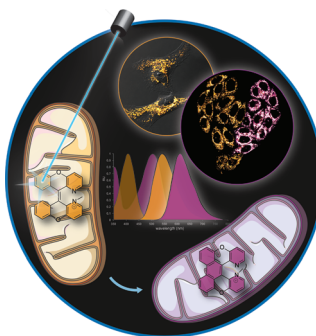


... difluoromethyl diazomethane ( $\text{CF}_2\text{HCHN}_2$ ) was generated in situ for the first time and employed in [3+2] cycloaddition reactions with alkynes. In his Communication on page 6558 ff., P. Mykhailiuk describes that this one-pot process for the synthesis of difluoromethylated pyrazoles is very practical as it does not require a catalyst or the isolation of the potentially toxic and explosive gaseous intermediate and can be easily scaled up.

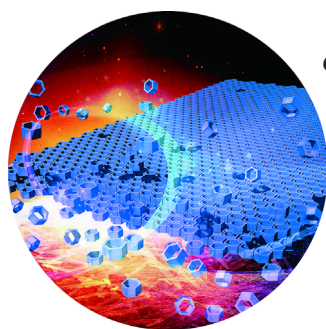
## Fluorescent Probes

A photoactivatable organelle-specific live-cell imaging probe that is based on a  $6\pi$  electrocyclization/oxidation mechanism is described by D. M. Chenoweth and M. N. Tran in their Communication on page 6442 ff.



## Controlling Pore Size

A new method allows porous carbon fibers to be prepared without inorganic templates. In their Communication on page 6466 ff., T. Ogoshi et al. show the pore dimensions can be controlled at the Ångström level.



## Clear Coatings

A graft-copolymer-based approach, described by M. Rabnawaz and G. Liu in their Communication on page 6516 ff., leads to clear polyurethane coatings that can protect surfaces from stains, fingerprints, and graffiti.



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## Service

6392 – 6395

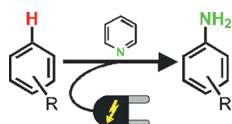


*“Meine größte Motivation ist die Schönheit der chemischen Welt zu erkunden. Ich verliere mein Zeitgefühl, wenn ich mich mit meinen Studenten unterhalte ...”*

This and more about Huanfeng Jiang can be found on page 6396.

## Author Profile

Huanfeng Jiang ————— 6396



Simply by applying electricity, the amination reaction of a broad variety of arenes, heteroarenes, and benzylic substrates is achieved. Pyridine serves as the nitrogen source and the intermediate cationic species are well-protected from over-oxidation.

## Highlights

### Oxidative Coupling

S. R. Waldvogel,\* S. Möhle – 6398 – 6399

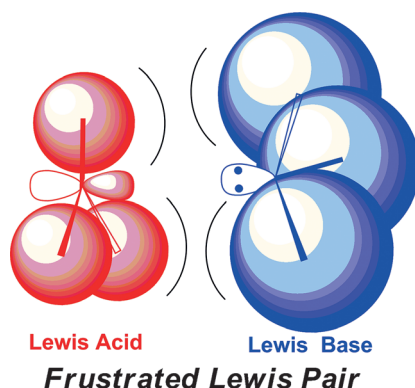
Versatile Electrochemical C–H Amination via Zincke Intermediates

## Reviews

### Frustrated Lewis Pairs

D. W. Stephan,\* G. Erker\* — 6400–6441

Frustrated Lewis Pair Chemistry:  
Development and Perspectives



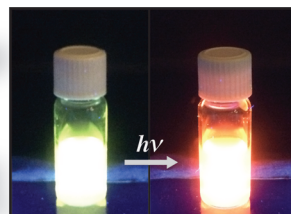
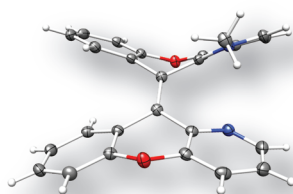
**Let's not get together:** Frustrated Lewis pairs (FLP) are combinations of Lewis acids and Lewis bases that are prevented from forming a stable adduct by steric or electronic hindrance. The growth of the field of FLP chemistry during the last four years has been rapid, including small-molecule activation, applications in catalysis, and the development of unprecedented reactions.

## Communications

### Fluorescent Probes

M. N. Tran,  
D. M. Chenoweth\* — 6442–6446

Photoelectrocyclization as an Activation  
Mechanism for Organelle-Specific Live-  
Cell Imaging Probes



A photoactivatable organelle-specific live-cell imaging probe based on a  $6\pi$  electrocyclization/oxidation mechanism is de-

scribed. This probe is water-soluble, non-cytotoxic, cell-permeable, and can be used for mitochondrial imaging.

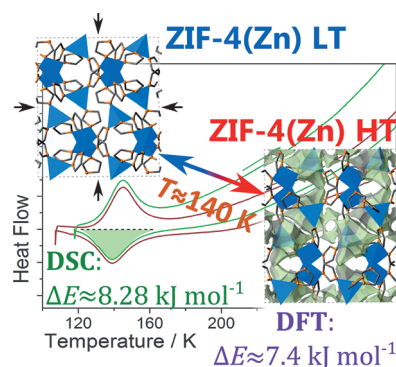
### Frontispiece

### Metal–Organic Frameworks

M. T. Wharmby, S. Henke, T. D. Bennett,  
S. R. Bajpe, I. Schwedler, S. P. Thompson,  
F. Gozzo, P. Simoncic,  
C. Mellot-Draznieks, H. Tao, Y. Yue,  
A. K. Cheetham\* — 6447–6451

Extreme Flexibility in a Zeolitic  
Imidazolate Framework: Porous to Dense  
Phase Transition in Desolvated ZIF-4

ZIF-4(Zn) undergoes a porous to non-porous transition on cooling from the high-temperature (HT) to low-temperature (LT) phase. The nature of this transition is elucidated by a combined approach of structure solution from powder diffraction, DSC measurement, and DFT calculations.



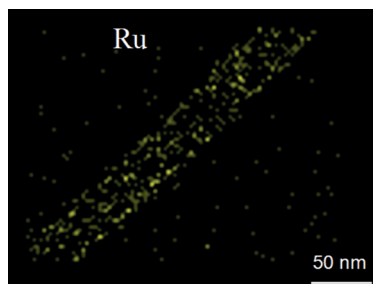
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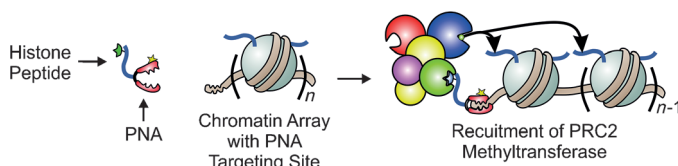
**A well-tailored coat:** As-synthesized  $\text{RuO}_2$ -coated  $\text{Na}_3\text{V}_2\text{O}_2(\text{PO}_4)_2\text{F}$  nanowires showed ultrahigh rate capability and excellent cycling stability when used as a cathode material for sodium-ion batteries.



## Sodium-Ion Batteries

M. Peng, B. Li, H. Yan, D. Zhang, X. Wang,\* D. Xia,\* G. Guo – **6452 – 6456**

Ruthenium-Oxide-Coated Sodium Vanadium Fluorophosphate Nanowires as High-Power Cathode Materials for Sodium-Ion Batteries



**Chromatin PNArrays:** A peptide nucleic acid (PNA) targeting compound bearing a modified histone peptide was used to recruit the histone methyltransferase PRC2 to a designated site on a nucleosome array. This recapitulation of hetero-

typic “designer” chromatin was used to investigate how PRC2 is both activated and inhibited with respect to neighboring nucleosomes from a particular location within the array.

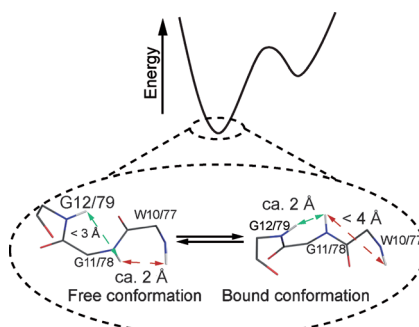
## Epigenetics

Z. Z. Brown, M. M. Müller, H. E. Kong, P. W. Lewis, T. W. Muir\* — **6457 – 6461**

Targeted Histone Peptides: Insights into the Spatial Regulation of the Methyltransferase PRC2 by using a Surrogate of Heterotypic Chromatin



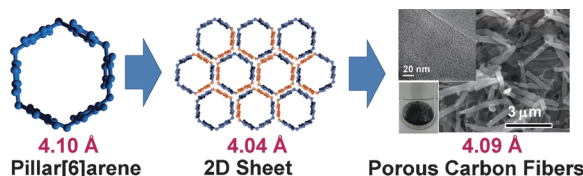
**Nothing to get excited about:** NMR spectroscopic studies revealed that a lectin with activity against the human immunodeficiency virus recognizes high-mannose sugars by conformational selection within the ground state, in contrast to the popular “excited-state” model. In the absence of sugars, both the sugar-free and sugar-bound protein conformations observed by X-ray crystallography (see picture) exist as conformational substates in solution.



## Protein Dynamics

M. G. Carneiro, L. M. I. Koharudin, D. Ban, T. M. Sabo, P. Trigo-Mourino, A. Mazur, C. Griesinger, A. M. Gronenborn, D. Lee\* **6462 – 6465**

Sampling of Glycan-Bound Conformers by the Anti-HIV Lectin *Oscillatoria agardhii* agglutinin in the Absence of Sugar



**The hole story:** Two dimensional (2D) supramolecular polymerization of pillar[6]arenes afforded hexagonal 2D porous sheets. Carbonization of these

sheets gives a carbon material containing pores with a size that is precisely controlled at the Ångstrom level by the cavity size of the precursor pillar[6]arene.

## Porous Materials

T. Ogoshi,\* K. Yoshikoshi, R. Sueto, H. Nishihara, T. Yamagishi **6466 – 6469**

Porous Carbon Fibers Containing Pores with Sizes Controlled at the Ångstrom Level by the Cavity Size of Pillar[6]arene



**Inside Back Cover**





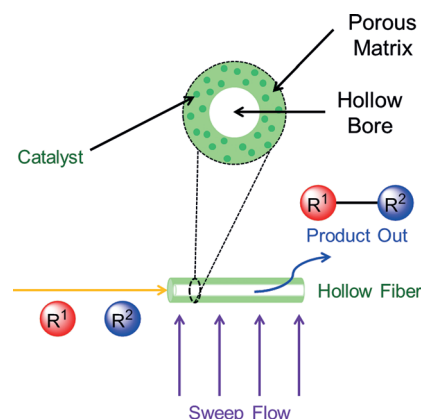
## Catalysis in Flow

E. G. Moschetta, S. Negretti,  
K. M. Chepiga, N. A. Brunelli, Y. Labreche,  
Y. Feng, F. Rezaei, R. P. Lively, W. J. Koros,  
H. M. L. Davies,\*  
C. W. Jones\* — 6470–6474



Composite Polymer/Oxide Hollow Fiber  
Contactors: Versatile and Scalable Flow  
Reactors for Heterogeneous Catalytic  
Reactions in Organic Synthesis

**Go with the flow:** Composite polymer/oxide hollow fibers have been used as a flow reactor platform for heterogeneously catalyzed reactions in organic synthesis. Embedding catalysts in the fiber walls avoids clogging of the flow channels and provides a short catalyst bed. Three different catalysts and reaction types were successfully performed in flow, thereby demonstrating the versatility of the fibers as reactors.



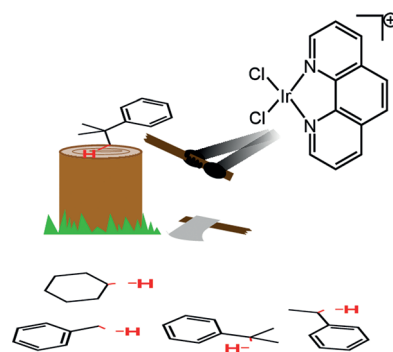
## C–H Activation

C. A. Swift, S. Gronert\* — 6475–6478



Intermolecular C–H Bond Activation by  
a Cationic Iridium(III) Dichloride  
Phenanthroline Complex

**Iridium(III) unleashed:** A cationic phenanthroline complex of Ir<sup>III</sup> can cleave C–H bonds of unactivated secondary carbons as well as benzylic carbons but not bonds to sp<sup>2</sup> or primary carbons in the gas phase. The unique reactivity pattern likely stems from the suboptimum bite angle provided by the phenanthroline ligand. Computational modeling suggests that the C–H activation process is concerted, without a stable oxidative addition intermediate.

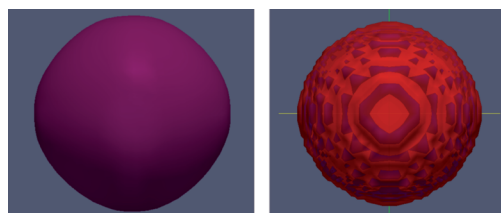


## Mass Spectrometry

Z. Farrell, S. Merz, J. Seager, C. Dunn,  
S. Egorov,\* D. L. Green\* — 6479–6482



Development of Experiment and Theory to  
Detect and Predict Ligand Phase  
Separation on Silver Nanoparticles



**Two different mixtures:** MALDI mass spectrometry and self-consistent mean-field calculations are combined to detect and predict ligand phase separation on Ag nanoparticles after synthesis. The progression of the monolayer morphology

from a well-mixed random ligand distribution (see picture, left) to an intermediate degree of phase separation (right) with changes in ligand length is determined.

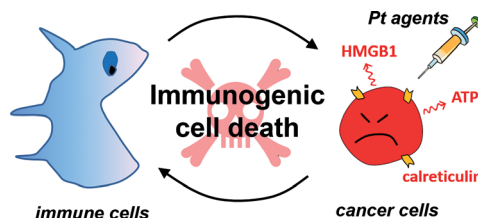


## Antitumor Agents

D. Y. Q. Wong, W. W. F. Ong,  
W. H. Ang\* — 6483–6487



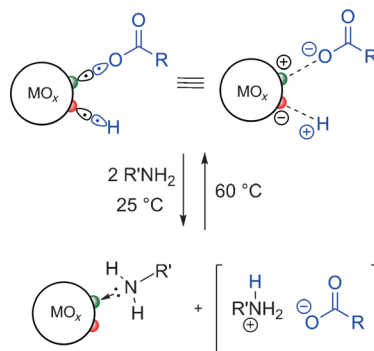
Induction of Immunogenic Cell Death by  
Chemotherapeutic Platinum Complexes



**For the long run:** Some chemotherapeutics can activate a long-term immune-mediated response against cancer by triggering an immunogenic mode of

cancer cell death (ICD). A library of platinum complexes were studied, and a potent Pt-based ICD inducer was thus identified.

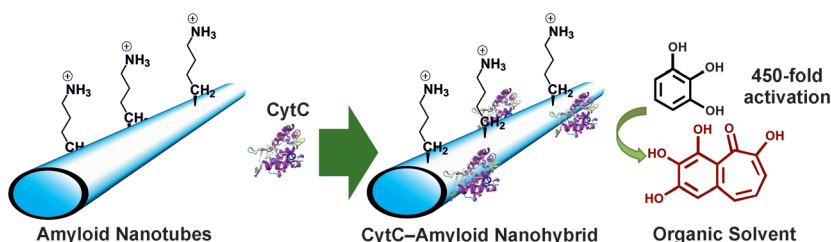
**Carboxylic acid** dissociatively self-adsorbs on metal oxide nanocrystals and can be reversibly displaced by L-type amines. Both observations are explained by an  $X_2$  binding motif, eliminating the need for an external proton source.



## Surface Chemistry

J. De Roo, Y. Justo, K. De Keukeleere, F. Van den Broeck, J. C. Martins, I. Van Driessche, Z. Hens\* — **6488–6491**

Carboxylic-Acid-Passivated Metal Oxide Nanocrystals: Ligand Exchange Characteristics of a New Binding Motif



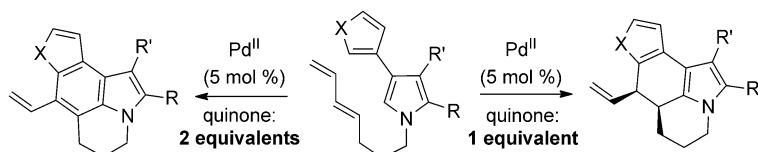
**Superactive nanohybrids:** Cytochrome C (CytC)-loaded homogenous amyloid nanohybrids were developed. The activity of CytC is enhanced up to 450-fold in the nanohybrids compared that of unbound

CytC in water. The exposed surface, morphology, and surface area of the amyloid play critical roles in modulating the enzymatic activity in organic solvents.

## Enzyme Nanotechnology

N. Kapil, A. Singh, D. Das\* — **6492–6495**

Cross- $\beta$  Amyloid Nanohybrids Loaded With Cytochrome C Exhibit Superactivity in Organic Solvents



**Don't overdo it:** A palladium(II)-catalyzed C–H activation cascade sequence for the synthesis of polyheterocycles is reported. Aromatization of the initially formed dihydro species occurred with a quinone

oxidant. In some cases the use of one equivalent of the oxidant enabled isolation of the dihydro species as a single isomer (see scheme; X = NMe, O, S).

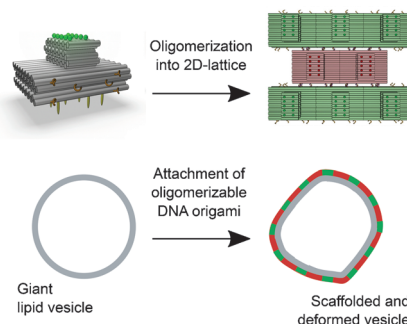
## Domino Cyclization

S. P. Cooper, K. I. Booker-Milburn\* — **6496–6500**

A Palladium(II)-Catalyzed C–H Activation Cascade Sequence for Polyheterocycle Formation



**Amphipathic DNA origami structures** were engineered, which have a flat membrane-binding interface decorated with cholesterol-derived anchors and sticky oligonucleotide overhangs enabling formation of ordered arrays on a membrane. Such DNA origami structures are capable of deforming free-standing lipid membranes (see picture), mimicking the biological activity of coat-forming proteins.



## Lipid Membranes

A. Czogalla, D. J. Kauert, H. G. Franquelim, V. Uzunova, Y. Zhang, R. Seidel, P. Schwille\* — **6501–6505**

Amphipathic DNA Origami Nanoparticles to Scaffold and Deform Lipid Membrane Vesicles

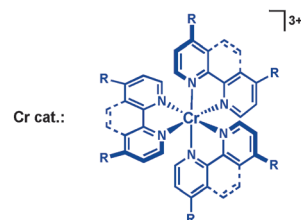
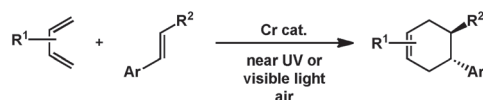


## Photoredox Catalysis

S. M. Stevenson, M. P. Shores,\*  
E. M. Ferreira\* ————— 6506–6510



Photooxidizing Chromium Catalysts for Promoting Radical Cation Cycloadditions



**Spotlight on chromium:** Selected Cr<sup>III</sup> complexes were investigated for promoting radical cation cycloadditions. These species have sufficiently long-lived excited states to oxidize electron-rich alkenes, thereby initiating [4+2] processes. These

metal complexes augment the spectrum of catalysts explored in photoredox systems, featuring properties that can result in differential reactivity from the more common Ru or Ir catalysts.

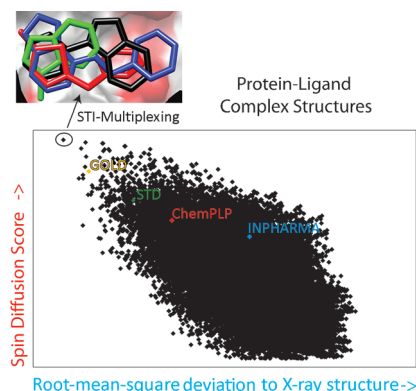
## Medicinal Chemistry

J. Pilger, A. Mazur, P. Monecke,  
H. Schreuder, B. Elshorst, S. Bartoschek,  
T. Langer, A. Schiffer, I. Krimm,  
M. Wegstroth, D. Lee, G. Hessler,  
K.-U. Wendt, S. Becker,  
C. Griesinger\* ————— 6511–6515



A Combination of Spin Diffusion Methods for the Determination of Protein–Ligand Complex Structural Ensembles

**Protein–ligand complexes:** A combination of the spin-diffusion-based NMR methods INPHARMA, trNOE, and STD (STI; see picture) results in an accurate scoring function for docking modes and therefore determination of protein–ligand complex structures. Applications are shown on the model system protein kinase A and the drug targets glycogen phosphorylase and soluble epoxide hydrolase.



## Coatings

M. Rabnawaz, G. Liu\* ————— 6516–6520



Graft-Copolymer-Based Approach to Clear, Durable, and Anti-Smudge Polyurethane Coatings



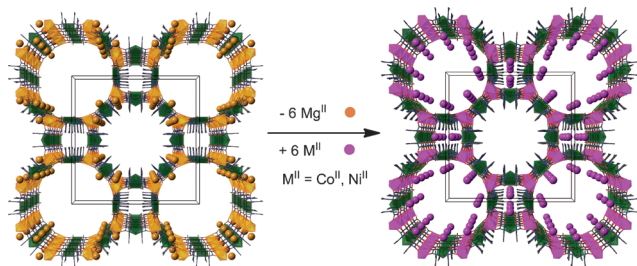
Red Graffiti Paint



**No more smudges:** A graft-copolymer-based approach was used to prepare clear polyurethane coatings that repel water, diiodomethane, hexadecane, ink, and an artificial fingerprint liquid. Different coat-

ing methods can be used to apply the coatings to different surfaces, which can thus be protected from fingerprints, stains, and graffiti.

**Back Cover**



**Synthesis à la carte:** A single crystal to single crystal transmetallation process is reported in a metal–organic framework in which  $\text{Mg}^{\text{II}}$  ions within the coordination network (see picture; orange polyhedra)

and those hosted in the channels (orange spheres) are replaced entirely by either  $\text{Co}^{\text{II}}$  or  $\text{Ni}^{\text{II}}$  ions (purple spheres and polyhedra).

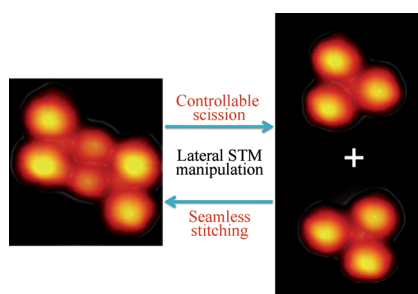
## Metal–Organic Frameworks

T. Grancha, J. Ferrando-Soria,\*  
H.-C. Zhou, J. Gascon,\* B. Seoane,  
J. Pasán, O. Fabelo, M. Julve,  
E. Pardo\* \_\_\_\_\_ **6521 – 6525**

Postsynthetic Improvement of the Physical Properties in a Metal–Organic Framework through a Single Crystal to Single Crystal Transmetallation



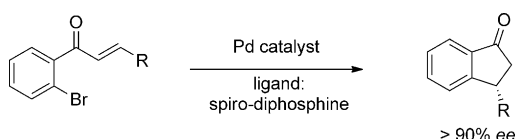
**Lateral STM manipulations** enable the controllable scission of a complicated metal–organic cluster consisting of nickel atoms and uracil molecules (see scheme, left) into its elementary structural motifs (right). Furthermore, the elementary units can be seamlessly stitched back together into the original cluster. STM = scanning tunneling microscopy.



## Metal–Organic Clusters

H. Kong, L. Wang, Q. Sun, C. Zhang,  
Q. Tan, W. Xu\* \_\_\_\_\_ **6526 – 6530**

Controllable Scission and Seamless Stitching of Metal–Organic Clusters by STM Manipulation



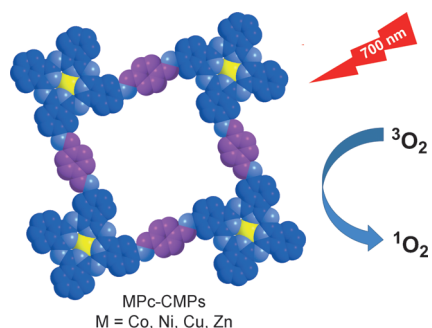
**Hydrogen-bond donors** promote halide dissociation from neutral arylpalladium halides to access an enantioselective cationic pathway. The use of trialkylam-

monium salts in a glycol solvent enables asymmetric reductive Heck reaction of aryl halides in high stereoselectivity.

## Asymmetric Catalysis

G. Yue, K. Lei, H. Hirao,  
J. Zhou\* \_\_\_\_\_ **6531 – 6535**

Palladium-Catalyzed Asymmetric Reductive Heck Reaction of Aryl Halides



**In the red:** The extended  $\pi$ -conjugation systems of metallophtalocyanine-based conjugated microporous polymers (MPC-CMPs) results in an enhanced light-harvesting capability in the far-red region. The microporous structure of the MPC-CMPs and their excellent absorption capability for long-wavelength photons, result in them (especially ZnPC-CMP and CuPC-CMP) being promising photosensitizers with a high efficiency for  $^1\text{O}_2$  generation.

## Photosensitizers

X. Ding, B.-H. Han\* \_\_\_\_\_ **6536 – 6539**

Metallophtalocyanine-Based Conjugated Microporous Polymers as Highly Efficient Photosensitizers for Singlet Oxygen Generation



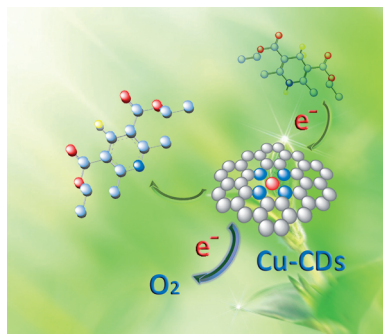


## Carbon Dots

W. T. Wu, L. Y. Zhan, W. Y. Fan, J. Z. Song,  
X. M. Li, Z. T. Li, R. Q. Wang, J. Q. Zhang,  
J. T. Zheng, M. B. Wu,\*  
H. Zeng\* 6540–6544



Cu–N Dopants Boost Electron Transfer and Photooxidation Reactions of Carbon Dots



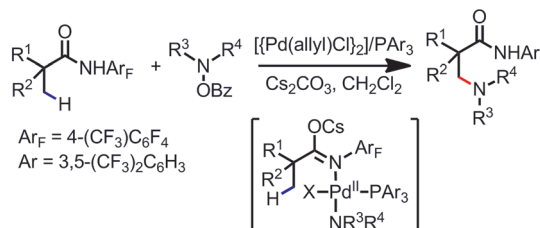
**Doped dots:** Cu–N-doped carbon dots (Cu-CDs) were fabricated by a one-step pyrolytic synthesis using  $\text{Na}_2[\text{Cu}(\text{EDTA})]$  as the precursor. Cu–N dopants concomitantly boost the conductivity and the electron-accepting and -donating abilities of the CDs, enhancing the electron-transfer process in the photooxidation of 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate (see picture; H yellow, N blue, C light blue, O red).

## C–H Activation

J. He, T. Shigenari, J.-Q. Yu\* 6545–6549



Palladium(0)/ $\text{PAr}_3$ -Catalyzed Intermolecular Amination of  $\text{C}(\text{sp}^3)\text{--H}$  Bonds: Synthesis of  $\beta$ -Amino Acids



**Zero in:** The title reaction begins with oxidative addition of  $\text{R}_2\text{N--OBz}$  to a  $\text{Pd}^0/\text{PAr}_3$  catalyst and subsequent cleavage of a  $\text{C}(\text{sp}^3)\text{--H}$  bond by the generated  $\text{Pd--NR}_2$  intermediate. The catalytic cycle pro-

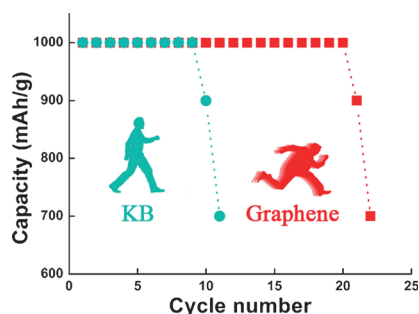
ceeds without the need for external oxidants. The electron-deficient triarylphosphine ligand is crucial for this  $\text{C}(\text{sp}^3)\text{--H}$  amination reaction to occur. Bz = benzoyl.

## Lithium Batteries

Z. Zhang, Q. Zhang, Y. N. Chen, J. Bao,  
X. Zhou, Z. J. Xie, J. P. Wei,  
Z. Zhou\* 6550–6553



The First Introduction of Graphene to Rechargeable  $\text{Li--CO}_2$  Batteries



**A different cathode:** The introduction of graphene as a cathode material to  $\text{Li--CO}_2$  batteries significantly improves their performance. The resulting batteries feature a superior discharge capacity and enhanced cycle stability. A novel approach for simultaneously capturing  $\text{CO}_2$  and storing energy has thus been developed.

## Amine Sensors

S. F. Liu, A. R. Petty, G. T. Sazama,  
T. M. Swager\* 6554–6557

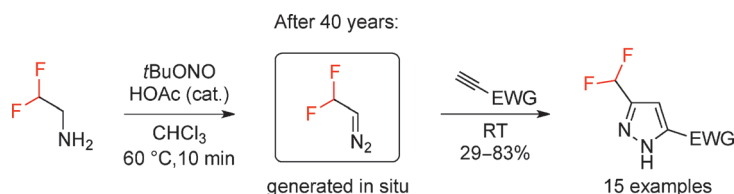


Single-Walled Carbon Nanotube/Metalloporphyrin Composites for the Chemiresistive Detection of Amines and Meat Spoilage



**Dead meat:** Chemiresistive detectors for amines were created from single-walled carbon nanotubes by noncovalent modification with Co *meso*-arylporphyrins. The devices demonstrated sub-ppm sensitiv-

ity and high selectivity toward amines. The use of the detectors to monitor meat spoilage was also demonstrated.  $-\Delta G/G_0$  = change in conductance upon exposure to meat.



**A new reagent:** The elusive chemical reagent  $\text{CF}_2\text{HCHN}_2$  was generated in situ for the first time and further reacted with alkynes in a [3+2] cycloaddition reaction.

This transformation constitutes a novel and efficient approach to agrochemically important difluoromethylated pyrazoles.

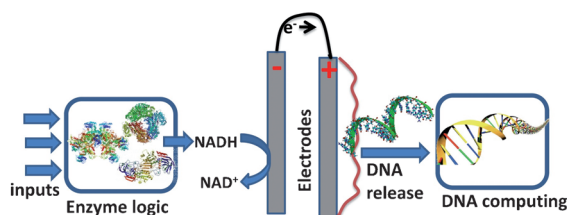
## Difluoromethylation

P. K. Mykhailiuk\* 6558 – 6561

In Situ Generation of Difluoromethyl Diazomethane for [3+2] Cycloadditions with Alkynes



Front Cover



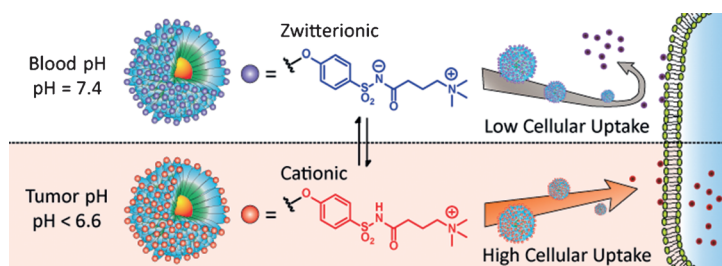
**Interface development:** The communication between enzymatic and DNA logic

systems was enabled by the development of a corresponding interface.

## Electrochemistry

S. Mailloux, Y. V. Gerasimova, N. Guz, D. M. Kolpashchikov,\* E. Katz\* 6562 – 6566

Bridging the Two Worlds: A Universal Interface between Enzymatic and DNA Computing Systems



**Tumor selective:** A pH-responsive zwitterionic alkoxyphenyl acylsulfonamide ligand is used to functionalize the surface of gold nanoparticles (AuNPs) to form zwitterionic NPs. The NPs reversibly

become cationic at tumor pH (< 6.6) with concomitant enhancement of cellular uptake and cytotoxicity in tumor cells, providing scope for pH-controlled NP delivery.

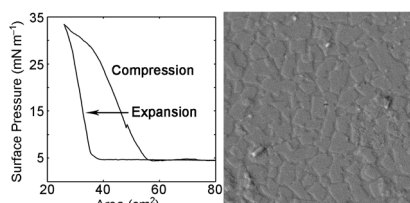
## Antitumor Agents

T. Mizuhara, K. Saha, D. F. Moyano, C. S. Kim, B. Yan, Y.-K. Kim, V. M. Rotello\* 6567 – 6570

Acylsulfonamide-Functionalized Zwitterionic Gold Nanoparticles for Enhanced Cellular Uptake at Tumor pH



**Zeolite films:** Acid treatment was used to prepare stable suspensions of MFI zeolite nanosheets in ethanol. Nanosheets from these suspensions showed high surface activity and could be transferred using the Langmuir–Schaefer technique to obtain monolayer coatings (3 nm thick). Secondary growth of the monolayer coatings resulted in sub-12 nm intergrown zeolite thin films.



## Mesoporous Materials

N. Rangnekar, M. Shete, K. V. Agrawal, B. Topuz, P. Kumar, Q. Guo, I. Ismail, A. Alyoubi, S. Basahel, K. Narasimharao, C. W. Macosko, K. A. Mkhoyan, S. Al-Thabaiti, B. Stottrup,\* M. Tsapatsis\* 6571 – 6575

2D Zeolite Coatings: Langmuir–Schaefer Deposition of 3 nm Thick MFI Zeolite Nanosheets

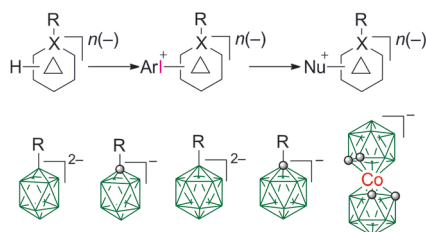


## Boron Cluster Anions

P. Kaszyński,\*  
B. Ringstrand ————— 6576–6581



Functionalization of *closo*-Borates via Iodonium Zwitterions



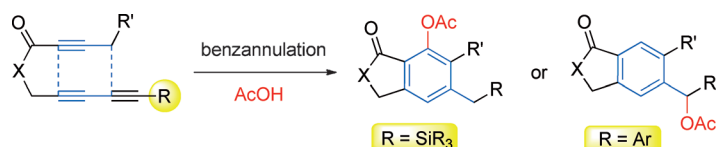
**Openo to change:** The simple preparation of iodonium zwitterions of *closo*-borates and their reactions with nucleophiles (see scheme) provided access to a broad spectrum of cluster derivatives with potential as new classes of pharmaceuticals and materials with tailored properties. The presented reactions demonstrate the synthetic versatility of *closo*-borate aryliodonium zwitterions.

## Synthetic Methods

R. Karmakar, S. Y. Yun, J. Chen, Y. Xia,\*  
D. Lee\* ————— 6582–6586



Benzannulation of Triynes to Generate Functionalized Arenes by Spontaneous Incorporation of Nucleophiles



**Small but profound:** In the benzannulation reaction of 1,3,8-triynes, a small structural difference has a profound impact on the structure of the products. When R is a silyl group, a nucleophile is

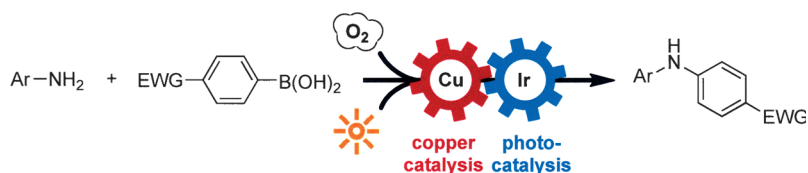
incorporated into the newly formed benzene core, whereas when R is an aryl group, nucleophile trapping occurs at the benzylic carbon atom connected to the aryl group.

## Cross-Coupling

W.-J. Yoo, T. Tsukamoto,  
S. Kobayashi\* ————— 6587–6590



Visible-Light-Mediated Chan–Lam Coupling Reactions of Aryl Boronic Acids and Aniline Derivatives



**Two are better than one:** The copper(II)-catalyzed aerobic oxidative coupling reaction between aryl boronic acids and anilines is significantly improved by the addition of visible-light-mediated photo-

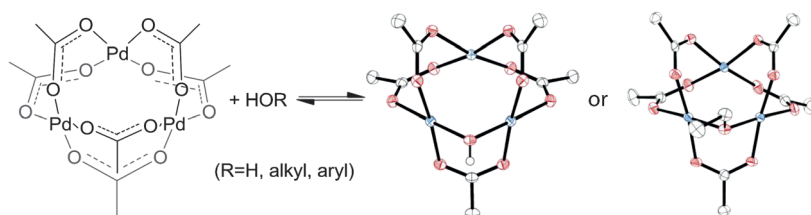
redox catalysts. The substrate scope of this Chan–Lam reaction was thus expanded to include electron-deficient aryl boronic acids.

## Palladium Complexes

R. B. Bedford,\* J. G. Bowen,  
R. B. Davidson, M. F. Haddow,  
A. E. Seymour-Julen, H. A. Sparkes,  
R. L. Webster ————— 6591–6594

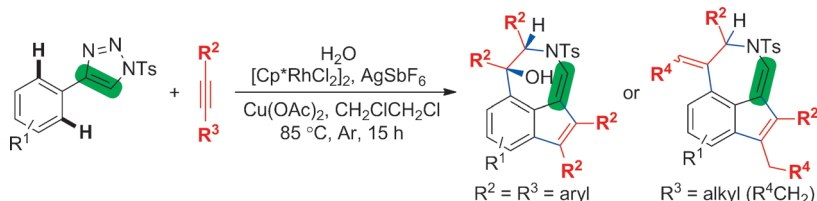


Facile Hydrolysis and Alcoholysis of Palladium Acetate



**When is palladium acetate** not palladium acetate? Anywhere near trace amounts of water or alcohols. Palladium acetate is extremely sensitive to hydrolysis in solution and moderately so in the solid state.

The resulting hydroxide complex is likely to be the true starting point for many reactions and catalytic processes that are reported as using palladium acetate.



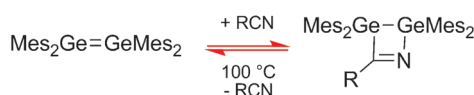
**A quantum leap in complexity:** A general strategy based on rhodium(III) azavinyl carbene intermediates was established for the oxidative [3+2]/[5+2] annulation of 4-aryl 1-tosyl-1,2,3-triazoles with alkynes. This general method provided densely

functionalized indeno[1,7-*cd*]azepine architectures with excellent selectivity through the functionalization of two C-(sp<sup>2</sup>)-H bonds (see scheme; Cp\* = pentamethylcyclopentadienyl, Ts = *p*-toluenesulfonyl).

## Synthetic Methods

Y. Yang, M.-B. Zhou, X.-H. Ouyang, R. Pi, R.-J. Song, J.-H. Li\* — 6595 – 6599

Rhodium(III)-Catalyzed [3+2]/[5+2] Annulation of 4-Aryl 1,2,3-Triazoles with Internal Alkynes through Dual C(sp<sup>2</sup>)-H Functionalization



**A tale of two digermenes:** The addition of acetonitrile, propionitrile, and acrylonitrile to tetramesityldigermene was examined to compare the structures of the molecular adducts with the structures of the nitrile adducts formed on the

Ge(100)-2×1 surface and to provide further insight into the surface chemistry. The addition of nitriles was found to be reversible, and no evidence for cyclic ketenimines was found.

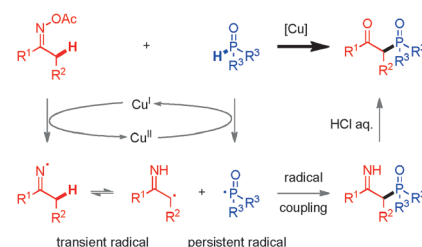
## Group 14 Elements

J. A. Hardwick, K. M. Baines\* — 6600 – 6603

The Addition of Nitriles to a Molecular Digermene: Reversible Addition and Comparison to Surface Reactivity



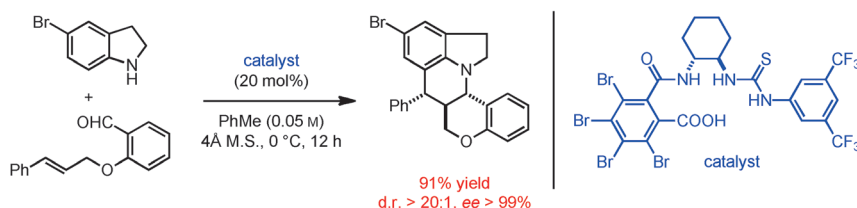
**A copper-catalyzed radical/radical cross-coupling reaction** enables C<sub>sp</sub><sup>3</sup>-P bond formation by direct oxidative C<sub>sp</sub><sup>3</sup>-H/P-H coupling. During the reaction, an α-C<sub>sp</sub><sup>3</sup> radical species (transient radical) and a phosphorus radical species (persistent radical) were generated in the same system by using an internal oxidant. The cross-coupling of the two radical species is selective based on the “persistent radical effect”.



## Cross-Coupling Reactions

J. Ke, Y. Tang, H. Yi, Y. Li, Y. Cheng, C. Liu, A. Lei\* — 6604 – 6607

Copper-Catalyzed Radical/Radical C<sub>sp</sub><sup>3</sup>-H/P-H Cross-Coupling: α-Phosphorylation of Aryl Ketone O-Acetyloximes



**In control:** A readily available chiral Brønsted acid was identified as an efficient catalyst for intramolecular Povarov reactions. Polycyclic amines containing three contiguous stereogenic centers were obtained with excellent stereocontrol in

a single step from secondary anilines and aldehydes possessing a pendent dienophile. These transformations constitute the first examples of catalytic enantioselective intramolecular aza-Diels-Alder reactions.

## Organocatalysis

C. Min, C. Lin, D. Seidel\* — 6608 – 6612

Catalytic Enantioselective Intramolecular Aza-Diels-Alder Reactions



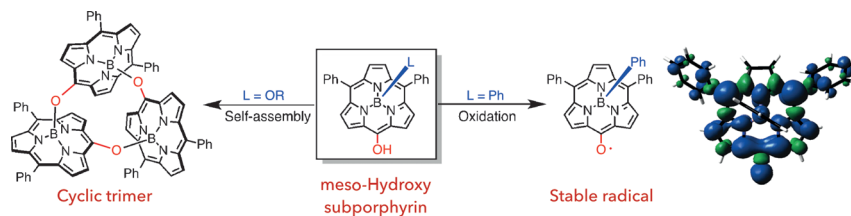


## Porphyrinoids

D. Shimizu, J. Oh, K. Furukawa,\* D. Kim,\*  
A. Osuka\* 6613–6617



meso-Hydroxysubporphyrins: A Cyclic Trimeric Assembly and a Stable meso-Oxy Radical



**A radical approach:** A recently developed  $S_NAr$  reaction was used to synthesize meso-hydroxysubporphyrin, which underwent self-assembly to form a cyclic trimer. This trimer was cleaved to the corresponding meso-hydroxy monomer with

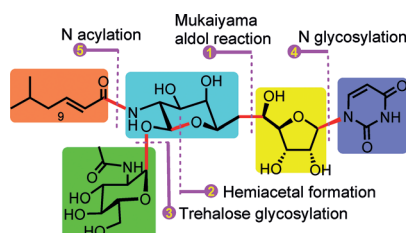
a phenyl Grignard reagent. Oxidation of the monomer gave a subporphyrin meso-oxy radical species which is exceptionally stable and can be stored in solution under open air for over a month.

## Total Synthesis

J. Li, B. Yu\* 6618–6621



A Modular Approach to the Total Synthesis of Tunicamycins



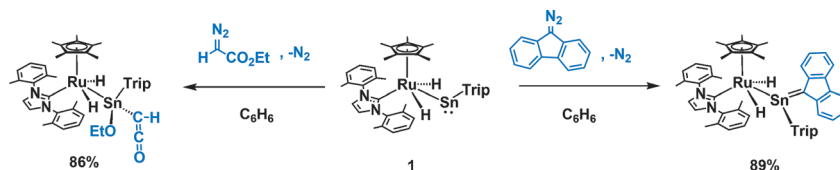
**The modular and stereoselective** synthesis of tunicamycins features a Mukaiyama aldol reaction, intramolecular acetal formation, gold(I)-catalyzed O and N glycosylation, and final N acylation as the key steps. These natural products are a unique type of nucleoside antibiotics with potent inhibitory activities against bacterial cell-wall synthesis and the N-glycosylation of eukaryotic proteins.

## Metallostannylene

H.-J. Liu, M. S. Ziegler,  
T. D. Tilley\* 6622–6626



The Ruthenostannylene Complex  $[Cp^*(IXy)H_2Ru-Sn-Trip]$ : Providing Access to Unusual Ru-Sn Bonded Stanna-imine, Stannene, and Ketenylstannyl Complexes



**Reactivity studies** of the thermally stable ruthenostannylene complex  $[Cp^*(IXy)(H)_2Ru-Sn-Trip]$  (1) towards a variety of organic substrates are described. This complex is used for the construction

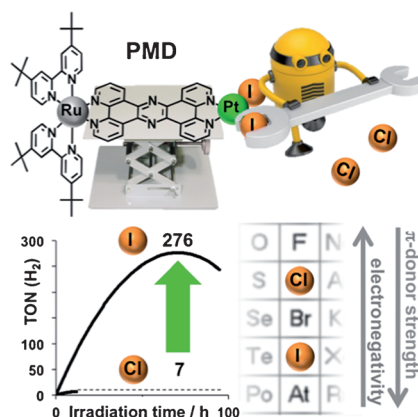
of new metal-tin complexes featuring low-valent or unsaturated tin centers.  $IXy = 1,3$ -bis(2,6-dimethylphenyl)imidazol-2-ylidene;  $Cp^* = \eta^5-C_5Me_5$ ;  $Trip = 2,4,6-iPr_3C_6H_2$ .

## Photocatalysis

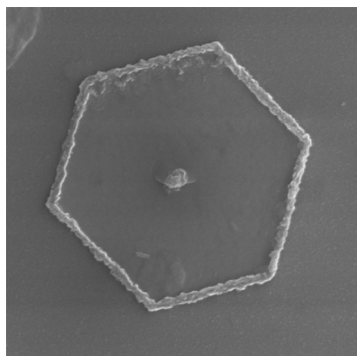
M. G. Pfeffer, T. Kowacs, M. Wächter,  
J. Guthmüller, B. Dietzek, J. G. Vos,  
S. Rau\* 6627–6631



Optimization of Hydrogen-Evolving Photochemical Molecular Devices



**The X files:** The catalytic activity of a photochemical molecular device (PMD) for light-driven hydrogen production, containing a  $PtX_2$  ( $X = Cl$  or  $I$ ) moiety as the catalytic center, is significantly enhanced by exchanging the terminal chloride ligands at the Pt center for iodide ligands. DFT calculations revealed a significantly increased electron density at the platinum center induced by the iodide ligands.



### Intermediates, served up on a plate:

Investigation of the formation mechanism of hexagonal  $\text{Sb}_2\text{Te}_3$  plates (HPs) in a solvothermal synthesis shows the structure is formed in an amorphous state and then subsequently crystallizes.

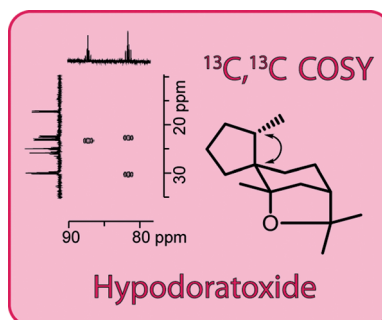
### Crystallization Processes

T. Saltzmann, M. Bornhöfft, J. Mayer, U. Simon\* 6632 – 6636

Shape without Structure: An Intriguing Formation Mechanism in the Solvothermal Synthesis of the Phase-Change Material  $\text{Sb}_2\text{Te}_3$



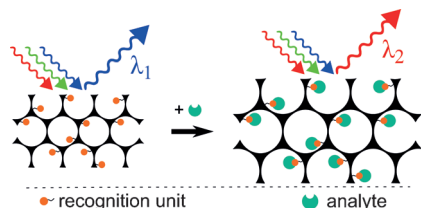
**Feeding** of (2,3,4,5,6- $^{13}\text{C}_5$ ) mevalonolactone to *Hypomyces odoratus* resulted in a completely  $^{13}\text{C}$ -labeled sesquiterpene ether. Its structure was elucidated by  $^{13}\text{C}$ ,  $^{13}\text{C}$  COSY and classic NMR experiments, resulting in a structural revision of hypodoratoxide. The absolute configuration was inferred from one of its co-metabolites. Feeding of other  $^{13}\text{C}$ -labeled mevalonolactone isotopologues confirmed skeletal rearrangements during terpene cyclization.



### Terpene Biosynthesis

L. Barra, K. Ibrom, J. S. Dickschat\* 6637 – 6640

Structural Revision and Elucidation of the Biosynthesis of Hypodoratoxide by  $^{13}\text{C}$ ,  $^{13}\text{C}$  COSY NMR Spectroscopy

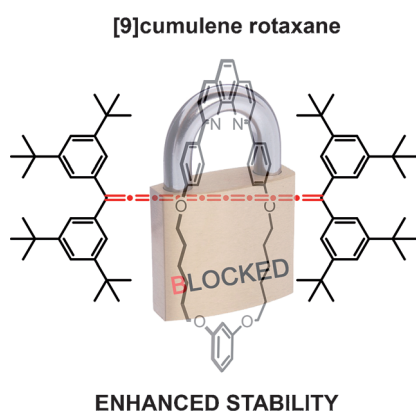


**A successful marriage:** The combination of smart hydrogels and inverse opal structures unites simplicity with efficacy for sensing macromolecules. While the inverse opal structure provides structural color and a large accessible interface for binding, the induced phase transition of the analyte-responsive hydrogel produces strong optical effects. The resulting spectral shifts can surpass 100 nm and are easily detected.

### Responsive Materials

J.-P. Couturier, M. Sütterlin, A. Laschewsky,\* C. Hettrich, E. Wischerhoff\* 6641 – 6644

Responsive Inverse Opal Hydrogels for the Sensing of Macromolecules



**Loaded and locked:** An approach to stabilizing  $[n]$ cumulenes was developed based on locking the cumulene within a rotaxane. The result is a stabilized  $[9]$ cumulene that enables the study of properties as a function of cumulene length in unprecedented detail, including by quantitative UV/Vis spectroscopy, cyclic voltammetry, and differential scanning calorimetry. The experimental results are supported by DFT calculations.

### Cumulated Double Bonds

M. Franz, J. A. Januszewski, D. Wendinger, C. Neiss, L. D. Movsisyan, F. Hampel, H. L. Anderson, A. Görling, R. R. Tykwinski\* 6645 – 6649

Cumulene Rotaxanes: Stabilization and Study of  $[9]$ Cumulenes



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



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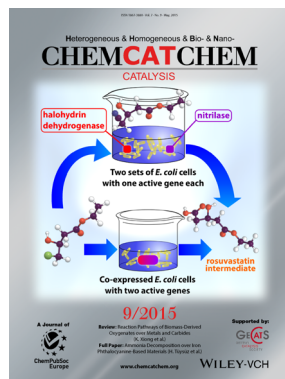


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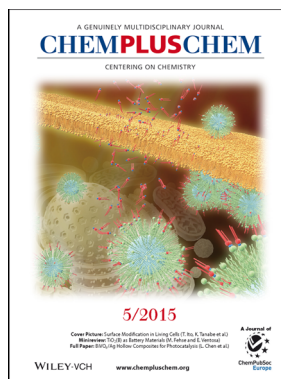
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