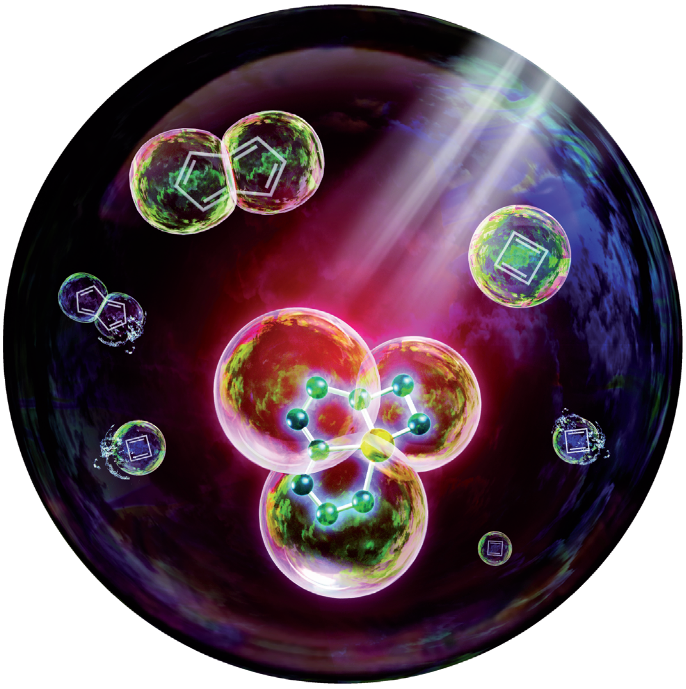
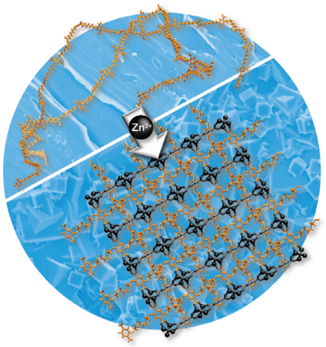
Two classical antiaromatic molecules ...



... cyclobutadiene (CBD) and pentalene, were stabilized by introduction of one metal fragment through a [2+2] cycloaddition reaction of osmapentalyne with alkynes. As shown by J. Zhu, H. Xia et al. in their Communication on page 6181 ff., the metalla-aromatic molecules absorb broadly from the UV to the near-IR region and show photoacoustic and photothermal effects. Theoretical calculations reveal that the antiaromaticity of both CBD and pentalene is decreased.

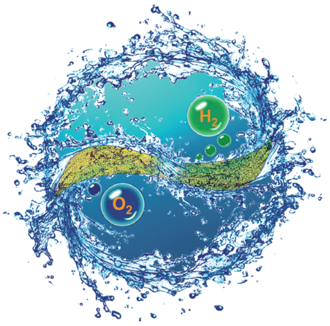
Hybrid Materials

In their Communication on page 6152 ff., S. M. Cohen et al. report the transformation of nonporous, one-dimensional, amorphous polymers into crystalline polymer-based metal–organic framework materials.



Water Splitting (1)

Heterostructures of p-Si microwires and orthorhombic $CoSe_2$ nanorods can function as an efficient photocathode for a solar-driven water-splitting system, as shown by S. F. Hu, R. S. Liu, and co-workers in their Communication on page 6211 ff.



Water Splitting (2)

Y. Sun et al. report bifunctional catalysts based on electrodeposited cobalt–phosphorous films in their Communication on page 6251 ff. These films give a high electrocatalytic performance in both the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER).

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Service

Author Profile

“The secret of being a successful scientist is to pursue excellence and not success.
The natural talent I would like to be gifted with is penning Urdu poetry …”
This and more about Kamal Kumar can be found on page 6092.

News

P. H. Seeberger

A. Seidel-Morgenstern

T. J. Colacot

Y. Xie

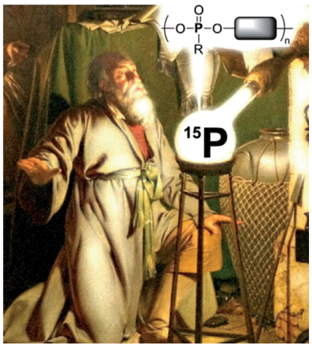
C. V. Robinson

Books

Minireviews

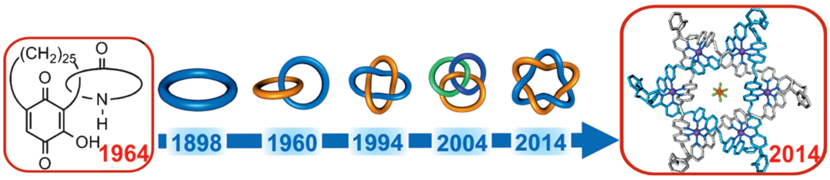
Degradable Polymers

Polymers with potential: Poly(phosphoester)s play an important role in nature (DNA, RNA, and pyrophosphates), but in contrast to classical polyesters they are rarely used for everyday applications. Recent developments are highlighted that may make phosphorus-based polymers attractive materials for future applications.



Reviews

Catenanes

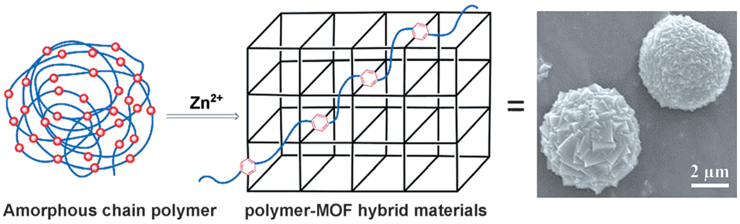


Half a century after Schill and Lüttringhaus carried out the first directed synthesis of a [2]catenane, a plethora of strategies now exist for the construction of interlocked molecular rings. Effective template synthesis enables the synthesis of higher order interlocked systems. This Review outlines the diverse strategies that exist for forming catenanes, their applications, and the important challenges that remain in the field of chemical topology.

Communications

Hybrid Materials

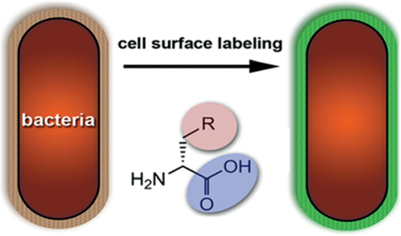
Frontispiece



A bottom-up strategy is used to generate porosity from non-porous, one-dimensional, amorphous polymeric materials by their transformation into crystalline polyMOF materials. These materials harness the advantages of the porosity and crystallinity of MOFs along with certain attributes of the polymers, such as facile film formation and greater chemical stability.

For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. US mailing agent: SPP, PO Box 437, Emigsville, PA 17318. Periodicals postage paid at Emigsville, PA. US POSTMASTER: send address changes to *Angewandte Chemie*, John Wiley & Sons Inc., C/O The Sheridan Press, PO Box 465, Hanover, PA 17331. Annual subscription price for institutions: US$ 11.738/10.206 (valid for print and electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

Transpeptidase domains of penicillin binding proteins catalyze the incorporation of exogenous D-amino acids onto bacterial cell surfaces. The substrates can have diverse side chains (see picture, pink), and this promiscuous enzyme can also accommodate C-terminus variations (blue). Most importantly, fluorescence labeling differences within and between bacterial species could be profiled using a panel of compounds.



Amino Acid Labeling

S. E. Pidgeon, J. M. Fura, W. Leon,
M. Birabaharan, D. Vezenov,
M. M. Pires* ______ **6158 – 6162**

Metabolic Profiling of Bacteria by Unnatural C-terminated D-Amino Acids

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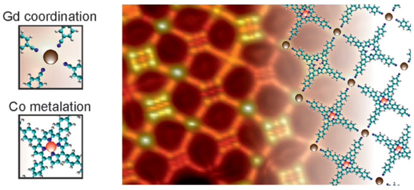


Surface-confined d–f bimetallic 2D coordination nanosystems have been achieved by using a three-step procedure that exploits orthogonal coordination interactions of CN-functionalized free-base porphyrin linkers with rare-earth and transition-metal centers. By systematic STM investigations the assembly process was established and the resulting nanoarchitectures characterized at the molecular level.

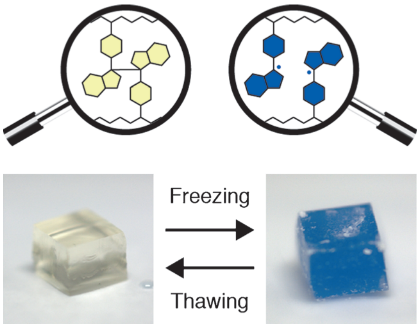
Surface Architectures

J. I. Urgel, D. Ecija,* W. Auwärter,*
D. Stassen, D. Bonifazi,*
J. V. Barth ______ **6163 – 6167**

Orthogonal Insertion of Lanthanide and Transition-Metal Atoms in Metal–Organic Networks on Surfaces

---

Freezing-induced mechanochemistry: A new diarylbibenzofuranone-based mechanophore showed reversible color change by external forces through radical mechanism. By incorporating the mechanophore into polymer chains, it was revealed that freezing gels induced mechanical force along the chains, but the force was not large enough to cleave common covalent bonds.



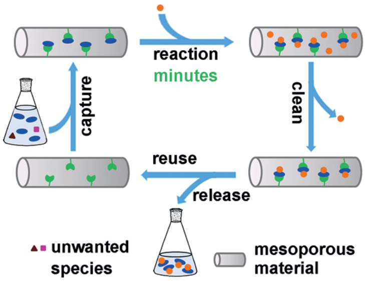
Mechanochemistry

K. Imato, A. Irie, T. Kosuge, T. Ohishi,
M. Nishihara, A. Takahara,*
H. Otsuka* ______ **6168 – 6172**

Mechanophores with a Reversible Radical System and Freezing-Induced Mechanochemistry in Polymer Solutions and Gels

---

A solid-phase approach is proposed for highly efficient labeling (see picture, orange) of saccharides (blue) by using boronic acid (green) functionalized mesoporous silica nanoparticles as a nanoreactor. Compared to conventional liquid-phase labeling, the solid-phase approach exhibited faster reaction speed (only 2 min), high product purity, and much lower applicable saccharide concentration (10^{-9} M).



Solid-Phase Labeling

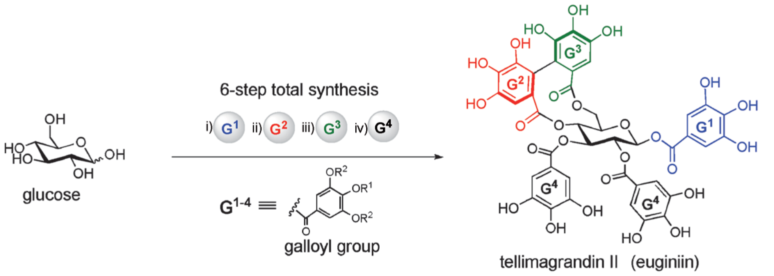
X. Pan, Y. Chen, P. Zhao, D. Li,
Z. Liu* ______ **6173 – 6176**

Highly Efficient Solid-Phase Labeling of Saccharides within Boronic Acid Functionalized Mesoporous Silica Nanoparticles

Regioselective Catalysis

H. Takeuchi, K. Mishiro, Y. Ueda,
Y. Fujimori, T. Furuta,
T. Kawabata* ______ 6177 – 6180

Total Synthesis of Ellagitannins through Regioselective Sequential Functionalization of Unprotected Glucose

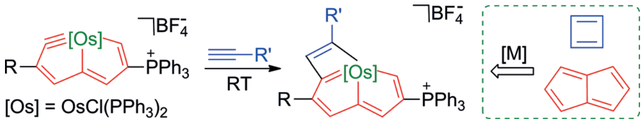


Short and sweet: Very short total syntheses of ellagitannins were achieved through sequential and regioselective functionalization of the hydroxy groups of unprotected glucose.

Metallacycles

C. Zhu, Y. Yang, M. Luo, C. Yang, J. Wu,
L. Chen, G. Liu, T. Wen, J. Zhu,*
H. Xia* ______ 6181 – 6185

Stabilizing Two Classical Antiaromatic Frameworks: Demonstration of Photoacoustic Imaging and the Photothermal Effect in Metalla-aromatics



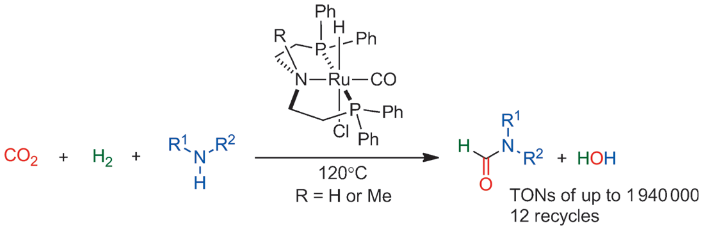
Two birds with one stone: Two classical antiaromatic molecules, cyclobutadiene and pentalene, were stabilized by introducing one metal fragment by a [2+2] cycloaddition reaction of osmapentalyne with alkynes. These metalla-aromatic molecules absorb broadly from the UV to the near-IR region and show significant photoacoustic and photothermal effects.

Front Cover

Hydrogenation

L. Zhang, Z. Han, X. Zhao, Z. Wang,
K. Ding* ______ 6186 – 6189

Highly Efficient Ruthenium-Catalyzed N-Formylation of Amines with H_2 and CO_2



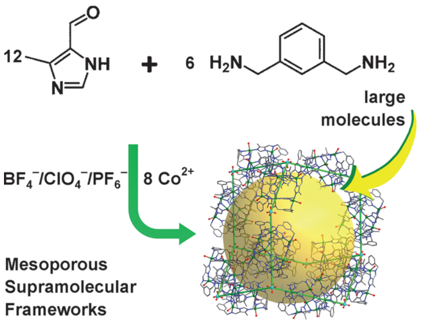
Just a pinch: CO_2 is efficiently hydrogenated for N-formylation of various amines using ruthenium-pincer catalysts, thus affording the corresponding formamides with extremely high turnover numbers (TONs). The catalyst was readily reused for 12 runs without significant loss of activity in *N*,*N*-dimethylformamide production, thus demonstrating potential for practical utilization of this cost-effective process.

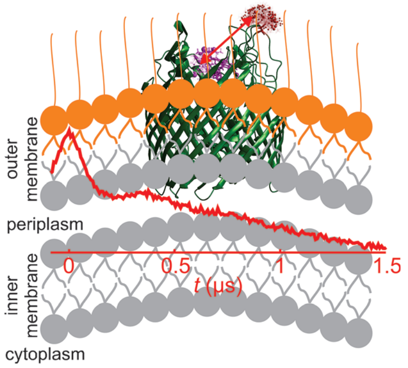
Self-Assembly

D. Luo, X.-P. Zhou,* D. Li* 6190 – 6195

Beyond Molecules: Mesoporous Supramolecular Frameworks Self-Assembled from Coordination Cages and Inorganic Anions

Caught in the middle: A series of diamond-like supramolecular frameworks featuring mesoporous cavities have been assembled through multiple interactions (covalent bonds, dative bonds, and weak C−H⋯X (X=O, F, and π) hydrogen bonds) between metal-imidazolate coordination cages and various anions. The mesoporous cavities are large enough to trap organic dye molecules, coordination cages, and vitamin B_{12}.





A novel general strategy was used for precise distance measurements on an outer membrane protein in whole *E. coli* cells and isolated outer membranes. This approach provides an elegant way to study conformational changes or protein–protein/ligand interactions under native conditions and provides a method to validate high-resolution structures of membrane proteins in their native environment.

EPR Spectroscopy

B. Joseph, A. Sikora, E. Bordignon, G. Jeschke, D. S. Cafiso,* T. F. Prisner* ______ **6196 – 6199**

Distance Measurement on an Endogenous Membrane Transporter in *E. coli* Cells and Native Membranes Using EPR Spectroscopy

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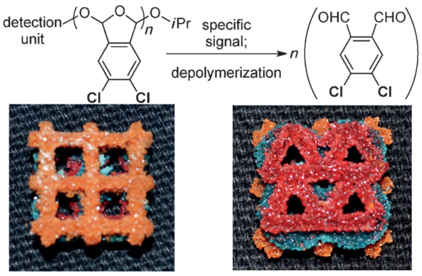


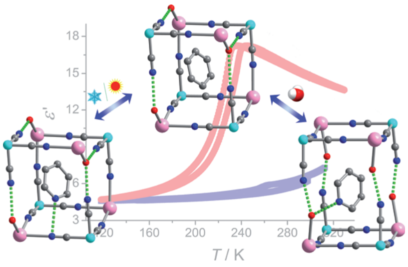
Selective laser sintering has been used to prepare synthetic materials from a new type of self-immolative polymer. These materials autonomously amplify macroscopic and nonlocalized changes in the material in response to specific molecular inputs, and alter the response of the material depending on the identity of an applied signal.

Polymers

A. M. DiLauro, G. G. Lewis, S. T. Phillips* ______ **6200 – 6205**

Self-Immolative Poly(4,5-dichlorophthalaldehyde) and its Applications in Multi-Stimuli-Responsive Macroscopic Plastics

---



A dielectric constant transition is observed in $(HPy)_2[Na(H_2O)Co(CN)_6]$ (HPy = pyridinium cation). This transition is chemically triggered by water in a single-crystal-to-single-crystal transformation (see picture; right) and thermally switched (left) in a structural phase transition.

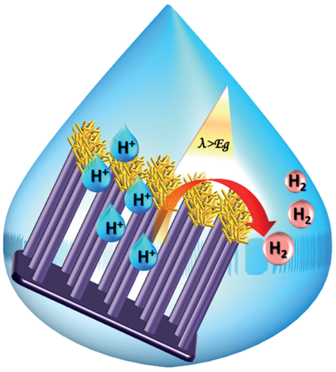
Phase Transitions

C. Shi, X. Zhang, Y. Cai, Y.-F. Yao,* W. Zhang* ______ **6206 – 6210**

A Chemically Triggered and Thermally Switched Dielectric Constant Transition in a Metal Cyanide Based Crystal

---

Heterostructures of semi-metallic $CoSe_2$ nanorods and p-Si microwires behave as an efficient photocathode for the solar-driven hydrogen evolution reaction. Photocurrents as high as 9 $mA\,cm^{-2}$ have been achieved at 0 V vs. reversible hydrogen electrode. The high photocurrents can be attributed to low charge transfer resistance between the Si and $CoSe_2$ interfaces and between the $CoSe_2$ and electrolyte interfaces.



Water Splitting

M. Basu, Z. W. Zhang, C. J. Chen, P. T. Chen, K. C. Yang, C.-G. Ma, C. C. Lin, S. F. Hu,* R. S. Liu* ______ **6211 – 6216**

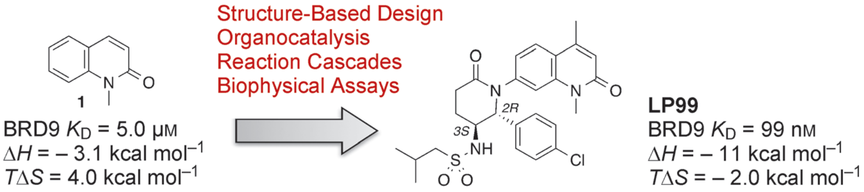
Heterostructure of Si and $CoSe_2$: A Promising Photocathode Based on a Non-noble Metal Catalyst for Photoelectrochemical Hydrogen Evolution

Inside Back Cover

Bromodomain Inhibitors

P. G. K. Clark, L. C. C. Vieira, C. Tallant, O. Fedorov, D. C. Singleton, C. M. Rogers, O. P. Monteiro, J. M. Bennett, R. Baronio, S. Müller, D. L. Daniels, J. Méndez, S. Knapp, P. E. Brennan,* D. J. Dixon* **6217 – 6221**

LP99: Discovery and Synthesis of the First Selective BRD7/9 Bromodomain Inhibitor

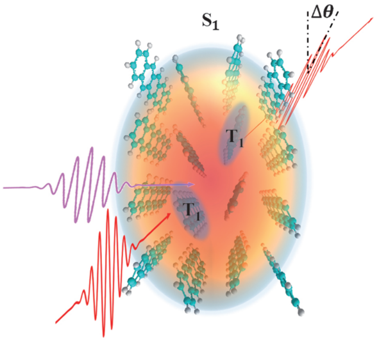


BRD7 and BRD9 are bromodomain proteins and part of some chromatin-remodeling complexes. A fragment lead was rapidly optimized through structure-based design and exploitation of a stereoselective nitro-Mannich/lactamization cascade process to give the first potent and selective BRD7/9 inhibitor, **LP99**. Treatment with **LP99** led to displacement of BRD7 and BRD9 from chromatin and down-regulation of the pro-inflammatory cytokine IL-6.

Nonlinear Optics

Y. Liu, C. Zhang,* R. Wang, B. Zhang, Z. Tan, X. Wang, M. Xiao* **6222 – 6226**

Large Optical Nonlinearity Induced by Singlet Fission in Pentacene Films

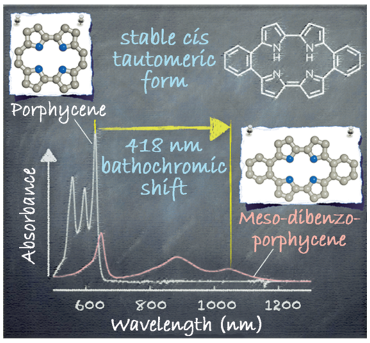


In pentacene films singlet-fission-induced nonlinear optical response with a magnitude of nonlinear susceptibility up to 10^{-9} esu is observed. Such efficient nonlinear optical response has been successfully applied to demonstrate ultrafast optical switching.

Porphycenes

K. Oohora, A. Ogawa, T. Fukuda, A. Onoda, J Hasegawa,* T. Hayashi* **6227 – 6230**

meso-Dibenzoporphycene has a Large Bathochromic Shift and a Porphycene Framework with an Unusual *cis* Tautomeric Form



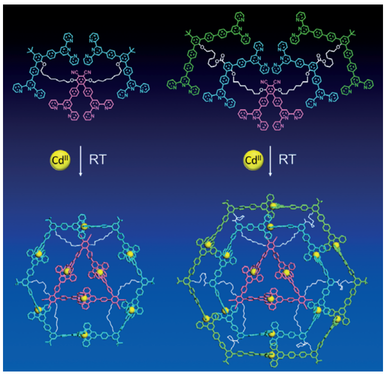
Put a ring on it: The insertion of two benzene moieties at the *meso* positions of a porphycene framework yields *meso*-dibenzoporphycene (mDBPc). The compound has a small electrochemical HOMO–LUMO gap (0.81 eV) and an NIR absorption band at 1047 nm. X-ray photoelectron spectroscopy and a theoretical study indicate that, unusually for a porphycene derivative, the *cis* tautomeric form of the porphycene framework is more stable than the *trans* form.

Supramolecular Chemistry

J.-H. Fu, Y.-H. Lee, Y.-J. He, Y.-T. Chan* **6231 – 6235**

Facile Self-Assembly of Metallo-Supramolecular Ring-in-Ring and Spiderweb Structures Using Multivalent Terpyridine Ligands

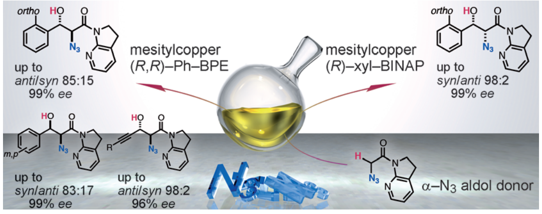
A nano-spiderweb: The complexation of multivalent terpyridine ligands with Cd^{II} ions afforded various linker-dependent ring-in-ring structures. The two-step self-assembly process through a tetratopic intermediate was deciphered by a mechanistic study. This ligand design strategy was successfully utilized in the construction of a trilayered metallo-supramolecular spiderweb.



Asymmetric Catalysis

K. Weidner, Z. Sun, N. Kumagai,*
M. Shibasaki* ____ **6236 – 6240**

Direct Catalytic Asymmetric Aldol Reaction of an α-Azido Amide

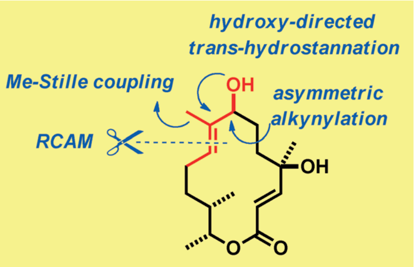


The direct aldol reaction of an α-azido 7-azaindolinylamide is promoted by a Cu-based catalyst. Aromatic aldehydes bearing an *ortho* substituent exhibited diastereodivergency depending on the nature of the chiral ligands used. A vicinal azido alcohol unit led to the corresponding aziridine, and facile hydrolysis of the 7-azaindolinylamide moiety furnished enantioenriched β-hydroxy-α-azido carboxylic acid derivatives.

Alkyne Metathesis

S. M. Rummelt, J. Preindl, H. Sommer,
A. Fürstner* ____ **6241 – 6245**

Selective Formation of a Trisubstituted Alkene Motif by *trans*-Hydrostannation/Stille Coupling: Application to the Total Synthesis and Late-Stage Modification of 5,6-Dihydrocineromycin B

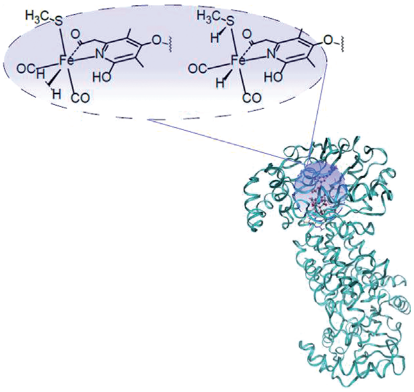


Directed although indirect: The antibiotic dihydrocineromyin B is one of countless natural products featuring an *E*-configured 2-methylbut-2-en-1-ol substructure (see picture, RCAM = ring-closing alkyne metathesis). The key step in the synthesis was a ruthenium-catalyzed hydroxy-directed *trans*-hydrostannation of an alkyne. The method is efficient, broadly applicable, and suited to late-stage diversification.

H_2 Activation by Hydrogenases

E. D. Hedegård,* J. Kongsted,
U. Ryde ____ **6246 – 6250**

Multiscale Modeling of the Active Site of [Fe] Hydrogenase: The H_2 Binding Site in Open and Closed Protein Conformations

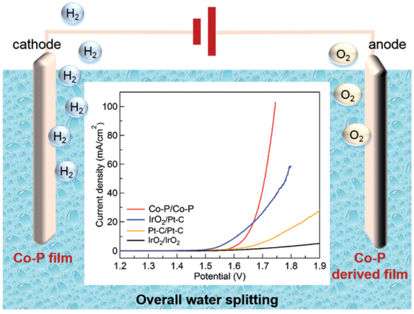


Hydrogenases mediate the conversion of H_2 into hydride and protons. Intermediates and transition structures for H_2 activation and hydride transfer in [Fe] hydrogenase were investigated (see picture, with a side-on bound dihydrogen and a hydride intermediate). Inclusion of the full protein with QM/MM is mandatory because of large electrostatic effects that cannot be described properly by vacuum calculations or continuum models.

Water Splitting

N. Jiang, B. You, M. Sheng,
Y. Sun* ____ **6251 – 6254**

Electrodeposited Cobalt-Phosphorous-Derived Films as Competent Bifunctional Catalysts for Overall Water Splitting



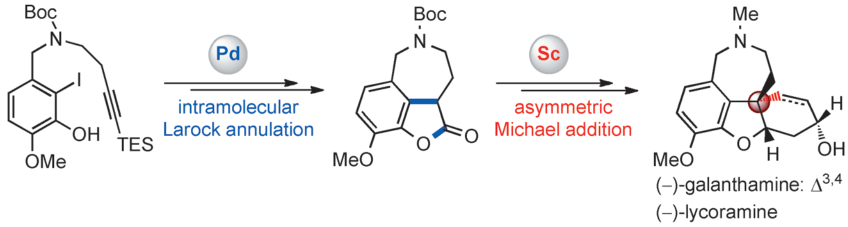
Split and polished: Electrodeposited cobalt-phosphorous-derived films (Co-P) can act as superior bifunctional catalysts for overall water splitting. When employed as catalysts on both the anode and cathode for water electrolysis, the Co-P/Co-P catalyst couple can rival the integrated performance of IrO_2 and Pt in alkaline media. Such a bifunctional Co-P film is a promising catalyst candidate for overall water-splitting electrolysis.

Back Cover

Alkaloids

L. Li, Q. Yang, Y. Wang,
Y. Jia* ________ 6255 – 6259

Catalytic Asymmetric Total Synthesis of (−)-Galanthamine and (−)-Lycoramine



How gallant: The catalytic asymmetric total synthesis of both (−)-galanthamine and (−)-lycoramine were achieved by using a conceptually new strategy. Two metal-catalyzed reactions were used as the key steps, and include a palladium-catalyzed intramolecular Larock annulation reaction and enantioselective conjugate addition reaction catalyzed by a Sc^{III}/*N*,*N*′-dioxide complex. Boc = *tert*-butoxycarbonyl, TES = triethylsilyl.

High-Energy-Density Materials

C. He, J. M. Shreeve* ________ 6260 – 6264

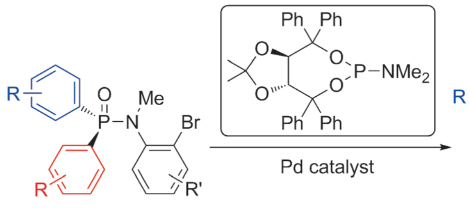
Energetic Materials with Promising Properties: Synthesis and Characterization of 4,4′-Bis(5-nitro-1,2,3-2*H*-triazole) Derivatives

The hunt for high energy: Derivatives of 4,4′-bis(5-nitro-1,2,3-2*H*-triazole) were synthesized by different functionalization strategies. Competitive detonation properties were achieved and compared to reported analogues of fully carbon-nitrated bis(azole) compounds.

C−H Activation

Z.-Q. Lin, W.-Z. Wang, S.-B. Yan,
W.-L. Duan* ________ 6265 – 6269

Palladium-Catalyzed Enantioselective C−H Arylation for the Synthesis of P-Stereogenic Compounds

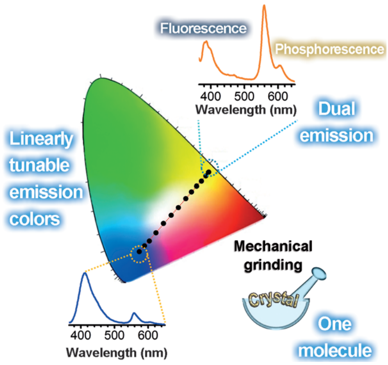


Dressing up phosphorus: The title reaction of *N*-(*o*-bromoaryl)-diarylphosphinic amides is described for the synthesis of phosphorus compounds bearing a P-stereogenic center. The method provides good enantioselectivities and high yields. The products were readily transformed into P-chiral biphenyl monophosphine ligands.

Mechanochromic Materials

Z. Mao, Z. Yang, Y. Mu, Y. Zhang,*
Y. Wang, Z. Chi,* C. Lo, S. Liu, A. Lien,
J. Xu* ________ 6270 – 6273

Linearly Tunable Emission Colors Obtained from a Fluorescent–Phosphorescent Dual-Emission Compound by Mechanical Stimuli

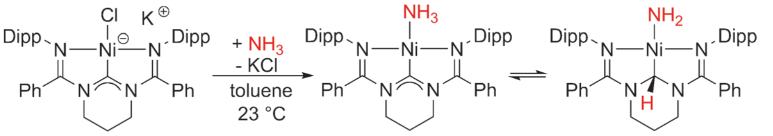


Grinding a rainbow: A purely organic compound with excellent room-temperature fluorescent–phosphorescent dual-emission (rFPDE) properties brought about by mechanical grinding has been demonstrated. It shows linearly tunable emission colors with a straight line across the white zone in the chromaticity diagram, following the principle of color mixing.

Ammonia Activation

R. M. Brown, J. Borau Garcia, J. Valjus, C. J. Roberts, H. M. Tuononen, M. Parvez, R. Roesler* ______ **6274 – 6277**

Ammonia Activation by a Nickel NCN-Pincer Complex featuring a Non-Innocent N-Heterocyclic Carbene: Ammine and Amido Complexes in Equilibrium

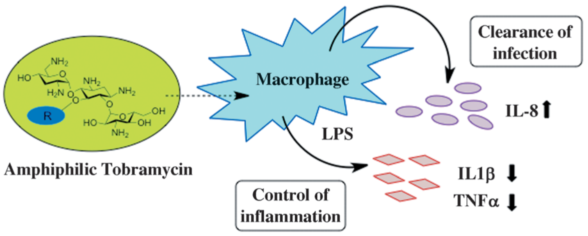


Fast and reversible ligand-assisted ammonia activation on a nickel-NCN pincer complex featuring a non-innocent N-heterocyclic carbene produced a solvent-dependent equilibrium mixture of ammine and amide complexes (see scheme, Dipp = 2,6-diisopropylphenyl). These species were present in solution in comparable proportions, and EXSY NMR experiments as well as exchange with ND_3 further supported the equilibrium.

Anti-infective Agents

G. Guchhait, A. Altieri, B. Gorityala, X. Yang, B. Findlay, G. G. Zhanel, N. Mookherjee, F. Schweizer* ______ **6278 – 6282**

Amphiphilic Tobramycins with Immunomodulatory Properties

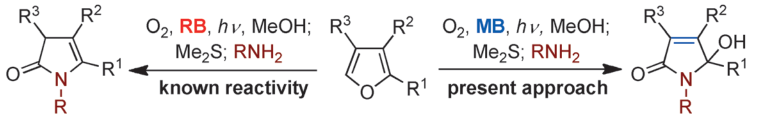


Double duty: Amphiphilic antibacterial aminoglycosides with additional immunomodulatory properties similar to those of host-defense peptides can be generated by appending a lipophilic R group (blue oval) to tobramycin. These amphiphilic tobramycin analogues can boost innate immune responses and control inflammatory responses related to septic shock.

Synthetic Methods

D. Kalaitzakis, A. Kouridaki, D. Noutsias, T. Montagnon, G. Vassilikogiannakis* ______ **6283 – 6287**

Methylene Blue as a Photosensitizer and Redox Agent: Synthesis of 5-Hydroxy-1*H*-pyrrol-2(5*H*)-ones from Furans

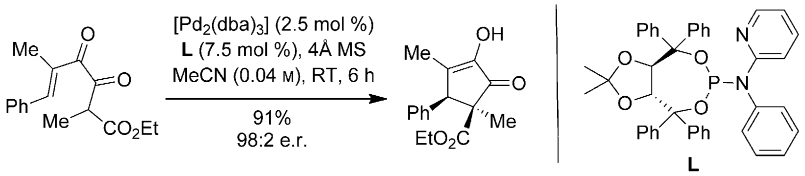


A reagent with two hats: A highly efficient and general singlet-oxygen-initiated one-pot transformation of readily accessible furans into 5-hydroxy-1*H*-pyrrol-2(5*H*)-ones was developed (see scheme, right) and extended to the synthesis of other high-value α,β-unsaturated γ-lactams. This useful set of transformations relies on both the photosensitizing ability and the redox properties of methylene blue (MB), the reactivity of which differs from that of Rose Bengal (RB).

Asymmetric Synthesis

K. Kitamura, N. Shimada, C. Stewart, A. C. Atesin, T. A. Ateşin,* M. A. Tius* ______ **6288 – 6291**

Enantioselective Palladium(0)-Catalyzed Nazarov-Type Cyclization

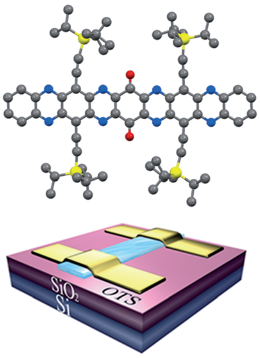


Stereoselective cycles: A Nazarov-type Pd^0-catalyzed asymmetric cyclization is reported. The reaction forms cyclopentenones as single diastereoisomers that incorporate two contiguous asymmetric centers in high yield and optical purity. The optimized ligand **L** incorporates a weakly coordinating pyridine ring into a TADDOL-derived phosphoramidite. dba = dibenzylideneacetone. MS = molecular sieves.

Electron Transport

C. Wang, J. Zhang, G. Long, N. Aratani,
H. Yamada, Y. Zhao,
Q. Zhang* ______ **6292 – 6296**

Synthesis, Structure, and Air-stable N-type Field-Effect Transistor Behaviors of Functionalized Octaazanonacene-8,19-dione



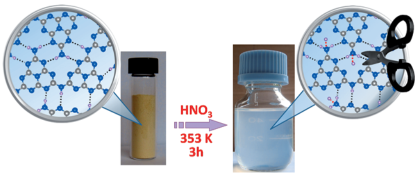
A field day: The large π-conjugated N-heteroquinone 6,10,17,21-tetra[(triisopropylsilyl)ethynyl]-5,7,9,11,16,18,20,22-octaazanonacene-8,19-dione (OANQ; see figure) has been successfully synthesized and characterized. A field-effect transistor device based on OANQ single crystals displays an electron mobility of up to 0.2 $cm^2 V^{-1} s^{-1}$ under ambient conditions.

Sol–Gel Processes

J. Zhang, M. Zhang, L. Lin,
X. Wang* ______ **6297 – 6301**

Sol Processing of Conjugated Carbon Nitride Powders for Thin-Film Fabrication

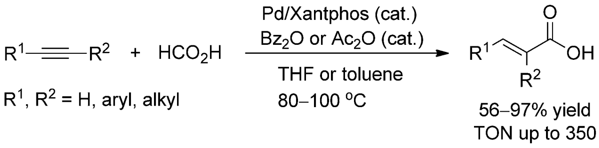
Going strong: Sol engineering of graphitic carbon nitride solids with strong oxidizing acids (e.g. HNO_3) generates a stable colloidal suspension, which can be translated into thin films by dip/disperse-coating techniques. The polymeric matrix and the reversible hydrogen bonding result in the thin-film electrodes derived from the sol solution having high mechanical stability with improved conductivity for charge transport.



Synthetic Methods

J. Hou, J.-H. Xie,
Q.-L. Zhou* ______ **6302 – 6305**

Palladium-Catalyzed Hydrocarboxylation of Alkynes with Formic Acid

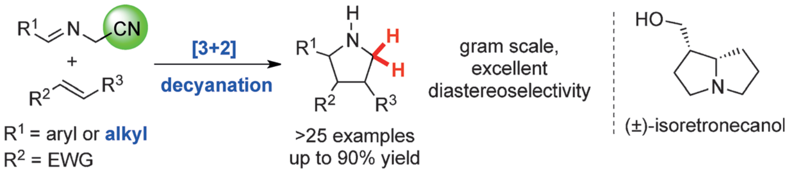


Nontoxic: Acrylic acids are an important chemical feedstock. The title reaction provides acrylic acid and derivatives in good yields with high regioselectivities without the need to handle toxic CO gas.

Heterocycle Synthesis

J. Li, H. Zhao, X. Jiang, X. Wang, H. Hu,
L. Yu, Y. Zhang* ______ **6306 – 6310**

The Cyano Group as a Traceless Activation Group for the Intermolecular [3+2] Cycloaddition of Azomethine Ylides: A Five-Step Synthesis of (±)-Isoretronecanol

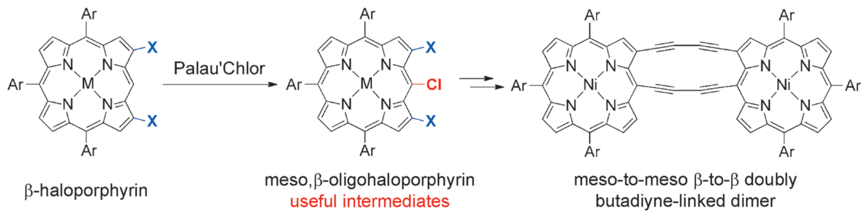


Without a trace... A highly stereoselective cycloaddition strategy provided efficient access to a diverse array of 5-unsubstituted pyrrolidines and enabled a five-step total synthesis of isoretronecanol (see scheme). A novel role of sodium borohydride in reductive decyanation was observed.

Porphyrinoids

N. Fukui, H. Yorimitsu,* A. Osuka* ____ **6311 – 6314**

meso,β-Oligohaloporphyrins as Useful Synthetic Intermediates of Diphenylamine-Fused Porphyrin and meso-to-meso β-to-β Doubly Butadiyne-Bridged Diporphyrin

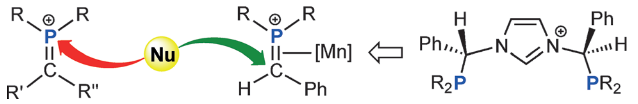


Doubled over: Chlorination of β-haloporphyrins with 2-chloro-1,3-bis(methoxycarbonyl)guanidine (Palau'Chlor) proceeded selectively at the neighboring unsubstituted meso position to afford meso,β-oligohaloporphyrins, which are useful intermediates of porphyrin-based extended π systems. For example, meso-chloro-β-iodoporphyrin was transformed stepwise into an efficiently conjugated meso-to-meso,β-to-β doubly butadiyne-linked porphyrin dimer.

Manganese Complexes

D. A. Valyaev,* O. A. Filippov, N. Lugan,* G. Lavigne, N. A. Ustynyuk ____ **6315 – 6319**

Umpolung of Methylenephosphonium Ions in Their Manganese Half-Sandwich Complexes and Application to the Synthesis of Chiral Phosphorus-Containing Ligand Scaffolds

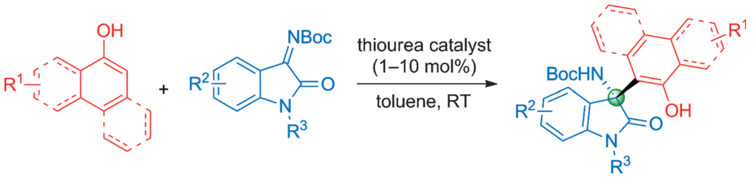


Reactivity trend reversal: Methylenephosphonium salts coordinated to a manganese center were found to exhibit "iminium-like" reactivity towards nucleophiles (see scheme). This unprecedented umpolung enables the instant formation of carbon–heteroatom bonds, highlighted by the synthesis of novel chiral pincer-type phosphine–NHC–phosphine ligands.

Asymmetric Catalysis

M. Montesinos-Magraner, C. Vila, R. Cantón, G. Blay, I. Fernández, M. C. Muñoz, J. R. Pedro* ____ **6320 – 6324**

Organocatalytic Asymmetric Addition of Naphthols and Electron-Rich Phenols to Isatin-Derived Ketimines: Highly Enantioselective Construction of Tetrasubstituted Stereocenters



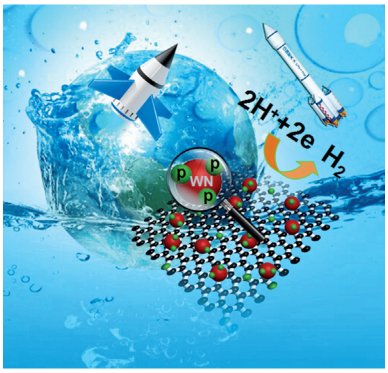
Gentle persuasion: A quinine-derived thiourea organocatalyst was found to promote the asymmetric addition of naphthols and activated phenols to ketimines derived from isatins (see scheme; Boc = *tert*-butoxycarbonyl). The reaction under mild conditions afforded chiral 3-amino-2-oxindoles containing a quaternary stereocenter in high yields (up to 99%) with excellent enantioselectivity (up to 99% *ee*).

Electrocatalysis

H. Yan, C. Tian,* L. Wang, A. Wu, M. Meng, L. Zhao, H. Fu* ____ **6325 – 6329**

Phosphorus-Modified Tungsten Nitride/Reduced Graphene Oxide as a High-Performance, Non-Noble-Metal Electrocatalyst for the Hydrogen Evolution Reaction

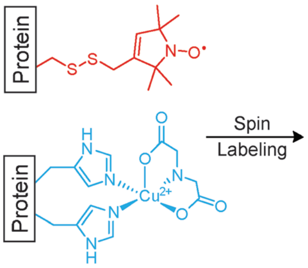
Boosting HER activity by phosphorus modification of tungsten nitride/reduced graphene oxide leads to a low-cost, high-performance, non-noble metal electrocatalyst for the hydrogen evolution reaction. The catalyst has a very small onset overpotential, a low Tafel slope, a large exchange current density in acid, and was stable in accelerated durability testing.



Protein Structure Determination

T. F. Cunningham, M. R. Putterman,
A. Desai, W. S. Horne,*
S. Saxena* ——— **6330 – 6334**

The Double-Histidine Cu^{2+}-Binding Motif: A Highly Rigid, Site-Specific Spin Probe for Electron Spin Resonance Distance Measurements



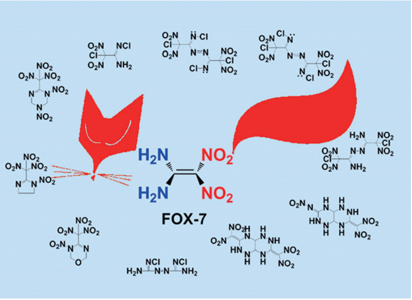
That's great, DEER! When a double-histidine Cu^{2+}-binding motif (shown in blue) assembled in situ from natural amino acid residues and a metal salt was used as a rigid spin probe for double electron–electron resonance (DEER) distance measurements, dramatically narrower and readily interpretable distance distributions were observed than with a commonly used flexible spin label (red). Molecular modeling of an unlabeled protein gave a distance within 0.5 Å of the experimental value.

Energetic Materials

H. Gao,* J. M. Shreeve* ——— **6335 – 6338**

The Many Faces of FOX-7: A Precursor to High-Performance Energetic Materials

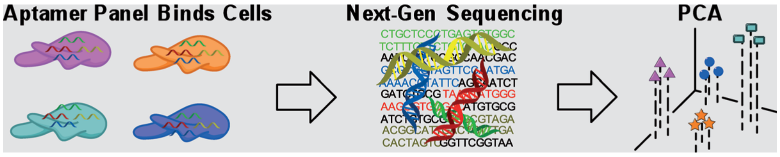
Fox in a box: New derivatives created from 1,1-diamino-2, 2-dinitroethene (FOX-7) often have properties superior to those of RDX. The compounds exhibit good thermal stability, high density, positive heats of formation, an acceptable oxygen balance, and excellent detonation properties. These findings contribute to the value of FOX-7 as an energetic precursor.



Sensors

S. Goodwin, A. M. Gade, M. Byrom,
B. Herrera, C. Spears, E. V. Anslyn,*
A. D. Ellington* ——— **6339 – 6342**

Next-Generation Sequencing as Input for Chemometrics in Differential Sensing Routines

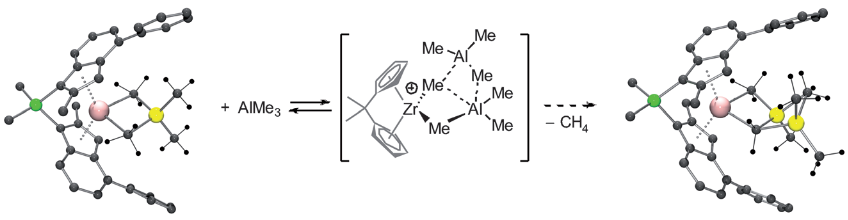


Keeping score: Nucleic acid sequences and sequence counts were used as multivariate data without the necessity of a spatial array. Aptamers were used as semi-specific receptors for cell line differentiation, and cross-reactivity between the aptamers was observed. The principal component analysis (PCA) generates high-dimensionality score plots, thus differentiating a mixture of complex and subtly different analytes.

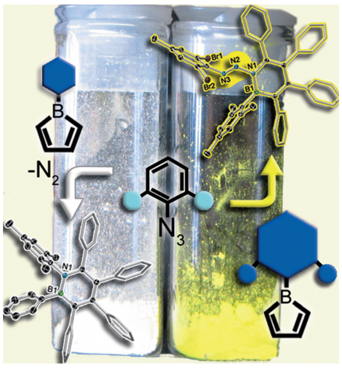
Polymerization Catalysts

G. Theurkauff, A. Bondon, V. Dorcet,
J.-F. Carpentier,* E. Kirillov* **6343 – 6346**

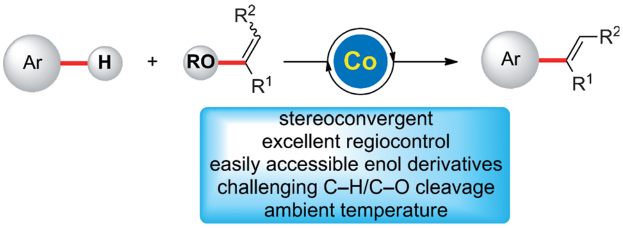
Heterobi- and -trimetallic Ion Pairs of Zirconocene-Based Isoselective Olefin Polymerization Catalysts with $AlMe_3$



Zirconocene-based $AlMe_3$ adducts bind an additional $AlMe_3$ molecule reversibly, affording heterotrimetallic intermediates. One of the $AlMe_3$ adducts undergoes slow decomposition via C–H activation in a bridging methyl unit to yield a new species with a trimetallic $\{Zr(\mu\text{-}CH_2)(\mu\text{-}Me)AlMe(\mu\text{-}Me)AlMe_2\}$ core.

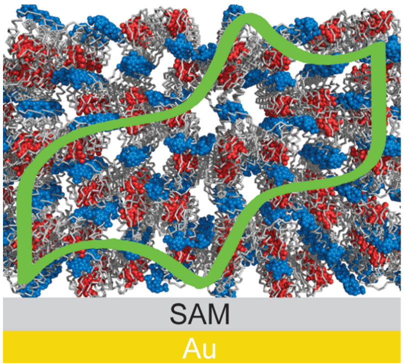


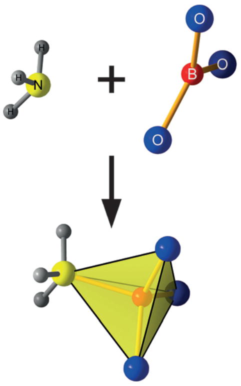
Azo borealis: The first 1,2-azaborinine-substituted azo dyes have been synthesized using sterically demanding boroles and organic azides. The ring-expansion mechanism of the unexpected formation of the bright yellow chromophores was investigated by DFT calculations.



Inexpensive cobalt catalysis enabled the C–H alkenylation of unactivated (hetero)arenes with enol derivatives at ambient temperature. The versatile cobalt catalyst was employed for challenging C–H/C–O cleavage reactions with alkenyl acetates, carbamates, carbonates, and phosphates in a stereoconvergent fashion.

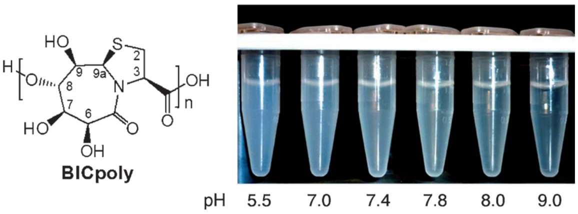
Crystal contact. A calixarene "molecular glue" (blue) can be used to grow crystals of cytochrome *c* (gray; heme red) directly on Au–SAM electrodes. Characterization by cyclic voltammetry revealed remarkable electroactivity in the crystals. The amount of electrode-addressable protein is several orders of magnitude larger than in standard multilayer systems.





Ammonize me! The first compound in the class of ammine borates has been synthesized by a multi-anvil high-pressure/high-temperature experiment. The previously unknown adduct of ammonia to an inorganic BO_3 group of a borate can be stabilized with this method, resulting in a $BO_3(NH_3)$ tetrahedron as a new structural element.

Drug Carriers



Polyhydroxycarboxylic acid for nanoscale carrier formation: By ring-opening polymerization with high regioselectivity, a polyester (BICpoly) is obtained which can be precipitated in water as nanoparticles or as a thin film. Its complete stability at low pH values, its residue-free hydrolysis to biocompatible monomers at higher pH values, and its capability for drug loading and sustained drug release, make BICpoly an attractive carrier material for medical applications.

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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