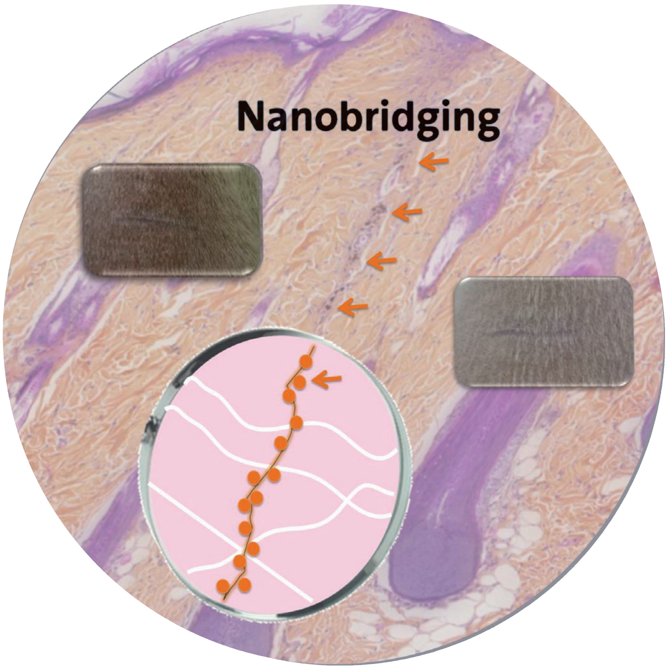
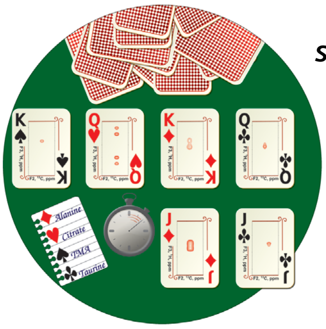
Rapid and efficient repair in vivo ...



… by the concept of nanobridging—adhesion by aqueous solutions of nanoparticles—even under hemorrhagic conditions in soft organs, such as the liver, for which sutures are traumatic, is described by D. Letourneur, L. Leibler et al. in their Communication on page 6369 ff. The method also leads to the remarkably aesthetic healing of deep skin wounds. Nanobridging also allows medical devices to be fixed to tissues, thereby opening new avenues for surgery and regenerative medicine.

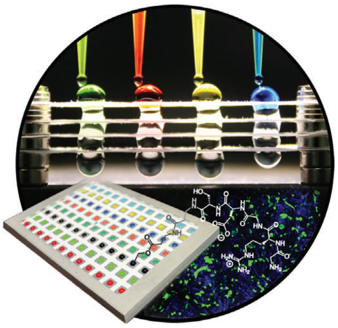
Protein Structures

B. Song, X. Gao, F. Huang et al. describe in their Communication on page 6358 ff. the ability of Al ions to induce the formation of backbone ring structures in a wide range of peptides, including neurodegenerative disease related motifs.



Sparse Sampling Techniques

In their Communication on page 6464 ff., K. Kazimierczuk et al. show how diffusion-ordered multidimensional NMR spectroscopy can be accelerated by exploiting the principles of compressed sensing.



Solid-Phase Synthesis

Teflon-patterned paper that enables the flow-through synthesis of multiple peptides in parallel is described by R. Derda and co-workers in their Communication on page 6374 ff. The resulting arrays can then be used for cell-based assays.

How to contact us:

Editorial Office:
E-mail: angewandte@wiley-vch.de
Fax: (+49) 6201–606-331
Telephone: (+49) 6201–606-315

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Courier Services:
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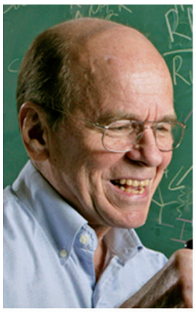
Author Profile

"My greatest achievement has been the success of my students and postdocs.
The most exciting thing about my research is the ability to move to new topics and explore exciting frontiers ..."
This and more about Joseph Wang can be found on page 6304.

News



K. B. Sharpless

E. A. Carter

J. F. Hartwig

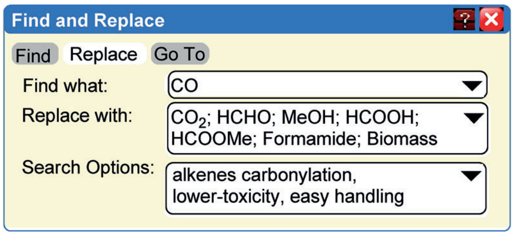
Books

Minireviews

Carbonylation

L. Wu, Q. Liu, R. Jackstell,
M. Beller* ______________ **6310 – 6320**

Carbonylations of Alkenes with CO Surrogates



Find what: CO

Replace with: CO_2; HCHO; MeOH; HCOOH; HCOOMe; Formamide; Biomass

Search Options: alkenes carbonylation, lower-toxicity, easy handling

All current industrial carbonylation processes rely on highly toxic and flammable carbon monoxide. Since these properties impede the wider use of carbonylation reactions in industry and academia, performing carbonylations with CO surrogates is highly desired and will contribute to further advances in sustainable chemistry. This Minireview summarizes the carbonylations of alkenes using different CO surrogates.

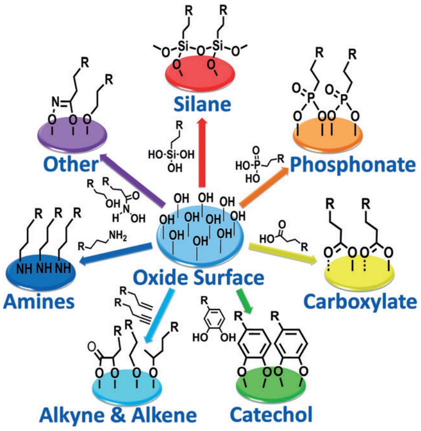
Reviews

Covalent Monolayers

S. P. Pujari, L. Scheres, A. T. M. Marcelis,
H. Zuilhof* ______________ **6322 – 6356**

Covalent Surface Modification of Oxide Surfaces

Not just scratching the surface: Covalently attached monolayers on oxide surfaces are reviewed with an eye to improved robustness, increased functionalization, understanding structural details, and the resulting potential for applications. Such monolayers, provided they are robust enough, provide a way of improving the properties of the bulk oxide material.

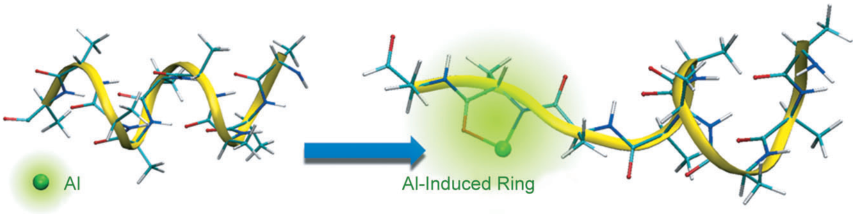


Communications

Protein Structures

B. Song,* Q. Sun, H. Li, B. Ge, J. S. Pan,
A. T. S. Wee, Y. Zhang, S. Huang, R. Zhou,
X. Gao,* F. Huang,*
H. Fang ______________ **6358 – 6363**

Irreversible Denaturation of Proteins through Aluminum-Induced Formation of Backbone Ring Structures



A good Al-rounder: Al ions can induce the formation of backbone ring structures in a wide range of peptides, including neurodegenerative disease related motifs. The rings are formed by the Al ion forming bonds simultaneously with the amide nitrogen and carbonyl oxygen atoms on the peptide backbone, which destabilizes the protein and results in irreversible denaturation.

Frontispiece

For the USA and Canada:
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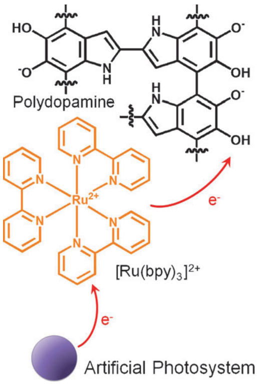


Nature as role model: Comparable to quinones that extract electrons from chlorophyll in the natural photosystem II, polydopamine (PDA) accelerates proton-coupled electron transfer and enables efficient charge separation of $[Ru(bpy)_3]^{2+}$. The introduction of PDA as an electron gate as well as a versatile adhesive significantly increases the efficiency of photochemical water oxidation.

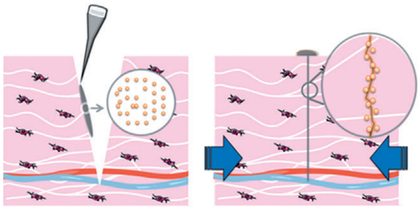
Biomimetic Materials

J. H. Kim, M. Lee,
C. B. Park* ——— **6364 – 6368**

Polydopamine as a Biomimetic Electron Gate for Artificial Photosynthesis

Inside Cover

Nanobridging is obtained by spreading a drop of aqueous nanoparticle solution on a wound edge and bringing edges into contact. In less than a minute, a strong closure and hemostasis can be achieved even within a wet and dynamic environment. Nanoparticle solutions can be also used to attach medical devices to organs.



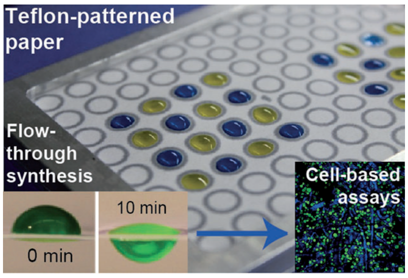
Organ Repair

A. Meddahi-Pellé, A. Legrand,
A. Marcellan, L. Louedec, D. Letourneur,*
L. Leibler* ——— **6369 – 6373**

Organ Repair, Hemostasis, and In Vivo Bonding of Medical Devices by Aqueous Solutions of Nanoparticles

Front Cover

On the same page: The patterned deposition of Teflon on paper creates barriers resistant to organic solvents. The solvents confined by the pattern flow through the paper at a controlled flow-rate, which permits the flow-through synthesis of 96 peptides in parallel on one sheet of paper. The resulting peptide arrays can be used to perform cell-based assays and discover 3D materials that support cell adhesion and growth.



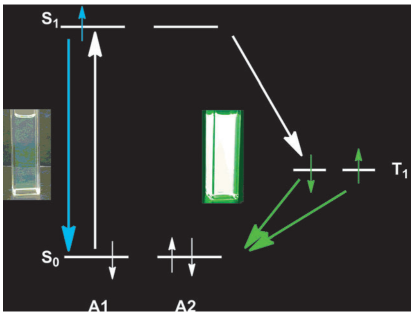
Solid-Phase Synthesis

F. Deiss, W. L. Matochko,
N. Govindasamy, E. Y. Lin,
R. Derda* ——— **6374 – 6377**

Flow-Through Synthesis on Teflon-Patterned Paper To Produce Peptide Arrays for Cell-Based Assays

Back Cover

By taking advantage of the singlet fission process highly efficient phosphorescent emitters based on metal- and heavy atom-free boron compounds were synthesized. The combination of a suitable molecular scaffold and appropriate electronic properties of the substituents was utilized to tailor the phosphorescence emission properties in solution, neat solid, and in doped PMMA films.

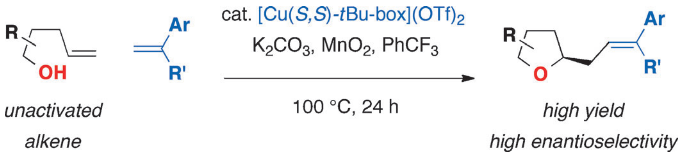


Organic Phosphorescence

M. Koch, K. Perumal, O. Blacque,
J. A. Garg, R. Saiganesh, S. Kabilan,
K. K. Balasubramanian,
K. Venkatesan* ——— **6378 – 6382**

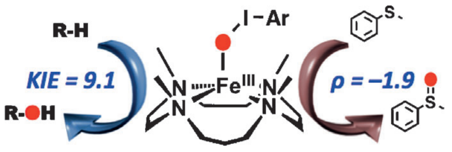
Metal-Free Triplet Phosphors with High Emission Efficiency and High Tunability

Asymmetric Catalysis



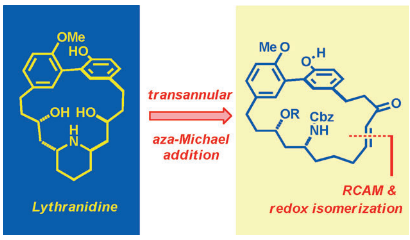
A general scheme: A highly enantioselective copper-catalyzed carboetherification of 4-pentenols has been developed. Both intramolecular (formal C–H functionalization) and intermolecular (net alkyl Heck-type coupling; see scheme) C–C bond formation can occur, thus forming a range of chiral functionalized tetrahydrofurans. DFT transition-state calculations provide a rationale for the observed asymmetric induction.

Enzyme Models



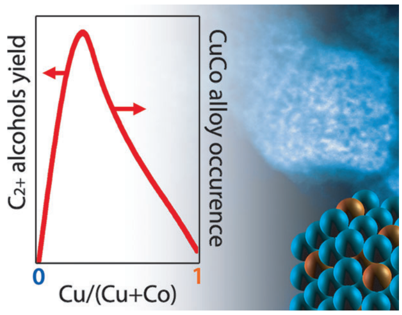
An iron boost: High-spin iron(III) iodosylarene complexes bearing an N-methylated cyclam ligand are prepared. The nonheme high-spin iron(III) iodosylarene intermediates are highly reactive oxidants capable of activating strong C–H bonds of alkanes. The electrophilic character of the iron(III) iodosylarene complexes is demonstrated in sulfoxidation reactions.

Natural Products

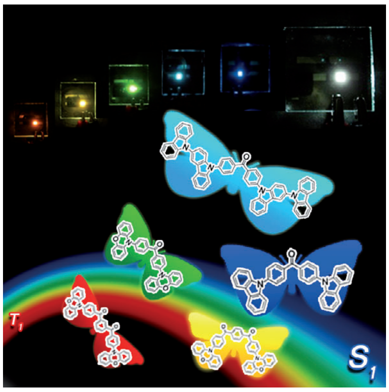


Triple: The distinguishing piperidine-metacyclophane framework of the *Lythraceum* alkaloid lythanidine was formed by ring-closing alkyne metathesis (RCAM) of a propargylic alcohol derivative followed by redox isomerization and a proton-catalyzed transannular aza-Michael addition as the key steps. This straightforward approach illustrates the enabling power of catalytic alkyne chemistry for target-oriented synthesis.

Heterogeneous Catalysis



Coupling DFT simulations, microkinetic modeling and synthesis tools allowed the development of supported CuCo bimetallic nanoparticles as highly efficient catalysts for the selective conversion of synthesis gas $(CO + H_2)$ into ethanol and longer-chain alcohols. As predicted by theory, maximizing the contribution from mixed Cu–Co sites, while preventing Cu phase segregation, results in superior yields to high alcohols.

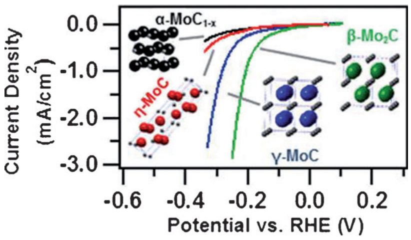


Lighting up: Butterfly-shaped benzophenone derivatives with small excited singlet–triplet energy gaps are demonstrated to exhibit efficient full-color delayed fluorescence. Organic light-emitting diodes employing these benzophenones as emitters can generate electroluminescence across most of the color gamut range, including white.

Hyperfluorescence

S. Y. Lee, T. Yasuda,* Y. S. Yang, Q. Zhang, C. Adachi* ______ **6402 – 6406**

Luminous Butterflies: Efficient Exciton Harvesting by Benzophenone Derivatives for Full-Color Delayed Fluorescence OLEDs

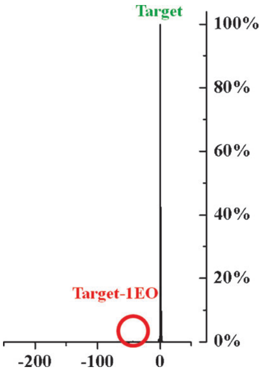


Four phases of Mo-C, including γ-MoC which was stabilized for the first time as a nanomaterial, were synthesized and investigated for their catalytic activity and stability in the hydrogen evolution reaction (HER). X-ray photoelectron spectroscopy and valence band studies were also conducted for the first time on γ-MoC.

Nanocarbide Catalysts

C. Wan, Y. N. Regmi, B. M. Leonard* ______ **6407 – 6410**

Multiple Phases of Molybdenum Carbide as Electrocatalysts for the Hydrogen Evolution Reaction

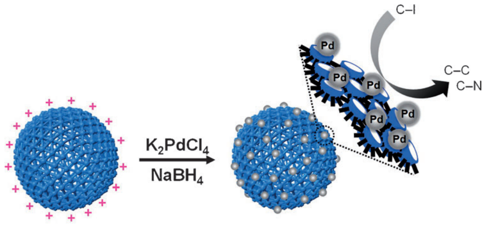


Counting mers: Poly(ethylene oxide) (PEO) is one of the most widely used polymers, but polydispersity hinders establishing its structure–property relationships. A synthetic procedure that provides PEO with an unprecedented low level of dispersity is reported. In addition a mass spectrometric method is presented to measure such low dispersity.

Monodispersed Polymers

K. Maranski, Y. G. Andreev, P. G. Bruce* ______ **6411 – 6413**

Synthesis of Poly(ethylene oxide) Approaching Monodispersity



Desirable tailoring: Hollow polymer nanocapsules (PNs) made of cucurbit[6]uril (CB) serve as a versatile platform since various metal nanoparticles (NPs) can be introduced on the surface. They allow for a controlled synthesis, prevent self-aggregation, and provide high stability and dispersibility. Pd@CB-PNs show outstanding properties as heterogeneous catalysts in C–C and C–N bond-forming reactions in water.

Metal Nanoparticles

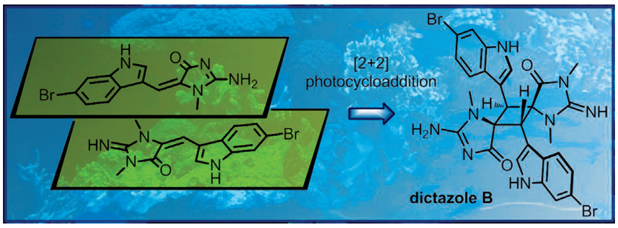
G. Yun, Z. Hassan, J. Lee, J. Kim, N.-S. Lee, N. H. Kim, K. Baek, I. Hwang, C. G. Park, K. Kim* ______ **6414 – 6418**

Highly Stable, Water-Dispersible Metal-Nanoparticle-Decorated Polymer Nanocapsules and Their Catalytic Applications

Biomimetic Synthesis

A. Skiredj, M. A. Beniddir, D. Joseph, K. Leblanc, G. Bernadat, L. Evanno,* E. Poupon* ______ **6419 – 6424**

Spontaneous Biomimetic Formation of (±)-Dictazole B under Irradiation with Artificial Sunlight

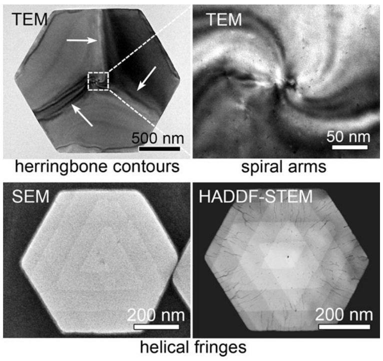


Always the sun? Biosynthetic considerations guided the first total synthesis of dictazole B. Furthermore, insights into the biosynthetic pathway towards the aplysinopsin family were gained, and an easy access to challenging cyclobutane alkaloids of marine origin, which are often postulated to be biosynthetic precursors of more complex structures, was developed.

Nanocrystal Growth

A. Zhuang, J.-J. Li, Y.-C. Wang, X. Wen, Y. Lin, B. Xiang, X. Wang, J. Zeng* ______ **6425 – 6429**

Screw-Dislocation-Driven Bidirectional Spiral Growth of Bi_2Se_3 Nanoplates

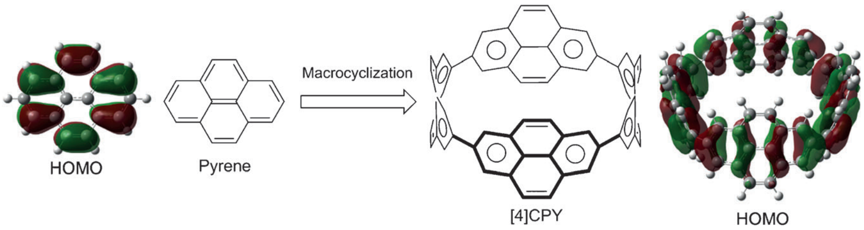


Interesting faces with chiseled features: No longer limited to nanoribbons and smooth nanoplates, Bi_2Se_3 nanostructures in the form of spiral-type nanoplates with a bipyramid-like shape characterized by two sets of centrosymmetric helical fringes on the top and bottom faces were formed by a bidirectional growth process. Other evidence for the unique structure and growth mode include herringbone contours, spiral arms, and hollow cores (see picture).

Nanostructures

T. Iwamoto, E. Kayahara, N. Yasuda, T. Suzuki, S. Yamago* ______ **6430 – 6434**

Synthesis, Characterization, and Properties of [4]Cyclo-2,7-pyrenylene: Effects of Cyclic Structure on the Electronic Properties of Pyrene Oligomers

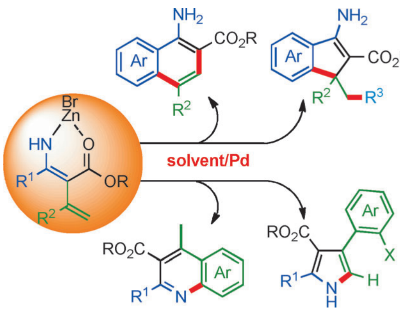


Changing the landscape: A cyclic tetramer of pyrene, [4]cyclo-2,7-pyrenylene ([4]CPY), was synthesized by the platinum-mediated cyclotetramerization and subsequent dehydrogenation. DFT calculations and electrochemical analyses showed that the electronic structure of [4]CPY was completely altered from that of pyrene and linear oligopyrenes. The results clearly show there is modulation of the topology of molecular orbitals upon formation of a cyclic structure.

Tandem Reactions

J. H. Kim, J. Bouffard, S.-g. Lee* ______ **6435 – 6438**

Formation of Four Different Aromatic Scaffolds from Nitriles through Tandem Divergent Catalysis

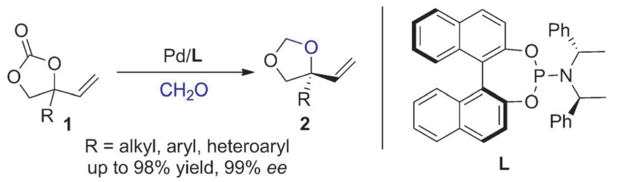


Four roads diverged: A zinc bromide complex, generated by the sequential reaction of nitriles with a Reformatsky reagent and 1-alkynes, is used as an intermediate for divergent palladium-catalyzed reactions. The reaction pathway depends on the choice of reaction solvents and palladium catalysts. The method provides a simple and efficient approach to four different frameworks starting from readily available nitriles.

Asymmetric Catalysis

A. Khan, R. Zheng, Y. Kan, J. Ye, J. Xing, Y. J. Zhang* **6439 – 6442**

Palladium-Catalyzed Decarboxylative Cycloaddition of Vinylethylene Carbonates with Formaldehyde: Enantioselective Construction of Tertiary Vinylglycols

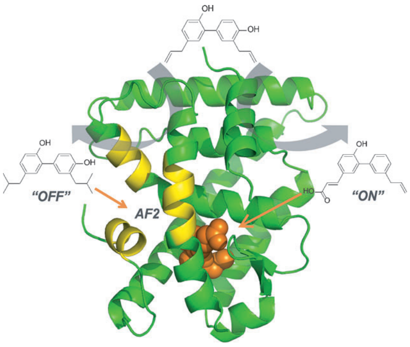


A Pd complex: An efficient method for the enantioselective construction of tertiary vinylglycols by the title reaction was developed. The palladium complex generated from $[Pd_2(dba)_3]\cdot CHCl_3$ and **L** catalyzes the cycloaddition under mild reaction conditions, thus converting racemic **1** into the corresponding 1,3-dioxolanes **2** in high yields with good to excellent enantioselectivities. dba = dibenzylideneacetone.

Protein–Protein Interactions

M. Scheepstra, L. Nieto, A. K. H. Hirsch, S. Fuchs, S. Leysen, C. V. Lam, L. in het Panhuis, C. A. A. van Boeckel, H. Wienk, R. Boelens, C. Ottmann, L.-G. Milroy,* L. Brunsveld* **6443 – 6448**

A Natural-Product Switch for a Dynamic Protein Interface

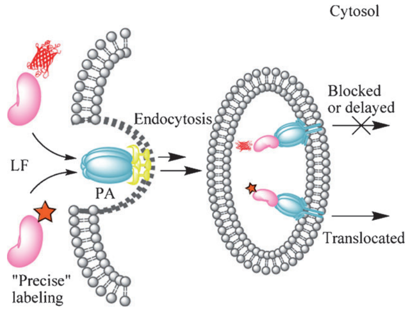


Rational splitting of the dual-binding properties of a natural product delivers two mechanistically different ligands, which selectively target opposite sides of a dynamic protein interface (see picture; AF2 = activation function 2). This work highlights the value of screening natural products against transient protein complexes.

Protein Labeling

S. Zheng, G. Zhang, J. Li, P. R. Chen* **6449 – 6453**

Monitoring Endocytic Trafficking of Anthrax Lethal Factor by Precise and Quantitative Protein Labeling

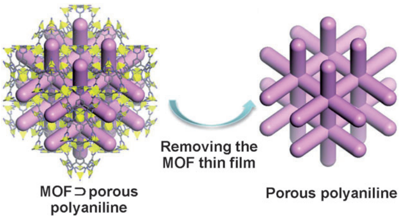


Visualizing toxin trafficking: Coupling the genetic-code expansion strategy with bioorthogonal reactions allowed site-specific fluorescent labeling of anthrax lethal factor (LF) with little perturbation to its native structure and function. Time-lapse visualization of the endocytic trafficking of a precisely labeled LF revealed molecular details underlying its virulence mechanism inside host cells. PA = protective antigen.

Conductive Polymers

C. J. Lu, T. Ben,* S. X. Xu, S. L. Qiu* **6454 – 6458**

Electrochemical Synthesis of a Microporous Conductive Polymer Based on a Metal–Organic Framework Thin Film

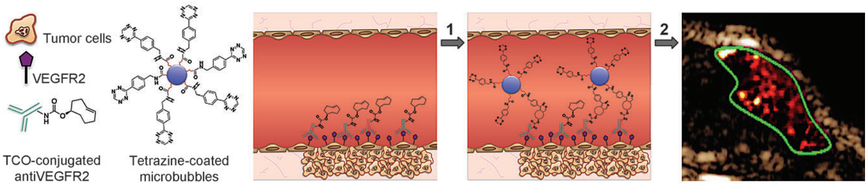


A 3D microporous conductive polymer has been achieved in the electrochemical synthesis of a porous polyaniline network with a MOF thin film. The prepared microporous polyaniline with well-defined uniform micropores of 0.84 nm exhibits a high BET surface area of 986 $m^2\,g^{-1}$ and a high electric conductivity of 0.125 $S\,cm^{-1}$ when doped with I_2.

Imaging Agents

A. Zlitni, N. Janzen, F. S. Foster,
J. F. Valliant* ———— **6459 – 6463**

Catching Bubbles: Targeting Ultrasound Microbubbles Using Bioorthogonal Inverse-Electron-Demand Diels–Alder Reactions



Catching bubbles: Tetrazine-functionalized microbubbles were prepared for use as ultrasound contrast agents, and shown to selectively localize on cells labeled with a TCO-derivatized antibody against VEGFR2. This capture approach based on labeling and bioorthogonal chemistry was validated in a flow-chamber assay and in vivo through ultrasound imaging of VEGFR2-positive and VEGFR2-negative murine tumor models. TCO = *trans*-cyclooctene.

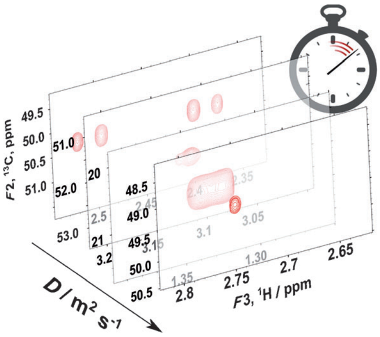
Sparse Sampling Techniques

M. Urbańczyk, W. Koźmiński,
K. Kazimierczuk* ———— **6464 – 6467**

Accelerating Diffusion-Ordered NMR Spectroscopy by Joint Sparse Sampling of Diffusion and Time Dimensions

Inside Back Cover

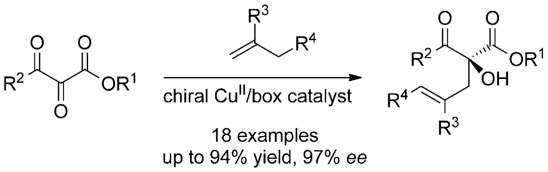
Diffusion-ordered multidimensional NMR spectroscopy is a valuable technique for the analysis of complex mixtures, but the sampling of a multidimensional signal can be very time-consuming. Various sparse sampling techniques have been proposed to accelerate the measurement, but they have always been limited to frequency dimensions of NMR spectra. It is now revealed how sparse sampling can be extended to diffusion dimensions.



Asymmetric Catalysis

P. M. Truong, P. Y. Zavalij,
M. P. Doyle* ———— **6468 – 6472**

Highly Enantioselective Carbonyl–Ene Reactions of 2,3-Diketoesters: Efficient and Atom-Economical Process to Functionalized Chiral α-Hydroxy-β-Ketoesters



Outside the box: Carbonyl–ene reactions of 2,3-diketoesters, catalyzed by [Cu{(*S*,*S*)-*t*Bu-box}](SbF$_6$)$_2$ [box = bis(oxazoline)], generate chiral α-functionalized α-hydroxy-β-ketoesters in up to 94 % yield and 97 % *ee*. The 2,3-diketoesters are conveniently accessed from the corresponding α-diazo-β-ketoester, and a catalyst loading as low as 1.0 mol % can be used.

Phase-Transfer Catalysis

H. Dang, M. Mailig,
G. Lalic* ———— **6473 – 6476**

Mild Copper-Catalyzed Fluorination of Alkyl Triflates with Potassium Fluoride

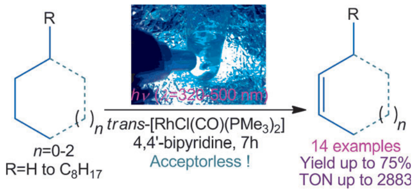
$$\text{R–OTf} + \text{KF}_{(s)} \xrightarrow[\text{1,4-dioxane, 45 °C, 1 h}]{\text{[IPrCuOTf] (2 mol \%)}} \text{R–F} \quad \begin{array}{c}\text{>80\% yield}\\ \text{(20 examples)}\end{array}$$

Teacher's PET: The title reaction delivers excellent yields of the desired alkyl fluorides by using potassium fluoride as a fluoride source in the presence of the copper catalyst [IPrCuOTf]. This procedure is potentially suited for the preparation of ^{18}F-labeled PET probes. IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, Tf = trifluoromethanesulfonyl.

Photocatalysis

A. D. Chowdhury, N. Weding, J. Julis, R. Franke, R. Jackstell, M. Beller* ——— 6477–6481

Towards a Practical Development of Light-Driven Acceptorless Alkane Dehydrogenation

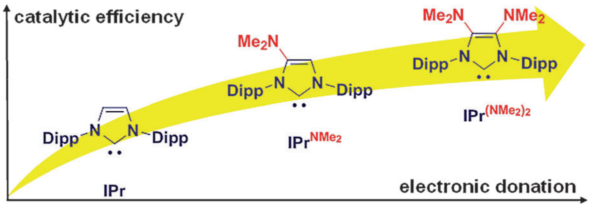


Blue (light) is green: The efficient light-induced atom-economical alkane dehydrogenation of various linear and cyclic alkanes (including shale gas constituents and liquid organic hydrogen carriers) was accomplished using *trans*-[Rh(PMe_3)$_2$(CO)Cl] as a catalyst in the presence of a specific nitrogenous additive. It provides a benign alternative to the direct use of alkanes as olefin feedstocks.

Carbene Chemistry

Y. Zhang, V. César,* G. Storch, N. Lugan, G. Lavigne* ——— 6482–6486

Skeleton Decoration of NHCs by Amino Groups and its Sequential Booster Effect on the Palladium-Catalyzed Buchwald–Hartwig Amination

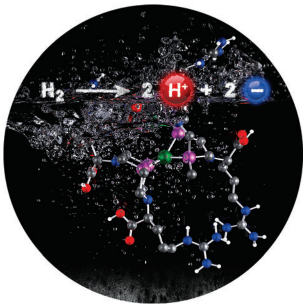


Boosting the PEPPSI: A sequential enhancement of the activity of the PEPPSI NHC-based palladium pre-catalyst in the Buchwald–Hartwig amination was obtained by a rational modification of its standard N-heterocyclic carbene (IMes or IPr), consisting of a "simple" incorporation of one, and then two, dimethylamino groups as substituents. These results highlight the valuable benefits of NHC-skeleton decoration in C–N cross-coupling.

Bioinspired Catalysts

A. Dutta, J. A. S. Roberts,* W. J. Shaw* ——— 6487–6491

Arginine-Containing Ligands Enhance H_2 Oxidation Catalyst Performance

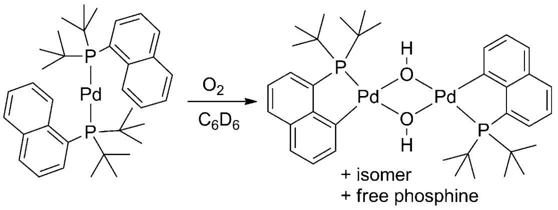


Learning from nature: An amino acid-based outer coordination sphere results in the homogeneous [Ni($P^{Cy}_2N^{Arg}_2$)]$^{8+}$ complex that can electrochemically oxidize H_2 in water with a turnover frequency of 210 s^{-1} at acidic pH. The outer coordination sphere improves the H_2 addition and H^+ movement from the active center.

O_2-Promoted C–H Activation

M. L. Scheuermann, D. W. Boyce, K. A. Grice, W. Kaminsky, S. Stoll, W. B. Tolman, O. Swang, K. I. Goldberg* ——— 6492–6495

Oxygen-Promoted C–H Bond Activation at Palladium

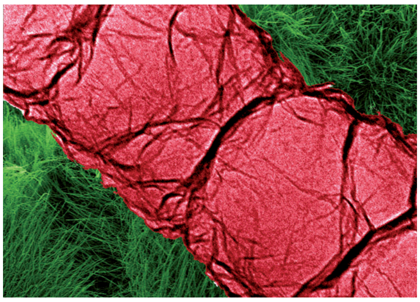


Oxygen leads the way: [Pd(P(Ar)(*t*Bu)$_2$)$_2$] (Ar = naphthyl) undergoes a reaction with molecular oxygen in which C–H and O–O bonds are cleaved. Observation of the reaction at low temperature suggests the initial formation of a superoxo complex, which then generates a peroxo complex prior to the C–H activation step. The transition state for an energetically viable C–H activation across a Pd–peroxo bond was located computationally.

Carbon Nanomaterials

Z. Wen, S. Ci, Y. Hou, J. Chen* ________ 6496 – 6500

Facile One-Pot, One-Step Synthesis of a Carbon Nanoarchitecture for an Advanced Multifunctonal Electrocatalyst

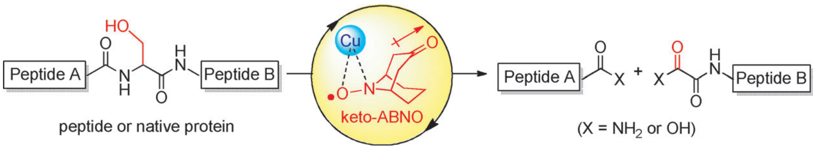


Not ones to laze about on the lawn, nitrogen-doped graphene/carbon-nanotube (CNT) hybrids showed high electrocatalytic activity for a series of important electrochemical reactions as a result of nitrogen doping and their unique structure with the graphene nanosheets entrapped in the inner void of the CNTs. The hybrids were prepared by a facile low-cost method from solid-phase sources with high efficiency.

Peptide Bond Cleavage

Y. Seki, K. Tanabe, D. Sasaki, Y. Sohma, K. Oisaki,* M. Kanai* ________ 6501 – 6505

Serine-Selective Aerobic Cleavage of Peptides and a Protein Using a Water-Soluble Copper–Organoradical Conjugate

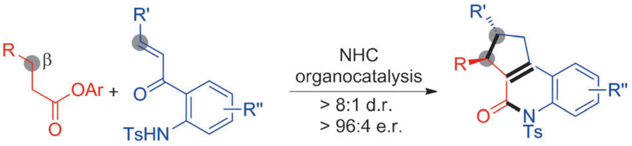


Peptides and proteins can be cleaved selectively at serine residues under mild (room temperature, near neutral pH value) aerobic conditions by a water-soluble copper–organoradical conjugate. The method is applicable to the site-selective cleavage of polypeptides that possess various functional groups, D-amino acids, or sensitive disulfide pairs. The system was also used for the site-selective cleavage of a native protein comprising more than 70 amino acid residues.

Heterocycles

Z. Fu, K. Jiang, T. Zhu, J. Torres, Y. R. Chi* ________ 6506 – 6510

Access to Oxoquinoline Heterocycles by N-Heterocyclic Carbene Catalyzed Ester Activation for Selective Reaction with an Enone

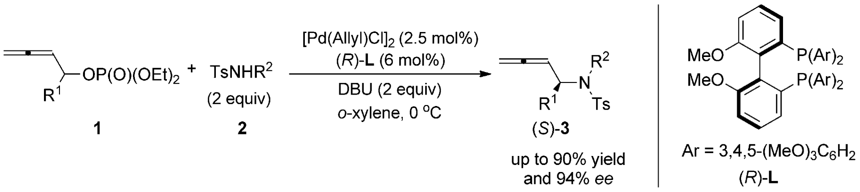


Under construction: A single-step enantioselective access to multicyclic oxoquinoline-type heterocycles is possible. The process takes advantage of the unique reaction patterns of esters under N-heterocyclic carbene (NHC) catalysis. It involves activation of the β-carbon atom of an ester as the key step with a subsequent chemoselective cascade reaction with amino enone substrates. Ts = 4-toluenesulfonyl.

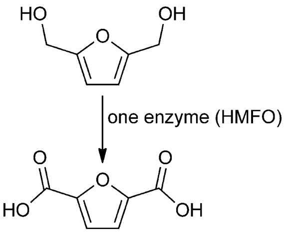
Asymmetric Catalysis

Q. Li, C. Fu, S. Ma* ________ 6511 – 6514

Palladium-Catalyzed Asymmetric Amination of Allenyl Phosphates: Enantioselective Synthesis of Allenes with an Additional Unsaturated Unit



Chiral 2,3-allenyl amines with or without (an) additional C–C double or triple bond(s) can be prepared through asymmetric Pd-catalyzed amination of allenyl phosphates. Under the optimized conditions, which involve the use of (*R*)-3,4,5-(MeO)$_3$-MeOBIPHEP as the ligand and the reaction being performed at 0 °C, the products were obtained with up to 90 % yield and 88–94 % *ee*.



A fourpeat: The recently discovered 5-hydroxymethylfurfural oxidase (HMFO) was found to perform a quadruple oxidation of [5-(hydroxymethyl)furan-2-yl]methanol (see scheme). The biocatalyst can also be used to convert 5-hydroxymethylfurfural into furan-2,5-dicarboxylic acid, thus providing a biobased platform chemical for the production of polymers. The oxidase acts on alcohol groups only and therefore depends on the hydration of aldehyde groups.

Biocatalysis

W. P. Dijkman, D. E. Groothuis,
M. W. Fraaije* ____________ **6515 – 6518**

Enzyme-Catalyzed Oxidation of 5-Hydroxymethylfurfural to Furan-2,5-dicarboxylic Acid

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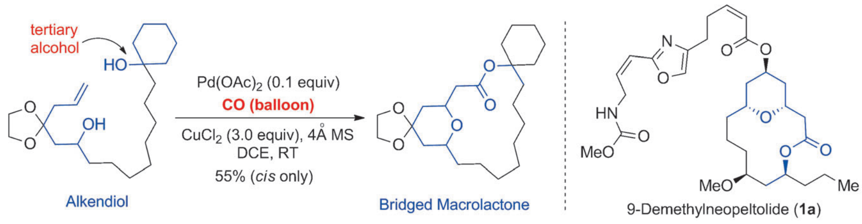

CO for bridged macrolides: An efficient Pd-catalyzed cascade alkoxycarbonylative macrolactonization to synthesize various THP/THF-containing macrolactones in one step from relatively simple alkendiols is possible. Challenging macrolactones involving tertiary alcohols were synthesized smoothly as well. The method was applied to the synthesis of the potent anticancer compound 9-demethylneopeltolide.

Macrolide Synthesis

Y. Bai, D. C. Davis, M. Dai* **6519 – 6522**

Synthesis of Tetrahydropyran/Tetrahydrofuran-Containing Macrolides by Palladium-Catalyzed Alkoxycarbonylative Macrolactonizations

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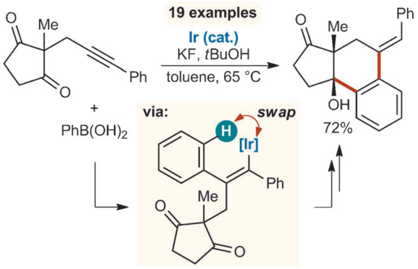
Migrating to iridium: Iridium catalysis enables the arylative cyclization of alkynones with arylboronic acids to give complex polycycles with high stereoselectivities. These reactions involve the first reported examples of 1,4-iridium migration.



C–H Activation

B. M. Partridge, J. Solana González,
H. W. Lam* ____________ **6523 – 6527**

Iridium-Catalyzed Arylative Cyclization of Alkynones by 1,4-Iridium Migration

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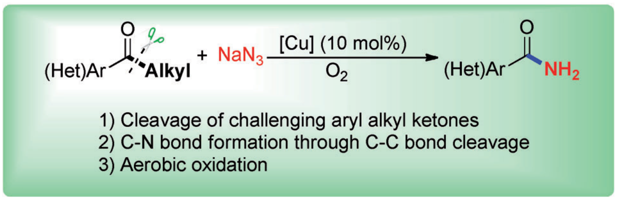


1) Cleavage of challenging aryl alkyl ketones
2) C-N bond formation through C-C bond cleavage
3) Aerobic oxidation

A copper-catalyzed aerobic oxidative C(CO)–C(alkyl) bond cleavage of aryl alkyl ketones for C–N bond formation proceeds with high chemoselectivity. A series of acetophenone derivatives as well as more challenging aryl ketones with long-chain alkyl groups could be cleaved efficiently to give the corresponding amides, which are frequently found in biologically active compounds and pharmaceuticals.

C–C Bond Cleavage

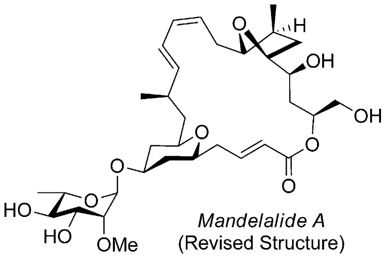
C. Tang, N. Jiao* ____________ **6528 – 6532**

Copper-Catalyzed Aerobic Oxidative C–C Bond Cleavage for C–N Bond Formation: From Ketones to Amides

Total Synthesis

H. Lei, J. Yan, J. Yu, Y. Liu, Z. Wang,
Z. S. Xu,* T. Ye* ____________ **6533 – 6537**

Total Synthesis and Stereochemical Reassignment of Mandelalide A



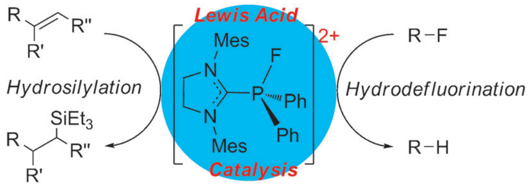
Mandelalide A
(Revised Structure)

Structural revision: A revised configurational assignment for the marine macrolide mandelalide A is proposed and validated by total synthesis. This study is one of several recent examples in a growing list of investigations that correct misassigned structures of natural products by stereocontrolled total synthesis.

P Dication

M. H. Holthausen, M. Mehta,
D. W. Stephan* ____________ **6538 – 6541**

The Highly Lewis Acidic Dicationic Phosphonium Salt: [(SIMes)PFPh$_2$][B(C$_6$F$_5$)$_4$]$_2$

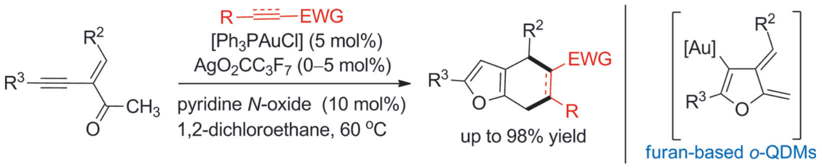


Versatile phosphonium salt: The dication [(SIMes)PFPh$_2$][B(C$_6$F$_5$)$_4$]$_2$ is prepared by oxidation of an NHC-derived cationic phosphine followed by fluoride abstraction. This species exhibits remarkable Lewis acidity in stoichiometric reactions as well as in Lewis acid catalysis of hydrodefluorination of fluoroalkanes and the hydrosilylation of olefins and acetylenes.

Heterocycle Synthesis

L. Zhou, M. Zhang, W. Li,
J. Zhang* ____________ **6542 – 6545**

Furan-Based *o*-Quinodimethanes by Gold-Catalyzed Dehydrogenative Heterocyclization of 2-(1-Alkynyl)-2-alken-1-ones: A Modular Entry to 2,3-Furan-Fused Carbocycles

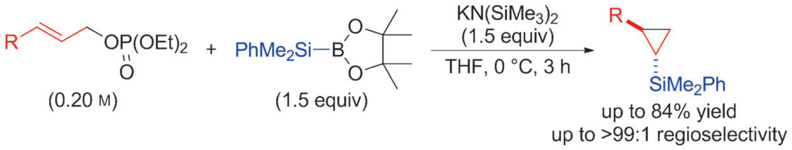


Caught in a trap: A novel strategy for in situ generation of furan-based *ortho*-quinodimethanes (*o*-QDMs) using the title reaction was developed. These furan-based *o*-QDMs were trapped by electron-deficient olefins and alkynes, thus leading to various 2,3-furan-fused carbocycles in good yields with high diastereo- and regioselectivities. EWG = electron-withdrawing group.

Small Ring Systems

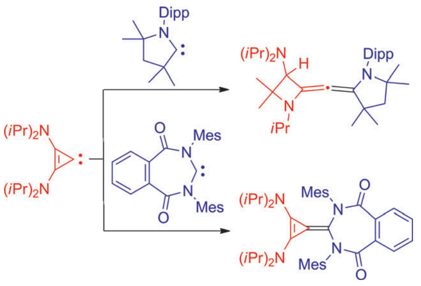
R. Shintani,* R. Fujie, M. Takeda,
K. Nozaki* ____________ **6546 – 6549**

Silylative Cyclopropanation of Allyl Phosphates with Silylboronates



β attack! A potassium-bis(trimethylsilyl)amide-mediated cyclopropanation of allyl phosphates with silylboronates has been developed. Unlike the reported copper-catalyzed allylic substitution reactions, the nucleophile selectively attacks at the β-position of the allylic substrates under the present conditions. The reaction mechanism has also been investigated, thus indicating the involvement of a silylpotassium species as the active nucleophilic component.

A couple of carbenes: By utilizing stable carbenes with low-lying LUMOs, coupling with the stable nucleophilic diaminocyclopropenylidene was achieved. This coupling resulted in the formation of two new and rare examples of a bent allene as well as the isolation of the first carbene–carbene heterodimer. Dipp = 2,6-$iPr_2C_6H_3$, Mes = 2,4,6-$Me_3C_6H_2$.

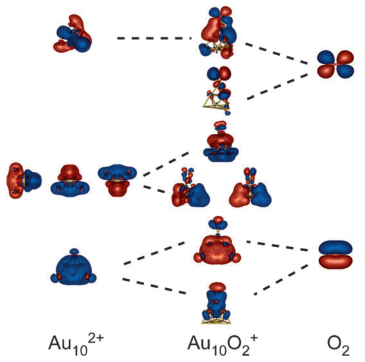


Dimerization

C. M. Weinstein, C. D. Martin, L. Liu, G. Bertrand* ———— 6550–6553

Cross-Coupling Reactions between Stable Carbenes

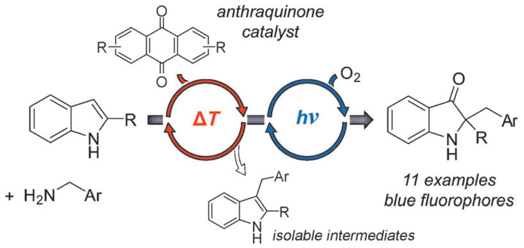
Act(ivat)ing positively: Cationic gold clusters are found to react with molecular oxygen and activate it by forming a superoxide (O_2^-), as confirmed by vibrational spectroscopy. This process is spontaneous in clusters, which attain a closed shell within the spherical jellium model, whereas other cluster sizes exhibit a self-promoting effect whereby the presence of multiple oxygen ligands is required for activation.



Oxygen Activation

A. P. Woodham, A. Fielicke* 6554–6557

Superoxide Formation on Isolated Cationic Gold Clusters



Orthogonal reactivities: Anthraquinone derivatives catalyze the thermal C3-alkylation of indoles with benzylamines in sequence with a visible-light-driven photooxidation/1,2-shift reaction to provide new fluorescent 2,2-disubstituted indoline-3-one derivatives. Quinones function as H_2 shuttles in the indole C3-alkylation with amines and the subsequent photooxidation of the intermediate 3-arylmethyl-1*H*-indoles is remarkably selective.

Tandem Catalysis

S. Lerch, L.-N. Unkel, M. Brasholz* ———— 6558–6562

Tandem Organocatalysis and Photocatalysis: An Anthraquinone-Catalyzed Indole-C3-Alkylation/Photooxidation/1,2-Shift Sequence

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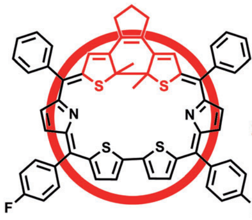
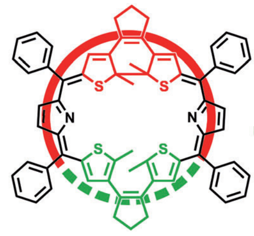


1
26 π aromatic



2
nonaromatic

Tuning aromaticity: Two stable core-modified rubyrins bearing one (**1**) and two (**2**) dithienylethene (DTE) units have been synthesized. Compound **1**, with a "closed-form" DTE unit, has a cyclic conjugated system with 26 π-electrons. In contrast, macrocycle **2** containing one "open-form" DTE unit has nonaromatic properties.

Heteroporphyrins

Z. Zhou, Y. Chang, S. Shimizu, J. Mack, C. Schütt, R. Herges, Z. Shen,* N. Kobayashi* ———— 6563–6567

Core-Modified Rubyrins Containing Dithienylethene Moieties

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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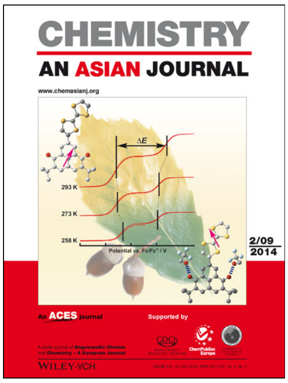

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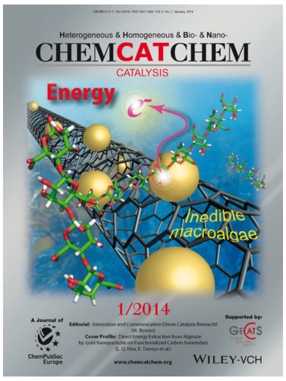

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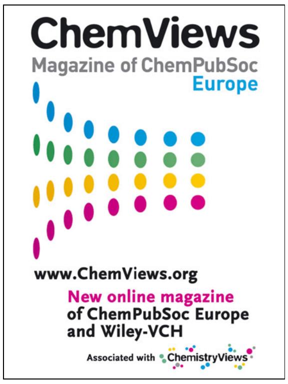

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Angewandte Corrigendum

Intact P_4 Tetrahedra as Terminal and Bridging Ligands in Neutral Complexes of Manganese

S. Heinl, E. V. Peresypkina, A. Y. Timoshkin, P. Mastrorilli, V. Gallo, M. Scheer* ———— **10887–10891**

Angew. Chem. Int. Ed. **2013**, *52*

DOI: 10.1002/anie.201303515

Figure 3 of this Communication does not show the EXSY NMR of compound **2** but that of compound **3**. The correct Figure 3 with the spectrum of compound **2** is shown below.

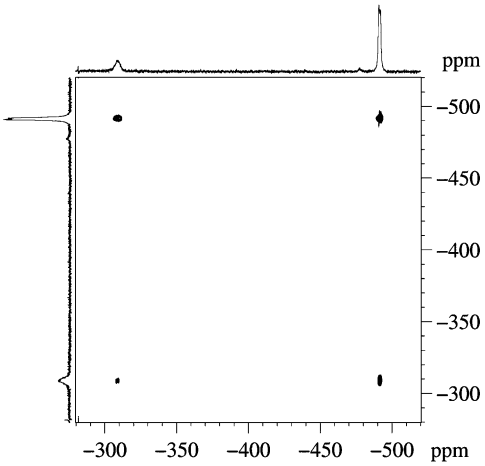

Figure 3. $^{31}P\{^1H\}$ EXSY spectrum of **2** ($[D_8]$toluene, 298 K).