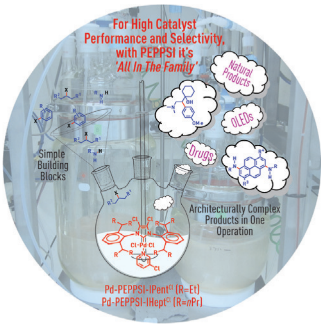
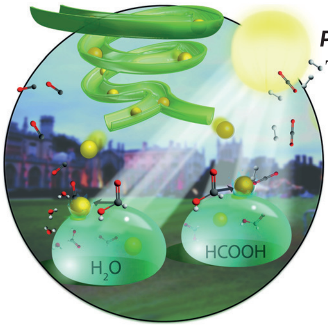
# A series of butterfly-like molecules ...

… that undergo controlled photoinduced structural change (PSC) and exhibit tunable dual emission are reported by B. Ma, C. Huang, and co-workers in their Communication on page 9591 ff. The precise control of the PSC processes and the dual emission is achieved by molecular engineering of the potential energy surface of the excited state.

***Cross-Coupling***

In their Communication on page 9502 ff., M. G. Organ et al. describe the cross-coupling of five-membered-ring heterocycles with secondary alkyl zinc reagents in the presence of the new precatalysts Pd-PEPPSI-IPent$^{Cl}$ and Pd-PEPPSI-IHept$^{Cl}$.





***Photocatalysis***

The selective room-temperature conversion of formic acid into either hydrogen or carbon monoxide is described by E. Reisner et al. in their Communication on page 9627 ff. The reaction is catalyzed by inexpensive CdS nanocrystals under irradiation with visible light.

***Lithium-Ion Batteries***

In their Communication on page 9663 ff., K. Kang et al. report a rechargeable Li–$SO_2$ battery with an energy efficiency that is significantly better than that of the Li–$O_2$ system.

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***Spotlight on Angewandte's*** Sister Journals **9442 – 9445**

## Author Profile

*"I advise my students to work hard and not to accept mediocrity.*
*Chemistry is fun because you can make a career out of your favorite hobby. ..."*
This and more about Ross A. Widenhoefer can be found on page 9446.

Ross A. Widenhoefer ———— **9446**

## News


A. E. Ashley


M. Arenz


K. Koszinowski


M. S. Sanford

BASF Catalysis Award:
A. E. Ashley ———— **9447**

Hellmuth Fischer Medal:
M. Arenz ———— **9447**

Mattauch–Herzog Prize:
K. Koszinowski ———— **9447**

OMCOS Prize:
M. S. Sanford ———— **9447**

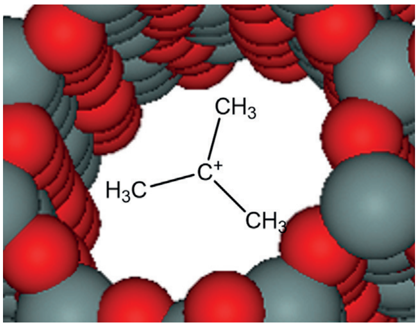
## Highlights

### Reaction Mechanisms

G. Buntkowsky,*
T. Gutmann ____________ 9450 – 9451

A Mousetrap for Carbenium Ions: NMR Detectives at Work

**The combined efforts** of German and Chinese scientists applying solid-state NMR spectroscopy, DFT calculations, and chemical modeling provided experimental proof of the *tert*-butyl cation as a reaction intermediate in the butene/isobutene conversion on acidic zeolites.



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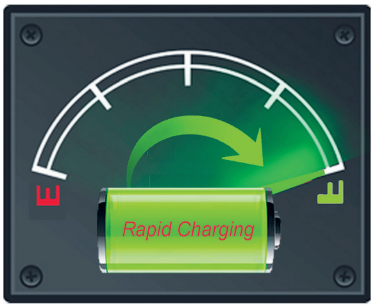
### Batteries

S. Lee, J. Cho* ____________ 9452 – 9455

Critical Requirements for Rapid Charging of Rechargeable Al- and Li-Ion Batteries



**On a charge**: Currently, considerable demand exists for rechargeable batteries with both high energy density and low manufacturing cost, for use in mobile electronic devices and electric vehicles. Rapid charging is also a highly desirable criterion. Various recent approaches to realizing these requirements are presented.

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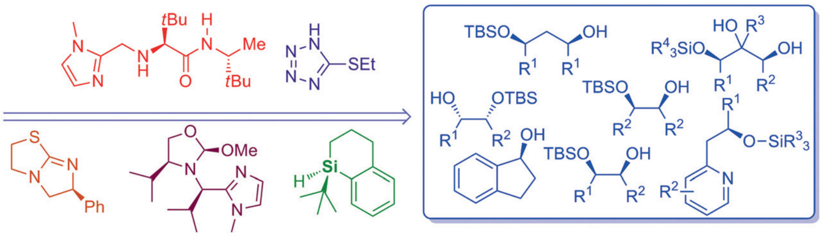
## Minireviews

### Silylation

L.-W. Xu,* Y. Chen, Y. Lu* __ 9456 – 9466

Catalytic Silylations of Alcohols: Turning Simple Protecting-Group Strategies into Powerful Enantioselective Synthetic Methods



**Silicon talks**: Owing to the development of methods for the site- and stereoselective functionalization of hydroxy groups, silyl ether formation has evolved from being a simple reaction for functional-group protection into a powerful enantioselective process. This Minireview highlights recent findings in the emerging field of enantioselective alcohol silylation.

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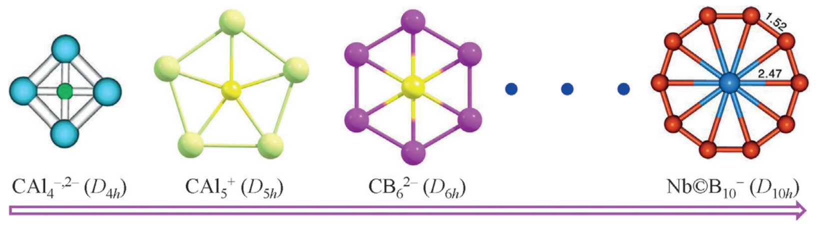
# Reviews

## Theoretical Chemistry

L.-M. Yang,* E. Ganz, Z. Chen,*
Z.-X. Wang, P. v. R. Schleyer **9468 – 9501**

Four Decades of the Chemistry of Planar Hypercoordinate Compounds



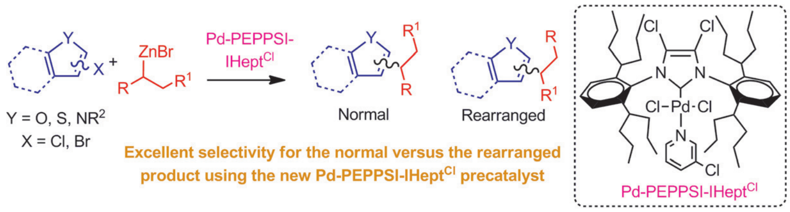
**Where the great plains begin**: Planar hypercoordinate chemistry has emerged as an exciting field with the discovery of unique molecules with unusual bonding configurations. Starting with planar tetragonal carbon, molecules of increasing complexity and hypercoordinate bond numbers from four up to ten have been predicted, and some have been synthesized. This Review covers the evolution and rapid growth of the field of planar hypercoordinate chemistry over the last four and a half decades.

# Communications

## Cross-Coupling

B. Atwater, N. Chandrasoma, D. Mitchell,
M. J. Rodriguez, M. Pompeo,
R. D. J. Froese,
M. G. Organ* __________ **9502 – 9506**

The Selective Cross-Coupling of Secondary Alkyl Zinc Reagents to Five-Membered-Ring Heterocycles Using Pd-PEPPSI-IHept$^{Cl}$



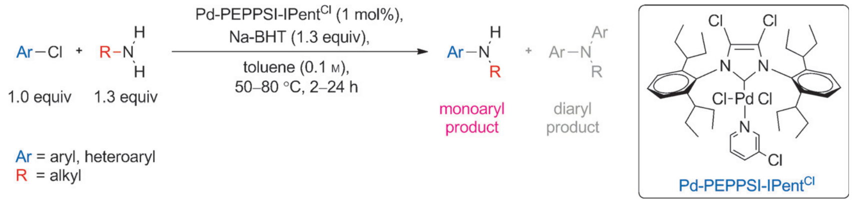
**A wide variety** of five-membered-ring heterocycles were successfully cross-coupled to secondary alkyl zinc reagents with the new precatalyst Pd-PEPPSI-IHept$^{Cl}$, which features a bulky N-heterocyclic carbene ligand. This catalyst suppresses migratory-insertion (rearrangement) pathways, and the desired products are thus formed with high selectivity.

**Frontispiece**

## Cross-Coupling

S. Sharif, R. P. Rucker, N. Chandrasoma,
D. Mitchell, M. J. Rodriguez,
R. D. J. Froese,
M. G. Organ* __________ **9507 – 9511**

Selective Monoarylation of Primary Amines Using the Pd-PEPPSI-IPent$^{Cl}$ Precatalyst

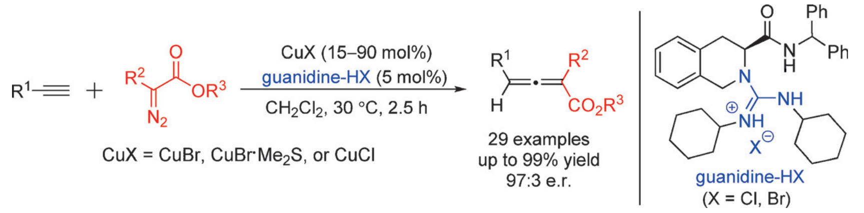


**PEPPSI hits the spot**: A single set of reaction conditions for the palladium-catalyzed amination of a wide variety of (hetero)aryl halides using primary alkyl amines has been developed. By combining the exceptionally high reactivity of the Pd-PEPPSI-IPent$^{Cl}$ with the sodium salt of BHT (BHT = 2,6-di-*tert*-butyl-hydroxytoluene), both six- and five-membered (hetero)aryl halides undergo efficient and selective monoamination.

## Asymmetric Catalysis

Y. Tang, Q. G. Chen, X. H. Liu,* G. Wang, L. L. Lin, X. M. Feng ——— **9512 – 9516**

### Direct Synthesis of Chiral Allenoates from the Asymmetric C–H Insertion of α-Diazoesters into Terminal Alkynes



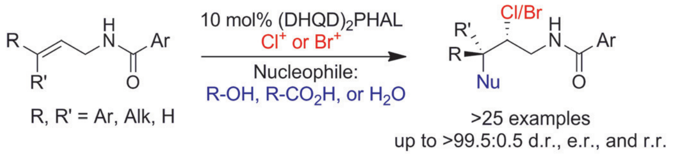
**Salt down**: The title reaction was achieved using chiral cationic guanidinium salts with copper(I) complexes. Optically active 2,4-disubstituted allenoates were generated under mild reaction conditions from various α-diazoesters and 1-alkynes in high yield and enantioselectivity. Control experiments excluded the possibility of an asymmetric isomerization.

---

## Organocatalysis

B. Soltanzadeh, A. Jaganathan, R. J. Staples, B. Borhan* —— **9517 – 9522**

### Highly Stereoselective Intermolecular Haloetherification and Haloesterification of Allyl Amides



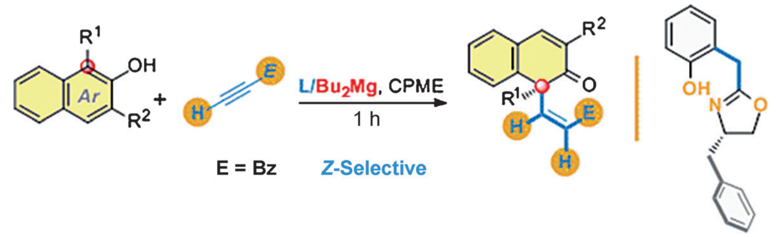
**A highly regioselective** intermolecular haloetherification that proceeds with excellent enantioselectivity, catalyzed by cinchona alkaloid dimers, is reported. The regioselectivity is preserved for unbiased alkyl substituted allyl amides with either *E* or *Z* geometry. $(DHQD)_2PHAL$ = hydroquinidine 1,4-phthalazinediyl diether.

---

## Aromaticity

D. Yang, L. Wang, M. Kai, D. Li, X. Yao, R. Wang* ——— **9523 – 9527**

### Application of a C–C Bond-Forming Conjugate Addition Reaction in Asymmetric Dearomatization of β-Naphthols



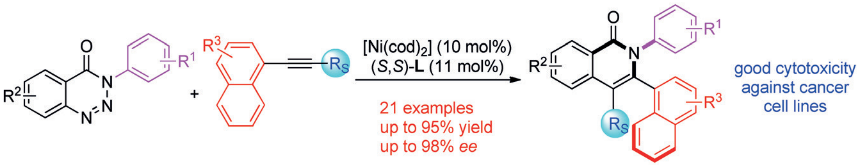
**Aromatic or nonaromatic?** The successful development of the title reaction was achieved for the first time. An in situ generated magnesium catalyst was employed to provide functionalized β-naphthalenones, having a quaternary stereocenter. The *Z*-configured C–C double bond in the products can be isomerized in the presence of $AlCl_3$. Bz = benzoyl, CPME = cyclopentyl methyl ether.

---

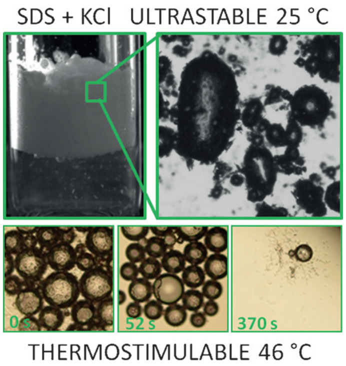
## Heterocycles

Z.-J. Fang, S.-C. Zheng, Z. Guo, J.-Y. Guo, B. Tan,* X.-Y. Liu* ——— **9528 – 9532**

### Asymmetric Synthesis of Axially Chiral Isoquinolones: Nickel-Catalyzed Denitrogenative Transannulation



**Getting the axe**: Reported is the first enantioselective $Ni^0$/bis(oxazoline)-catalyzed asymmetric transannulation of 1,2,3-benzotriazin-4(3*H*)-ones with internal alkynes in an atroposelective manner to form novel axially chiral isoquinolones. DFT calculations show data for the preferred transition state in the annulation step. The products show good cytotoxicity against cancer cell lines.



**Ultrastable foams** are made very simply by adding NaCl or KCl to sodium dodecyl sulfate. Below the Krafft boundary, bubbles with solid surfaces can be obtained, which arrest foam ageing and lead to foams that are stable indefinitely. They can however be easily destroyed by heating. This provides a means to cheap and simple thermostimulable foams.

### Thermostimulable Materials

L. Zhang, A. Mikhailovskaya, P. Yazhgur, F. Muller, F. Cousin, D. Langevin, N. Wang, A. Salonen* ______ **9533 – 9536**

Precipitating Sodium Dodecyl Sulfate to Create Ultrastable and Stimulable Foams

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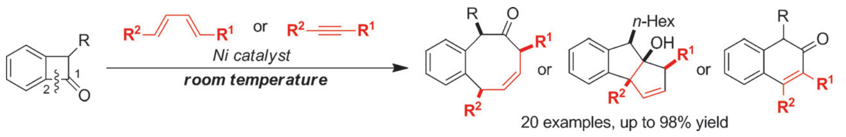


**Mild and economical**: The first catalytic intermolecular bond formation through proximal C1–C2 cleavage of benzocyclobutenones without prior carbonyl activation or employing noble metals is described. The reaction operates at room temperature and is characterized by excellent chemo-, regio- and diastereoselectivities, providing access to complex carbocyclic skeletons.

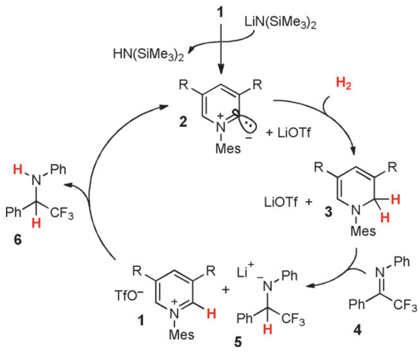
### C–C Bond Activation

F. Juliá-Hernández, A. Ziadi, A. Nishimura, R. Martin* __ **9537 – 9541**

Nickel-Catalyzed Chemo-, Regio- and Diastereoselective Bond Formation through Proximal C–C Cleavage of Benzocyclobutenones

---

**Deprotonation** of pyridinium salt **1** (R = 2,6-$Me_2C_6H_3$) produces pyridylidene **2**, which reacts with $H_2$ to give dihydropyridine **3**. This $H_2$ activation process can be combined with hydride transfer from the dihydropyridine to an imine in a catalytic process. Treatment of imine **4** with **1** (5–20 mol %) and $LiN(SiMe_3)_2$ (0.3–1.0 equiv) under hydrogen atmosphere (50 bar) resulted in high conversion into the corresponding amine.



### Dihydrogen Activation

J. Auth, J. Padevet, P. Mauleón,* A. Pfaltz* ______ **9542 – 9545**

Pyridylidene-Mediated Dihydrogen Activation Coupled with Catalytic Imine Reduction

**Inside Cover**

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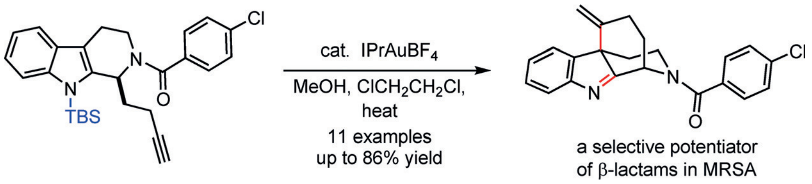


**Resurrecting β-lactams**: A gold-catalyzed desilylative cyclization was developed to construct bridged tetracyclic indolenines, a common motif of natural indole alkaloids. One cyclization product was discovered to selectively potentiate β-lactam antibiotics in methicillin-resistant *S. aureus* (MRSA). IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene, TBS = *tert*-butyldimethylsilyl.

### Antibiotics

W. Xu, W. Wang, X. Wang* _ **9546 – 9549**

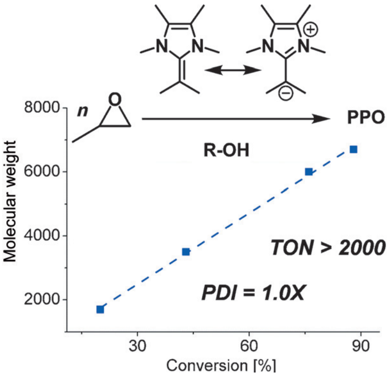
Gold-Catalyzed Cyclization Leads to a Bridged Tetracyclic Indolenine that Represses β-Lactam Resistance

## *Ring-Opening Polymerization*

S. Naumann,* A. W. Thomas,
A. P. Dove* ______ **9550 – 9554**

N-Heterocyclic Olefins as Organocatalysts for Polymerization: Preparation of Well-Defined Poly(propylene oxide)

**One carbon makes a difference**: The efficient and controlled formation of poly(propylene oxide) (PPO) at a very low catalyst loading of N-heterocyclic olefins showcases the use of this group of highly polarized alkenes as catalysts for organopolymerization. A strong structure–activity relationship is found, which is fundamentally different from the reactivity of N-heterocyclic carbenes (TON = turnover number, PDI = polydispersity index).



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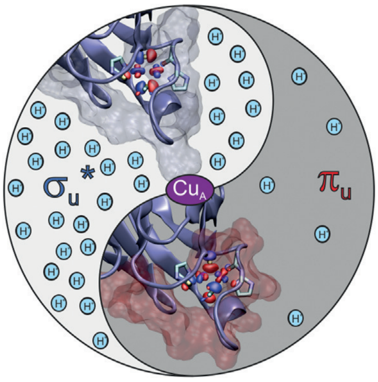
## *Bioelectrochemistry*

U. Zitare, D. Alvarez-Paggi,
M. N. Morgada, L. A. Abriata, A. J. Vila,
D. H. Murgida* ______ **9555 – 9559**

Reversible Switching of Redox-Active Molecular Orbitals and Electron Transfer Pathways in $Cu_A$ Sites of Cytochrome *c* Oxidase



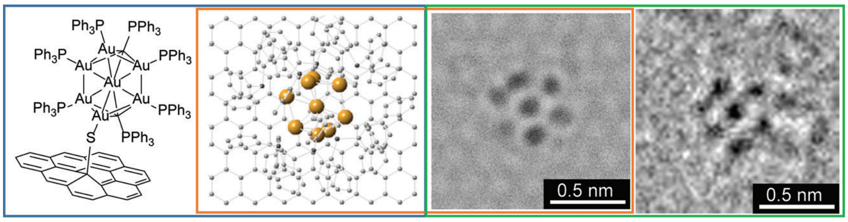
**Biological electron hub:** The $Cu_A$ site of cytochrome *c* oxidase is shown to switch between electron pathways optimized for reduction and oxidation, respectively, through reversible modulation of the energy gap separating alternative electronic ground states ($\sigma_u^*$ and $\pi_u$; see picture). This behavior explains the efficiency and directionality of the site in cytochrome *c* oxidase.

---

## *Surface Chemistry*

C. Bosch-Navarro,* Z. P. L. Laker,
H. R. Thomas, A. J. Marsden, J. Sloan,
N. R. Wilson,* J. P. Rourke* **9560 – 9563**

Covalently Binding Atomically Designed $Au_9$ Clusters to Chemically Modified Graphene



Synthesis & chemical design Image simulation Direct identification

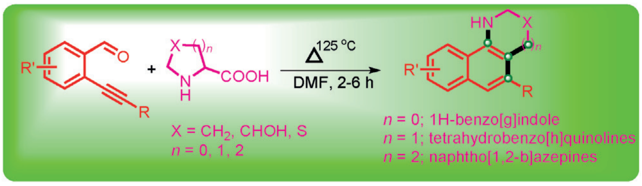
**Clusters last stand**: Graphene has been chemically modified and functionalized with atomically designed $Au_9$ clusters. Aberration-corrected transmission electron microscopy has allowed individual clusters, and their rotational motion, to be imaged directly and correlated to image simulation.

---

## *Azomethine Ylides*

S. Samala, G. Singh, R. Kumar,
R. S. Ampapathi, B. Kundu* **9564 – 9567**

Metal-Free Decarboxylative Cyclization/Ring Expansion: Construction of Five-, Six-, and Seven-Membered Heterocycles from 2-Alkynyl Benzaldehydes and Cyclic Amino Acids

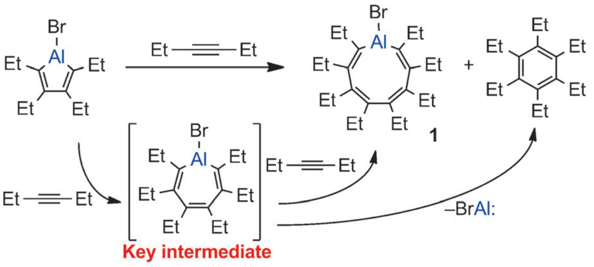


**Expansion project**: A series of rigid cyclic amino acids were subjected to metal-free condensation with 2-alkynyl benzaldehyde to afford 1*H*-benzo[g]indoles, tetrahydrobenzo[h]quinolines, and naphtho[1,2-b]azepines. The reaction demonstrates a broad substrate scope and can deliver five-, six-, and seven-membered heterocycles in good yields. DMF = *N*,*N*-dimethylformamide.

## Aluminum Compounds

T. Agou, T. Wasano, T. Sasamori, J.-D. Guo, S. Nagase, N. Tokitoh* ______ **9568 – 9571**

Ring Expansion to 1-Bromo-1-alumacyclonona-2,4,6,8-tetraene by Insertion of Two Alkyne Molecules into the Al—C Bonds



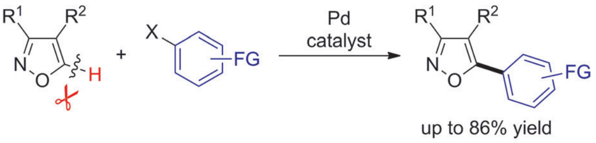
**Expanding Al's horizons**: A stable alumacyclononatetraene **1** was obtained by the reaction of the corresponding alumole with 3-hexyne accompanied by the formation of hexaethylbenzene. Deuterium-labeling experiments and DFT calculations suggested that an alumacycloheptatriene is the key intermediate (see picture).

---

## Cross-Coupling

M. Shigenobu, K. Takenaka,* H. Sasai* ______ **9572 – 9576**

Palladium-Catalyzed Direct C—H Arylation of Isoxazoles at the 5-Position



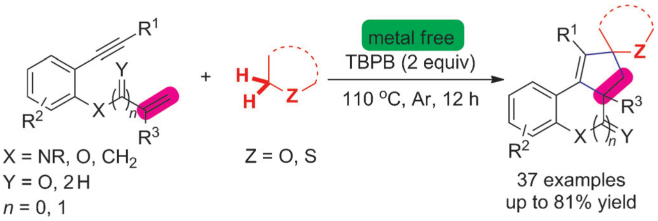
**Knock your 'sox' off**: A palladium catalyst promotes the cross-coupling of isoxazoles with aryl iodides through the selective C—H bond activation at the 5-position of the heteroaromatic compound. The use of 1,2-bis(diphenylphosphino)benzene as the ligand and silver fluoride as the activator was found to be crucial for this direct arylation. FG = functional group.

---

## Heterocycles

M. Hu, J.-H. Fan, Y. Liu, X.-H. Ouyang, R.-J. Song, J.-H. Li* ______ **9577 – 9580**

Metal-Free Radical [2+2+1] Carbocyclization of Benzene-Linked 1,*n*-Enynes: Dual C($sp^3$)—H Functionalization Adjacent to a Heteroatom



**An oxidative functionalization** of two C($sp^3$)—H bonds adjacent to a same heteroatom for the [2+2+1] carbocyclization with benzene-linked 1,*n*-enynes is presented. This method successfully proceeds using a radical mechanism and provides straightforward access to a variety of fused five-membered carbocyclic hydrocarbons. TBPB = *tert*-butyl perbenzoate.

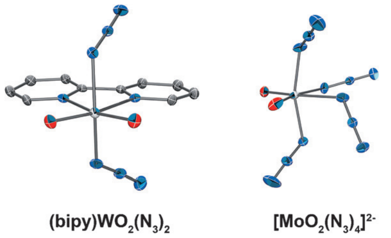
---

## Oxoazides

R. Haiges,* J. Skotnitzki, Z. Fang, D. A. Dixon, K. O. Christe ______ **9581 – 9585**

The First Molybdenum(VI) and Tungsten(VI) Oxoazides $MO_2(N_3)_2$, $MO_2(N_3)_2{\cdot}2CH_3CN$, (bipy)$MO_2(N_3)_2$, and $[MO_2(N_3)_4]^{2-}$ (M = Mo, W)

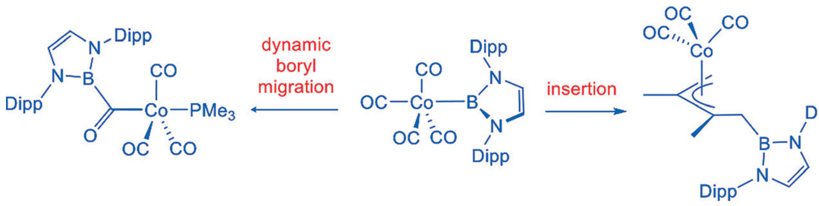
**A fluoride–azide exchange** enables the preparation of the first molybdenum(VI) and tungsten(VI) oxoazides $MO_2(N_3)_2$ (M = Mo, W) from $MO_2F_2$ and $Me_3SiN_3$ as very friction- and impact-sensitive solids. The reactions of $MO_2(N_3)_2$ with 2,2′-bipyridine (bipy) and $PPh_4N_3$ afforded (bipy)$MO_2(N_3)_2$ and $[PPh_4]_2[MO_2(N_3)_4]$, which were characterized by their X-ray crystal structures.



## Boryl Complexes

R. Frank,* J. Howell, J. Campos, R. Tirfoin, N. Phillips, S. Zahn, D. M. P. Mingos,* S. Aldridge* ______ 9586 – 9590

Cobalt Boryl Complexes: Enabling and Exploiting Migratory Insertion in Base-Metal-Mediated Borylation



**The insertion of CO** into M–R bonds is a fundamental step in organometallic chemistry but was unknown for boryl ($BR_2$) ligands; the reverse de-insertion of CO from bora-acyl complexes is invariably spontaneous. CO migratory insertion is now demonstrated in cobalt boryl complexes. Applications are shown in alkene functionalization, a well-known reaction for noble metals such as Rh or Pt.

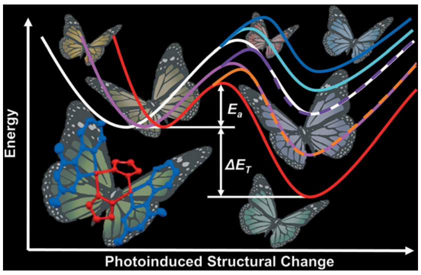
## Photochemistry

C. Zhou, Y. Tian, Z. Yuan, M. Han, J. Wang, L. Zhu, M. S. Tameh, C. Huang,* B. Ma* ______ 9591 – 9595

Precise Design of Phosphorescent Molecular Butterflies with Tunable Photoinduced Structural Change and Dual Emission

**Front Cover**

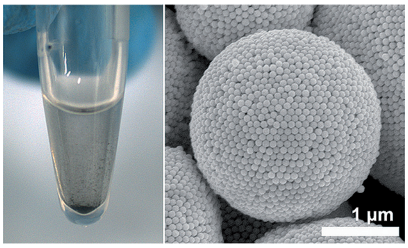
**Spread your wings and fly**: A series of butterfly-like phosphorescent binuclear platinum complexes can undergo controlled photoinduced structural change (PSC) by Pt–Pt distance shortening and exhibit tunable dual emission in the steady state. The precise manipulation of the PSC processes and the dual emission is achieved by molecular engineering of the excited-state potential energy surface.



## Plasmonics

D. Liu, F. Zhou, C. Li,* T. Zhang, H. Zhang, W. Cai, Y. Li* ______ 9596 – 9600

Black Gold: Plasmonic Colloidosomes with Broadband Absorption Self-Assembled from Monodispersed Gold Nanospheres by Using a Reverse Emulsion System

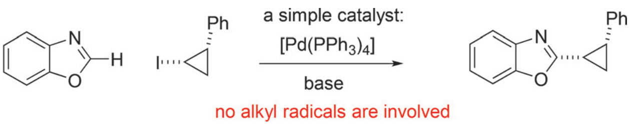


**Black colloidosomes**: 3D hollow plasmonic colloidosomes (see picture) composed of hexagonal close-packed gold nanospheres were self-assembled by a new reverse water-in-1-butanol emulsion system. These gold colloidosomes display a strong plasmonic coupling effect with broadband light absorption, show black color intrinsically, and are therefore denoted as black gold.

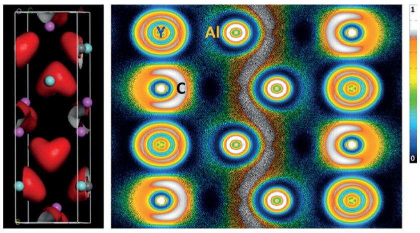
## Heterocycle Synthesis

X. Wu, C. Lei, G. Yue, J. Zhou* ______ 9601 – 9605

Palladium-Catalyzed Direct Cyclopropylation of Heterocycles



**The cyclopropylation** reaction shown in the scheme proceeds by concerted oxidative addition of the C–I bond to palladium. Notably, the relative configuration on the three-membered rings is retained in the products. Control experiments confirm that radicals are not involved in this reaction.



**YAlC** belongs to a compound class with prospects for thermoelectrics. It is a borderline chemical species where aluminum and carbon form a polymeric Zintl anion that is related to but distinct from polyacetylene. The strong polarization of carbon manifests itself in a heart-shaped localization feature and points to a unique kind of Al–Al bonding.

## Intermetallic Phases

M. R. Kotyrba,* E. Cuervo-Reyes,*
R. Nesper* ______ **9606–9609**

YAlC: A Bonding Chameleon with Heteropolyacetylene Features

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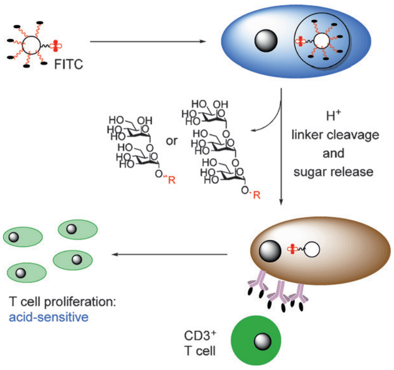
**A pathogen mimic,** glycodendrimer-coated latex beads with acid-labile linkers (see picture; top left), allows interactions with antigen-presenting molecules. The beads (both covalently linked and with acid-cleavable linkers) were efficiently internalized by macrophages (blue). Released sugars were presented to CD3$^+$ T cells, leading to T-cell proliferation. FITC = fluorescein isothiocyanate.



## Carbohydrates

R. Roychoudhury, P. A. Martinez,
T. Grinnage-Pulley, R. G. Schaut,
C. A. Petersen,
N. L. B. Pohl* ______ **9610–9613**

Acid-Triggered Degradable Reagents for Differentiation of Adaptive and Innate Immune Responses to *Leishmania*-Associated Sugars

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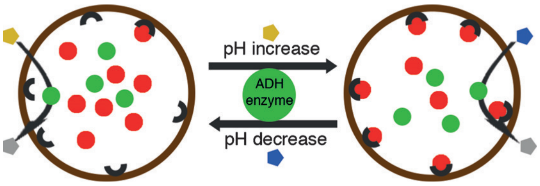

**Small-molecule triggers** are used to reversibly control protein–ligand interactions in giant vesicles (see picture; yellow and blue pentagons denote NADH and NAD$^+$, respectively). The results show that GUVs can mimic the ability of cells to react to external stimuli by starting a signaling event to induce a reversible structural change inside the vesicle.

## Cell Mimics

R. J. R. W. Peters, M. Nijemeisland,
J. C. M. van Hest* ______ **9614–9617**

Reversibly Triggered Protein–Ligand Assemblies in Giant Vesicles

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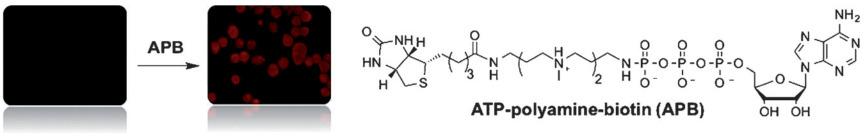


**A cell-permeable ATP analogue**, ATP–polyamine–biotin (APB), acts as a cosubstrate for kinase-catalyzed biotinylation in cellulo. APB provides a foundation for the development of additional cell-permeable ATP analogues for cell-signaling research.

## ATP Analogues

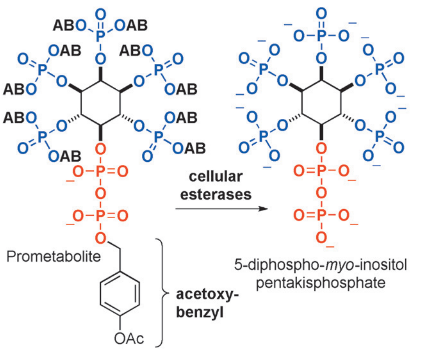
A. E. Fouda,
M. K. H. Pflum* ______ **9618–9621**

A Cell-Permeable ATP Analogue for Kinase-Catalyzed Biotinylation

### Prometabolites

I. Pavlovic, D. T. Thakor, L. Bigler,
M. S. C. Wilson, D. Laha, G. Schaaf,
A. Saiardi, H. J. Jessen* ____ **9622 – 9626**

Prometabolites of 5-Diphospho-*myo*-inositol Pentakisphosphate



**Precursors** of 5-diphospho-*myo*-inositol pentakisphosphate with biolabile protecting groups were synthesized, and their in vitro/in cellulo metabolism was studied. Acetoxybenzyl phosphates and phosphoanhydrides were rapidly removed in mammalian tissue and cell homogenates. This process was analyzed by polyacrylamide gel electrophoresis, which also led to the identification of unexpected side products.

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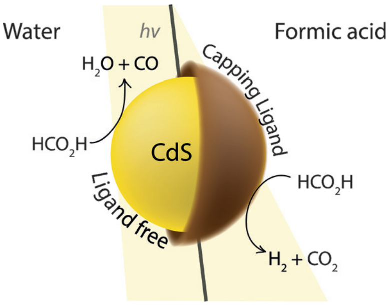
### Photocatalysis

M. F. Kuehnel, D. W. Wakerley,
K. L. Orchard, E. Reisner* __ **9627 – 9631**

Photocatalytic Formic Acid Conversion on CdS Nanocrystals with Controllable Selectivity for $H_2$ or CO

**Inside Back Cover**

**Take your cap off**: Selective photocatalytic conversion of formic acid into either $H_2$ or CO is achieved in the presence of inexpensive CdS nanocrystals under irradiation with visible light. Product selectivity is controlled by the solvent and particle capping ligand, and high photoactivity is sustained for several days under ambient conditions.



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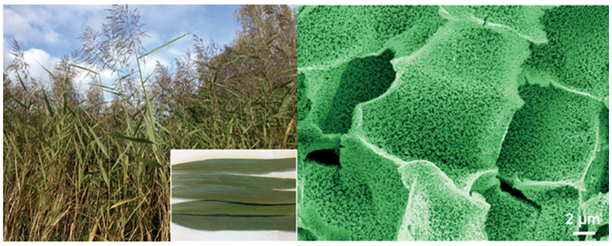
### Anode Materials

J. Liu, P. Kopold, P. A. van Aken, J. Maier,
Y. Yu* ________________ **9632 – 9636**

Energy Storage Materials from Nature through Nanotechnology: A Sustainable Route from Reed Plants to a Silicon Anode for Lithium-Ion Batteries



**A 3D highly porous Si⊂C hierarchical anode** is successfully prepared by magnesiothermic reduction of a mesoporous silica precursor converted from reed leaves and a subsequent modification by coating with thin carbon layers. Both the highly porous 3D structure and the carbon coating contribute significantly to the high structure stability and astonishing electrochemical performance of the nanocomposites.

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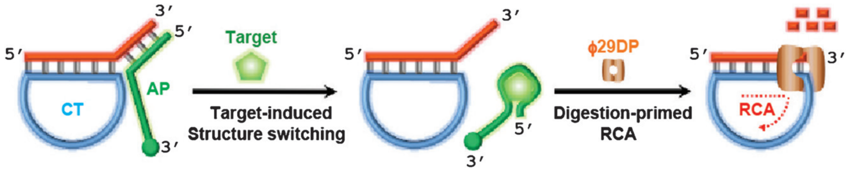
### DNA Amplification

M. Liu, W. Zhang, Q. Zhang,
J. D. Brennan,* Y. Li* ______ **9637 – 9641**

Biosensing by Tandem Reactions of Structure Switching, Nucleolytic Digestion, and DNA Amplification of a DNA Assembly

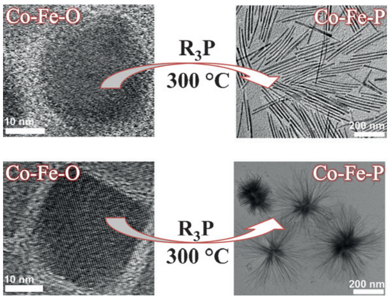


**Switching, cleaving, and copying**: The collaboration between a structure-switching DNA aptamer and ϕ29 DNA polymerase leads to amplified biosensing. The target-triggered structure-switching event yields a single-stranded DNA, which is converted by the polymerase into a mature primer to initiate rolling circle amplification (RCA). This process results in long-chain DNA amplicons that can be easily detected. CT = circular template.

### Bimetallic Nanophosphides

A. Mendoza-Garcia, H. Zhu, Y. Yu, Q. Li, L. Zhou, D. Su, M. J. Kramer, S. Sun* ——— **9642 – 9645**

Controlled Anisotropic Growth of Co-Fe-P from Co-Fe-O Nanoparticles



**Anisotropic bimetallic Co-Fe-P**: Anisotropic Co-Fe-P nanorods and sea urchins were synthesized by controlled phosphidation of Co-Fe-O nanoparticles of polyhedral and cubic shapes, respectively. The Co-Fe-P showed greatly enhanced catalysis for the oxygen evolution reaction. The synthesis may be generalized to prepare metallic phosphides/phosphates for catalysis and energy storage applications.

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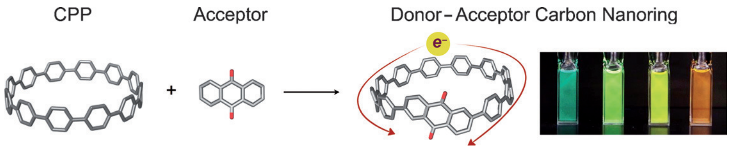
### Donor–Acceptor Systems

T. Kuwabara, J. Orii, Y. Segawa, K. Itami* ——— **9646 – 9649**

Curved Oligophenylenes as Donors in Shape-Persistent Donor–Acceptor Macrocycles with Solvatofluorochromic Properties



**I give this ring**: Cycloparaphenylenes bearing acceptor units (anthraquinone and tetracyanoanthraquinodimethane) were synthesized. These macrocycles may be regarded as donor–acceptor (D–A) molecules, as evidenced by their solvatofluorochromic behavior, well-separated HOMO and LUMO, and electrochemical behavior. These findings provide a new molecular design strategy for D–A systems that makes use of curved $\pi$-electron ring systems.

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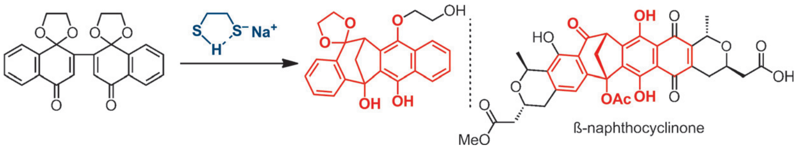
### Reductive Cyclization

Y. Ando, S. Hori, T. Fukazawa, K. Ohmori,* K. Suzuki* ——— **9650 – 9653**

Toward Naphthocyclinones: Doubly Connected Octaketide Dimers with a Bicyclo[3.2.1]octadienone Core by Thiolate-Mediated Cyclization



**Doubling up**: A viable method for the construction of bicyclo[3.2.1]octadienone scaffolds has been developed, involving the reductive cyclization of dimeric naphthoquinone monoacetal mediated by the monosodium salt of 1,2-ethanedithiol. Bicyclo[3.2.1]octadienones may serve as key core units in the synthesis of biologically relevant naphthocyclinones.

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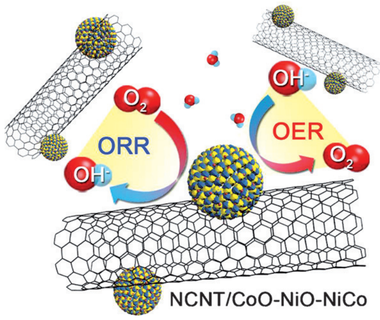
### Bifunctional Electrocatalysts

X. Liu, M. Park, M. G. Kim, S. Gupta, G. Wu,* J. Cho* ——— **9654 – 9658**

Integrating NiCo Alloys with Their Oxides as Efficient Bifunctional Cathode Catalysts for Rechargeable Zinc–Air Batteries

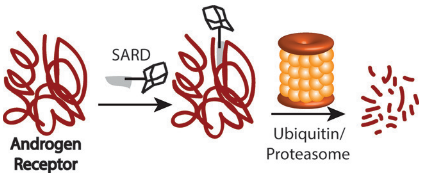


**A NiCo alloy-based** bifunctional electrocatalyst (NCNT/CoO-NiO-NiCo) exhibits excellent activity and stability in alkaline solutions for the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER). When integrated into air cathodes of primary and rechargeable zinc–air batteries, the performance of NCNT/CoO-NiO-NiCo is superior or comparable to Pt/C or (Pt/C + $IrO_2$)-based air cathodes.

## Antiproliferation

J. L. Gustafson, T. K. Neklesa, C. S. Cox, A. G. Roth, D. L. Buckley, H. S. Tae, T. B. Sundberg, D. B. Stagg, J. Hines, D. P. McDonnell, J. D. Norris, C. M. Crews* ________ **9659 – 9662**

Small-Molecule-Mediated Degradation of the Androgen Receptor through Hydrophobic Tagging



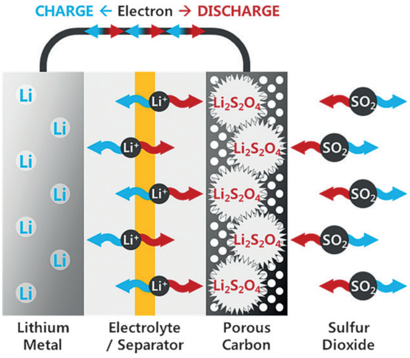
**Making the problem go away**: Most prostate tumor growth is driven by the action of the androgen receptor (AR). Resistance to current chemotherapies for prostate cancer can occur when the androgen receptor is either overexpressed or mutated. Coupling of an AR agonist to an adamantyl “hydrophobic tag” resulted in a molecule that induces AR degradation, even in drug-resistant prostate tumor cells.

## Lithium-Ion Batteries

H.-D. Lim, H. Park, H. Kim, J. Kim, B. Lee, Y. Bae, H. Gwon, K. Kang* _ **9663 – 9667**

A New Perspective on Li–$SO_2$ Batteries for Rechargeable Systems

**Back Cover**

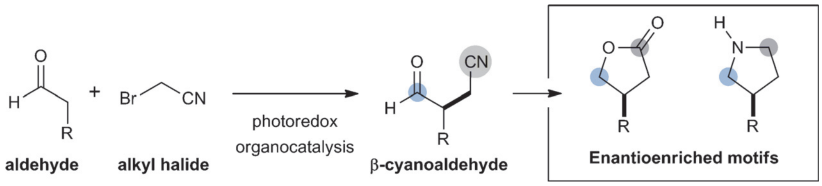


**Energy storage**: Although Li–$SO_2$ batteries have been used as primary batteries to date, the feasibility of a rechargeable Li–$SO_2$ battery is demonstrated based on the reversible formation and decomposition of the solid product $Li_2S_2O_4$ (see picture). The observed energy efficiency of the Li–$SO_2$ system is significantly better than that of the Li–$O_2$ system.

## Synthetic Methods

E. R. Welin, A. A. Warkentin, J. C. Conrad, D. W. C. MacMillan* ______ **9668 – 9672**

Enantioselective α-Alkylation of Aldehydes by Photoredox Organocatalysis: Rapid Access to Pharmacophore Fragments from β-Cyanoaldehydes



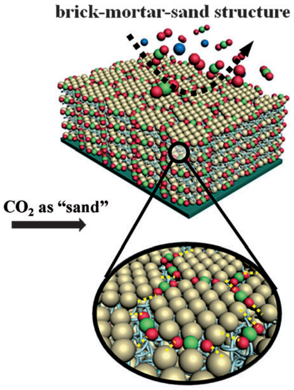
**A combination** of photoredox catalysis and enamine catalysis has enabled the development of an enantioselective cyanoalkylation of aldehydes. This synergistic catalysis protocol makes possible the coupling of two highly versatile yet orthogonal functionalities.

## Gas-Barrier Films

Y. Dou, T. Pan, S. Xu, H. Yan, J. Han,* M. Wei,* D. G. Evans, X. Duan ________ **9673 – 9678**

Transparent, Ultrahigh-Gas-Barrier Films with a Brick–Mortar–Sand Structure

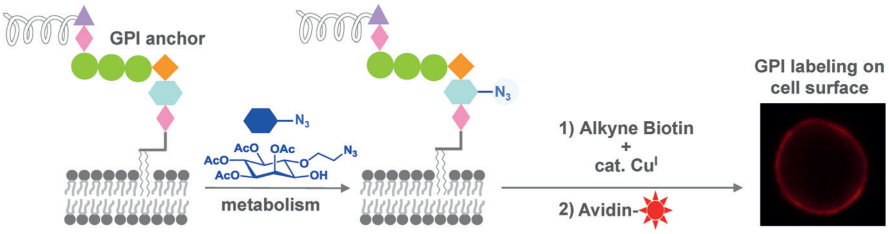
**Sand and deliver**: Transparent, ultrahigh-gas-barrier films with a “brick–mortar–sand” structure were fabricated by layer-by-layer assembly of XAl-layered double hydroxide (LDH, X = Mg, Ni, Zn, and Co) nanoplatelets (“bricks”) and polyacrylic acid (“mortar”) and subsequent $CO_2$ (“sand”, C green, O red) infilling. The films have very high gas-barrier properties, revealed by both experimental and theoretical studies.



## Glycolipids

L. Lu, J. Gao, Z. Guo* ______ **9679 – 9682**

Labeling Cell Surface GPIs and GPI-Anchored Proteins through Metabolic Engineering with Artificial Inositol Derivatives

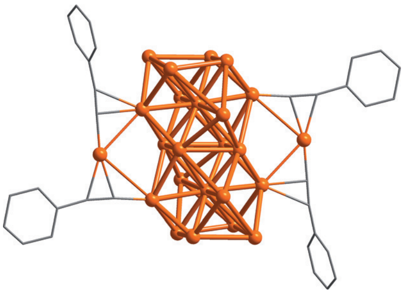


**Sweet and sticky**: An effective strategy was developed for the metabolic engineering of cell-surface glycosylphosphatidylinositols (GPIs) and GPI-anchored proteins by using azido-modified inositol (blue hexagon) derivatives. This strategy can be used to label GPI-anchored proteins with various tags through click chemistry in live cells for biological studies.

## Gold Nanoclusters

X.-K. Wan, W. W. Xu, S.-F. Yuan, Y. Gao,*
X. C. Zeng, Q.-M. Wang* ___ **9683 – 9686**

A Near-Infrared-Emissive Alkynyl-Protected $Au_{24}$ Nanocluster

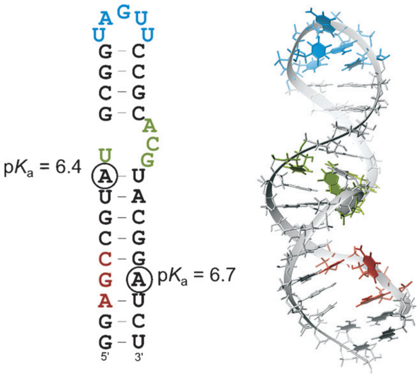


**Good as gold**: An alkynyl-protected gold nanocluster $[Au_{24}(C{\equiv}CPh)_{14}(PPh_3)_4](SbF_6)_2$ is reported which contains a $Au_{22}$ core composed of two $Au_{13}$ centered cuboctahedra that share a square face. Two staple-like PhC≡C−Au−C≡CPh motifs are located around the center of the rod-like $Au_{22}$ core. The $Au_{24}$ nanocluster is highly emissive in the near-infrared region ($\lambda_{max} = 925$ nm). Atom colors: Au = orange; C = gray.

## RNA Structures

M. Pechlaner, D. Donghi, V. Zelenay,
R. K. O. Sigel* __________ **9687 – 9690**

Protonation-Dependent Base Flipping at Neutral pH in the Catalytic Triad of a Self-Splicing Bacterial Group II Intron

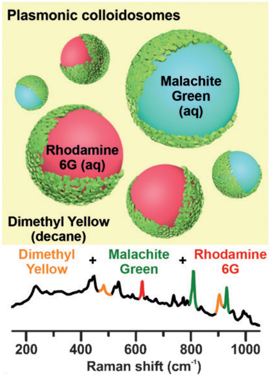


**Strongly shifted**: Two adenines in the highly conserved and catalytically essential domain 5 of group II introns become protonated near physiological pH values. The associated dynamic equilibria play an important role in group II intron assembly and catalysis.

## Sensors

G. C. Phan-Quang, H. K. Lee, I. Y. Phang,
X. Y. Ling* ___________ **9691 – 9695**

Plasmonic Colloidosomes as Three-Dimensional SERS Platforms with Enhanced Surface Area for Multiphase Sub-Microliter Toxin Sensing

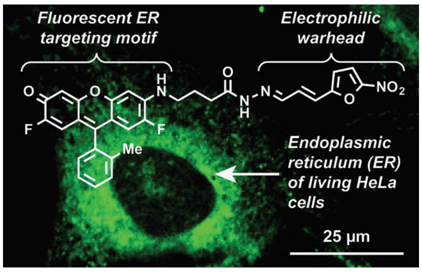


**Toxin detection**: Plasmonic colloidosomes constructed from silver nanocubes are fabricated as emulsion-based three-dimensional surface-enhanced surface scattering (SERS; see picture) platforms. The colloidosomes show excellent mechanical robustness, flexible size tunability, versatility to merge, and ultrasensitivity in SERS quantitation of sub-femtomole toxin.

## Subcellular Targeting

J. M. Meinig, L. Fu,
B. R. Peterson* ———— **9696 – 9699**

Synthesis of Fluorophores that Target Small Molecules to the Endoplasmic Reticulum of Living Mammalian Cells



**On target**: Fluorinated hydrophobic analogues of rhodol accumulate in the endoplasmic reticulum (ER) of HeLa cells. When this highly fluorescent ER-targeting motif was linked to a 5-nitrofuran warhead, the ubiquitin–proteasome system was selectively inhibited. These rhodol derivatives thus provide a new method for the delivery of small molecules for targeting ER-associated proteins and pathways.

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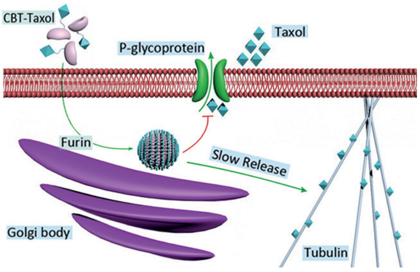
## Drug Resistance

Y. Yuan, L. Wang, W. Du, Z. Ding, J. Zhang, T. Han, L. An, H. Zhang,*
G. Liang* ———— **9700 – 9704**

Intracellular Self-Assembly of Taxol Nanoparticles for Overcoming Multidrug Resistance

**Resistance is futile**: By employing a biocompatible condensation reaction, a taxol derivative has been rationally designed which could be subjected to furin-controlled condensation and self-assembly of taxol nanoparticles. Slow release of the anticancer drug from the nanoparticles effectively overcomes multidrug resistance of taxol-resistant cancer cells and tumors.



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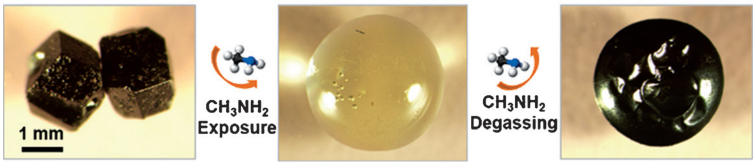
## Perovskite Solar Cells

Z. Zhou, Z. Wang, Y. Zhou, S. Pang,*
D. Wang, H. Xu, Z. Liu, N. P. Padture,
G. Cui* ———— **9705 – 9709**

Methylamine-Gas-Induced Defect-Healing Behavior of $CH_3NH_3PbI_3$ Thin Films for Perovskite Solar Cells

$$MAPbI_3 + xCH_3NH_2 \rightleftharpoons MAPbI_3{\bullet}xCH_3NH_2$$



**A perovskite smoothie**: Treating $CH_3NH_3PbI_3$ ($MAPbI_3$) perovskite thin films with methylamine gas induces a rapid collapse of the perovskite structure and formation of a liquid phase. Removing the gas causes conversion back into the perovskite structure giving a smooth defect-free film. Using the film in perovskite solar cells enhances their performance.

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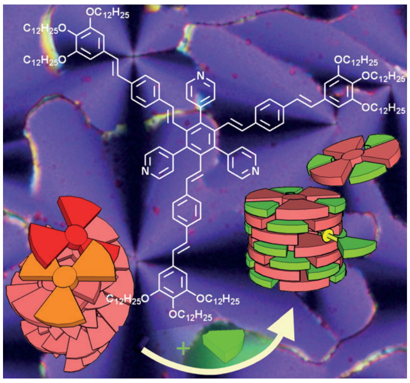
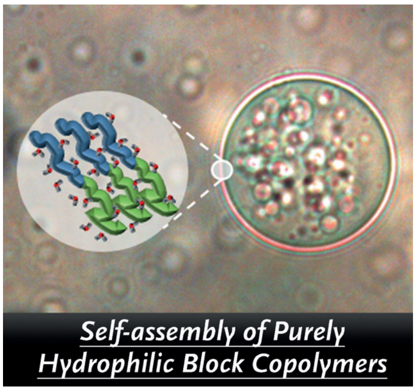
## Liquid Crystals

M. Lehmann,* P. Maier ———— **9710 – 9714**

Shape-Persistent, Sterically Crowded Star Mesogens: From Exceptional Columnar Dimer Stacks to Supermesogens



**Stilbenoid superstars**: Star mesogens that are sterically crowded at the core pack in an exceptional helical-columnar dimer phase (see Scheme, bottom left). Pyridyl groups in the interspace of the arms bind aromatic carboxylic acids and incrementally transform the dimer phase into a columnar phase of supermesogens (right).



**Water, water, everywhere**: In a purely aqueous environment, self-assembly of highly hydrophilic diblock copolymers into vesicle-like aggregates was demonstrated for various polysaccharide-based block copolymers. These hydrophilic materials can easily yield nanosized (< 500 nm) and microsized (> 5 μm) polymer vesicles depending on concentration and diblock composition.

***Vesicle Self-Assembly***

S. M. Brosnan,* H. Schlaad,*
M. Antonietti ———— **9715 – 9718**

Aqueous Self-Assembly of Purely Hydrophilic Block Copolymers into Giant Vesicles

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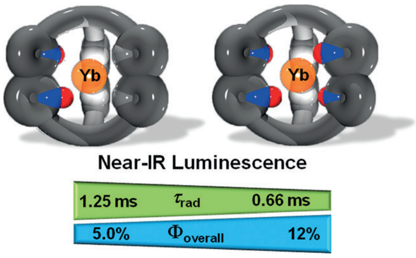
**Generating a warm glow indeed**: By a combination of conventional optimization strategies with a new approach, near-IR-emissive ytterbium cryptates with unprecedented photoluminescence quantum yields of up to 12 % have been realized. The key to these successful luminophores is the judicious chemical design that makes the metal-centered emissive transition much more competitive with respect to quenching processes.



***Near-Infrared Luminescence***

C. Doffek, M. Seitz* ———— **9719 – 9721**

The Radiative Lifetime in Near-IR-Luminescent Ytterbium Cryptates: The Key to Extremely High Quantum Yields

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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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# Angewandte Corrigendium

In this Communication inadvertently a wrong value was given for the redox potential in the caption of Figure 2. The chronoamperometry experiment was performed at −455 mV versus SHE, not at −340 mV versus SHE as reported.
The authors sincerely apologize for this mistake, which does not affect any results or conclusions of this Communication.

Induction of a Proton Gradient across a Gold-Supported Biomimetic Membrane by Electroenzymatic $H_2$ Oxidation

Ó. Gutiérrez-Sanz, C. Tapia,
M. C. Marques, S. Zacarias,
M. Vélez, I. A. C. Pereira,
A. L. De Lacey* ———— **2684–2687**

*Angew. Chem. Int. Ed.* **2015**, *54*

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