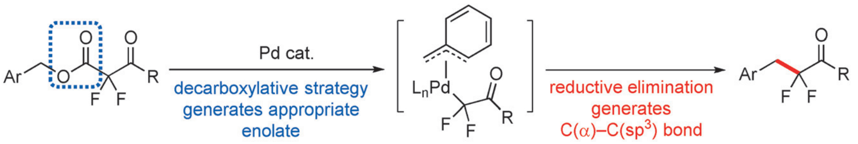


Growth agents: Through the combined use of in situ atomic force microscopy and mass spectrometry, several preformed cadmium-containing species that are present in the growth solution of the cadmium 2-ethylimidazolate metal–organic framework CdIF-4 were identified. Their presence was shown to be critical for surface nucleation.

Synthetic Methods

M.-H. Yang, J. R. Hunt, N. Sharifi,
R. A. Altman* ____ 9080 – 9083

Palladium Catalysis Enables Benzylation of α,α-Difluoroketone Enolates

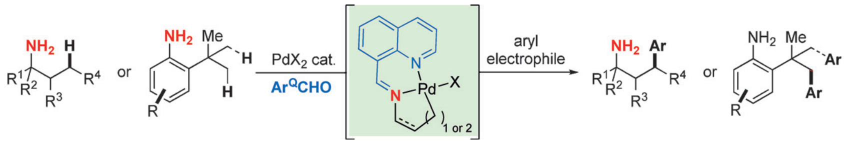


Alkylation reactions of α,α-difluoroketone enolates with sp^3-based electrophiles have been underdeveloped because of intrinsically weak nucleophilicity and chemoselective formation associated with this enolate. Reported herein is a palladium-catalyzed decarboxylative benzylation of α,α-difluoroketone enolates, in which the external α,α-difluoroenolate, formed in situ, underwent reductive elimination from a palladium(II) intermediate to generate the key C(α)–C(sp^3) bond.

C–H Activation

Y. Xu, M. C. Young, C. Wang,
D. M. Magness, G. Dong* ____ 9084 – 9087

Catalytic C(sp^3)–H Arylation of Free Primary Amines with an *exo* Directing Group Generated In Situ

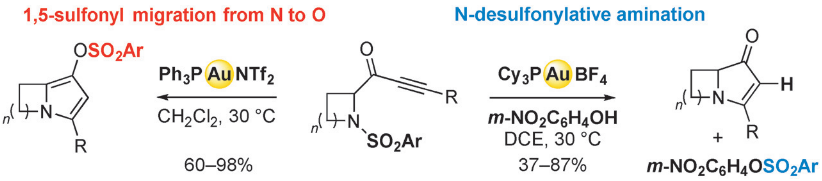


The direct arylation of unactivated aliphatic C–H bonds in free primary amines was achieved by using an *exo*-imine-type directing group (DG) that can be generated and removed in situ. Both primary aliphatic amines and anilines are suitable substrates, and methyl as well as cyclic and acyclic methylene groups smoothly underwent site-selective arylation.

Heterocycle Synthesis

S. Miaskiewicz, B. Gaillard, N. Kern,
J.-M. Weibel, P. Pale,*
A. Blanc* ____ 9088 – 9092

Gold(I)-Catalyzed N-Desulfonylative Amination versus N-to-O 1,5-Sulfonyl Migration: A Versatile Approach to 1-Azabicycloalkanes



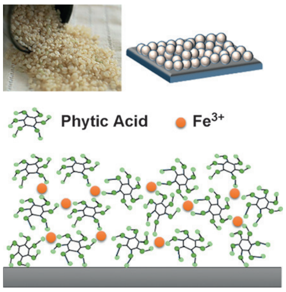
Worth their weight in gold: The great value of sulfonamides in gold catalysis is highlighted by two hydroamination reactions that occur by migration or cleavage of sulfonyl group (see scheme). These unprecedented gold-promoted sulfonyl-transfer reactions open the way to appealing synthetic applications of these robust nitrogen-protecting groups, as demonstrated by the formation of versatile azabicycles.

Superhydrophilic Surfaces

L. Li, G. Zhang, Z. Su* ____ **9093 – 9096**

One-Step Assembly of Phytic Acid Metal Complexes for Superhydrophilic Coatings

Wet, wet, wet: Natural phytic acid reacts with Fe^{III} ions to produce rough coatings of coordination complexes in one step to make a variety of substrates superhydrophilic. Coating deposition occurs in minutes. The coatings are ultrathin, colorless, transparent, and suitable for a range of applications, such as oil/water separation and antifogging.



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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