The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:

*J. Lu, C. Aydin, N. D. Browning, B. C. Gates**
Imaging Gold Atom Catalytic Sites in Zeolite NaY

F. Liao, Z. Zeng, C. Eley, Q. Lu, X. Hong, S. C. E. Tsang**
Electronic Modulation of a Cu–ZnO Catalyst by Heterojunction Establishment for Selective Hydrogenation of Carbon Dioxide to Methanol

*N. Metanis, D. Hilvert**
Strategic Use of Nonnative Diselenide Bridges to Steer Oxidative Protein Folding

*S. C. S. Lai, A. N. Patel, K. McKelvey, P. R. Unwin**
Definitive Evidence for Fast Electron Transfer at Pristine Basal Plane Graphite from High-Resolution Electrochemical Imaging

*B. Esser, J. M. Schnorr, T. M. Swager**
Selective Detection of Ethylene Gas Using Carbon-Nanotube-Based Devices for the Determination of Fruit Ripeness

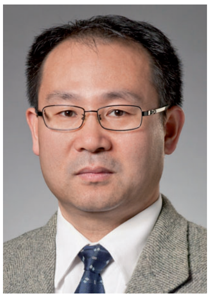
*A. Elahi, T. Fowowe, D. J. Caruana**
Dynamic Electrochemistry in Flame Plasma Electrolyte

J. Graton, Z. Wang, A.-M. Brossard, D. G. Monteiro, J.-Y. Questel, B. Linclau**
An Unexpected and Significantly Lower Hydrogen-Bond Donating Capacity of Fluorohydrins Relative to Nonfluorinated Alcohols

*M. Kessler, S. Schüler, D. Hollmann, M. Klahn, T. Beweries, A. Spannenberg, A. Brückner, U. Rosenthal**
Photoassisted Ti–O Activation in a Decamethyltitanocene Dihydroxo Complex: Insights into the Elemental Steps of Water Splitting

*T. Köchner, T. A. Engesser, H. Scherer, D. A. Plattner, A. Steffani, I. Krossing**
Positive at Last: $[P_9]^+[Al(OR^F)_4]^-$, the First Pure Phosphorus Cation Salt

Author Profile



"My favorite place on earth is my home town.
A good work day begins with a cup of Chinese tea …"
This and more about Zuowei Xie can be found on page 5037.

News

K. Kim

J. Nitschke

J. Wang

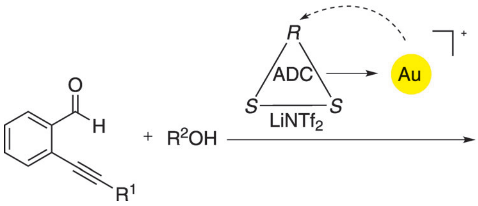
Books

Highlights

Ligand Design

H. G. Raubenheimer* ______ 5042 – 5044

Monomeric Linear Diaminocarbene Complexes of Gold(I) Show Merit in Enantioselective Catalysis

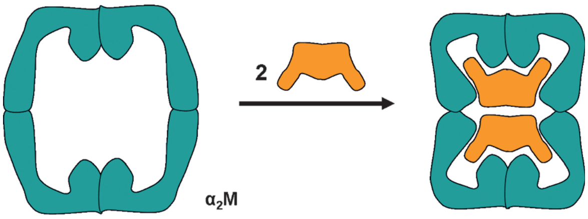


Striking gold: Rather simple aryl substituents are required to convert acyclic diaminocarbenes (ADCs) into useful pseudo-bidentate ligands for monomeric gold(I), which can enantioselectively catalyze a tandem acetylization/cycloisomerization reaction. Tf=trifluoromethanesulfonyl.

Proteinase Inhibitors

C. Meyer, W. Hinrichs,*
U. Hahn* ______ 5045 – 5047

Human α_2-Macroglobulin—Another Variation on the Venus Flytrap

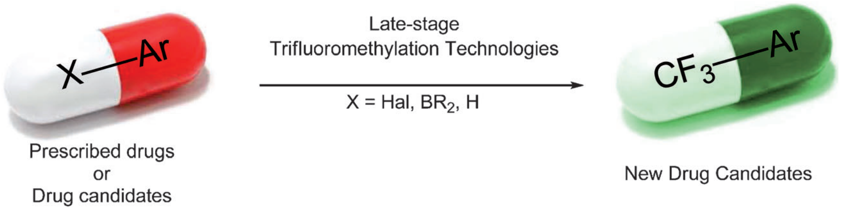


Trapping proteinases: The mechanism of the nonspecific human proteinase inhibitor α_2-macroglobulin (α_2M, about 6000 amino acid residues) is reminiscent of a Venus flytrap (see scheme). The structure of α_2M was solved recently with a resolution of 4.3 Å even though only one single crystal was available.

Trifluoromethylation

T. Besset, C. Schneider,
D. Cahard* ______ 5048 – 5050

Tamed Arene and Heteroarene Trifluoromethylation



A tri-ing transformation: The increasingly high demand for trifluoromethylated arenes and heteroarenes is a major challenge that has been addressed through the development of trifluoromethylation reactions. Several effective approaches for late-stage trifluoromethylation, as well as the use of practical and cheap trifluoromethylation reagents, are highlighted.

For the USA and Canada:
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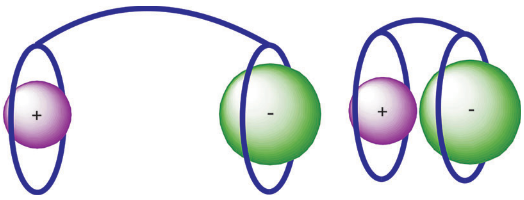
Minireviews

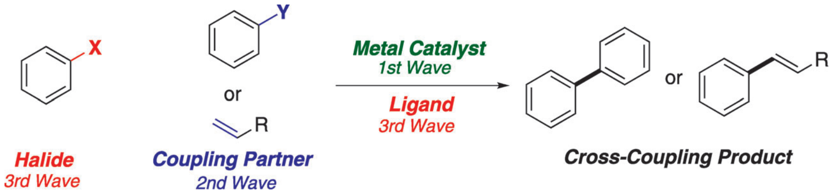
Coordination Chemistry



Paired up: Ion-pair recognition is an emerging field of research. This Minireview serves to introduce the topic by exploring the concepts behind ion-pair recognition including cooperativity and heteroditopic receptor design (see picture). The different types and applications of heteroditopic receptors for ion pairs are also discussed.

Reviews

Cross-Coupling

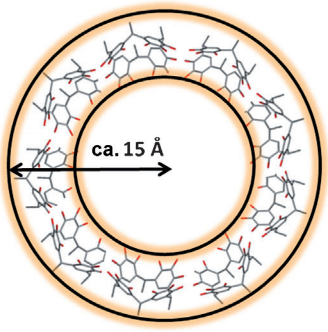


The 2010 Nobel Prize in Chemistry was awarded to Richard Heck, Ei-ichi Negishi, and Akira Suzuki for their contributions to the development of Pd-catalyzed C–C bond forming reactions. This Review traces the historical origins of the reactions these laureates discovered, and follows the three waves of research (see scheme) that led to the systematic evolution of "cross-coupling" and the resultant proliferation of discovery within the field of metal-catalyzed organic transformations to the present time.

Communications

Supramolecular Chemistry

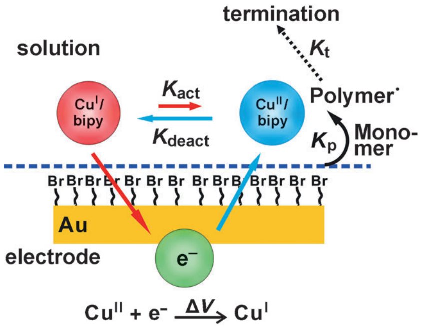
Hollow cylinders: Gallium- and gallium–zinc-seamed pyrogallol[4]arene nanoassemblies were studied in the solution phase through various methods. The results reveal their rearrangement from spheres in the solid state to toroids in solution (see, for example, PgC_4GaZn) illustrating the structural flexibility of gallium in the metal-seamed frameworks.



Frontispiece

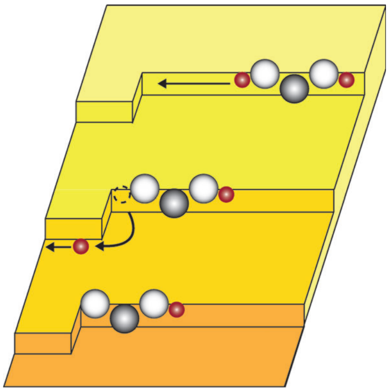
Surface Chemistry

Polymer brushes: Electrically induced atom-transfer radical polymerization allows polymer brushes to grow in air (see picture). The thickness of the brushes is controlled through the ratio of initiator and applied potential. The monomer solution can be reused, which renders this process promising for the polymerization of specialty monomers and for biocompatible polymer brushes grown on complex substrates.

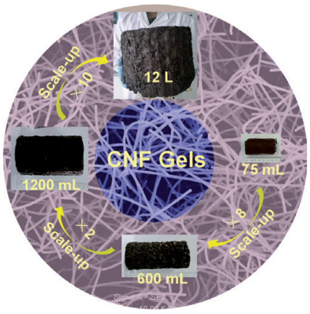


Surface Catalysis

Kinky catalysis: Surface defects, such as step edges and kinks, are thought to be the 'active sites' that induce site-specific chemical reactions on catalytic materials. The catalytic dissociation of a bromine atom from an organic molecule is shown to occur at kink sites on the stepped Au(10,7,7) surface (see scheme; Br = red). The anisotropic surface also facilitates the production of highly aligned polymers, formed by on-surface covalent coupling of monomer units.

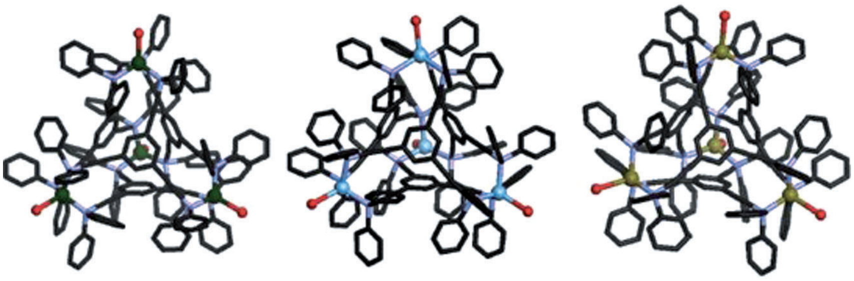


Nanofiber Gels



Robust nanofiber gels: Monolithic hydrogels and aerogels consisting of uniform carbonaceous nanofibers (CNFs) were fabricated on a macroscopic scale (12 L, see picture) by a simple template-directed, hydrothermal carbonization process. The high surface reactivity of the CNFs and high porosity and robust nature of the gels can be exploited in applications such as selective adsorbents and templates for creating functional composite gels.

Coinage-Metal Supramolecules

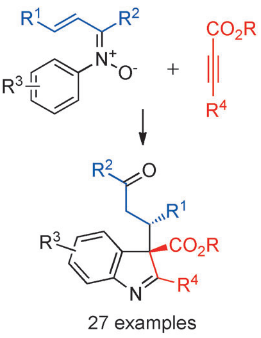


Treasure chests: The Group 11 metals Cu$^{\rm I}$, Ag$^{\rm I}$, and Au$^{\rm I}$ form tetrahedral supramolecular clusters with a rigid threefold-symmetric phosphine ligand. These supramolecular clusters, which assemble by metal–phosphine interactions, are the first to form across an entire group of the periodic table. Cu^+ green, Ag^+ pale blue, Au^+ green, I^- red, P purple.

Synthetic Methods

C. B. Huehls, T. S. Hood,
J. Yang* ______ 5110 – 5113

Diastereoselective Synthesis of C3-Quaternary Indolenines Using α,β-Unsaturated *N*-Aryl Ketonitrones and Activated Alkynes



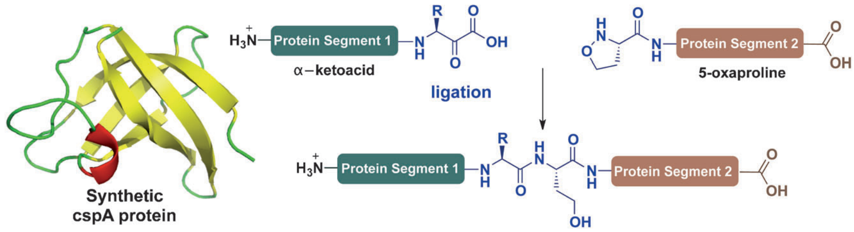
New trick for an old dog: C3-Quaternary indolenines were synthesized by combining readily available α,β-unsaturated *N*-aryl ketonitrones and activated alkynes. This remarkably simple and atom-economical transformation does not require transition-metal catalysis and involves the formation of the heterocycles with concomitant generation of two contiguous quaternary and tertiary chiral centers.

Protein Ligations

V. R. Pattabiraman, A. O. Ogunkoya,
J. W. Bode* ______ 5114 – 5118

Chemical Protein Synthesis by Chemoselective α-Ketoacid–Hydroxylamine (KAHA) Ligations with 5-Oxaproline

Front Cover



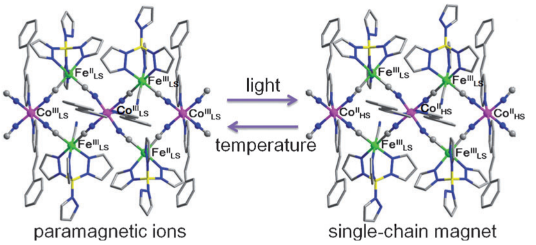
The chemical synthesis of proteins from unprotected peptide segments uses KAHA ligation with 5-oxaproline, which is incorporated readily into peptides by solid-phase peptide synthesis. Ligation of such protein segments in aqueous buffers with an α-ketoacid peptide gives an α-homoserine residue at the ligation site. The new ligation is used for the synthesis of two proteins, prokaryotic-ubiquitin like protein (Pup) and probable cold shock protein A (cspA; see scheme).

Switchable Materials

D.-P. Dong, T. Liu,* S. Kanegawa, S. Kang, O. Sato,* C. He,
C.-Y. Duan* ______ 5119 – 5123

Photoswitchable Dynamic Magnetic Relaxation in a Well-Isolated $\{Fe_2Co\}$ Double-Zigzag Chain

Inside Cover

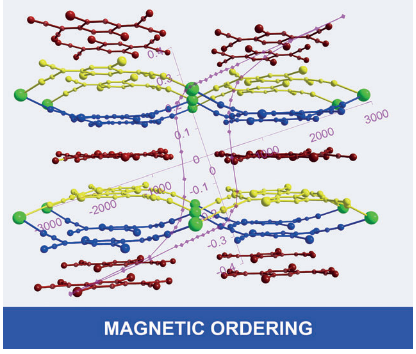


Charge-transfer-induced spin transition occurs cooperatively and reversibly in the isolated $Fe^{III}_2Co^{II}$ chains of $\{[Fe(pzTp)(CN)_3]_2Co(4\text{-styrylpyridine})_2\}\cdot 2\,H_2O\cdot 2\,CH_3OH$ (**1**). When **1** is irradiated with 532 nm light, it shows single-chain magnetic behavior with no antiferromagnetic ordering after irradiation (see picture; C gray, N blue, B yellow; LS = low spin, HS = high spin).

Cerium–Organic Magnets

M. Ballesteros-Rivas, H. Zhao, A. Prosvirin, E. W. Reinheimer, R. A. Toscano, J. Valdés-Martínez,
K. R. Dunbar* ______ 5124 – 5128

Magnetic Ordering in Self-assembled Materials Consisting of Cerium(III) Ions and the Radical Forms of 2,5-$TCNQX_2$ ($X = Cl$, Br)

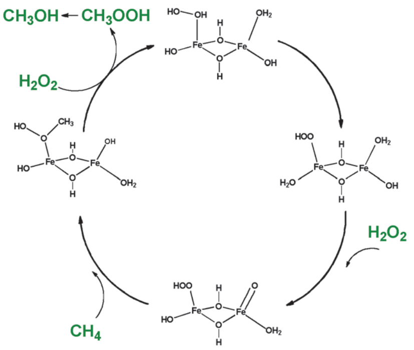


Ribbon-like coordination polymers composed of Ce^{III} ions and $TCNQX_2$ (TCNQ = tetracyanoquinodimethane; X = Cl, Br), but not TCNQ radicals, show unexpected magnetic ordering (see picture; Ce green). This behavior reveals remarkable subtlety for magnetic properties of lanthanide–organic materials.

Cool Methane Oxidation

C. Hammond, M. M. Forde,
M. H. Ab Rahim, A. Thetford, Q. He,
R. L. Jenkins, N. Dimitratos,
J. A. Lopez-Sanchez, N. F. Dummer,
D. M. Murphy, A. F. Carley, S. H. Taylor,
D. J. Willock, E. E. Stangland, J. Kang,
H. Hagen, C. J. Kiely,
G. J. Hutchings* ________ 5129 – 5133

Direct Catalytic Conversion of Methane to Methanol in an Aqueous Medium by using Copper-Promoted Fe-ZSM-5

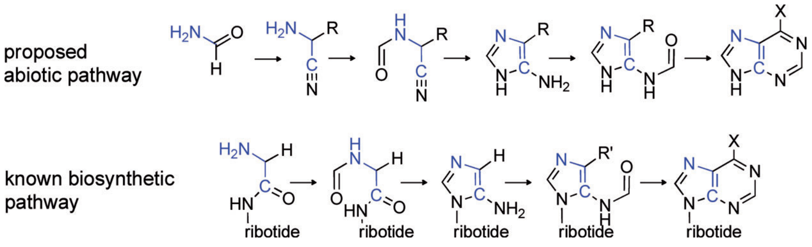


Iron copper zeolite (Fe-Cu-ZSM-5) with aqueous hydrogen peroxide is active for the selective oxidation of methane to methanol. Iron is involved in the activation of the carbon–hydrogen bond, while copper allows methanol to form as the major product. The catalyst is stable, reusable and activates methane giving $>90\%$ methanol selectivity and 10% conversion in a closed catalytic cycle (see scheme).

Prebiotic Synthesis

J. S. Hudson, J. F. Eberle, R. H. Vachhani,
L. C. Rogers, J. H. Wade,
R. Krishnamurthy,
G. Springsteen* ________ 5134 – 5137

A Unified Mechanism for Abiotic Adenine and Purine Synthesis in Formamide

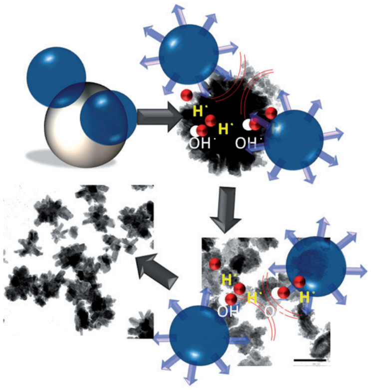


Form(am)idable beginning: Mechanistic pathways from formamide to purine and adenine have been proposed (see scheme, purine (R = H, X = H), adenine (R = CN, X = NH_2, R′ = $CONH_2$). Parallels between these plausible prebiotic syntheses and purine-ring biosynthesis may allude to the origins of the metabolic route.

Sonochemistry

E. V. Skorb,* D. V. Andreeva,
H. Möhwald ________ 5138 – 5142

Generation of a Porous Luminescent Structure Through Ultrasonically Induced Pathways of Silicon Modification

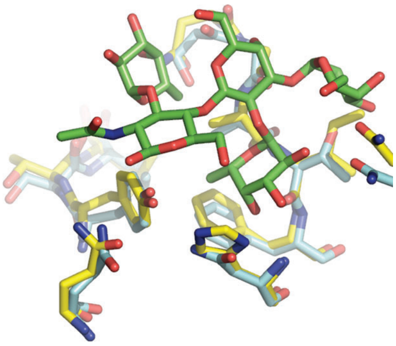


Porous silicon with unique optical properties was formed through an ultrasonication method. This technique allows the one-step formation of silicon with a purposefully variable porous structure, provides for the possibility of patterned surface-selective modification, and forms photoluminescent centers and defect states, which can act as centers for charge separation.

Bacterial Toxins

P. K. Mandal, T. R. Branson, E. D. Hayes,
J. F. Ross, J. A. Gavín, A. H. Daranas,
W. B. Turnbull* ________ 5143 – 5146

Towards a Structural Basis for the Relationship Between Blood Group and the Severity of El Tor Cholera



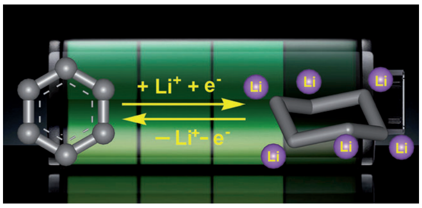
It has long been known that people with blood group O are more severely affected by El Tor cholera than those with blood groups A or B. Microcalorimetry and NMR spectroscopy are used to evaluate the ability of the B-subunits of cholera toxin and *E. coli* heat-labile toxin to bind to selected blood group oligosaccharides.

Electrode Materials

X. Han, G. Qing, J. Sun, T. Sun* ________ 5147 – 5151

How Many Lithium Ions Can Be Inserted onto Fused C_6 Aromatic Ring Systems?

Getting a charge out of lithium: The naphthalene derivative NTCDA is used to demonstrate a novel lithium ion insertion model in which each ring carbon atom can reversibly accept a lithium ion, giving discharge capacities of up to nearly 2000 mA h g^{-1}. This method provides a new strategy for the design of high-performance organic electrodes.

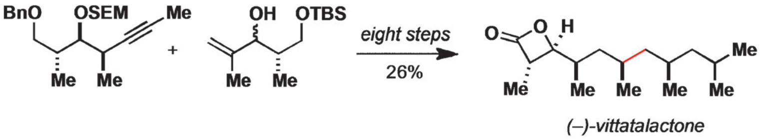


Back Cover

Natural Product Synthesis

P. S. Diez, G. C. Micalizio* _ 5152 – 5156

Convergent Synthesis of Deoxypropionates



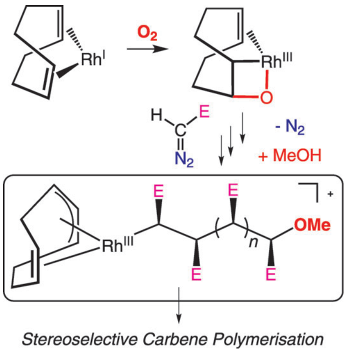
Metallacycle-mediated allylic alcohol–alkyne reductive cross-coupling is described as a convergent solution to the synthesis of deoxypropionates. This approach offers superior step-economy in comparison to available strategies based on multistep iterative chain elongation. The technique is demonstrated in a concise synthesis of the C1–C11 subunit of borrelidin, and a total synthesis of (−)-vittatalactone.

Carbene Polymerization

A. J. C. Walters, O. Troeppner, I. Ivanović-Burmazović, C. Tejel, M. P. del Río, J. N. H. Reek, B. de Bruin* ________ 5157 – 5161

Stereospecific Carbene Polymerization with Oxygenated Rh(diene) Species

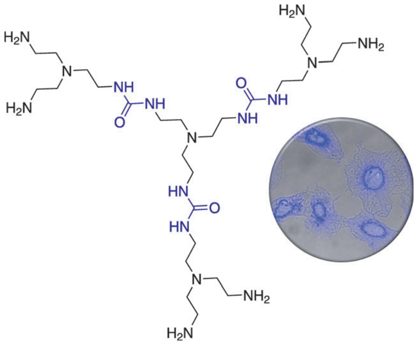
Breath-taking activation: Stereoregular carbene polymerization proceeds via cationic [(allyl)Rh^{III}–polymeryl]$^+$ species. These are most efficiently generated by oxygenation of the [(diene)Rh^{I}] precatalysts, which involves an unusual rearrangement of 2-rhodaoxetane intermediates. This discovery gives detailed insight in the reaction mechanism.



Supramolecular Chemistry

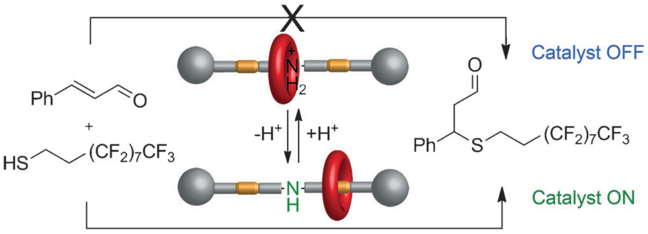
R. B. Restani, P. I. Morgado, M. P. Ribeiro, I. J. Correia, A. Aguiar-Ricardo, V. D. B. Bonifácio* ________ 5162 – 5165

Biocompatible Polyurea Dendrimers with pH-Dependent Fluorescence



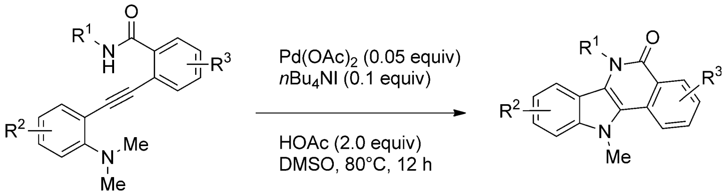
Blue: Biocompatible and biodegradable water-soluble dendrimers comprising ureas within the interior and amino groups on the periphery were synthesized in supercritical carbon dioxide (dendrimer of generation 1 shown in picture). This novel class of dendrimers shows a pH-dependent intrinsic blue fluorescence at very low concentrations, which makes them potential polymeric fluorescent cell markers.

Switchable Catalysts



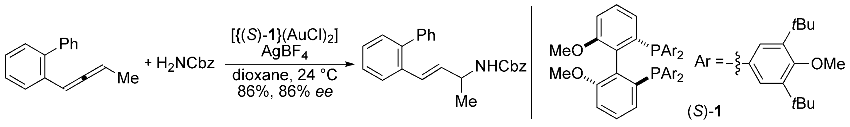
Switch it on! The activity of an organocatalytic group incorporated within a rotaxane architecture can be controlled by switching the position of the macrocycle. The system was used to mediate the progress of the Michael addition of an aliphatic thiol to *trans*-cinnamaldehyde.

Synthetic Methods



“I” did it: A sequential intramolecular amination/N-demethylation/amidation of internal acetylenes in the presence of a catalytic amount of $Pd(OAc)_2$ and nBu_4NI afforded indolo[3,2-*c*]isoquinolinones under mild aerobic conditions (see scheme, DMSO = dimethyl sulfoxide). The iodide ion was regenerated by reaction of in situ generated MeI with HOAc present in the reaction mixture.

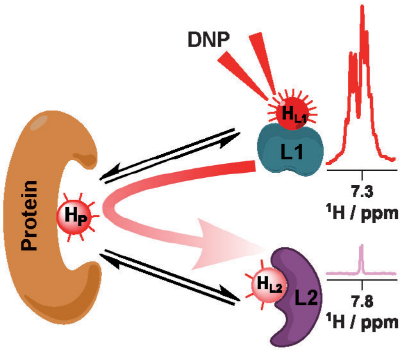
Asymmetric Catalysis



Gold and silver: A 1:2 mixture of $[\{(S)\text{-}\mathbf{1}\}(AuCl)_2]$ and $AgBF_4$ catalyzes the enantioselective hydroamination of chiral, racemic 1,3-disubstituted allenes with N-unsubstituted carbamates to form *N*-allylic carbamates in good yield, with high regio- and diastereoselectivity, and up to 92% *ee* (see scheme, Cbz = benzyloxycarbonyl).

NMR Spectroscopy in Solution

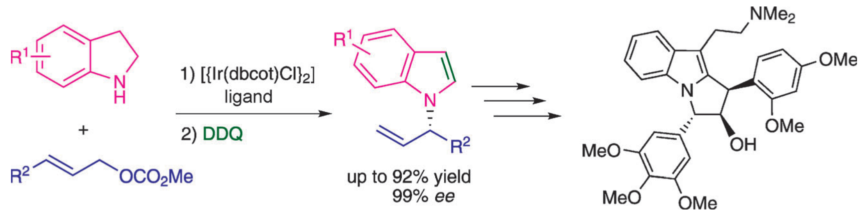
Protein-mediated polarization transfer: Ligands L1 and L2 that competitively bind to a protein are subject to indirect spin-polarization transfer through the binding site of the protein. If protons H_{L1} of one ligand are hyperpolarized by dynamic nuclear polarization (DNP, see picture), signal intensities in the NMR spectrum of the second ligand become enhanced. The relative build-up of signal of the second ligand yields information on its binding epitope.



Asymmetric Catalysis

W.-B. Liu, X. Zhang, L.-X. Dai, S.-L. You* ______ **5183 – 5187**

Asymmetric *N*-Allylation of Indoles Through the Iridium-Catalyzed Allylic Alkylation/Oxidation of Indolines

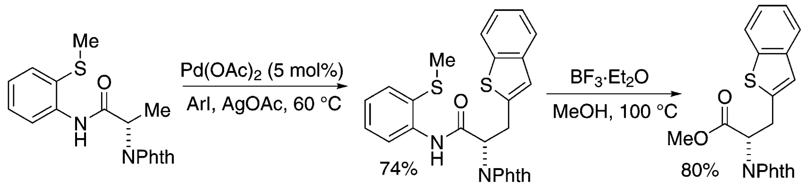


Two steps can be better than one: An efficient synthesis of enantioenriched *N*-allylindoles by a one-pot Ir-catalyzed asymmetric allylic alkylation/oxidation reaction of indolines has been realized. The current method features high regioselectivity and enantioselectivity together with a broad range of indoles with varying electronic properties. The utility of this method was demonstrated by the synthesis of dihydropyrrolo[1,2-*a*]indole derivatives.

C–H Bond Functionalization

L. D. Tran, O. Daugulis* ______ **5188 – 5191**

Nonnatural Amino Acid Synthesis by Using Carbon–Hydrogen Bond Functionalization Methodology

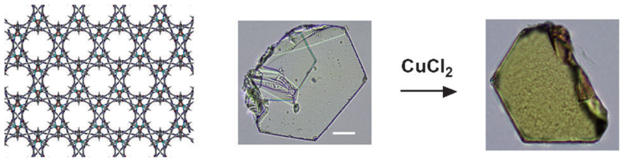


Taking direction well: Substituted phenylalanine derivatives were prepared by C–H bond functionalization (see scheme). The syntheses are highly convergent and employ an *N*-phthaloylalanine with a 2-thiomethylaniline directing group. The use of an 8-aminoquinoline directing group allows for the diarylation of methyl and the diastereoselective arylation of methylene groups.

Metal–Organic Frameworks

T. Jacobs, R. Clowes, A. I. Cooper, M. J. Hardie* ______ **5192 – 5195**

A Chiral, Self-Catenating and Porous Metal–Organic Framework and its Post-Synthetic Metal Uptake

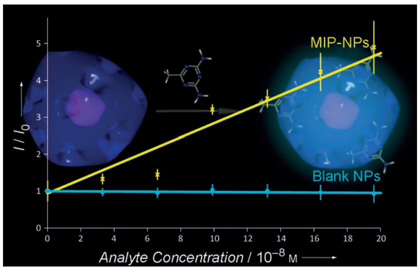


Free vacancies: A robust and porous metal–organic framework material with unique 4-connected self-catenating structure of {8^5·10} topology was synthesized. The structure features empty bipyridine metal-chelating sites that can be doped with copper cations in a single-crystal-to-single-crystal post-synthetic modification (see picture; scale bar 20 μm).

Optical sensing

P. K. Ivanova-Mitseva, A. Guerreiro, E. V. Piletska, M. J. Whitcombe,* Z. Zhou, P. A. Mitsev, F. Davis, S. A. Piletsky ______ **5196 – 5199**

Cubic Molecularly Imprinted Polymer Nanoparticles with a Fluorescent Core

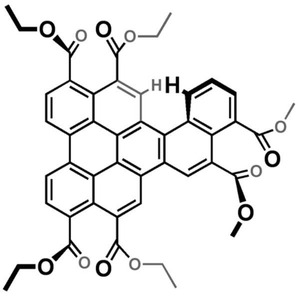


Building blocks for a bright future: A new method for the synthesis of organic nanoparticles (NPs) was developed combining a molecularly imprinted polymer shell and a fluorescent dendrimer biosensing core. Cubic organic nanoparticles are reported for the first time. The polymeric nanoparticles could be used as a direct replacement for antibodies in biosensor applications.

Liquid Crystals

J. Kelber, M.-F. Achard, F. Durola, H. Bock* ——— **5200 – 5203**

Distorted Arene Core Allows Room-Temperature Columnar Liquid-Crystal Glass with Minimal Side Chains

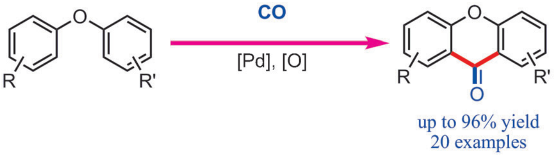


Atropoisomeric aromatic cores enhance disorder inside the supramolecular packing of disk-shaped mesogens. Core-extension of perylene with an atropoisomeric [4]helicene fragment thus gives rise to a room-temperature liquid crystal even with extremely short side chains. Replacement of diester moieties by imide substituents allows switching from donor- to acceptor-type electronic characteristics.

C–H Activation

H. Zhang, R. Shi, P. Gan, C. Liu, A. Ding, Q. Wang, A. Lei* ——— **5204 – 5207**

Palladium-Catalyzed Oxidative Double C–H Functionalization/Carbonylation for the Synthesis of Xanthones



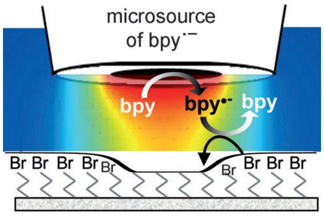
Two at once: Xanthones with different functional groups were obtained with CO (balloon) in the presence of a simple catalytic system that consists of Pd(OAc)$_2$, $K_2S_2O_8$, and trifluoroacetic acid (see scheme). Preliminary mechanism studies reveal that the second C–H functionalization might be the rate-determining step.

Surface Chemistry

S. Nunige, R. Cornut, H. Hazimeh, F. Hauquier, C. Lefrou, C. Combellas, F. Kanoufi* ——— **5208 – 5212**

Reactivity of Surfaces Determined by Local Electrochemical Triggering: A Bromo-Terminated Self-Assembled Monolayer

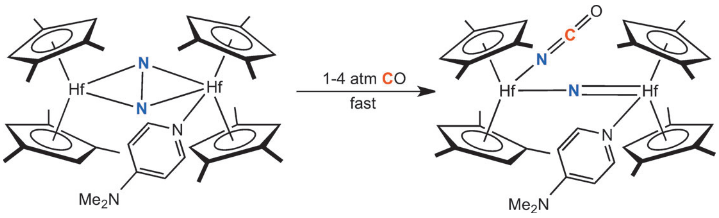
Magic ink: The chemical reactivity of a bromo-terminated self-assembled monolayer immobilized on an insulating substrate is quantified from the time evolution of patterns formed during the local reduction of the SAM (see picture; bpy = 2,2′-bipyridine). The potential of this lithographic strategy to determine the reactivity of the self-assembled monolayer is described and compared to surface interrogation by electrochemical microscopy.



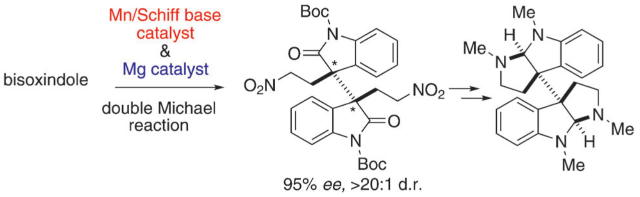
N_2 Cleavage

S. P. Semproni, C. Milsmann, P. J. Chirik* ——— **5213 – 5216**

Structure and Reactivity of a Hafnocene µ-Nitrido Prepared From Dinitrogen Cleavage



Carbonylation of the strongly activated hafnocene dinitrogen complex, $[\{(\eta^5\text{-C}_5\text{H}_2\text{-1,2,4-Me}_3)_2\text{Hf}\}_2(\mu_2,\eta^2,\eta^2\text{-N}_2)]$, in the presence of electron-rich 4-substituted pyridines resulted in isolation of rare µ-nitrido hafnocene complexes prepared from N_2 cleavage. The electronic and molecular structures as well as the intermediacy in N–C bond forming reactions has been determined.



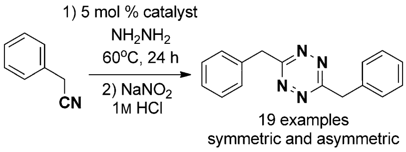
Direct access: Sterically hindered vicinal quaternary carbon stereocenters were constructed by catalytic enantio- and diastereoselective double Michael reaction, providing straightforward access to dimeric hexahydropyrroloindole alkaloids. A Mn(4-fluorobenzoate)$_2$/Schiff base complex and a Mg(OAc)$_2$/benzoic acid system were used as catalysts.

Synthetic Methods

H. Mitsunuma, M. Shibasaki, M. Kanai,* S. Matsunaga* ———— 5217 – 5221

Catalytic Asymmetric Total Synthesis of Chimonanthine, Folicanthine, and Calycanthine through Double Michael Reaction of Bisoxindole

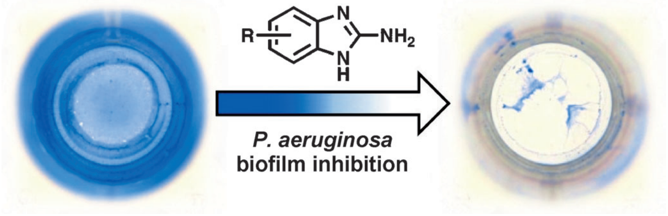
Paving the way: The lack of convenient synthetic methods is a significant roadblock to the broader use of 1,2,4,5-tetrazines in bioorthogonal chemistry and functional materials. Lewis acid metal catalysts—most notably divalent nickel and zinc salts— are described to catalyze the one-pot synthesis of 1,2,4,5-tetrazines directly from aliphatic nitriles (see scheme).



Synthetic Methods

J. Yang, M. R. Karver, W. Li, S. Sahu, N. K. Devaraj* ———— 5222 – 5225

Metal-Catalyzed One-Pot Synthesis of Tetrazines Directly from Aliphatic Nitriles and Hydrazine

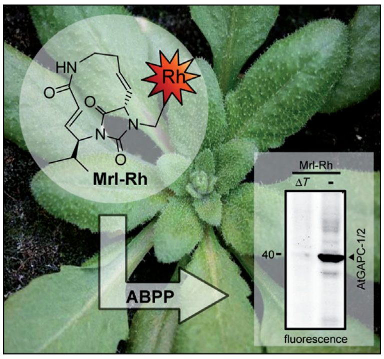


Bacterial biofilms are exceptionally difficult to clear using traditional antibiotics and constitute a significant health threat. 2-Aminobenzimidazole derivatives (see scheme) are capable of strongly inhibiting the growth of and dispersing *Pseudomonas aeruginosa* biofilms. These molecules were found to modulate quorum sensing in reporter strains, and represent some of strongest *P. aeruginosa* biofilm inhibitors known.

Inhibitors

R. Frei, A. S. Breitbach, H. E. Blackwell* ———— 5226 – 5229

2-Aminobenzimidazole Derivatives Strongly Inhibit and Disperse *Pseudomonas aeruginosa* Biofilms



Exceptionally specific: The natural-product-like structural complexity of a bicyclic hydantoin was exploited to generate the novel, highly specific activity-based profiling probe (ABPP) **Mrl-Rh** (Rh = rhodamine; see picture) for glyceraldehyde 3-phosphate dehydrogenases. This probe can be used to investigate activity changes of this enzyme class during plant–pathogen interactions.

Chemical Biology

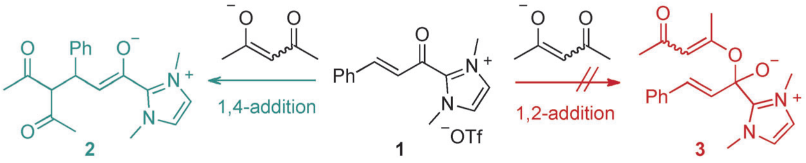
F. Kaschani, J. Clerc, D. Krahn, D. Bier, T. N. Hong, C. Ottmann, S. Niessen, T. Colby, R. A. L. van der Hoorn, M. Kaiser* ———— 5230 – 5233

Identification of a Selective, Activity-Based Probe for Glyceraldehyde 3-Phosphate Dehydrogenases

Organocatalysis

R. C. Samanta, B. Maji, S. De Sarkar,
K. Bergander, R. Fröhlich,
C. Mück-Lichtenfeld,* H. Mayr,*
A. Studer* ________ **5234 – 5238**

Nucleophilic Addition of Enols and Enamines to α,β-Unsaturated Acyl Azoliums: Mechanistic Studies



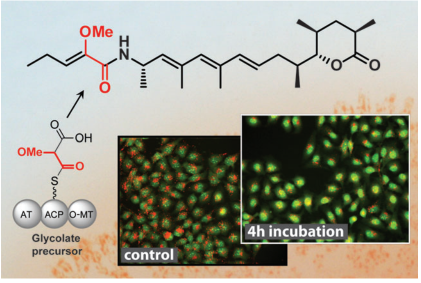
1,4 but not 1,2! The reactivity of **1** towards different nucleophiles (deprotonated β-diketones, enamines, and malonodinitrile) was investigated by NMR and kinetic experiments. These investigations proved that C–C bond formation occurs by a Michael-type 1,4-addition and not by a 1,2-addition and subsequent [3,3]-sigmatropic rearrangement. The first X-ray structure of an α,β-unsaturated acyl azolium salt (**1**) is also presented.

Natural Products

C. Jahns, T. Hoffmann, S. Müller, K. Gerth,
P. Washausen, G. Höfle, H. Reichenbach,
M. Kalesse,* R. Müller* ____ **5239 – 5243**

Pellasoren: Structure Elucidation, Biosynthesis, and Total Synthesis of a Cytotoxic Secondary Metabolite from *Sorangium cellulosum*

Genetic analysis of biosynthetic gene clusters is becoming an accepted tool to predict the stereochemical outcome of a biosynthesis. However, in the case of pellasoren, one chiral center was not predicted correctly. The absolute configuration was verified by total synthesis, which also demonstrated that stereoselective protonations can be successfully applied to natural products synthesis.

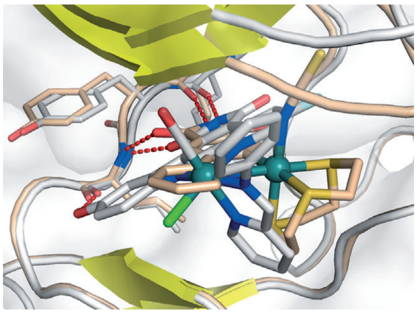


Bioorganometallic Chemistry

S. Blanck, J. Maksimoska, J. Baumeister,
K. Harms, R. Marmorstein,*
E. Meggers* ________ **5244 – 5246**

The Art of Filling Protein Pockets Efficiently with Octahedral Metal Complexes

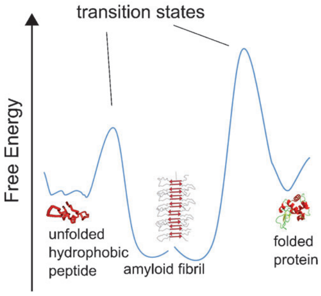
Better fit, less effort: An easy-to-synthesize ruthenium phthalimide complex (tan-colored carbon atoms in the picture) was designed to bind within the active site of the p21-activated kinase 1 in a novel fashion that differs from that of the previously established staurosporine-inspired metallopyridocarbazoles (gray-colored carbon atoms).



Amyloid Fibrils

A. K. Buell, A. Dhulesia, D. A. White,
T. P. J. Knowles, C. M. Dobson,*
M. E. Welland* ________ **5247 – 5251**

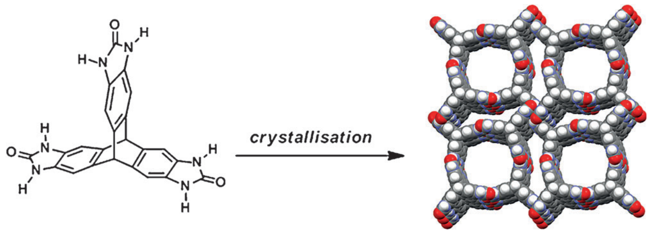
Detailed Analysis of the Energy Barriers for Amyloid Fibril Growth



The free energy barriers that determine the kinetics of the growth of amyloid fibrils have been measured for a series of peptides and proteins using a quartz crystal microbalance. The results indicate that the enthalpic contribution to the free energy barrier is invariably unfavorable and correlates with the size and structure of the soluble parent polypeptide, whereas the entropic contribution is favorable and linked to the hydrophobicity of the peptide sequence.

Porous Organic Crystals

Inside Back Cover



Small molecule, large surface area: A rigid triptycene derivative self-assembles by hydrogen bonds to a porous crystal with one-dimensional channels of about 14 Å diameter. Solvents in the channels can be removed to generate an extrinsic porous material with a specific BET surface area of 2796 $m^2 g^{-1}$. Furthermore, gases can be selectively adsorbed within the pores at 1 bar.

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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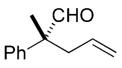
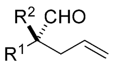
This article is accompanied by a cover picture (front or back cover, and inside or outside).

Angewandte Corrigendum

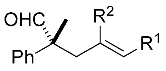
The wrong absolute configuration of products **3** was inadvertently displayed throughout this Communication. The correct configuration of these products is shown below. The authors apologize for this mistake.



3a



3



3l-o

Direct Asymmetric α-Allylation of Aldehydes with Simple Allylic Alcohols Enabled by the Concerted Action of Three Different Catalysts

G. Jiang, B. List* **9471–9474**

Angew. Chem. Int. Ed. **2011**, *50*

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Service