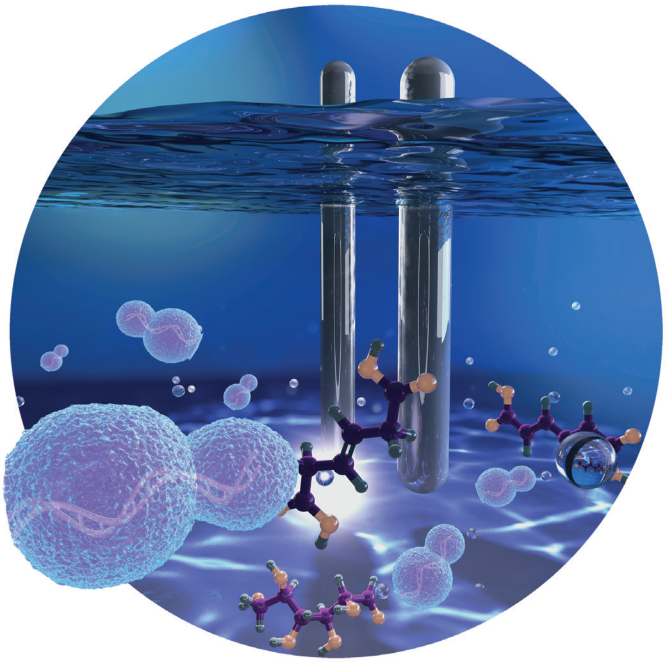
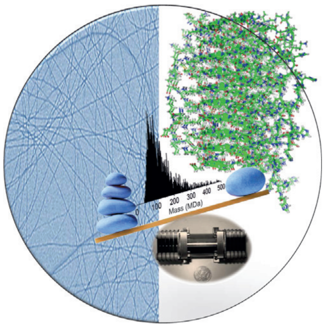
Innovative pathways ...

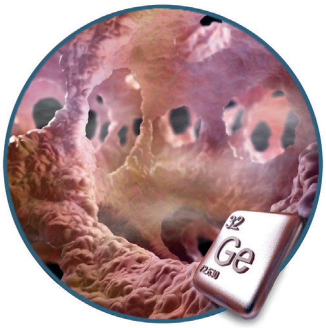


… for the production of biorenewable chemicals from sugars are generated by streamlining bio- and chemical catalysis. In their Communication on page 2368 ff., Z. Shao, J.-P. Tessonnier, et al. describe the electrocatalytic hydrogenation of muconic acid that had been produced from glucose using metabolically engineered yeast to 3-hexenedioic acid in the presence of all cells and biogenic impurities. The hydrogenation product was employed as a monomer for the synthesis of unsaturated nylon-6,6.

Proteins

In their Communication on page 2340 ff., V. Forge, R. Antoine, and co-workers report on the use of charge-detection mass spectrometry for the characterization of amyloid fibrils. This method can be used to monitor protein aggregation in real time.





Zintl Clusters

T. Fässler, D. Fattakhova-Rohlfing, et al. describe a general and controllable fabrication method for Ge nanomorphologies with tunable composition in their Communication on page 2441 ff.

Zeolite Catalysts

Using solid-state NMR spectroscopy F. Deng, J. Xu, and co-workers report in their Communication on page 2507 ff. the direct detection of supramolecular reaction centers composed of organic hydrocarbon-pool species and the zeolite framework.

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Service

Author Profile

"My favorite food is lobster.
My favorite place on earth is The Maldives …"
This and more about Yixin Lu can be found on page 2300.

News

G. Haufe

R. Baughman

G. Resnati

K. Müllen

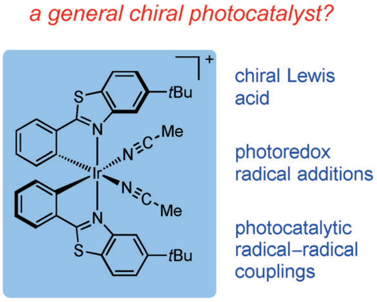
Highlights

Photocatalysis

A. G. Amador, T. P. Yoon* — **2304 – 2306**

A Chiral Metal Photocatalyst Architecture for Highly Enantioselective Photoreactions

A light in dark places: The discovery of catalysts that can both promote photochemical reactions and control their stereochemistry has been regarded as a central challenge in photochemical synthesis for several decades. The discovery of chiral-at-metal complexes that seem particularly successful in this context is an exciting new development that may provide a general solution to this long-standing problem.



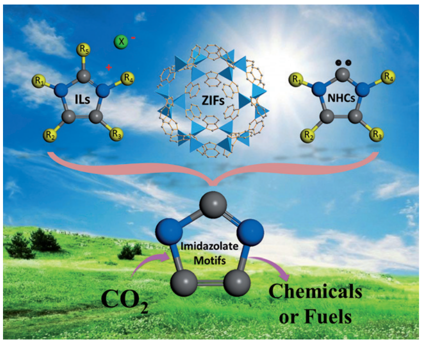
Minireviews

Photocatalysis

S. Wang, X. Wang* — **2308 – 2320**

Imidazolium Ionic Liquids, Imidazolylidene Heterocyclic Carbenes, and Zeolitic Imidazolate Frameworks for CO_2 Capture and Photochemical Reduction

Around the block: Imidazolate building blocks can be utilized in three different ways for the adsorption, activation, and photoreduction of CO_2: as components of ionic liquids, N-heterocyclic carbenes, or zeolitic imidazolate frameworks (see picture). The recent developments and existing shortcomings of imidazolate motifs for CO_2 utilization, with focus on CO_2 photoreduction catalysis, are summarized.



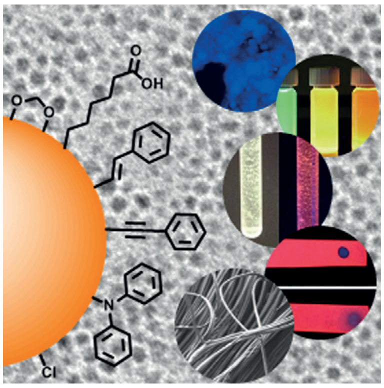
Reviews

Silicon Nanocrystals

M. Dasog, J. Kehrle, B. Rieger,*
J. G. C. Veinot* — **2322 – 2339**

Silicon Nanocrystals and Silicon-Polymer Hybrids: Synthesis, Surface Engineering, and Applications

The grand old newcomer: Silicon may be the "grand old semiconductor", however, it is a relative newcomer to the field of quantum dots. Silicon nanocrystals (Si-NCs) are emerging as a promising, non-toxic, and greener alternative to Group II–VI and III–V quantum dots. This Review highlights how surface chemistry can be used to engineer properties of Si-NCs and adapt them towards modern applications, such as sensors, photovoltaics, and light-emitting diodes.



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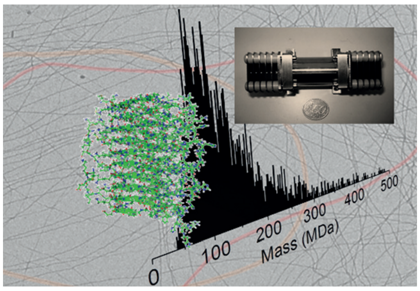
Communications

Mass media: The high aspect ratio of amyloid fibrils and the presence of some polymorphism mean that these self-assembled protein structures are difficult to characterize and basic information such as their mass is unknown. Charge-detection mass spectrometry can be used to provide such information in a straightforward manner, and thus monitor protein aggregation in real time.



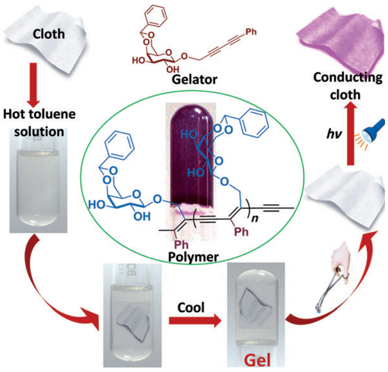
Proteins

T. Doussineau, C. Mathevon, L. Altamura, C. Vendrely, P. Dugourd, V. Forge,* R. Antoine* ________ 2340 – 2344

Mass Determination of Entire Amyloid Fibrils by Using Mass Spectrometry

Frontispiece

A diyne-functionalized sugar gelator was synthesized that, upon self-assembly, preorganizes the diyne motifs for photochemical polymerization to polydiacetylene. This was exploited to make semiconducting fabrics by in situ polymerization to PDA. While the diyne motif forms the conducting PDA, the carbohydrate motif anchors the monomer, and thus the polymer, to the fabric through hydrogen bonds.



Conducting Textile

B. P. Krishnan, S. Mukherjee, P. M. Aneesh, M. A. G. Namboothiry, K. M. Sureshan* ________ 2345 – 2349

Semiconducting Fabrics by In Situ Topochemical Synthesis of Polydiacetylene: A New Dimension to the Use of Organogels

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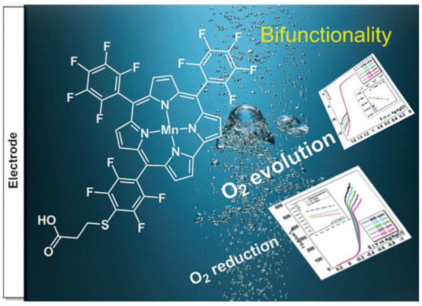

Leading a double life: A manganese corrole complex has been shown to serve as a bifunctional catalyst for the electrocatalytic generation of dioxygen and reduction of dioxygen in aqueous solution. The complex oxidizes hydroxide ions to molecular oxygen through a four-electron process in weak to moderate alkaline conditions and reduces O_2 in a two-electron process to hydrogen peroxide.

Electrocatalysis

W. Schöfberger,* F. Faschinger, S. Chattopadhyay, S. Bhakta, B. Mondal, J. A. A. W. Elemans, S. Müllegger, S. Tebi, R. Koch, F. Klappenberger, M. Paszkiewicz, J. V. Barth, E. Rauls, H. Aldahhak, W. G. Schmidt, A. Dey* ________ 2350 – 2355

A Bifunctional Electrocatalyst for Oxygen Evolution and Oxygen Reduction Reactions in Water

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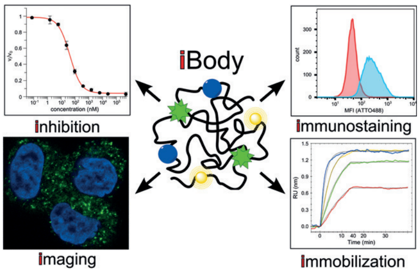


I spy with my little i: iBodies are antibody mimetics consisting of an HPMA copolymer decorated with low-molecular-weight compounds that function as targeting ligands (blue), affinity anchors (green), and imaging probes (yellow). These iBodies can be used for enzyme inhibition; protein isolation, immobilization, or quantification; and live-cell imaging.

Antibody Mimetics

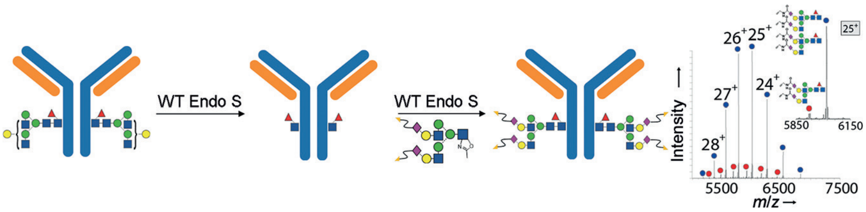
P. Šácha, T. Knedlík, J. Schimer, J. Tykvart, J. Parolek, V. Navrátil, P. Dvořáková, F. Sedlák, K. Ulbrich, J. Strohalm, P. Majer, V. Šubr,* J. Konvalinka* ________ 2356 – 2360

iBodies: Modular Synthetic Antibody Mimetics Based on Hydrophilic Polymers Decorated with Functional Moieties

Glycoproteins

T. B. Parsons, W. B. Struwe, J. Gault,
K. Yamamoto, T. A. Taylor, R. Raj, K. Wals,
S. Mohammed, C. V. Robinson,*
J. L. P. Benesch,
B. G. Davis* ________ **2361 – 2367**

Optimal Synthetic Glycosylation of a Therapeutic Antibody



You're the one that I want: The "blockbuster" antibody Herceptin was accessed with natural glycosylation through chemoenzymatic construction coupled with MS of the intact antibody (see picture). Herceptin was obtained with high purity (> 90%) when nonspecific, non-enzymatic reactions (glycation) revealed by precise MS analysis were minimized. Glycosylation with unnatural sugars bearing tags also enabled the site-selective attachment of cargo.

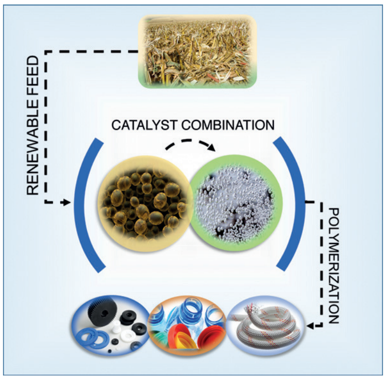
Biorefinery

M. Suastegui, J. E. Matthiesen,
J. M. Carraher, N. Hernandez,
N. Rodriguez Quiroz, A. Okerlund,
E. W. Cochran, Z. Shao,*
J.-P. Tessonnier* ________ **2368 – 2373**

Combining Metabolic Engineering and Electrocatalysis: Application to the Production of Polyamides from Sugar

Front Cover

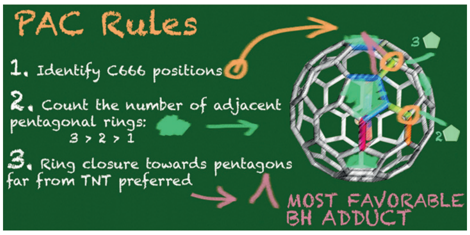
A metabolically engineered yeast strain was used to convert glucose into the platform molecule muconic acid, which was further electrocatalytically hydrogenated to 3-hexenedioic acid directly in the fermentation broth. Bio-based unsaturated nylon-6,6 was then obtained by polymerization of 3-hexenedioic acid with hexamethylenediamine.



Cage Compounds

M. Garcia-Borràs, M. R. Cerón, S. Osuna,*
M. Izquierdo, J. M. Luis,* L. Echegoyen,*
M. Solà* ________ **2374 – 2377**

The Regioselectivity of Bingel–Hirsch Cycloadditions on Isolated Pentagon Rule Endohedral Metallofullerenes

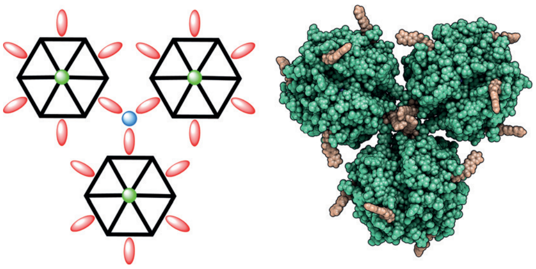


The Bingel–Hirsch (BH) addition of diethylbromomalonate to all non-equivalent bonds of $Sc_3N@D_{3h}$-C_{78} was studied using DFT calculations. A set of rules, the predictive aromaticity criteria (PAC), is proposed to identify the most reactive bonds of endohedral metallofullerenes. The PAC predictions are consistent with computational and experimental data, indicating their generality.

Self-Assembly

H. K. Munch, J. Nygaard,
N. J. Christensen, C. Engelbrekt,
M. Østergaard, T. Porsgaard,
T. Hoeg-Jensen, J. Zhang, L. Arleth,
P. W. Thulstrup,
K. J. Jensen* ______ **2378 – 2381**

Construction of Insulin 18-mer Nanoassemblies Driven by Coordination to Iron(II) and Zinc(II) Ions at Distinct Sites

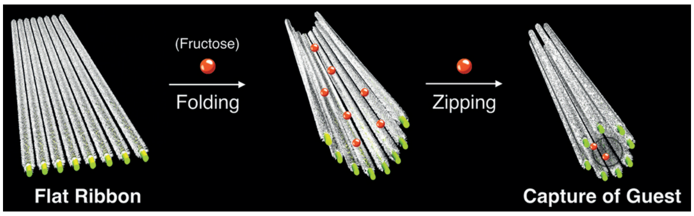


Careful planning: Well-defined insulin 18-mer nanoassemblies formed by metal-ion-mediated self-assembly (SA) of a modified human insulin molecule (HI) have been synthesized. Attachment of an abiotic 2,2′-bipyridine ligand (red oval) to each HI (black triangle) enabled Zn^{II}-binding hexamers to SA into trimers of hexamers driven by coordination to a Fe^{II} ion. Zn^{II} = green sphere; Fe^{II} = blue sphere.

Supramolecular Chemistry

B. Shen, Y. He, Y. Kim,* Y. Wang,
M. Lee* ______ **2382 – 2386**

Spontaneous Capture of Carbohydrate Guests through Folding and Zipping of Self-Assembled Ribbons



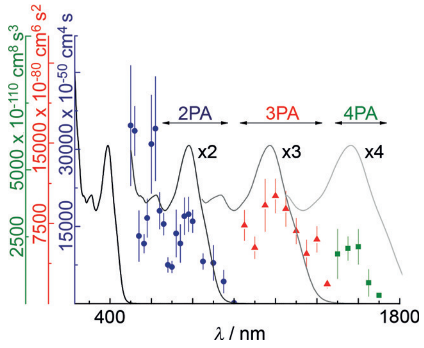
Ribbon zipping: A planar ribbon assembly is folded into closed tubules in response to fructose addition. The folding and then zipping of the flat ribbons is accompanied by spontaneous capture of the fructose molecules inside the tubular cavities, creating new opportunities for 2D structures to capture specific biomolecules.

Optically Active Materials

P. V. Simpson, L. A. Watson, A. Barlow,
G. Wang, M. P. Cifuentes,
M. G. Humphrey* ______ **2387 – 2391**

Record Multiphoton Absorption Cross-Sections by Dendrimer Organometalation

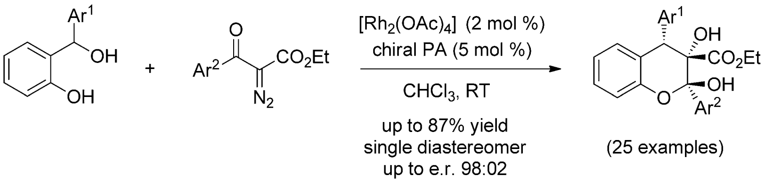
A significant increase in two-photon absorption (2PA) cross-section σ_2 (blue) at biologically important wavelengths, and the appearance of large 3PA (red) and record 4PA (green) cross-sections in the telecommunications region, is achieved by incorporation of ruthenium alkynyl units into a dendritic structure. Spectra are scaled along *x* axis as indicated.



Synergistic Catalysis

S. K. Alamsetti, M. Spanka,
C. Schneider* ______ **2392 – 2396**

Synergistic Rhodium/Phosphoric Acid Catalysis for the Enantioselective Addition of Oxonium Ylides to *ortho*-Quinone Methides

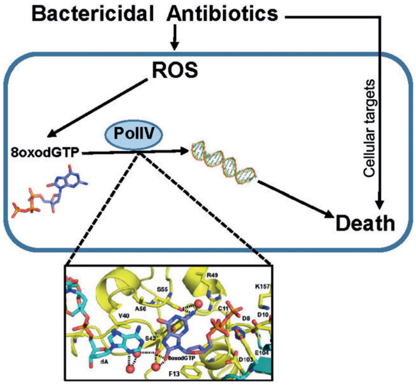


Hand in hand: A rhodium-catalyzed diazo ester decomposition with subsequent oxonium ylide formation and a phosphoric acid-catalyzed generation of an *ortho*-quinone methide from an *ortho*-hydroxy benzhydryl alcohol were efficiently coupled to furnish highly substituted and densely functionalized chromans with three contiguous chiral centers in one synthetic step and with generally good yields and excellent diastereo- and enantioselectivities (PA = phosphoric acid).

Reactive Oxygen Species

J. Kottur, D. T. Nair* ______ 2397 – 2400

Reactive Oxygen Species Play an Important Role in the Bactericidal Activity of Quinolone Antibiotics

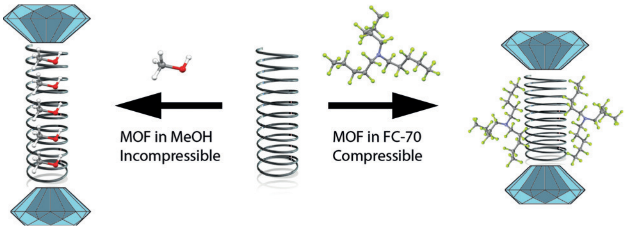


Double peril: Reactive oxygen species (ROS) oxidize the nucleotide pool and PolIV can incorporate the oxidized nucleotides into DNA. Structural and biochemical studies coupled with in vivo assays show that selective elimination of the ability of PolIV to incorporate 8oxodGTP results in improved survival of bacteria in the presence of antibiotics. These results indicate that the formation of ROS contributes substantially to the bactericidal activity of antibiotics.

Microporous Materials

C. L. Hobday, R. J. Marshall,
C. F. Murphie, J. Sotelo, T. Richards,
D. R. Allan, T. Düren, F.-X. Coudert,
R. S. Forgan,* C. A. Morrison,*
S. A. Moggach,*
T. D. Bennett* ______ 2401 – 2405

A Computational and Experimental Approach Linking Disorder, High-Pressure Behavior, and Mechanical Properties in UiO Frameworks

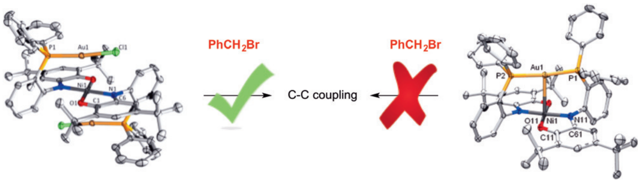


Bowed but unbroken: Two Zr-MOFs of the UiO family are reported. By including flexible azobenzene-based linkers into the frameworks, the lattices were shown to an exhibit moderate increase in flexibility, along with a dramatic increase in mechanical stability. These results may help design MOFs for useful industrial applications.

Metal–Metal Interactions

D. L. J. Broere, D. K. Modder, E. Blokker,
M. A. Siegler,
J. I. van der Vlugt* ______ 2406 – 2410

Metal–Metal Interactions in Heterobimetallic Complexes with Dinucleating Redox-Active Ligands



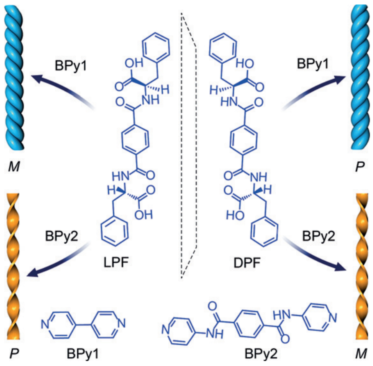
Aurophilic nickelaburger: Selective P coordination of a redox-active PNO ligand to $\mathrm{Au^I}$ followed by homoleptic metalation of the NO pocket with $\mathrm{Ni^{II}}$ affords a unique trinuclear Au–Ni–Au complex. A corresponding cationic dinuclear Au–Ni analogue with a stronger d^8–d^{10} interaction is also reported. However, only the trinuclear complex in its doubly reduced state facilitates electrocatalytic C−X bond activation of alkyl halides.

Helical Structures

G. F. Liu, L. Y. Zhu, W. Ji, C. L. Feng,*
Z. X. Wei ______ 2411 – 2415

Inversion of the Supramolecular Chirality of Nanofibrous Structures through Co-Assembly with Achiral Molecules

Inside Cover

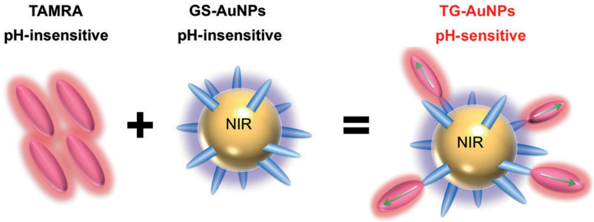


The chirality inversion of helical nanofibers was triggered by achiral bis(pyridinyl) derivatives through co-assembly with phenylalanine-based enantiomers. This process is mainly mediated by the formation of intermolecular hydrogen bonds, which may induce stereoselective interactions and different reorientations.

Antitumor Agents

Small yet mighty: The development of antibody–drug conjugates has been advanced by the combination of nanobodies and sortase-mediated protein modification. The small format of nanobodies allows quick in vivo target validation and leads to low systemic toxicity. The flexibility of sortase-mediated reactions enables switching between imaging and therapy activities in a quantitative and defined manner.

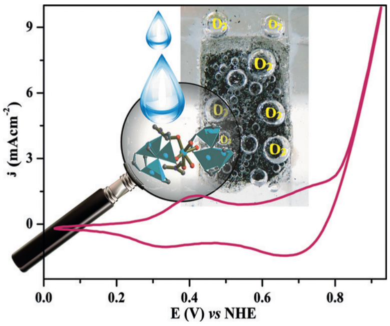
pH Nanosensors



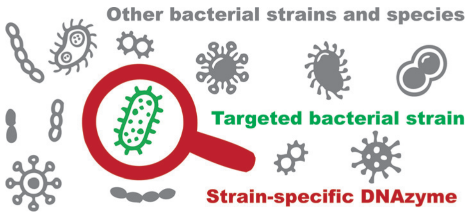
More than its parts: Dimerization of pH-insensitive fluorophores on ultrasmall luminescent gold nanoparticles creates a highly sensitive ratiometric probe of local pH. This conjugation process can also extend the range of pH-sensitive dyes, allowing for tunable sensing features.

Oxygen Evolution Reaction

Cat in a bottle: Efficient and sustained electrochemical oxidation of water to molecular oxygen has been achieved by a mononuclear Co^{II} complex entrapped, like a ship in a bottle, inside the void space of a three-dimensional metal–organic host. The catalyst operates best at pH 13 with a catalytic turnover frequency as high as 0.05 s^{-1} for oxygen evolution.



Bacterial Detection

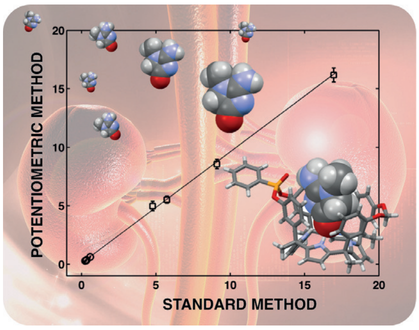


A DNA molecule that is picky: A method has been established for developing catalytic DNA probes that recognize a targeted infectious strain of a specific bacterium without cross-reactivities to non-pathogenic strains of the same species.

Sensors

T. Guinovart, D. Hernández-Alonso,
L. Adriaenssens, P. Blondeau,
M. Martínez-Belmonte, F. X. Rius,
F. J. Andrade,* P. Ballester* **2435 – 2440**

Recognition and Sensing of Creatinine



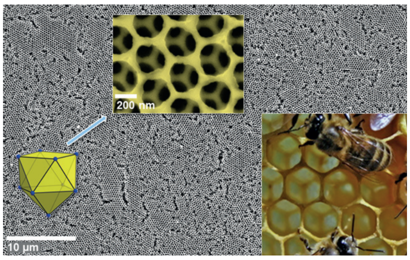
Creatinine quantification: A monophosphonate-bridge calix[4]pyrrole cavitand traps creatinine and the creatininium cation in its deep and polar aromatic cavity. The receptor offers complementary hydrogen-bonding sites to the polar functional groups of the guest. Its use as an ionophore enhances the analytical performance of ion-selective electrodes and enables the determination of creatinine levels in biological samples.

Zintl Clusters

M. M. Bentlohner, M. Waibel, P. Zeller,
K. Sarkar, P. Müller-Buschbaum,
D. Fattakhova-Rohlfing,*
T. F. Fässler* ____________ **2441 – 2445**

Zintl Clusters as Wet-Chemical Precursors for Germanium Nanomorphologies with Tunable Composition

Inside Back Cover

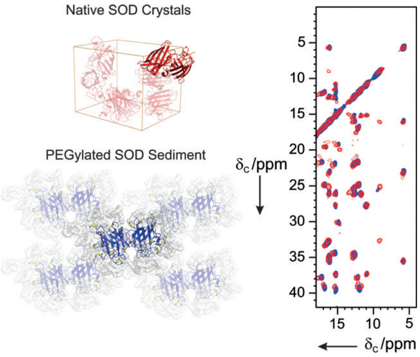


Inverse opals from Zintl clusters: Like a bees wax germanium forms a honeycomb structure around template beads. The controlled reaction of [Ge$_9$]$^{4-}$ Zintl anions to a solid germanium phase is presented and used for a general and controllable fabrication method for Ge nanomorphologies with tunable composition. This method is used for the fabrication of undoped and P-doped inverse opal-structured Ge films.

Protein NMR

E. Ravera, S. Ciambellotti, L. Cerofolini,
T. Martelli, T. Kozyreva, C. Bernacchioni,
S. Giuntini, M. Fragai, P. Turano,
C. Luchinat* ____________ **2446 – 2449**

Solid-State NMR of PEGylated Proteins

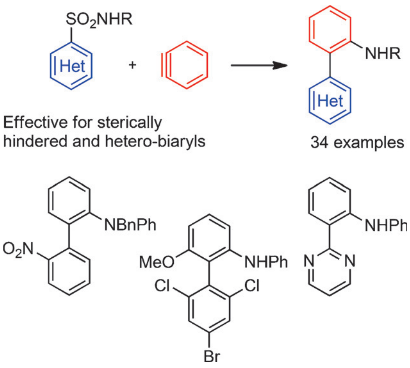


PEGging down proteins: PEGylated proteins are an elusive target for structure elucidation since they are usually too large for solution NMR and tend not to crystallize. Pelleted PEGylated proteins were demonstrated to yield high-resolution spectra that are suitable for structural characterization and allow the tracking of minor structural changes as a result of PEGylation.

Biaryls

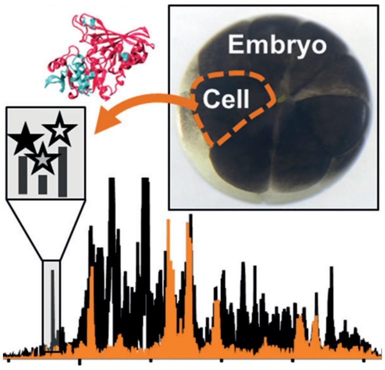
C. M. Holden, S. M. A. Sohel,
M. F. Greaney* ____________ **2450 – 2453**

Metal Free Bi(hetero)aryl Synthesis: A Benzyne Truce–Smiles Rearrangement

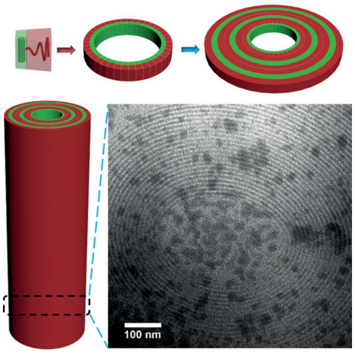


All smiles: Metal-free biaryl synthesis is achieved by adding benzyne to arylsulfonamides. A Smiles rearrangement enables C–C bond formation, thus accessing a variety of functionalized biaryls under mild reaction conditions.

Back to the beginning: the cell. The encoded proteome offers basic insight into normal development. Capillary electrophoresis, electrospray ionization, high-resolution mass spectrometry, and bottom-up proteomics were integrated to enable the identification of 1709 proteins in single embryonic *Xenopus* cells. Quantification of hundreds of proteins revealed translational differences between cells that give rise to different tissues during development.

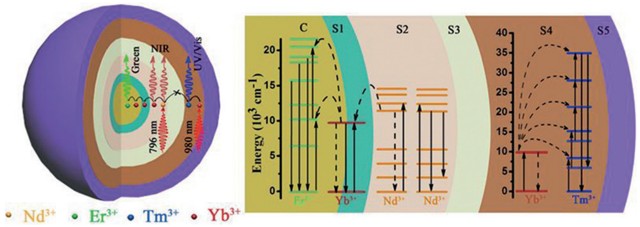


Proteomics



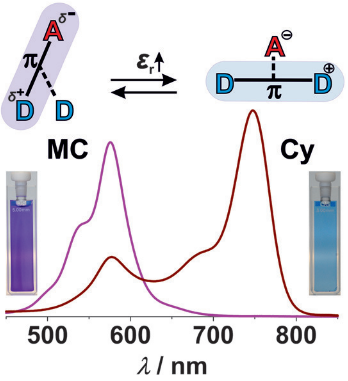
Ever-increasing circles: The spontaneous formation of curved/concentric lamellae was observed in the self-assembly of giant surfactants (see picture; scale bar: 100 nm). This behavior is induced by the molecular curvature originating from the asymmetrical sizes of the head and tail blocks and the rectangular shape of the molecular interface.

Giant Surfactants



A different light: Lanthanide-doped nanoparticles (NPs) with a filtration shell that separates two different luminescence processes and prevents them from interfering with each other are prepared. The filtration effects allow the core-multishell upconversion NPs to show power density independent orthogonal excitations-emissions luminescence and be used in anti-counterfeiting and imaging-guided combined therapy.

Upconversion



Solvent-dependent conformational switch: A bifurcated π-scaffold exhibits a conformational switch between a DA merocyanine-like and a zwitterionic DAD cyanine-like structure upon increasing solvent polarity, which is accompanied by an absorption maximum shift of $\Delta\lambda \approx 160$ nm from the visible (ca. 585 nm) to the near infrared region (ca. 750 nm). Both conformations were characterized by UV/Vis and fluorescence spectroscopy.

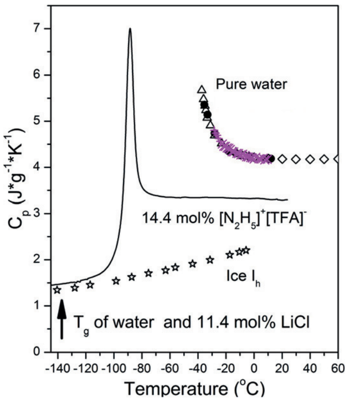
Solvatochromism

Supercooled Water

Z. Zhao, C. A. Angell* ______ **2474 – 2477**

Apparent First-Order Liquid–Liquid Transition with Pre-transition Density Anomaly, in Water-Rich Ideal Solutions

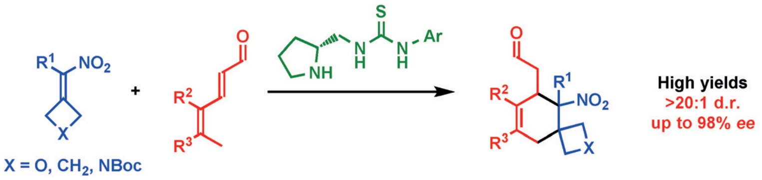
Heat capacities of an aqueous non-ideal salt solution (11.4 mol % LiCl) and an ideal salt solution (14.4 mol % hydrazinium trifluoroacetate) were measured and compared in the temperature range of water anomalies. Is the C_p “spike” the elusive liquid–liquid transition?



Organocatalysis

A. Monleón, F. Glaus, S. Vergura, K. A. Jørgensen* ______ **2478 – 2482**

Organocatalytic Strategy for the Enantioselective Cycloaddition to Trisubstituted Nitroolefins to Create Spirocyclohexene-Oxetane Scaffolds

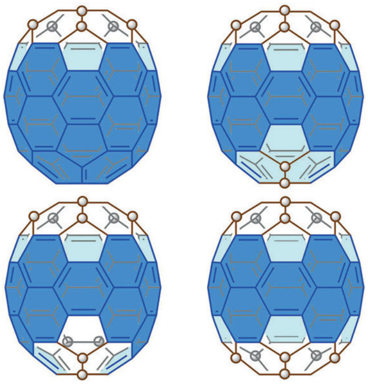


Challenging the crowds: The enantioselective cycloaddition reaction of α,β,β-trisubstituted nitroolefins with 2,4-dienals mediated by trienamine catalysis affords highly functionalized spirocyclohexene-oxetanes containing two tetrasubstituted carbon atoms in high yields (up to 86%) and enantioselectivities (up to 98% *ee*).

Fullerenes

Y. B. Li, D. Xu, L. B. Gan* ______ **2483 – 2487**

Selective Multiamination of C_{70} Leading to Curved π Systems with 60, 58, 56, and 50 π Electrons

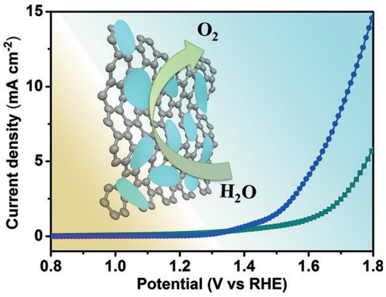


Throw a curve: Secondary aliphatic amines add to [70]fullerene in the presence of NFSI (*N*-fluorobenzenesulfonimide) to form cyclopentadienyl-type adducts. The addition occurs at the pole pentagon and was confirmed by X-ray analysis. Further contraction of the π system took place at the other pole pentagon and led to curved π systems, including the 50π electron Vögtle belt.

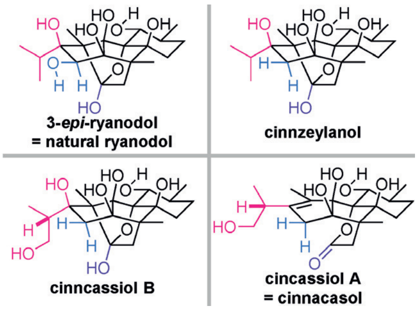
Electrocatalysis

P. Z. Chen, K. Xu, T. P. Zhou, Y. Tong, J. C. Wu, H. Cheng, X. L. Lu, H. Ding, C. Z. Wu,* Y. Xie ______ **2488 – 2492**

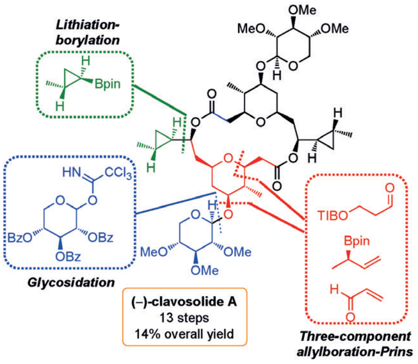
Strong-Coupled Cobalt Borate Nanosheets/Graphene Hybrid as Electrocatalyst for Water Oxidation Under Both Alkaline and Neutral Conditions



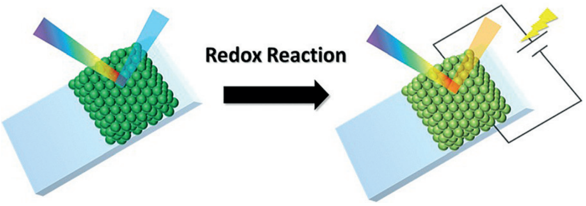
Amorphous Co-based borate ultrathin nanosheets/graphene hybrid was prepared by a room-temperature chemical approach and investigated as an OER electrocatalyst. This Co-B_i NS/G hybrid electrocatalyst showed high OER catalytic activity and superior stability in both alkaline and neutral solutions.



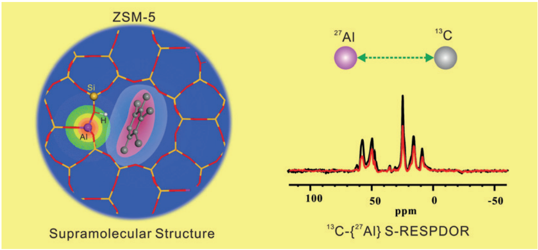
Ryanodane diterpenoids have an extremely complex fused ring system with distinct positions and orientations of the oxygen-based functionalities. Reported is the unified total syntheses of four diterpenoids, 3-*epi*-ryanodol, cinnzeylanol, cinncassiols B and A, from a common pentacycle. This work also served to revise the proposed structures of natural ryanodol and cinncasol to be those of 3-*epi*-ryanodol and cinncassiol A, respectively.



Growing complexity: A highly efficient and diastereoselective three-component allylboration–Prins reaction serves to construct the highly functionalised THP-ring of (−)-clavosolide A from simple starting materials. An early stage diastereoselective glycosidation and a late stage lithiation–borylation are used to complete the synthesis of this complex natural product in just 13 steps from ethanol in 14% overall yield.

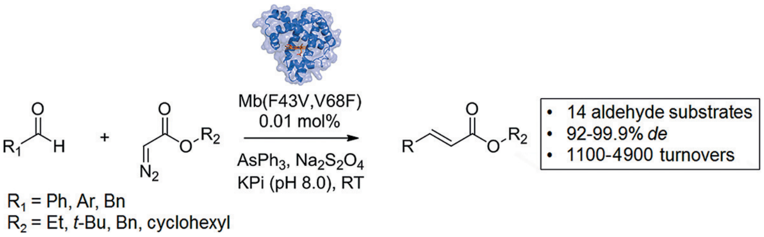


Coat of many colors: Ordered arrays of polyaniline@poly(methyl methacrylate) core–shell nanoparticles act as electroresponsive structurally colored materials. The colors, which range from greenish-yellow to light-blue, depend on the size of the nanoparticles, and can also be varied by the application of a voltage.



Pooled resources: The formation of supramolecular reaction centers composed of organic hydrocarbon-pool (HP) species and a zeolite framework is shown by ^{13}C–^{27}Al double-resonance solid-state NMR spectroscopy. The distance between ^{13}C atoms (HP species) and ^{27}Al atoms (zeolite) determines the reactivity of the HP species in the methanol-to-olefins conversion over H-ZSM-5 zeolite.

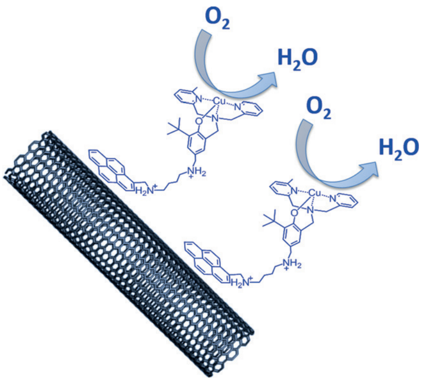
Biocatalysis



A whale of an olefination: Engineered variants of sperm whale myoglobin can serve as biocatalysts for the conversion of aldehydes and α-diazo esters into the corresponding α,β-unsaturated esters. This transformation proceeds with high catalytic efficiency and high *E* diastereoselectivity and could be applied to a variety of different aldehyde substrates and α-diazoesters.

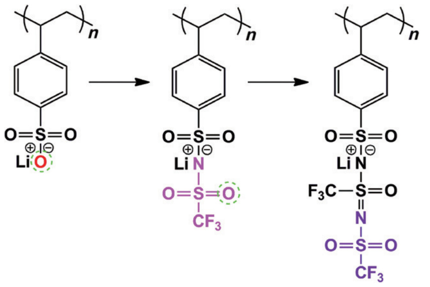
Electrocatalysis

From enzyme to nanotube: A carbon-nanotube-supported copper phenolato complex for biomimetic oxygen reduction was synthesized. The immobilized complex exhibits a 4 H^+/4 e^- electrocatalytic activity and may guide the development of future catalysts.

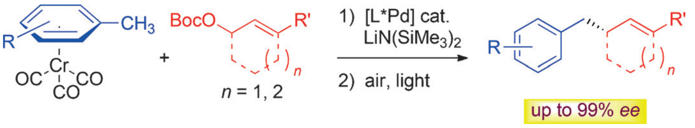


Ion Conductors

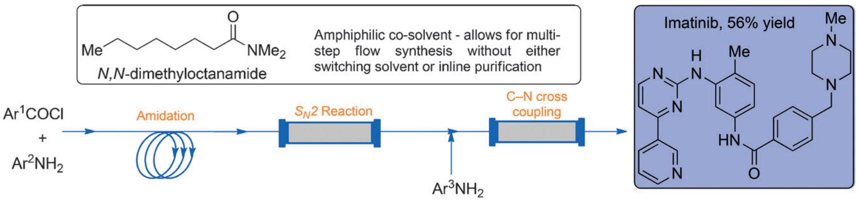
A super-delocalized polyanion is used for a single lithium-ion conducting polymer electrolyte. The neat LiPSsTFSI ionomer displays a low glass-transition temperature (44.3 °C), and its blended polymer electrolyte of the LiPSsTFSI/PEO exhibits a high Li-ion transference number (t_{Li^+} = 0.91) and high ionic conductivities of individual Li^+ cations, which are comparable to those for the classic ambipolar LiTFSI/PEO SPEs above 70 °C (the melting point).



Homogeneous Catalysis

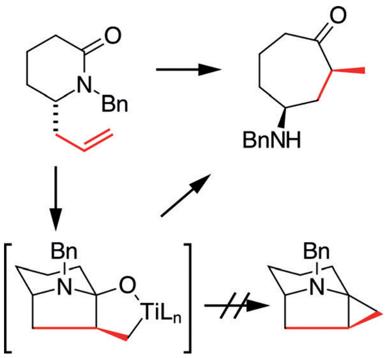


A softer touch: Coordination of the tricarbonylchromium group to toluene derivatives not only facilitates deprotonation with lithium silylamide base, but convinces the resulting benzylic organolithium to reconsider its hardened ways and participate in palladium-catalyzed asymmetric allylic alkylation reactions with high enantioselectivity.



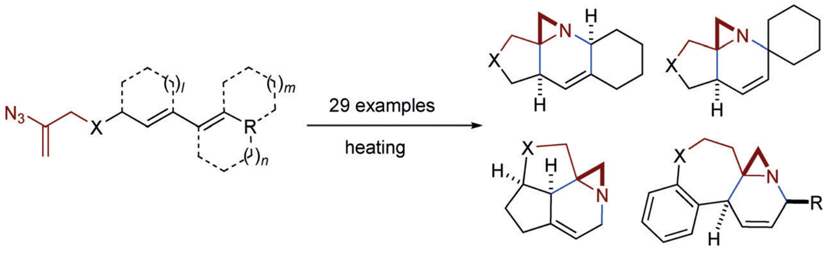
Going with the flow: A general flow method developed for C–N cross-coupling using *N*,*N*-dimethyloctanamide as a catalytic cosolvent was integrated into a two-step sequence which converted phenols into biarylamines via either triflates or tosylates. It was applied to a three-step synthesis of imatinib, the API of Gleevec, in good yield without the need of solvent switches.

Cross-Coupling



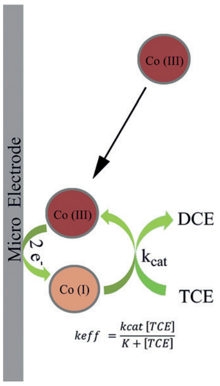
Frustrated by Bredt’s rule: An inability to consummate a Kulinkovich–de Meijere cyclopropanation that would involve a bridgehead double bond transforms the reaction into a transannular cyclization of an unsaturated lactam yielding an amino ketone product with potential for alkaloid synthesis.

Synthetic Methods



Cycling through: 5-6-3 and 6-6-3 tricycles, as well as more complex polycycles having a fused aziridine ring were constructed through an unprecedented intramolecular aza-Diels–Alder reaction of 2*H*-azirine with high stereoselectivity. The use of vinyl azide as the in situ azirine precursor precludes difficulties encountered in the direct handling of the corresponding azirine.

Heterocycles



Nano-impacting B_{12}: The electrocatalytic dehalogenation of trichloroethylene (TCE) by single soft nanoparticles in the form of Vitamin B_{12}-containing droplets is reported. The turnover number of the catalytic reaction was quantified at the single soft nanoparticle level. The kinetic data shows that the binding of TCE with the electro-reduced vitamin in the Co^{I} oxidation state is chemically reversible.

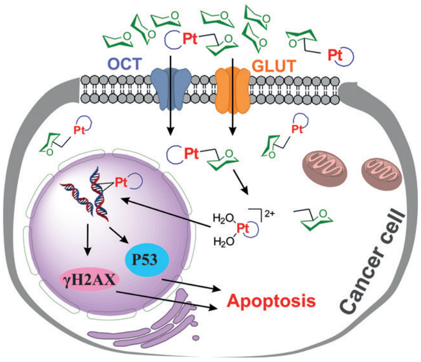
Nanoparticle Catalysis

Medicinal Inorganic Chemistry

M. Patra, T. C. Johnstone,
K. Suntharalingam,
S. J. Lippard* ______ **2550 – 2554**

A Potent Glucose–Platinum Conjugate Exploits Glucose Transporters and Preferentially Accumulates in Cancer Cells

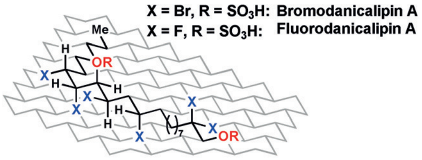
Glucose–platinum conjugates for targeted delivery: A rationally designed potent glucose–platinum conjugate exploits glucose transporters, which are widely overexpressed in cancers, for internalization and selectively accumulates in and annihilates cancer cells.



Chlorosulfolipids

S. Fischer, N. Huwyler, S. Wolfrum,
E. M. Carreira* ______ **2555 – 2558**

Synthesis and Biological Evaluation of Bromo- and Fluorodanicalipin A

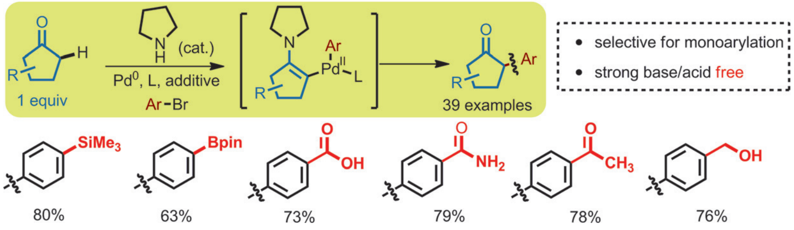


Halologs: The syntheses of bromo- and fluorodanicalipin A are reported and the ground-state conformation was determined by *J*-based configuration analysis (see scheme, R = H). A preliminary comparative study of their toxicology suggests that the adverse effect arises from the lipophilicity of the halogens which counterbalance the polar C14 sulfate.

Synthetic Methods

Y. Xu, T. Su, Z. Huang,
G. Dong* ______ **2559 – 2563**

Practical Direct α-Arylation of Cyclopentanones by Palladium/Enamine Cooperative Catalysis

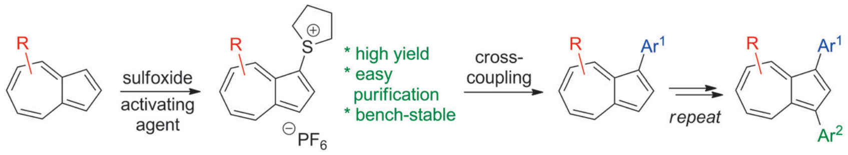


Be direct: A direct α-C–H arylation of normal cyclopentanones with aryl bromides, enabled by palladium/amine cooperative catalysis, features an exceptionally high selectivity for monoarylation, use of readily available starting materials, good scalability, and broad functional-group tolerance.

Synthetic Methods

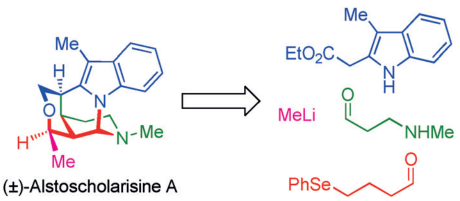
P. Cowper,* Y. Jin, M. D. Turton,
G. Kociok-Köhn,
S. E. Lewis* ______ **2564 – 2568**

Azulenesulfonium Salts: Accessible, Stable, and Versatile Reagents for Cross-Coupling



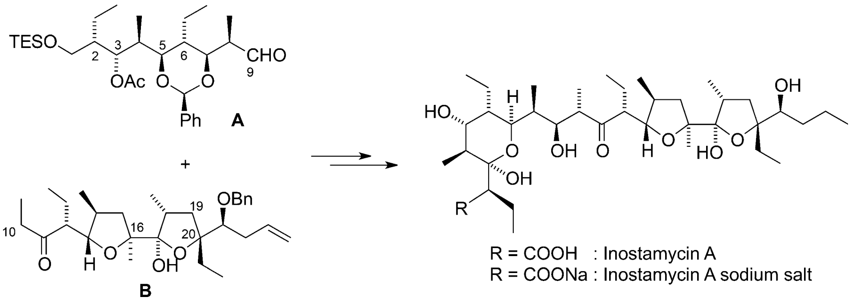
Az u like it! Azulenesulfonium salts, which can be synthesized in one step from the corresponding azulenes, acted as pseudohalide electrophilic cross-coupling reagents in Suzuki–Miyaura reactions with a variety of aryl and heteroaryl boronic acids (see scheme). The sulfonium salts possess several advantages over azulenyl halides in terms of their ease of preparation and purification, as well as their superior stability.

Alkaloid Synthesis



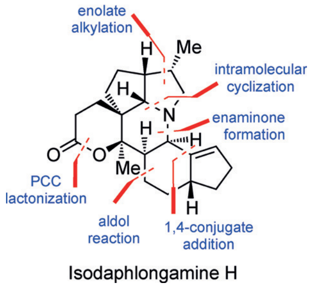
A change of mind: The first total synthesis of the neuroactive indole alkaloid (±)-alstoscholarisine A is reported. The key step of the concise synthesis is an efficient domino sequence that was used to assemble the 2,8-diazabicyclo-[3.3.1]nonane core through the formation of two C–N bonds and one C–C bond in a single step.

Inostamycin A



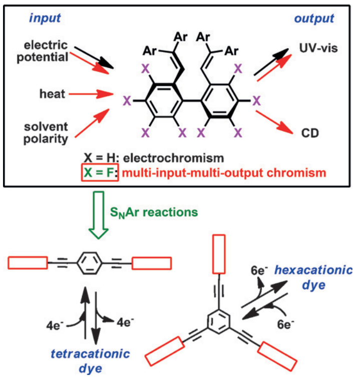
The total synthesis of inostamycin A sodium salt was completed through a stereoselective and efficient aldol condensation of aldehyde **A** with the lithium enolate of ethyl ketone **B**. The two quaternary carbons at C20 and C16 of **B** were installed by diastereoselective addition reactions of the transmetalated species from iodides to ketones.

Total Synthesis



The missing link? A concise and highly convergent total synthesis of isodaphlongamine H was accomplished in 24 linear steps. The molecule exhibited promising inhibitory activity against a panel of human cancer cell lines. PCC = pyridinium chlorochromate.

Electrochromism

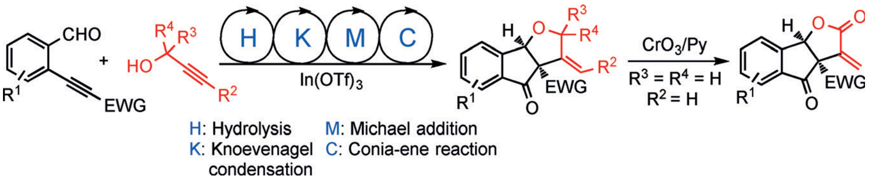


Attachment of fluorine atoms endows a biphenyl-based dynamic redox donor with the multi-input/multi-output response properties. The S_NAr reaction at the F atom enabled construction of the optically pure dyad and triad electron donors, which undergo multielectron-oxidation to tetra- and hexacationic dyes, respectively, and exhibit electrochiroptical responses.

Heterocycle Synthesis

R. Liang, K. Chen, Q. Zhang, J. Zhang, H. Jiang, S. Zhu* ———— **2587 – 2591**

Rapid Access to 2-Methylene Tetrahydrofurans and γ-Lactones: A Tandem Four-Step Process

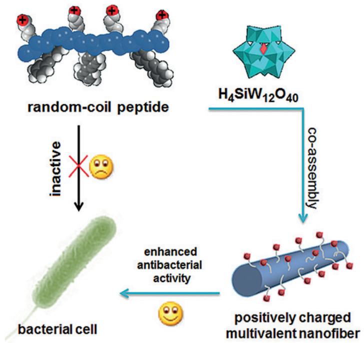


Four in one: A one-pot tandem process (see scheme; EWG = electron-withdrawing group) has been developed for the efficient synthesis of indanone-fused 2-methylene tetrahydrofurans from enynals and propynols. Two rings and four bonds were generated with 100% atom economy and high step efficiency. The resulting tetrahydrofurans were oxidized into α-methylene γ-lactones, which are important substructures in natural and bioactive compounds.

Ionic Self-Assembly

J. F. Li, Z. J. Chen, M. C. Zhou, J. B. Jing, W. Li,* Y. Wang, L. X. Wu,* L. Y. Wang, Y. Q. Wang, M. S. Lee* ———— **2592 – 2595**

Polyoxometalate-Driven Self-Assembly of Short Peptides into Multivalent Nanofibers with Enhanced Antibacterial Activity

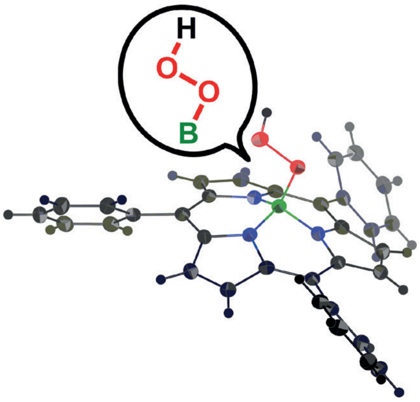


Fatal attraction: Polyoxometalates were able to drive the self-assembly of short peptides into well-defined nanofibers through multivalent electrostatic attraction. The resulting fibrillar nanostructures with lysine residues concentrated on the surface showed enhanced antimicrobial activity and biological stability (see picture).

Boron Peroxides

E. Tsurumaki, J. Sung, D. Kim,* A. Osuka* ———— **2596 – 2599**

Stable Boron Peroxides with a Subporphyrinato Ligand



Acid-catalyzed exchange reactions of a subporphyrinatoboron methoxide with a range of hydroperoxides have resulted in the synthesis of a series of boron peroxides with a subporphyrinato ligand. The boron peroxides are prepared in good yields and are fairly stable under ambient conditions, thus allowing their isolation and full characterization as the first examples of structurally authenticated neutral and acyclic boron peroxides.

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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