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

*Q. Zhang, T. P. Chou, B. Russo, S. A. Jenekhe, G. Cao**
**Aggregation of ZnO Nanocrystallites for High Conversion Efficiency in Dye-Sensitized Solar Cells**

*S. Arita, T. Koike, Y. Kayaki, T. Ikariya**
**Aerobic Oxidative Kinetic Resolution of Racemic Secondary Alcohols with Chiral Bifunctional Amido Complexes**

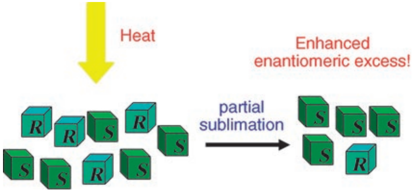
*T. Z. Forbes, J. G. McAlpin, R. Murphy, P. C. Burns**
**Metal–Oxygen Isopolyhedra Assembled into Fullerene Topologies**

*T. A. Rokob, A. Hamza, A. Stirling, T. Soós,* I. Pápai**
**Turning Frustration into Bond Activation: A Theoretical Mechanistic Study on Heterolytic Hydrogen Splitting by Frustrated Lewis Pairs**

## Obituary

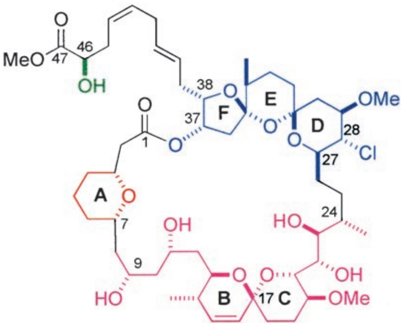
## Books

## Highlights



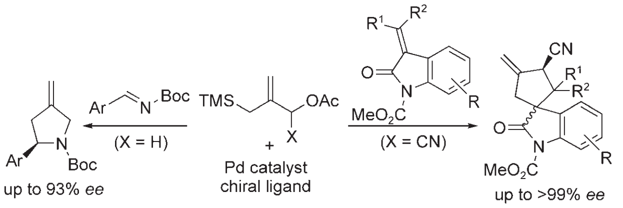
**Some like it hot!** Fractional sublimation of chiral organic compounds may improve substantially a small enantiomeric excess and result in a useful protocol for resolving racemates. This simple yet insightful concept has been revisited with extra vistas on stereoisomer discrimination mechanisms.

***Resolution by Sublimation***



**Problem solved**: Spirastrellolide A methyl ester (see picture) is a potent phosphatase 2A inhibitor and has been the subject of considerable synthetic interest since its isolation in 2003. Paterson and co-workers have now succeeded in the total synthesis of this compound by using a flexible modular strategy. This total synthesis and previous studies towards fragments for spectroscopic comparison and stereochemical determination is summarized.

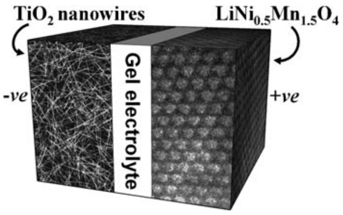
***Natural Product Synthesis***



**Advances in selectivity**: The use of chiral phosphoramidite ligands in asymmetric Pd-catalyzed [3+2] cycloadditions of trimethylenemethane derivatives affords *exo*-methylenecyclopentanes. This type of reaction has been used to prepare diverse compounds such as pyrrolidines and spirocyclic oxindolic cyclopentanes in good yields and with excellent selectivity (see scheme).

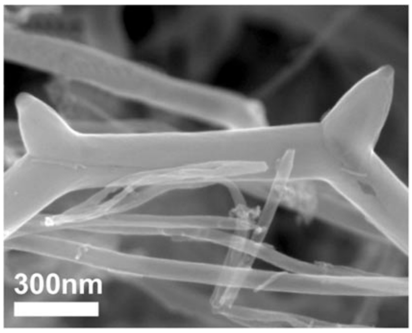
## Reviews

**Rechargeable lithium batteries** have developed into the dominant energy source for portable electronic devices because of their high energy density. Nanomaterials are pivotal for further development in this area, as their special properties can greatly increase the efficiency of such batteries. The picture shows a lithium nanobattery incorporating a $TiO_2$(B) nanowire anode and nanoparticulate $Li(Ni_{1/2}Mn_{3/2})O_4$ cathode.



## Communications

**Going out on a limb**: A combination of theoretical techniques, high-resolution microscopy, and energy-dispersive X-ray spectroscopy shows the role sulfur plays in branching phenomena during carbon nanotube (CNT) network growth. A model is proposed in which small amounts of sulfur are enough to trigger the growth of a bud in a CNT, leading to kink formation and subsequent branch growth (see SEM image).

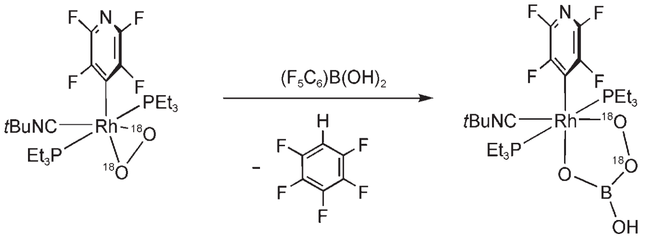


**For the USA and Canada:** ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Wiley-VCH, 111 River Street, Hoboken, NJ 07030. Annual subscription price for institutions: US$ 7225/6568 (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.

## Peroxo Complexes

M. Ahijado, T. Braun* ______ 2954 – 2958

Rhodium Derivatives of Peroxoboronic Acids and Peroxoboric Acid: Formation of Metallatrioxaborolanes from an η²-Peroxo Complex



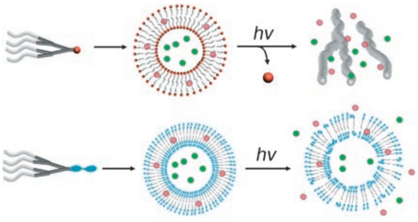
**Heterocyclic peroxides** with a five-membered RhOOBO ring have been isolated by reaction of a rhodium peroxo complex with phenylboronic acids. They can be considered to be rhodium derivatives of perboric acid (see scheme) and phenylperboronic acids.

---

## Self-Assembly

C. Park, J. Lim, M. Yun, C. Kim* ______ 2959 – 2963

Photoinduced Release of Guest Molecules by Supramolecular Transformation of Self-Assembled Aggregates Derived from Dendrons



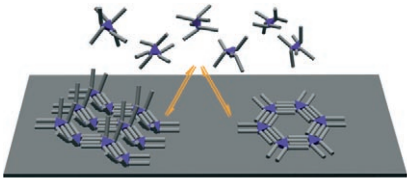
**The missing link**: Supramolecular transformation from a vesicle to a fibrous nanostructure has been achieved by photolytic cleavage and supramolecular reorganization of a dendritic building block containing a 2-nitrobenzyl group (see picture). Furthermore, supramolecular aggregates of an amide dendron with a photoisomerizable azobenzene unit exhibit controlled release of encapsulated molecules upon photoirradiation in the aqueous phase.

---

## Self-Assembly on Surfaces

S. Lei, K. Tahara, F. C. De Schryver, M. Van der Auweraer, Y. Tobe,* S. De Feyter* ______ 2964 – 2968

One Building Block, Two Different Supramolecular Surface-Confined Patterns: Concentration in Control at the Solid–Liquid Interface



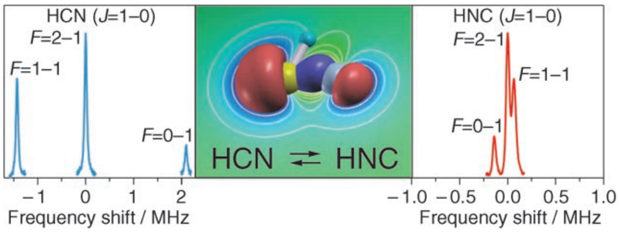
**New tool for surface modification**: The 2D pattern formed by physisorbed dehydrobenzoannulene molecules on a graphite surface depends on their concentration in solution. The concentration dependence is directly related to the difference in stability between the linear and the honeycomb polymorphs and their respective molecular densities (see picture).

---

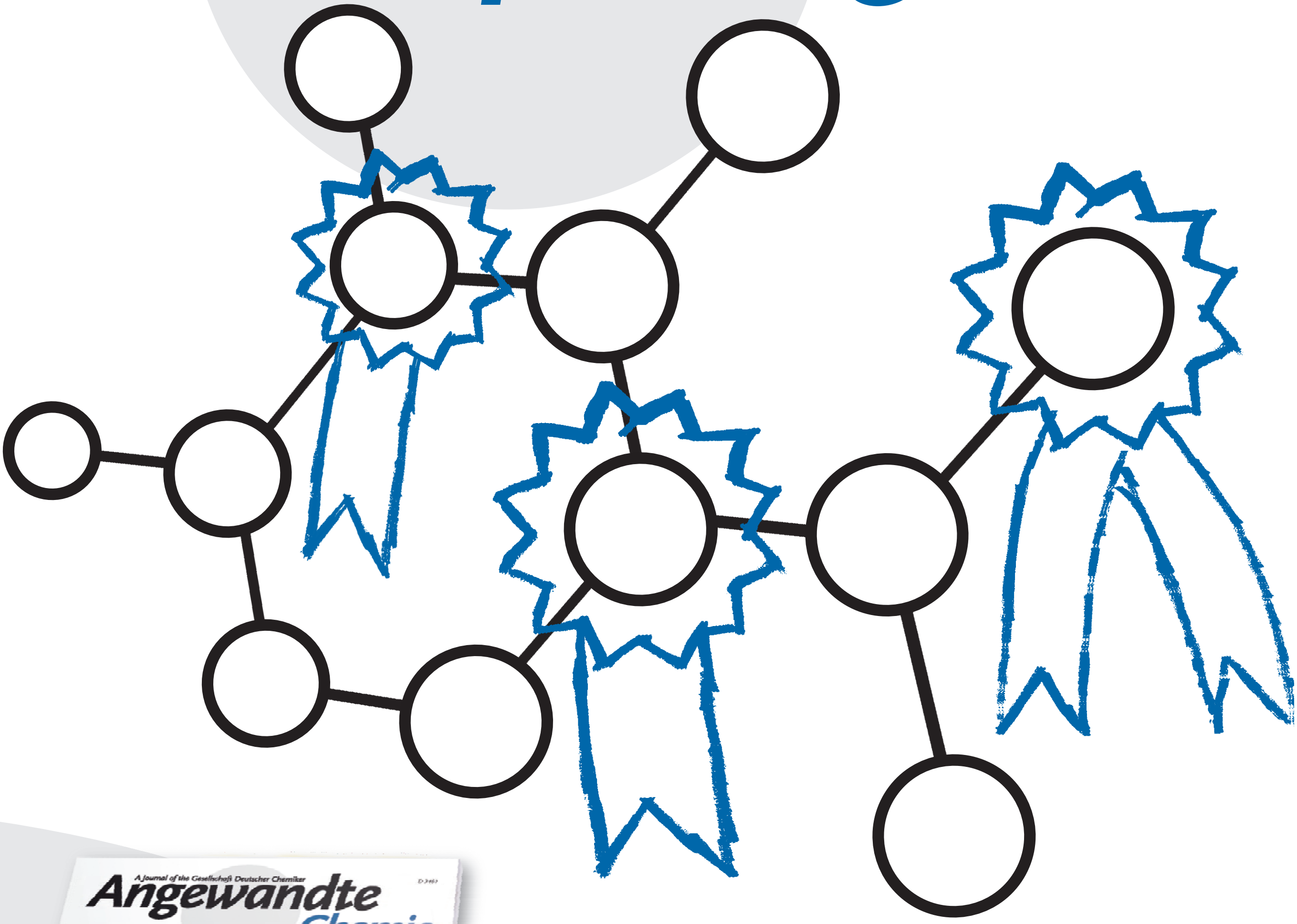
## Chemical Bonding

H. A. Bechtel, A. H. Steeves, B. M. Wong, R. W. Field* ______ 2969 – 2972

Evolution of Chemical Bonding during HCN⇄HNC Isomerization as Revealed through Nuclear Quadrupole Hyperfine Structure



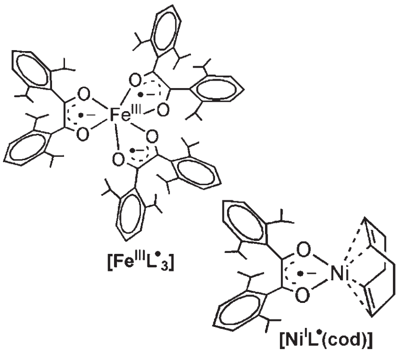
**Hyperfine reporter**: Millimeter-wave absorption measurements and ab initio calculations show that nuclear quadrupole hyperfine structure (hfs) is highly sensitive to the extent of bending excitation in HCN and HNC. These results indicate that hfs serves as a reporter of progress along the isomerization reaction coordinate and can reveal mechanistic information about this process.



### $\pi$-Radical Complexes

G. H. Spikes, E. Bill, T. Weyhermüller, K. Wieghardt* ———— 2973 – 2977

Transition-Metal Complexes with Singly Reduced 1,2-Diketone Radical Ligands



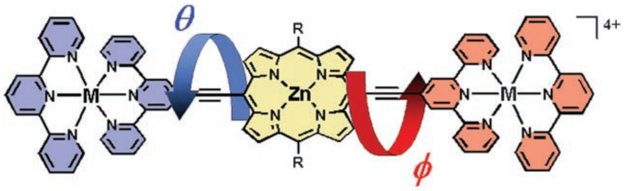
**Radically single**: Two complexes featuring a singly reduced 1,2-diketonate(1−) $\pi$-radical ligand, namely the tris(ligand) radical iron complex $[Fe^{III}L^{\bullet}_3]$ ($S=1$) and the low-valent organometallic nickel complex $[Ni^{I}L^{\bullet}(cod)]$ ($S=0$; cod = cycloocta-1,5-diene), are isolated and characterized (see picture).

---

### Chromophores

T. V. Duncan, K. Song, S.-T. Hung, I. Miloradovic, A. Nayak, A. Persoons, T. Verbiest, M. J. Therien,* K. Clays* ———— 2978 – 2981

Molecular Symmetry and Solution-Phase Structure Interrogated by Hyper-Rayleigh Depolarization Measurements: Elaborating Highly Hyperpolarizable $D_2$-Symmetric Chromophores



**Strongly coupled oscillators** with $D_2$ and $D_{2d}$ symmetry can act as potent octopolar chromophores with nonlinear optical properties according to Hyper-Rayleigh light-scattering measurements, which demonstrate that small solution-phase structural subpopulations having these symmetries ($\theta \approx -\phi$ and $\theta = -\phi = |45°|$, respectively, for the chromophore shown in the picture) can exhibit exceptional hyperpolarizabilities.

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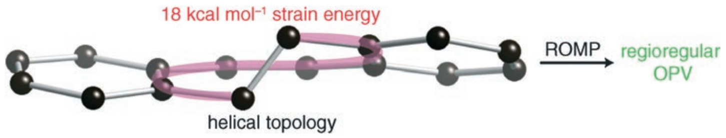
### Olefin Metathesis

M. Carnes, D. Buccella, J. Decatur, M. L. Steigerwald, C. Nuckolls* ———— 2982 – 2985

Helical (5*Z*, 11*E*)-Dibenzo[*a*,*e*]cyclooctatetrene: A Spring-Loaded Monomer



**ROMP with a kinky olefin**: An [8]-annulene in which one of the double bonds is kinked into a *trans* configuration is wound into a helical conformation, and is spring-loaded with circa 18 kcal mol$^{-1}$ strain energy. This annulene acts as an active monomer for ring-opening polymerization (ROMP), which produces a living oligo(phenylene vinylene) (OPV) with all-*ortho* linkages. The polymer has an equal number of *cis* and *trans* double bonds.

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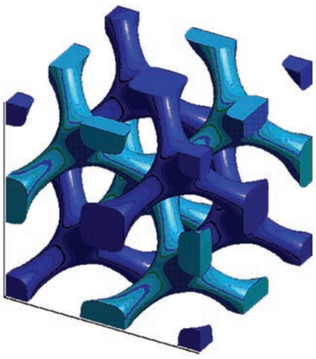
### Cell-Penetrating Peptides

A. Mishra, V. D. Gordon, L. Yang, R. Coridan, G. C. L. Wong* – 2986 – 2989

HIV TAT Forms Pores in Membranes by Inducing Saddle-Splay Curvature: Potential Role of Bidentate Hydrogen Bonding



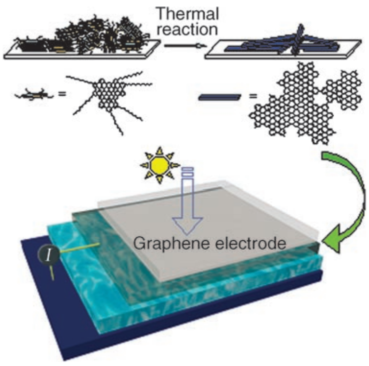
**Pore performance**: The TAT protein of HIV can cross cell membranes with remarkable efficiency. By applying ideas from coordination chemistry, soft-condensed-matter physics, and differential geometry, it has been shown that TAT induces saddle-splay curvature in cell membranes, a process that is required for pore formation (see picture of two nonintersecting networks of pores). The results have potential implications for the design of cell-penetrating peptides.

### Nanostructures

X. Wang, L. Zhi,* N. Tsao, Ž. Tomović,
J. Li, K. Müllen* ____________ **2990 – 2992**

Transparent Carbon Films as Electrodes in Organic Solar Cells

**A window of opportunity**: A transparent graphene film has been obtained by a new bottom-up chemical approach involving the thermal reaction of synthetic nanographene molecules of giant polycyclic aromatic hydrocarbons which are cross-linked with each other and further fused into larger graphene sheets. Such graphene films have been applied as window electrodes in organic solar cells (see picture).



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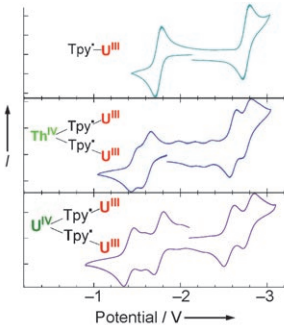
### Actinide Complexes

E. J. Schelter, R. Wu, B. L. Scott,
J. D. Thompson, D. E. Morris,*
J. L. Kiplinger* ____________ **2993 – 2996**

Mixed Valency in a Uranium Multimetallic Complex

**Hetero- and homo-trimetallic** thorium and uranium complexes with mixed-valent metal centers have been prepared and studied by electrochemical (see picture; Tpy = 2,2′:6′,2″-terpyridine), spectroscopic, and magnetic analyses. Appreciable electronic interaction has been detected in this system with the $U^{IV}$ ion facilitating communication to the $U^{III}$ center better than $Th^{IV}$.



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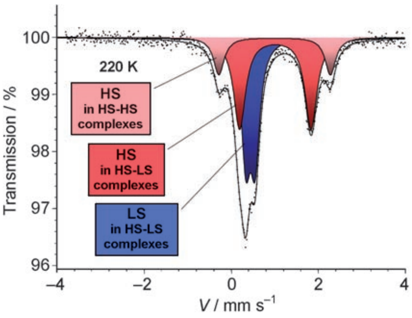
### Spin Crossover

C. M. Grunert, S. Reiman, H. Spiering,
J. A. Kitchen, S. Brooker,*
P. Gütlich* ____________ **2997 – 2999**

Mixed Spin-State [HS-LS] Pairs in a Dinuclear Spin-Transition Complex: Confirmation by Variable-Temperature $^{57}Fe$ Mössbauer Spectroscopy



**Exquisite sensitivity** of Mössbauer spectroscopy for tiny local molecular distortion is demonstrated in $[Fe^{II}_2(pmat)_2](BF_4)_4 \cdot DMF$: high-spin (HS) iron(II) in [HS-HS] and in [LS-HS] (low-spin–high-spin) pairs is clearly distinguished (see picture) for the first time without the need to apply a magnetic field. This dinuclear complex clearly shows that spin crossover via a [LS-HS] species is promoted by the use of a highly constrained bridging ligand (the bis-terdentate pmat).

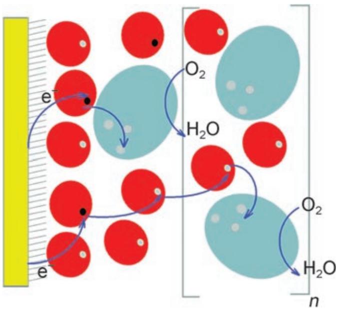
---

### Signal-Transfer Models

R. Dronov, D. G. Kurth, H. Möhwald,
F. W. Scheller, F. Lisdat* ____ **3000 – 3003**

Communication in a Protein Stack: Electron Transfer between Cytochrome *c* and Bilirubin Oxidase within a Polyelectrolyte Multilayer

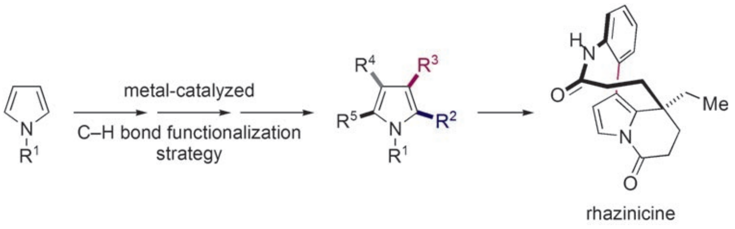
**Assemblies of proteins and enzymes** can serve as a model for mimicking biological signal transfer. A polyelectrolyte multilayer (see picture) of an electron-transfer protein (cytochrome *c*, red) and a copper enzyme (bilirubin oxidase, blue) has catalytic properties for four-electron oxygen reduction. The proposed architecture guarantees efficient protein–protein interaction without an additional redox mediator.



## C–H Activation

E. M. Beck, R. Hatley,
M. J. Gaunt* ———— 3004 – 3007

Synthesis of Rhazinicine by a Metal-Catalyzed C–H Bond Functionalization Strategy



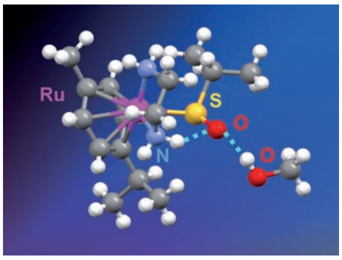
**Iterative and regioselective** metal-catalyzed C–H bond functionalization has been utilized to develop a strategy for the first total synthesis of the pyrrole alkaloid rhazinicine (see scheme).

---

## Sulfur Complexes

H. Petzold, J. Xu,
P. J. Sadler* ———— 3008 – 3011

Metal and Ligand Control of Sulfenate Reactivity: Arene Ruthenium Thiolato-Mono-*S*-Oxides



**Going OS**: Oxygenation of thiolate sulfur atoms can control biological signaling processes. Rare examples of a monodentate sulfenate ligands stabilized by hydrogen bonding to a diamine ligand within organometallic ruthenium arene complexes of pharmaceutical interest and their unusual acid/base properties are reported.

---

## Nanoemulsions

J. Zhang, B. Han,* C. Zhang, W. Li,
X. Feng ———— 3012 – 3015

Nanoemulsions Induced by Compressed Gases

**Pressure makes the difference!** Compressed gases, such as $CO_2$, ethylene, ethane, and propane, can induce the formation of nanoemulsions with special characteristics. The application of $CO_2$-induced nanoemulsions in the preparation of cross-linked porous polystyrene materials and the ability of $CO_2$ to stabilize emulsions for enhanced oil recovery are studied. A possible mechanism for the formation of the nanoemulsions is discussed (see picture).

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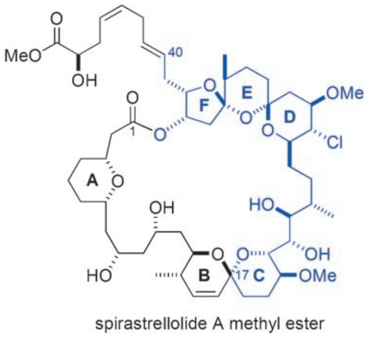
## Natural Product Synthesis

I. Paterson,* E. A. Anderson, S. M. Dalby,
J. H. Lim, J. Genovino, P. Maltas,
C. Moessner ———— 3016 – 3020

Total Synthesis of Spirastrellolide A Methyl Ester—Part 1: Synthesis of an Advanced C17–C40 Bis-spiroacetal Subunit

**Out of the blue**: The marine macrolide spirastrellolide A is a potent and selective inhibitor of protein phosphatase 2A and a lead for anticancer therapies. A flexible and modular synthetic strategy has been developed with two routes for the construction of the DEF bis-spiroacetal subunit. The optimized Suzuki coupling approach results in the efficient preparation of a C17–C40 aldehyde that forms the cornerstone of the first total synthesis.

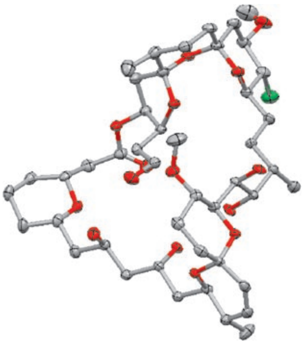


## Natural Product Synthesis

VIP

I. Paterson,* E. A. Anderson, S. M. Dalby,
J. H. Lim, J. Genovino, P. Maltas,
C. Moessner ______________ **3021 – 3025**

Total Synthesis of Spirastrellolide A Methyl Ester—Part 2: Subunit Union and Completion of the Synthesis

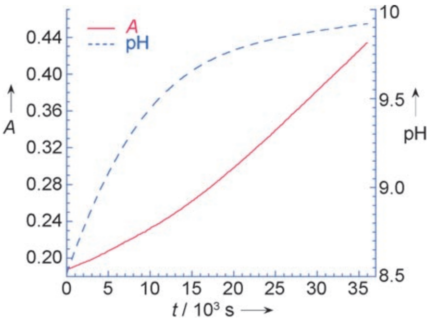


**Succumbing to synthesis**: The stereocontrolled total synthesis of spirastrellolide A methyl ester is reported. The union of two key C1–C16 and C17–C40 subunits is followed by macrolactonization and late-stage side chain attachment by a cross-metathesis reaction and a π-allyl Stille coupling reaction with a C43–C47 stannane, thus confirming the 46*R* configuration. The full configuration and conformation of the 38-membered macrolide is revealed by single-crystal X-ray analysis of an advanced pentaol intermediate.

## Molecular Devices

G. Alibrandi* ______________ **3026 – 3028**

Cryptand 111: A Chemical Device for Variable-pH Kinetic Experiments

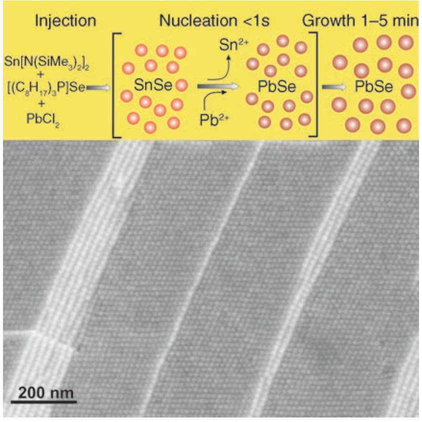


**An internal molecular device**, namely, cryptand 111, as opposed to an external physical one (e.g., an autoburette), was used to change the pH with time in a variable-pH kinetic (VpHK) experiment and thus obtain the pH–rate profile of the hydrolysis of aspirin in the alkaline range in a single run. The picture shows the change in absorbance due to aspirin hydrolysis during the VpHK experiment while the pH changed with time.

## Nanocrystal Growth

M. V. Kovalenko,* D. V. Talapin, M. A. Loi,
F. Cordella, G. Hesser, M. I. Bodnarchuk,
W. Heiss ______________ **3029 – 3033**

Quasi-Seeded Growth of Ligand-Tailored PbSe Nanocrystals through Cation-Exchange-Mediated Nucleation

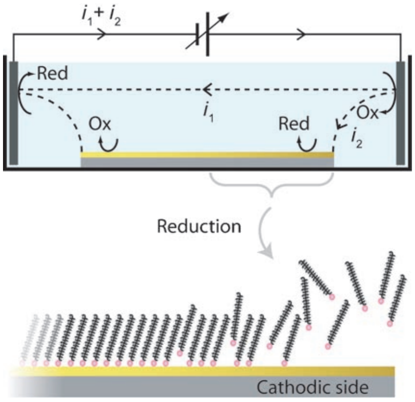


**Seeds of change**: An unusually fast cation-exchange reaction at the nanoscale is an efficient tool for precise control of the nucleation of nanocrystals. As a model system, 3.2–14-nm PbSe nanocrystals are produced by the nucleation reaction of $Pb^{2+}$ with transient SnSe nuclei (see picture). The synthesis allows surface derivatization of the PbSe nanocrystals with various ligands.

## Molecular Gradients

C. Ulrich, O. Andersson, L. Nyholm,
F. Björefors* ______________ **3034 – 3036**

Formation of Molecular Gradients on Bipolar Electrodes

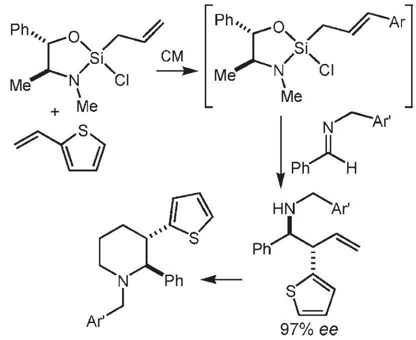


**Intelligent surfaces**: Electrochemical reactions can be induced on a conducting surface placed in an electric field. In this way, a bipolar electrode is formed, and this effect can be used to create molecular gradients (see picture). The major advantage of the technique is that the electrode can be of virtually any thickness, shape, and material—as long as it is conductive.

## Asymmetric Synthesis

J. D. Huber, N. R. Perl,
J. L. Leighton* ——— 3037 – 3039

Allylsilane–Vinylarene Cross-Metathesis Enables a Powerful Approach to Enantioselective Imine Allylation



**“Cinnamylation-flavored” synthesis**: Cross-metathesis (CM) reactions between an allylsilane and vinylarenes enable the rapid generation of various cinnamylsilanes, which may be used in situ for the highly enantioselective, and diastereodivergent, cinnamylation of imines (see example in scheme). Under this new, simple, and efficient protocol, the potential of imine cinnamylation to produce stereochemically and functionally complex products has been more fully realized. Ar = thienyl, Ar′ = 2-hydroxyphenyl.

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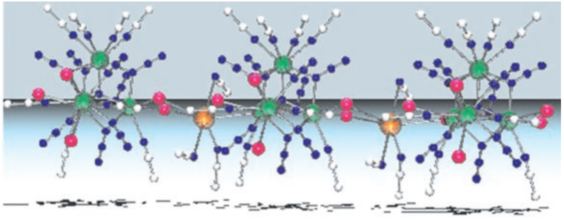
## Uranium Complexes

G. Nocton, J. Pécaut,
M. Mazzanti* ——— 3040 – 3042

A Nitrido-Centered Uranium Azido Cluster Obtained from a Uranium Azide



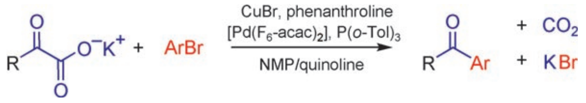
**Caught in the actinide**: A tetranuclear azido/nitrido uranium anion containing eight end-on bridging azido ligands and a $\mu_4$ interstitial nitrido ligand has been isolated and structurally characterized (see 1D chain; U green, Cs orange, I magenta, N blue, C white). A new two-step procedure has been developed to promote the cluster assembly by oxidation of $[UI_3(thf)_4]$ with a preformed uranium heptaazido complex.

---

## Cross-Coupling

L. J. Gooßen,* F. Rudolphi, C. Oppel,
N. Rodríguez ——— 3043 – 3045

Synthesis of Ketones from α-Oxocarboxylates and Aryl Bromides by Cu/Pd-Catalyzed Decarboxylative Cross-Coupling



**The power of two metals**: A Pd/Cu catalyst system mediates the in situ formation of acyl nucleophiles by decarboxylation of readily accessible and stable salts of α-oxocarboxylic acids and their cross-coupling with aryl or heteroaryl bromides to give ketones. The reaction may be used in the presence of many functional groups and provides good yields.

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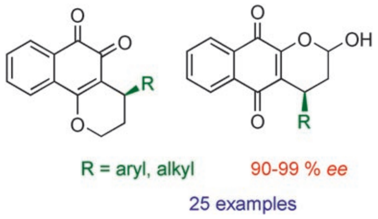
## Organocatalysis

M. Rueping,* E. Sugiono,
E. Merino ——— 3046 – 3049

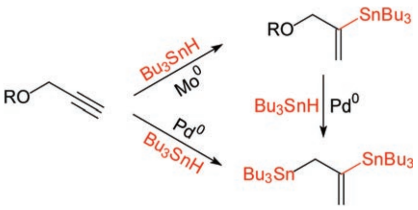
Asymmetric Iminium Ion Catalysis: An Efficient Enantioselective Synthesis of Pyranonaphthoquinones and β-Lapachones



**An addition–cyclization reaction cascade** triggered by an organocatalyst was used for the enantioselective preparation of a series of biologically active 1,2- and 1,4-pyranonaphthoquinones from aliphatic and aromatic α,β-unsaturated aldehydes and 2-hydroxy-1-4-naphthoquinone. A trimethylsilyl-protected diarylprolinol serves as the Lewis base organocatalyst.

# Contents

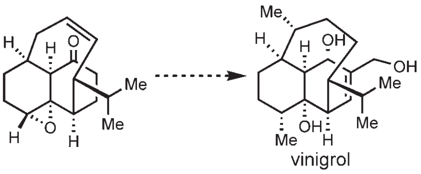
## Metalations



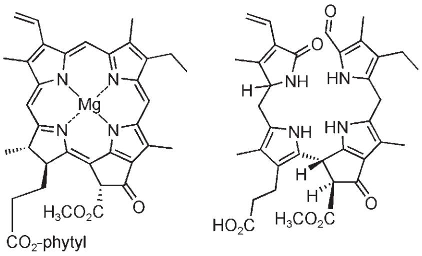
**Propargylic ethers and acetates** can be converted into distannylated alkenes in the presence of Bu$_3$SnH and a Pd catalyst. The reaction proceeds via a stannylated allyl alcohol derivative, which undergoes elimination and subsequent dimetalation. If a molybdenum catalyst is used in the hydrostannylation step, and the stannylated intermediates can be reacted with other dimetallic compounds.

## Natural Products

**Short and sweet**: A simple and practical route to the unusual tricyclic ring system found in the biologically active diterpene vinigrol is described. A remarkable proximity-induced intramolecular cycloaddition and mild Grob fragmentation allow rapid construction of the core ring system in less than 10 steps and with a minimal reliance on protecting groups.



## Synthetic Chlorophyll Catabolites



chlorophyll *a*

NCC

**Colorless** nonfluorescent chlorophyll catabolites (NCCs), the final products of endogenous chlorophyll breakdown in higher plants, were prepared by biomimetic partial synthesis from chlorophyll *a*. A nonstereoselective variant of the synthesis also provided an entry to the enantiomers of natural NCCs.

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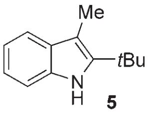
Supporting information is available on www.angewandte.org (see article for access details).

A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

## Service

# Corrigendum

The regiochemistry of indole **5** in Table 2, entry 2 of this Communication was inadvertently inverted. The correct structure is shown below.



**5**

One-Pot Multicomponent Synthesis of Indoles from 2-Iodobenzoic Acid

O. Leogane, H. Lebel* ______ **350–352**

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