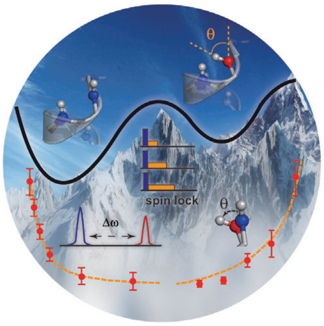
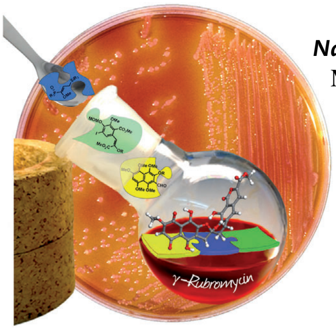
A 12-step chemoenzymatic total synthesis ...

… of *ent*-hydromorphone from β-bromoethylbenzene is described by T. Hudlicky and V. Varghese in their Communication on page 4355 ff. The key steps consist of enzymatic dihydroxylation, Mitsunobu coupling, and oxidative dearomatization followed by intramolecular [4 + 2] cycloaddition. This approach holds potential for further optimization of morphine alkaloid syntheses. We acknowledge the legendary efforts of the chemists pictured, who dedicated their careers to the chemistry of morphine. Cover design: Dennis Ceci, Tomas Hudlicky, Jordan Froese (Brock University).

Solid-State NMR Spectroscopy

In their Communication on page 4312 ff., P. Schanda et al. describe an NMR method used to probe conformational states of proteins. Information about the exchange kinetics, relative populations, and structures of the short-lived state can be obtained.





Natural Product Synthesis

M. Wilsdorf and H.-U. Reissig describe a convergent total synthesis of (±)-γ-rubromycin in their Communication on page 4332 ff. Three highly functionalized building blocks are combined through selective organometallic chemistry.

Functional Polymer Layers

In their Communication on page 4465 ff., Y. Wang et al. report functional polymer layers on paper. Near-infrared light was used to change the conductivity and wettability of the polymers.

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Service

Author Profile

"My favorite piece of research is the hunt for the polio vaccine.
If I were not a scientist, I would be a farmer ..."
This and more about Michael G. Organ can be found on page 4272.

News

M. D. Walter

D. Uraguchi

J. W. Goodby

P. Schreiner

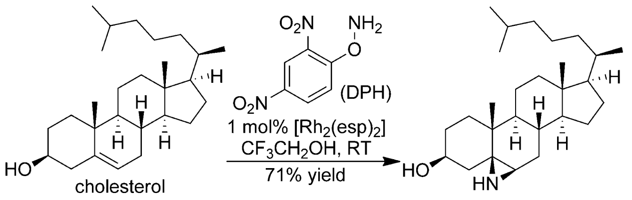
Books

Highlights

Heterocycles

D. T. Smith,
J. T. Njardarson* ________ **4278 – 4280**

A Scalable Rhodium-Catalyzed Intermolecular Aziridination Reaction



The amine has landed! By employing the rhodium catalyst $[Rh_2(esp)_2]$ in the presence of a readily available amine source (DPH), unactivated and styrene-type olefins can now be stereospecifically transformed, in high yields at room temperature, into valuable NH aziridine products. esp = α,α,α′,α′-tetramethyl-1,3-benzenedipropionic acid.

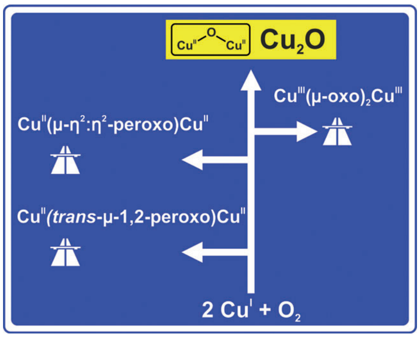
Minireviews

Copper Oxo Complexes

P. Haack, C. Limberg* ____ **4282 – 4293**

Molecular Cu^{II}-O-Cu^{II} Complexes: Still Waters Run Deep

Cu-ltivating new areas: Complexes featuring Cu^{II}-O-Cu^{II} units do not have a developed chemistry. Recently, however, findings suggest such Cu_2O units are the methane-oxidizing species of heterogeneous catalysts and are relevant in biological methane monoxygenation, too. This Minireview outlines the spectroscopy, the structures, and reactivities of the few examples reported to date.

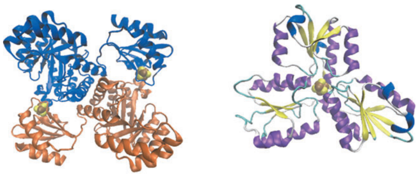


Reviews

Bioorganometallic Chemistry

W. Wang, E. Oldfield* ____ **4294 – 4310**

Bioorganometallic Chemistry with IspG and IspH: Structure, Function, and Inhibition of the $[Fe_4S_4]$ Proteins Involved in Isoprenoid Biosynthesis



IspG
Structure

IspH
Function Inhibition

A mission based on inside information: The methylerythritol phosphate pathway is an attractive anti-infective drug target. The last two enzymes of this pathway, IspG and IspH, are $[Fe_4S_4]$ proteins that catalyze $2H^+/2e^-$ dehydroxylation reactions. Recent progress in the elucidation of their biosynthetic mechanisms opens up new routes to the design of inhibitors that target these $[Fe_4S_4]$ enzymes.

For the USA and Canada:
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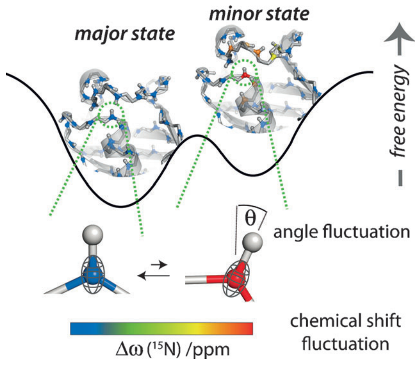
Communications

Protein Dynamics

P. Ma, J. D. Haller, J. Zajakala, P. Macek,
A. C. Sivertsen, D. Willbold, J. Boisbouvier,
P. Schanda* ——— **4312 – 4317**

Probing Transient Conformational States of Proteins by Solid-State $R_{1\rho}$ Relaxation-Dispersion NMR Spectroscopy

Functionally relevant states of proteins are often only short-lived, and thus difficult to detect. Relaxation-dispersion experiments in magic-angle-spinning solid-state NMR spectroscopy provide access to such transient states. Information about the exchange kinetics, relative populations, and structures of the short-lived state can be obtained.



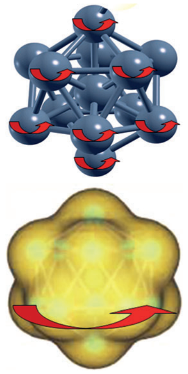
Frontispiece

Giant Diamagnetism

E. Roduner,* C. Jensen, J. van Slageren,
R. A. Rakoczy, O. Larlus,
M. Hunger ——— **4318 – 4321**

Anomalous Diamagnetic Susceptibility in 13-Atom Platinum Nanocluster Superatoms

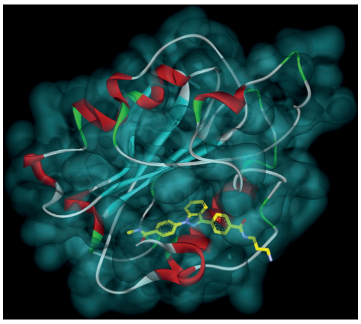
As predicted: The diamagnetic susceptibility per atom of hydride-coated $\{Pt_{13}\}$ nanoclusters supported by a zeolite, exceeds that of Pt^{2+} ions by a factor of 37–50. The observation verifies an earlier theoretical prediction and can be understood on the basis of the superatom nature of the spherical cluster. The two main contributions come from ring currents in cluster molecular orbitals hosting the Pt 5d and Pt 6s electrons and from the delocalized hydride shell.



PPI Activators

M. Hintersteiner,* J. Kallen, M. Schmied,
C. Graf, T. Jung, G. Mudd, S. Shave,
H. Gstach, M. Auer* ——— **4322 – 4326**

Identification and X-ray Co-crystal Structure of a Small-Molecule Activator of LFA-1-ICAM-1 Binding



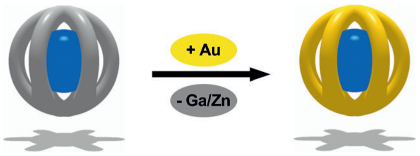
Tuned up: The LFA-1 ICAM-1 interaction is a fundamental step in T-cell activation in response to antigen encounter. A small-molecule activator of LFA-1, IBE-667, was identified by confocal on-bead screening. The identified activator binds to LFA-1 I domain, as revealed by the co-crystal structure, and increases the affinity of LFA-1 for ICAM-1 on activated T-cells.

Inside Cover

Interstitial Clusters

A. Puls, P. Jerabek, W. Kurashige,
M. Förster, M. Molon, T. Bollermann,
M. Winter, C. Gemel, Y. Negishi,
G. Frenking,* R. A. Fischer* **4327 – 4331**

A Novel Concept for the Synthesis of Multiply Doped Gold Clusters $[(M@Au_nM'_m)L_k]^{q+}$

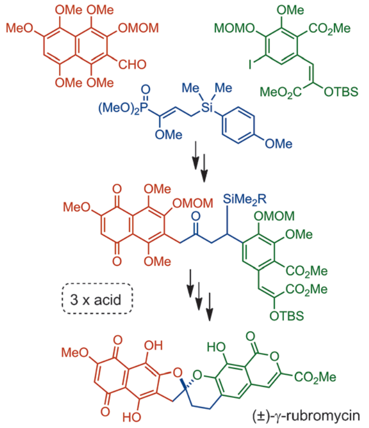


Golden cages: When complexes $[M(M'R)_a]$ (M = Mo, Ni, Pd, Pt; M' = Al, Ga; R = CH_3, C_5Me_5; $a \geq 4$) react with $ClAuPR_3$ (R = Ph, Me), the interstitial metal atom M (blue) is transferred from the M'_a cage (gray) to a Au_n shell (yellow). Multiply metal-doped gold clusters $[(M@Au_nM'_m)L_k]^{q+}$ ($n + m \geq 9$; $q = 0, 1, 3$) result. The design rule of the new clusters is based on the 18 valence electron count for the central metal atom M and agrees with the unified superatom concept based on the jellium model.

Natural Product Synthesis

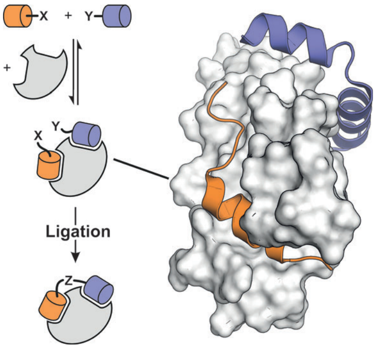
Inside Back Cover

3 building blocks + 3 acids→natural product: After the assembly of the crucial precursor from three highly functionalized building blocks, the pivotal spiroketalization was achieved with trifluoromethanesulfonic acid, the isocoumarin formation with fluoroboric acid, and the O-demethylation with the Lewis acid boron tribromide. (±)-γ-Rubromycin was thus synthesized in 18 steps with an overall yield of 3.8% from commercially available precursors.

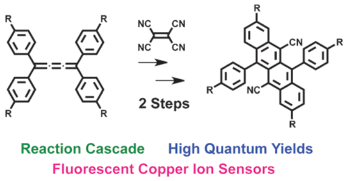


Bioorthogonal Reactions

Come together: A protein template was used to mediate the ligation reaction between two peptides which were equipped with suitable electrophilic and nucleophilic groups. These templated reactions were accelerated by more than three orders of magnitude relative to the nontemplated reactions and proved to be highly selective when used to label proteins within crude cell lysate.



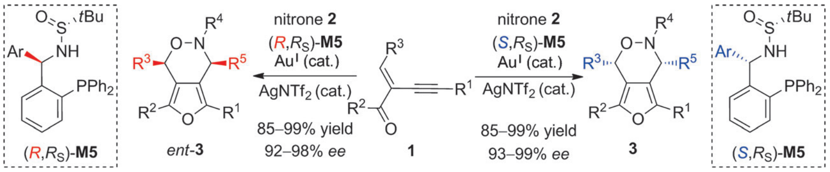
Tetracenes



Condensed sensors: The title reaction starts with the cycloaddition of tetracyanoethylenene to the central C=C bond of cumulenes, followed by a multi-reaction cascade to yield tetracyanodihydrotetracenes. Elimination of $(CN)_2$ provides tetracenes with a rubrene-like substitution pattern as highly fluorescent chromophores that can be used as molecular chemosensors for Cu^+ and Ag^+ ions.

Ash Dieback

The largely unknown secondary metabolism of the plant pathogenic fungus *Hymenoscyphus pseudoalbidus* was investigated by use of the closed-loop stripping apparatus (CLSA) method. A set of volatile lactones was identified by GC/MS. The lactones were synthesized and used in bioassays in which one of the compounds was found to be a strong germination inhibitor for ash seeds.

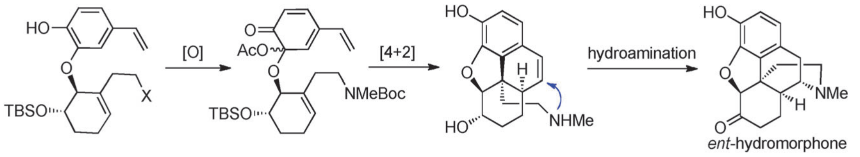


Ming-Phos: A new type of simple chiral sulfinamide monophosphine ligands, the so-called Ming-Phos ligands, can be easily prepared from inexpensive and commercially available starting materials. The enantioselectivity of the reaction of yne–enones **1** with nitrones can be controlled by the diastereomeric ligands (R,R_S)-**M5** and (S,R_S)-**M5**.

Enantioselective Gold Catalysis

Z.-M. Zhang, P. Chen, W. Li, Y. Niu,
X.-L. Zhao, J. Zhang* ——— **4350–4354**

A New Type of Chiral Sulfinamide Monophosphine Ligands: Stereodivergent Synthesis and Application in Enantioselective Gold(I)-Catalyzed Cycloaddition Reactions



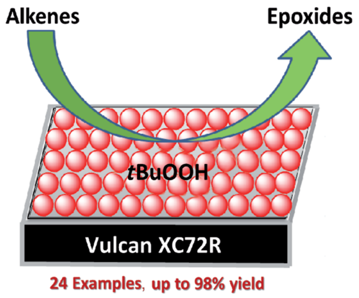
A short synthesis of *ent*-hydromorphone has been achieved in twelve steps from β-bromoethylbenzene. The key transformations involved the enzymatic dihydroxylation of the arene to the corresponding *cis*-dihydrodiol, oxidative dearomatization, subsequent [4+2] cycloaddition to form ring B of the morphinan, and intramolecular amination at C9. Boc = *tert*-butoxycarbonyl, TBS = *tert*-butyldimethylsilyl.

Natural Products

V. Varghese, T. Hudlicky* —— **4355–4358**

Short Chemoenzymatic Total Synthesis of *ent*-Hydromorphone: An Oxidative Dearomatization/Intramolecular [4+2] Cycloaddition/Amination Sequence

Front Cover

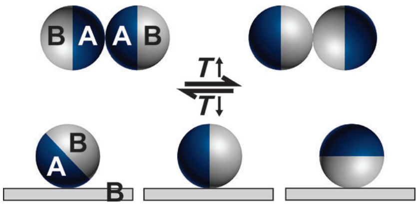


A general epoxidation of aromatic and aliphatic olefins under mild conditions using recyclable heterogeneous Co_xO_y–N/C (x = 1,3; y = 1,4) catalysts and *tert*-butyl hydroperoxide as the terminal oxidant has been developed. Various stilbenes and aliphatic alkenes were successfully transformed into the corresponding epoxides with high selectivity and good yields.

Heterogeneous Catalysis

D. Banerjee, R. V. Jagadeesh, K. Junge,
M.-M. Pohl, J. Radnik, A. Brückner,
M. Beller* ———————— **4359–4363**

Convenient and Mild Epoxidation of Alkenes Using Heterogeneous Cobalt Oxide Catalysts



Thermal wetting reversibly joins patchy colloidal particles into clusters and crystals. This is demonstrated with Janus particles made of gold (A) half-coated silica (B) spheres immersed in a mixture of water and 2,6-lutidine such that the relative strength of gold–gold bonding through hydrophobic interaction and silica–silica bonding through wetting-induced attraction is reversibly switched by temperature changes of only 1–2 °C.

Reconfigurable Materials

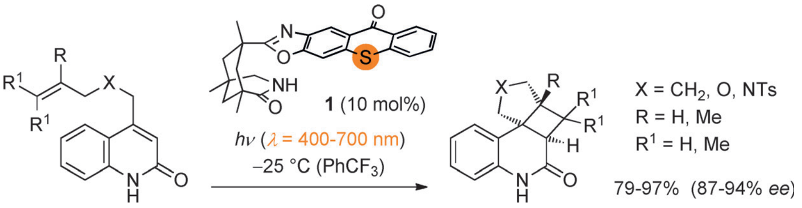
C. Yu, J. Zhang, S. Granick* **4364–4367**

Selective Janus Particle Assembly at Tipping Points of Thermally-Switched Wetting

Photochemistry

R. Alonso, T. Bach* ——— **4368 – 4371**

A Chiral Thioxanthone as an Organocatalyst for Enantioselective [2+2] Photocycloaddition Reactions Induced by Visible Light

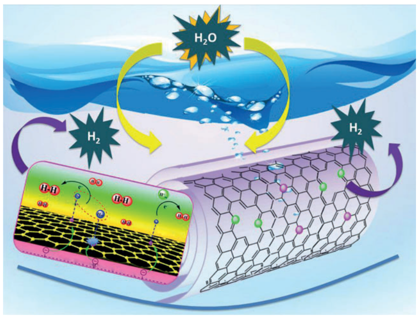


Lighting up S: The thioxanthone **1**, which was synthesized in a concise fashion from methyl thiosalicylate, exhibits a significant absorption in the visible-light region. It allows for an efficient enantioselective catalysis of intramolecular [2+2] photocycloaddition reactions, presumably by triplet-energy transfer. Ts = 4-toluenesulfonyl.

Hydrogen Evolution Reaction

X. Zou, X. Huang, A. Goswami, R. Silva, B. R. Sathe, E. Mikmeková, T. Asefa* ——— **4372 – 4376**

Cobalt-Embedded Nitrogen-Rich Carbon Nanotubes Efficiently Catalyze Hydrogen Evolution Reaction at All pH Values

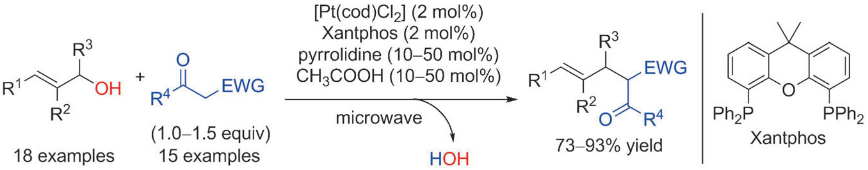


The water-splitting reaction still remains far from being practically feasible because of the unavailability of effective catalysts for the hydrogen evolution reaction (HER). A simple synthetic route gives to nitrogen-rich carbon nanotubes that electrocatalyze HER with activities close to that of Pt, and function well under acidic, neutral, or basic media allowing them to be coupled with the best oxygen-evolving catalysts available.

Synthetic Methods

R. Shibuya, L. Lin, Y. Nakahara, K. Mashima,* T. Ohshima* **4377 – 4381**

Dual Platinum and Pyrrolidine Catalysis in the Direct Alkylation of Allylic Alcohols: Selective Synthesis of Monoallylation Products

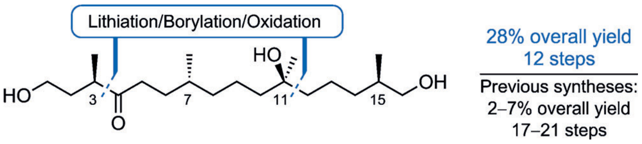


Two cats are better than one: The combined use of platinum and pyrrolidine catalysts enabled the direct alkylation of allylic alcohols with reactive methylene compounds. Pyrrolidine was essential for obtaining high selectivity of the monoallylation products, which were produced without the use of excess nucleophiles. cod = 1,5-cyclooctadiene, EWG = electron-withdrawing group.

Natural Product Synthesis

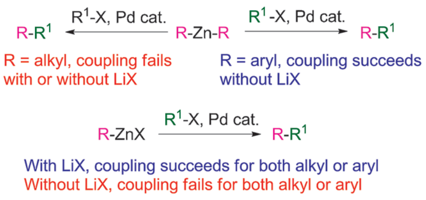
A. P. Pulis, P. Fackler, V. K. Aggarwal* ——— **4382 – 4385**

Short Stereoselective Synthesis of the *Phytophthora* Universal Mating Hormone α1 Using Lithiation/Borylation Reactions



In search of a mate: The universal mating hormone α1 of the virulent plant pathogen *Phytophthora* has been synthesized in 12 steps and 28% overall yield. Key C–C bond-forming steps involved the use of two lithiation/borylation reactions to couple together enantioenriched building blocks, one of which also set up the stereochemistry of the tertiary alcohol at C11. The diastereomeric purity of the target molecule is > 91%, the highest obtained to date.

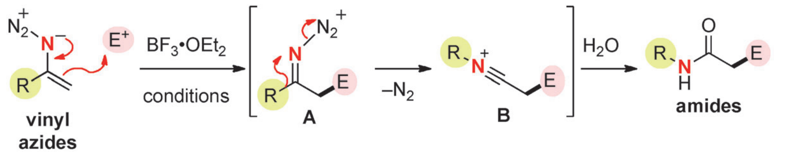
Pass the salt! Alkyl- and arylzinc halides both require salt (e.g., LiBr, $MgCl_2$) in order to undergo the Negishi cross-coupling reaction—but not for the same reason: Whereas alkylzinc halides must form high-order zincates to undergo transmetallation, in the aryl case the role of the salt is to increase solvent dielectric. Conversely, the analogous diarylzinc much more readily undergoes coupling without salt and in low dielectric solvents.



Negishi Reaction Mechanism

L. C. McCann,
M. G. Organ* ______ **4386 – 4389**

On The Remarkably Different Role of Salt in the Cross-Coupling of Arylzincs From That Seen With Alkylzincs

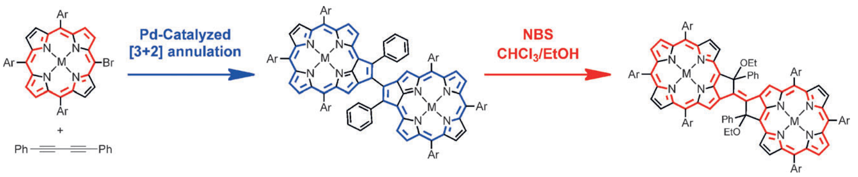


Nitrilium intermediate: A new method for amide synthesis employs vinyl azides as enamine-type nucleophiles towards carbon electrophiles in the presence of $BF_3{\cdot}OEt_2$. After nucleophilic attack of the vinyl azide, a substituent of the resulting iminodiazonium ion intermediate **A** migrates to form nitrilium ion **B**, which is hydrolyzed to afford the corresponding amide.

Amide Synthesis

F.-L. Zhang, Y.-F. Wang, G. H. Lonca,
X. Zhu, S. Chiba* ______ **4390 – 4394**

Amide Synthesis by Nucleophilic Attack of Vinyl Azides



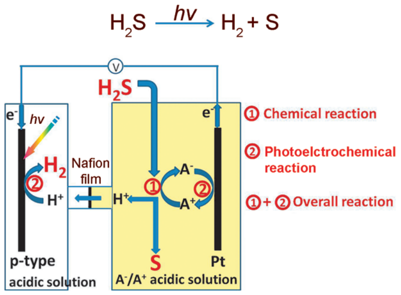
Bridging the networks: 7,8-Dehydropurpurin dimers were synthesized by twofold Pd-catalyzed [3+2] annulation of *meso*-bromoporphyrin with 1,4-diphenylbutadiyne. Treatment of this dimer with *N*-bromosuccinimide (NBS) in $CHCl_3$ and ethanol gave the title porphyrin dimers, which exhibited well-conjugated electronic networks and constrained conformations.

Porphyrinoids

N. Fukui, H. Yorimitsu,* J. M. Lim,
D. Kim,* A. Osuka* ______ **4395 – 4398**

Synthesis of 7,8-Dehydropurpurin Dimers and Their Conversion into Conformationally Constrained β-to-β Vinylene-Bridged Porphyrin Dimers

Trash to Treasure: A photochemical–chemical loop for the overall H_2S splitting was developed by integrating photoelectrochemical H_2 production and H_2S chemical absorption redox reactions with the link of a redox couple (Fe^{2+}/Fe^{3+} or I^-/I_3^-). Using functionalized silicon as photoelectrode, simultaneous extraction of H_2 and elemental sulfur from H_2S was successfully achieved (see picture).



H_2S Splitting

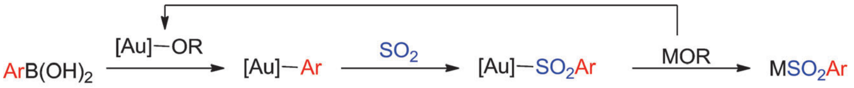
X. Zong, J. F. Han, B. Seger, H. J. Chen,
G. Q. (Max) Lu, C. Li,*
L. Z. Wang* ______ **4399 – 4403**

An Integrated Photoelectrochemical–Chemical Loop for Solar-Driven Overall Splitting of Hydrogen Sulfide

Sulfination

M. W. Johnson, S. W. Bagley,
N. P. Mankad, R. G. Bergman,
V. Mascitti,* F. D. Toste* ___ **4404–4407**

Application of Fundamental Organometallic Chemistry to the Development of a Gold-Catalyzed Synthesis of Sulfinate Derivatives



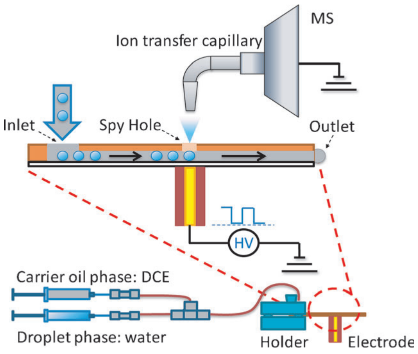
À la mode: A gold(I)-catalyzed synthesis of sulfinates has been accomplished. Preparation of proposed intermediates, X-ray studies, and a number of mechanistic experiments suggest that an unprecedented mode of reactivity for gold(I) has been achieved. The resulting sulfinates from this reaction can be functionalized in situ to form sulfones and sulfonamides.

Microdroplet Mass Spectrometry

N. Gasilova, Q. Yu, L. Qiao,
H. H. Girault* ___ **4408–4412**

On-Chip Spyhole Mass Spectrometry for Droplet-Based Microfluidics

Microdroplets are coupled in a simple and efficient manner with electrostatic-spray ionization mass spectrometry using a microchip with a spyhole. Such a set-up allows direct dilution-free droplet ionization with high detection sensitivity. It is suitable for the performance of various single-phase and biphasic reactions, as demonstrated for peptide/protein tryptic digestion and β-lactoglobulin/α-tocopheryl acetate interaction.

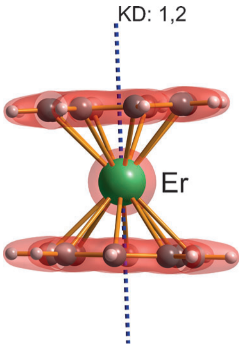


Single-Molecule Magnets

L. Ungur, J. J. Le Roy, I. Korobkov,
M. Murugesu,*
L. F. Chibotaru* ___ **4413–4417**

Fine-tuning the Local Symmetry to Attain Record Blocking Temperature and Magnetic Remanence in a Single-Ion Magnet

A record blocking capability of a single-ion magnet has been predicted and obtained. Ab initio calculations on the Er and the isostructural Dy analogue allowed deeper insight into the reasons for the strong magnetic blocking, explaining the striking differences between magnetic behaviors of these two compounds. Dashed line: Calculated orientation of the main magnetic axis in the ground and first excited Kramers doublet.

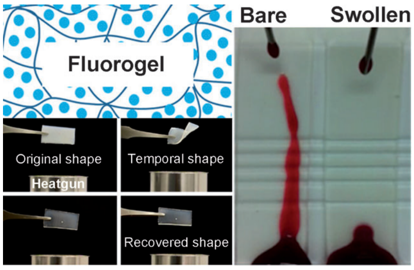


Polymeric Gels

X. Yao,* S. S. Dunn, P. Kim, M. Duffy,
J. Alvarenga, J. Aizenberg* ___ **4418–4422**

Fluorogel Elastomers with Tunable Transparency, Elasticity, Shape-Memory, and Antifouling Properties

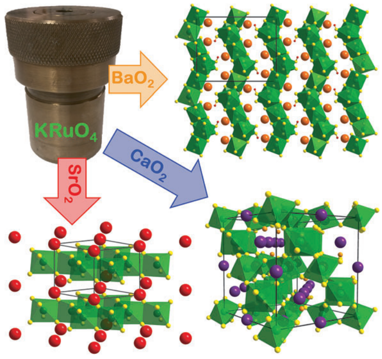
Slippery surfaces: Multifunctional fluorogel elastomers with tunable transparency, mechanics, and shape memory properties are reported. After infusing with fluorinated lubricants, the fluorogels demonstrated broad omniphobicity and antifouling against water, hydrocarbon oils, proteins, biological cells, and blood (see picture) while maintaining excellent cytocompatibility.



Solid-State Structures

C. I. Hiley, M. R. Lees, J. M. Fisher,
D. Thompsett, S. Agrestini, R. I. Smith,
R. I. Walton* ———— **4423 – 4427**

Ruthenium(V) Oxides from Low-Temperature Hydrothermal Synthesis

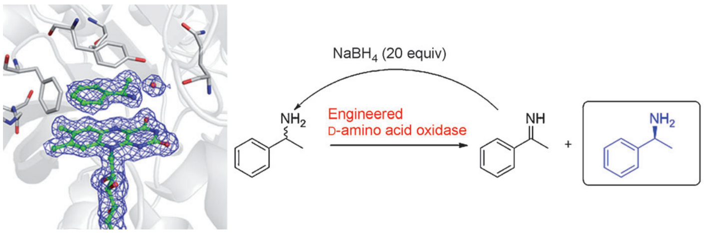


Hydrothermal synthesis yields the ruthenium(V)-containing oxides $Ca_{1.5}Ru_2O_7$, $SrRu_2O_6$, and $Ba_2Ru_3O_9(OH)$. These oxides show a range of structures and magnetic properties. $SrRu_2O_6$ is a hexagonal layered oxide that exhibits antiferromagnetic ordering to at least 230 °C, whilst the orthorhombic $Ba_2Ru_3O_9(OH)$ is a ferromagnetic oxyhydroxide. All three ruthenates are metastable and readily collapse to other oxides at 300–500 °C.

Enzymatic Deracemization

K. Yasukawa, S. Nakano,
Y. Asano* ———— **4428 – 4431**

Tailoring D-Amino Acid Oxidase from the Pig Kidney to *R*-Stereoselective Amine Oxidase and its Use in the Deracemization of α-Methylbenzylamine

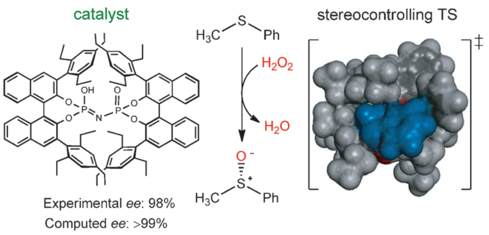


A change in selectivity: An engineered porcine kidney D-amino acid oxidase (pkDAO) with markedly changed substrate selectivity towards *R* amines was obtained by directed evolution. The mutant enzyme exhibited a high preference towards the substrate α-methylbenzylamine and was used to synthesize the *S*-configured amine through deracemization.

Asymmetric Catalysis

G. Jindal, R. B. Sunoj* ———— **4432 – 4436**

Axially Chiral Imidodiphosphoric Acid Catalyst for Asymmetric Sulfoxidation Reaction: Insights on Asymmetric Induction



Turn the stereo up: The first transition-state (TS) model for a new class of axially chiral imidodiphosphoric acid catalysts in the title reaction is proposed using DFT-(M06-2X) calculations. The recognition of the substrate in the chiral pocket and a series of weak noncovalent interactions are responsible for stereoinduction. This stereoelectronic model differs from the commonly employed models which rely on steric interactions.

MOF Memristor

S. M. Yoon, S. C. Warren,
B. A. Grzybowski* ———— **4437 – 4441**

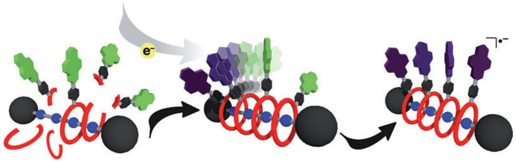
Storage of Electrical Information in Metal–Organic-Framework Memristors

Memories are forever: The sub-nanometer pore size that exists in a metal–organic framework allows electrical information to be written, read, and re-written when that MOF is infiltrated with an ionic electrolyte.

Self-Assembly

A.-J. Avestro, D. M. Gardner,
N. A. Vermeulen, E. A. Wilson,
S. T. Schneebeli, A. C. Whalley,
M. E. Belowich, R. Carmieli,
M. R. Wasielewski,*
J. F. Stoddart* ________ **4442 – 4449**

Gated Electron Sharing Within Dynamic Naphthalene Diimide-Based Oligorotaxanes

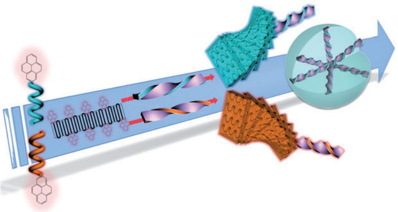


Birds of a feather flock together: Mutually π-stacked small-molecule naphthalene diimide (NDI) [24]crown-8 derivatives self-assemble dynamically on a repeating $-(CH_2CH_2\mathbf{NH_2}^+CH_2)-$ template to afford the stepwise evolution of discrete-length oligorotaxanes, which are shown to communicate electronically through their cofacially interacting π-surfaces, sharing electrons across linear arrays containing one, two, three, and four NDI units as determined by cyclic voltammetry and EPR/ENDOR spectroscopies.

Helical Structures

M.-C. Li, H.-F. Wang, C.-H. Chiang,
Y.-D. Lee, R.-M. Ho* ________ **4450 – 4455**

Lamellar-Twisting-Induced Circular Dichroism of Chromophore Moieties in Banded Spherulites with Evolution of Homochirality

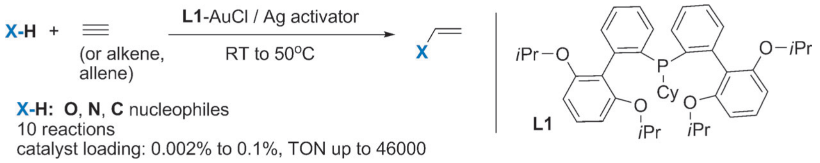


Supramolecular chirality: By evolution of homochirality from helical polymer chains (conformational chirality) to twisting lamellae (hierarchical chirality), banded spherulites with preferential handedness are formed by crystallization of chiral polymers end-capped with chromophore through cooperative intramolecular and intermolecular interactions, changing the chromophore moiety from “optically inactive” to “optically active”.

Gold Catalysis

D. Malhotra, M. S. Mashuta,
G. B. Hammond,* B. Xu* ___ **4456 – 4459**

A Highly Efficient and Broadly Applicable Cationic Gold Catalyst

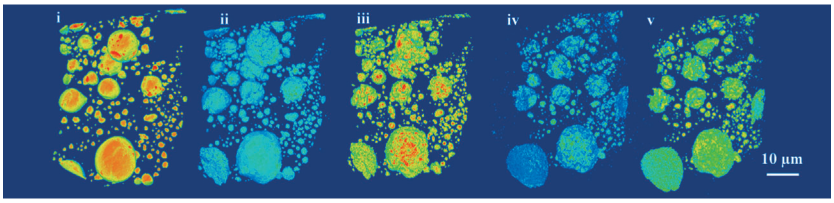


Less is better: A broadly applicable cationic gold catalyst was developed that works at extremely low loading and relatively low temperature. The new gold catalyst containing a bis(biphenyl) phosphane ligand was tested in many common types of gold-catalyzed reactions including intra- and intermolecular X–H (X = C, N, O) additions to alkynes (see example) and cycloisomerizations of enyne and allenone.

Lithium-Ion Batteries

J. J. Wang, Y. K. Chen-Wiegart,
J. Wang* ________ **4460 – 4464**

In Situ Three-Dimensional Synchrotron X-Ray Nanotomography of the (De)lithiation Processes in Tin Anodes



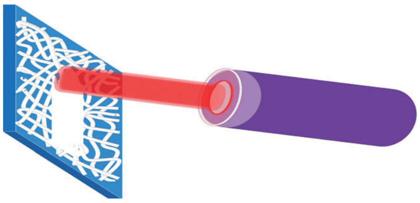
Microstructural evolution: In situ synchrotron X-ray nanotomography has been developed to track the microstructural evolution of battery materials during the cycling of a battery. This three-dimensional quantitative analysis and visualization on the nanometer scale should contribute to our understanding of energy materials and lead to improvements of their synthetic processing.

Photo-annealing

Q. Qian, J. Wang, F. Yan,
Y. Wang* ______________ 4465 – 4468

A Photo-annealing Approach for Building Functional Polymer Layers on Paper

Back Cover



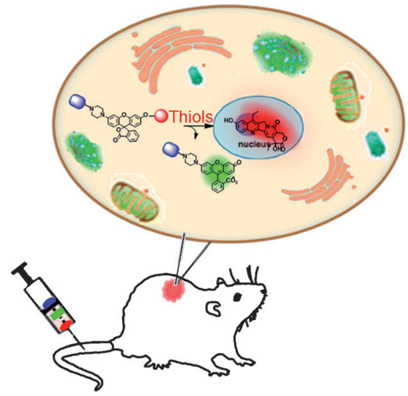
Red hot: A photo-annealing approach was developed for building functional polymer layers on paper. Conducting polyaniline that can undergo photothermal conversion can be readily annealed by near-infrared light. The porous structure is retained in the annealed polymer but it becomes insulating and hydrophobic. Selective photo-annealing produces a functional layer with patterned conductive arrays, which exhibits real-time response to ammonia gas.

Drug Delivery

S. Bhuniya, S. Maiti, E. J. Kim, H. Lee,
J. L. Sessler,* K. S. Hong,*
J. S. Kim* ______________ 4469 – 4474

An Activatable Theranostic for Targeted Cancer Therapy and Imaging

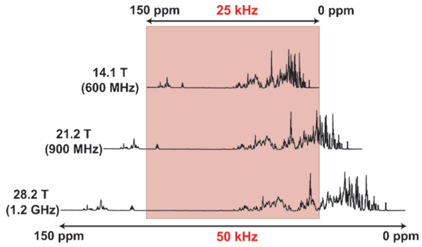
All in one: A new theranostic prodrug was developed containing a biotinylated piperazine-rhodol conjugate linked to the drug SN-38 through a self-immolative disulfide spacer. When exposed to cellular thiols in cancer cells, it is able to release the active chemotherapeutic, SN38, along with a diagnostic fluorophore. This theranostic framework permits the targeted delivery, release of an active agent (SN-38), and its facile monitoring in vitro and in vivo.



NMR Spectroscopy

F. Schilling, L. R. Warner,
N. I. Gershenzon, T. E. Skinner,*
M. Sattler,* S. J. Glaser* ___ 4475 – 4479

Next-Generation Heteronuclear Decoupling for High-Field Biomolecular NMR Spectroscopy

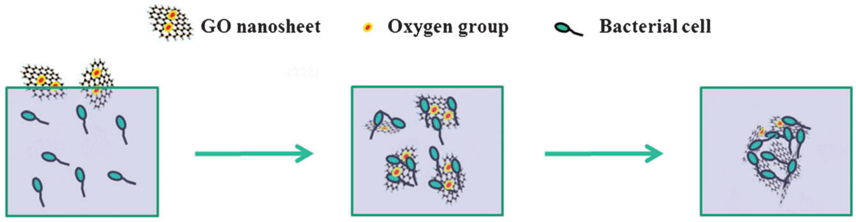


Availability of ultra-high magnetic fields in NMR spectroscopy requires increased bandwidth for heteronuclear decoupling. While composite pulse decoupling is limited in the achievable bandwidth, adiabatic pulse decoupling is compromised by sideband artifacts. A novel low-power decoupling pulse that achieves broadband uniform sideband suppression (BUSS) is reported.

Electroactive Biofilms

Y. C. Yong, Y. Y. Yu, X. Zhang,
H. Song* ______________ 4480 – 4483

Highly Active Bidirectional Electron Transfer by a Self-Assembled Electroactive Reduced-Graphene-Oxide-Hybridized Biofilm

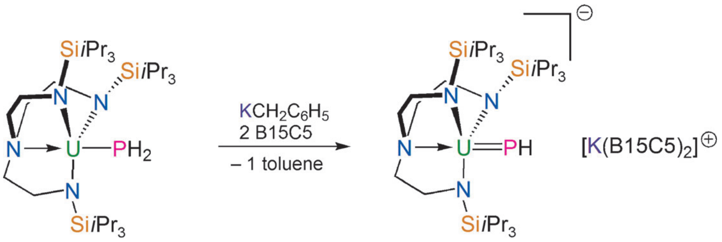


Shocking bacteria! The title biofilm was constructed by the one-step in situ bioreduction and self-assembly of graphene oxide (GO) with *Shewanella oneidensis*. The resulting 3D macroporous rGO/bacteria hybrid biofilm gave a 25-fold increase in maximum oxidation current in microbial fuel cells, and a 74-fold increase in reduction current in microbial electrosynthesis over that of the naturally occurring biofilms.

Metal Phosphinidenes

B. M. Gardner, G. Balázs, M. Scheer,*
F. Tuna, E. J. L. McInnes, J. McMaster,
W. Lewis, A. J. Blake,
S. T. Liddle* ________ **4484 – 4488**

Triamidoamine–Uranium(IV)-Stabilized Terminal Parent Phosphide and Phosphinidene Complexes



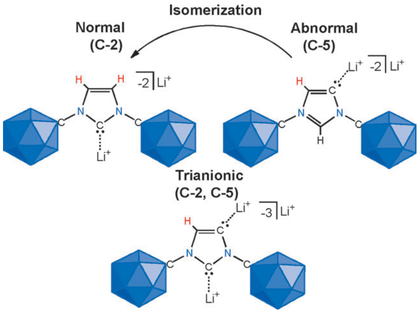
Straightforward deprotonation of the first f-block terminal parent phosphide complex and potassium abstraction results in the isolation of an unprecedented structurally authenticated metal-stabilized terminal parent phosphinidene complex. B15C5 = benzo-15-crown-5 ether.

N-Heterocyclic Carbenes

A. El-Hellani, V. Lavallo* ___ **4489 – 4493**

Fusing N-Heterocyclic Carbenes with Carborane Anions

Three in one: A novel family of polyanionic N-heterocyclic carbene–lithium adducts are reported, that feature two N-bonded weakly coordinating carborane anions. Judicious choice of base allows the selective deprotonation of an anionic imidazolium to form either a normal C2 or an abnormal C5 imidazolylidene. When treated with *n*BuLi the monoanionic imidazolium produces a doubly deprotonated trianionic C2,C5 dilithium complex.



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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