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:*

*B. L. Merner, L. N. Dawe, G. J. Bodwell**
1,1,8,8-Tetramethyl[8](2,11)teropyrenophane: Half of an Aromatic Belt and a Segment of an (8,8) Single-Walled Carbon Nanotube

*B. Liu, H. Wang, H. Xie, B. Zeng, J. Chen, J. Tao, T. B. Wen, Z. Cao, H. Xia**
Osmapyridine and Osmapyridinium from a Formal [4+2] Cycloaddition Reaction

*J. L. Alonso-Gómez, P. Rivera-Fuentes, N. Harada, N. Berova, F. Diederich**
An Enantiomerically Pure Alleno-Acetylenic Macrocycle: Synthesis and Rationalization of Its Outstanding Chiroptical Response

*P. García-García, M. A. Fernández-Rodríguez, E. Aguilar**
Gold-Catalyzed Cycloaromatization of 2,4-Dien-6-yne Carboxylic Acids: Synthesis of 2,3-Disubstituted Phenols and Unsymmetrical Bi- and Terphenyls

P. A. Rupar, R. Bandyopadhyay, B. F. T. Cooper, M. R. Stinchcombe, P. J. Ragogna, C. L. B. Macdonald, K. M. Baines**
Cationic Crown Ether Complexes of Germanium(II)

*X. Zeng, H. Beckers, H. Willner**
Difluoro-λ^5-Phosphinonitrile $F_2P{\equiv}N$: Matrix Isolation and Photoisomerization into FP=NF

A. D. Payne, G. Bojase, M. N. Paddon-Row, M. S. Sherburn**
Practical Synthesis of the Dendralene Family Reveals Alternation in Behavior

*T. J. Kucharski, Z. Huang, Q.-Z. Yang, Y. Tian, N. C. Rubin, C. D. Concepcion, R. Boulatov**
Kinetics of Thiol/Disulfide Exchange Correlates Weakly with the Restoring Force in the Disulfide Moiety

*W. Xu, X. Xue, T. Li, H. Zeng, X. Liu**
Ultrasensitive and Selective Colorimetric DNA Detection by Nicking Endonuclease-Assisted Nanoparticle Amplification

Author Profile

My favorite subject at school was Chemistry. I chose chemistry as a career because I love the fact we can "Just Do It" without over-thinking.
This and more about Wenbin Lin can be found on page 4472.

News

C. A. Mirkin

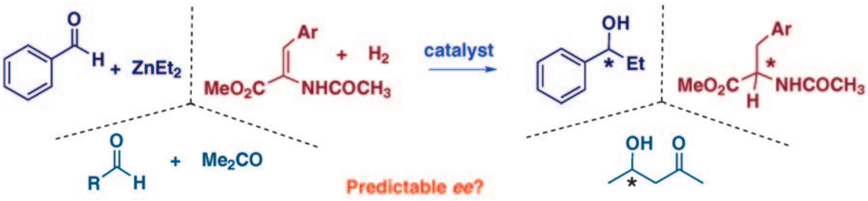
M. Shokat

A. Warshel

Books

Highlights

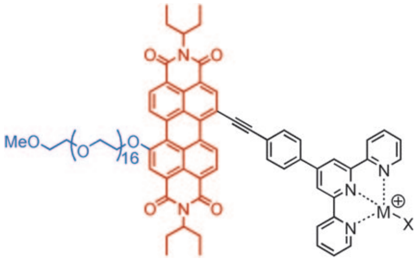
Asymmetric Catalysis



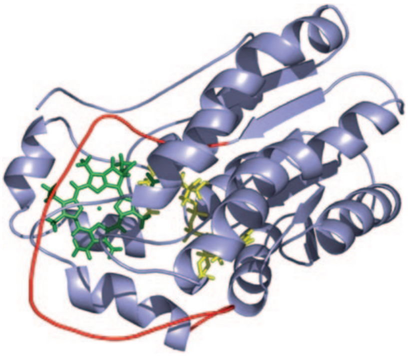
Seeing into the future: A range of computational methods have been applied to harmonize predicted *ee* values with experimental values. Novel ways of combining quantum mechanics and molecular mechanics feature prominently.

Supramolecular Chemistry

A limited number of poly(ethylene oxide)-substituted perylene bisimides, some of which are equipped with terpyridine ligands for transition-metal coordination (see structure), combine different types of noncovalent interactions to yield opto-electronically active organic materials with different types of supramolecular morphologies.



Enzyme Catalysis



In a new light: The NADPH:protochlorophyllide (Pchlide) oxidoreductase (POR; see structure, green Pchlide, yellow NADPH) is a good model to investigate catalytical processes in enzymes, as its light activation allows an immediate start of the catalyzed reaction. By irradiation with weak, short laser pulses it is possible to detect conformation changes during the reaction and thus to uncover the elementary steps of the catalytic process.

For the USA and Canada:
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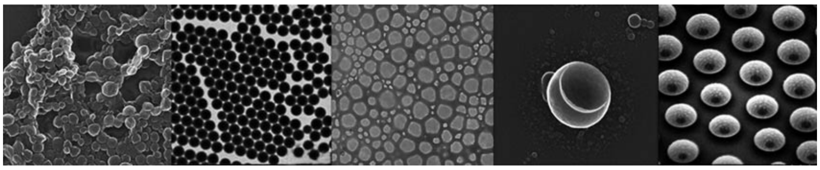
Reviews

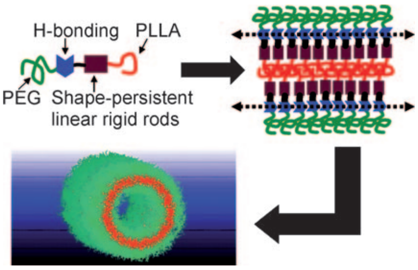
Structures in Miniemulsions



The miniemulsion process allows the formation of complex polymer nanoparticles and the encapsulation of widely varying materials into a polymer shell (see examples). Functionalization of the nanoparticles can be easily carried out, and polymerization to form polymer nanoparticles can be performed in environmentally friendly solvents, such as water.

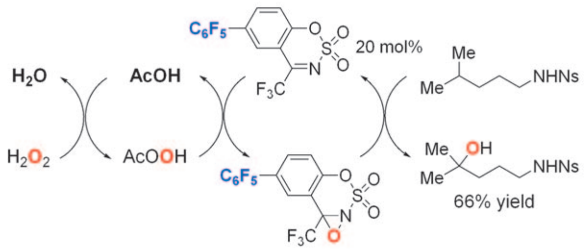
Communications

Polymeric Nanostructures



Once around the block: Incorporation of a rigid hydrogen-bonding benzamide unit, placed at the interface between two polymer blocks, in poly(ethylene glycol) (PEG)–(thio)urea–poly(L-lactide) (PLLA) block copolymers transforms the morphology of the block copolymers, from spherical micelles, as formed by PEG-PLLA diblock copolymers, into nanotubes in solution.

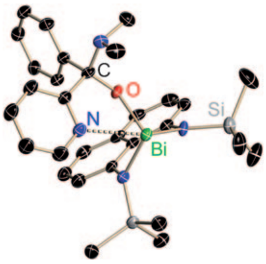
Synthetic Methods

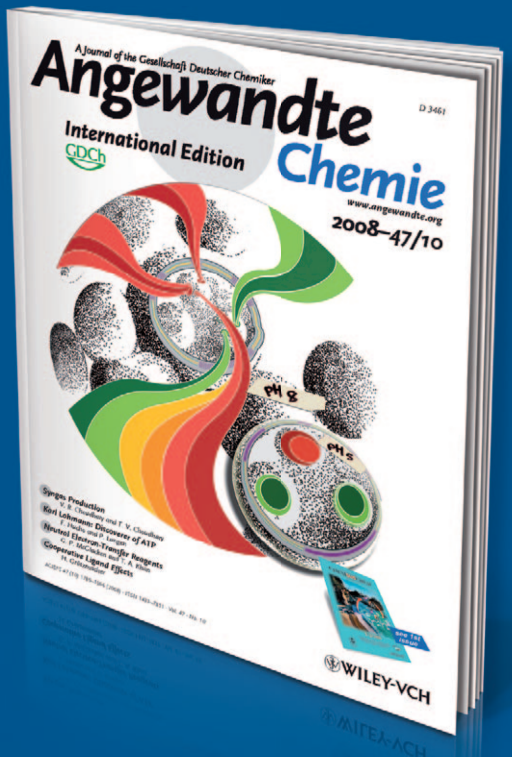


Substituted benzoxathiazines function as catalysts for the selective hydroxylation of tertiary C–H bonds. Mechanistic studies have revealed an unanticipated disparity between oxaziridine reactivity and catalyst performance and have given way to a new catalyst and an aqueous H_2O_2 reaction protocol that greatly facilitate such transformations (see scheme).

Bismuth Compounds

Bi–O chemistry: A direct regioselective route to bismuth bis(amino)naphthalene compounds, incorporating Bi–O and Bi–C bonds is described, in which an amide precursor is treated with aldehydes, ketones, alkenes, and alkynes, leading to insertion into the Bi–NMe_2 bond.

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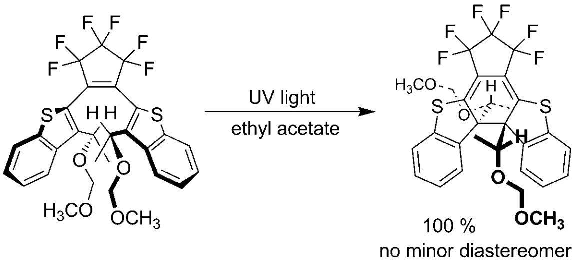
Photochromism

Y. Yokoyama,* T. Shiozawa, Y. Tani, T. Ubukata ______ 4521–4523

A Unified Strategy for Exceptionally High Diastereoselectivity in the Photochemical Ring Closure of Chiral Diarylethenes

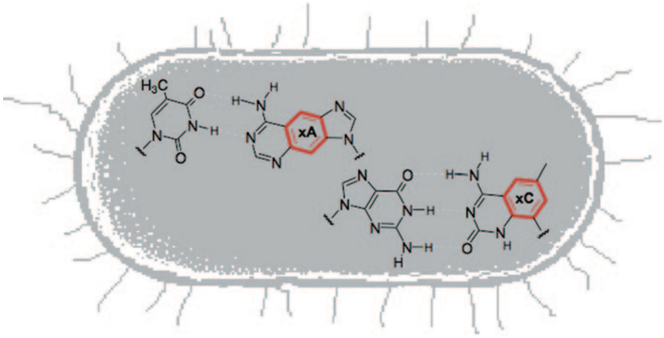


Into my arms: Photochemical cyclization of diarylethenes that have two chiral side arms showed up to 100% *de* (see scheme). Introduction of these chiral side arms onto the carbon atoms where ring closure occurs is a general strategy for the highly diastereoselective cyclization of diarylethenes.

Unnatural DNA Bases

J. C. Delaney, J. Gao, H. Liu, N. Shrivastav, J. M. Essigmann,* E. T. Kool* ______ 4524–4527

Efficient Replication Bypass of Size-Expanded DNA Base Pairs in Bacterial Cells

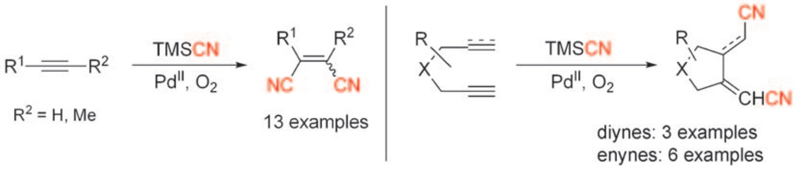


Supersize me! Size-expanded DNA bases (xDNA) are able to encode natural DNA sequences in replication. In vitro experiments with a DNA polymerase show nucleotide incorporation opposite the xDNA bases with correct pairing. In vivo experiments using *E. coli* show that two xDNA bases (xA and xC, see picture) encode the correct replication partners.

Palladium Catalysis

S. Arai,* T. Sato, Y. Koike, M. Hayashi, A. Nishida ______ 4528–4531

Palladium-Catalyzed Cyanation of Carbon–Carbon Triple Bonds Under Aerobic Conditions

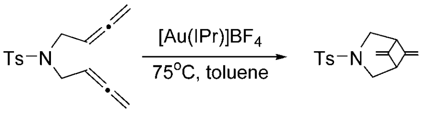


Essential oxygen: The title transformation involves two different modes of cyanation, *syn* and *anti* cyanopalladation, as the key steps in this catalytic reaction. These processes enable successful dicyanative cyclization of diyne and enyne derivatives (see scheme).

N-Heterocyclic Carbenes

S. M. Kim, J. H. Park, Y. K. Kang,* Y. K. Chung* ______ 4532–4535

N-Heterocyclic Carbene Gold(I) Catalyzed Transformation of N-Tethered 1,5-Bisallenes to 6,7-Dimethylene-3-azabicyclo[3.1.1]heptanes

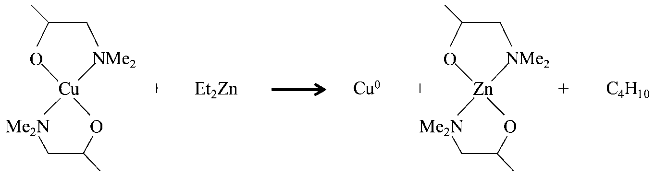


Tying up loose ends: The reaction of bisallenes tethered with *N*-(*p*-tolylsulfonamide) in the presence of a cationic gold N-heterocyclic carbene catalyst gave new cycloisomerization products, 6,7-dimethyleneazabicyclo[3.1.1]heptanes, in high yields (see scheme; IPr = *N*,*N'*-bis(2,6-diisopropylphenyl)imidazol-2-ylidene).

Thin Films

B. H. Lee, J. K. Hwang, J. W. Nam,
S. U. Lee, J. T. Kim, S. Koo, A. Baunemann,
R. A. Fischer, M. M. Sung* — **4536 – 4539**

Low-Temperature Atomic Layer Deposition of Copper Metal Thin Films: Self-Limiting Surface Reaction of Copper Dimethylamino-2-propoxide with Diethylzinc

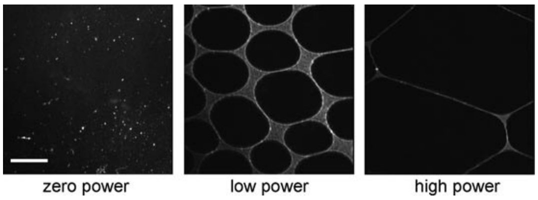


A uniform, conformal, pure copper metal thin film was grown at very low substrate temperatures (100–120 °C) on Si(100) substrates by atomic layer deposition involving the ligand exchange of [Cu(OCHMeCH$_2$NMe$_2$)$_2$] with Et$_2$Zn (see scheme). Patterned copper thin films of Cu nanotubes (diameter 150 nm, length 12 μm) were fabricated.

Nanostructures

R. Volinsky, R. Jelinek* — **4540 – 4542**

Laser-Modulated Ordering of Gold Nanoparticles at the Air/Water Interface

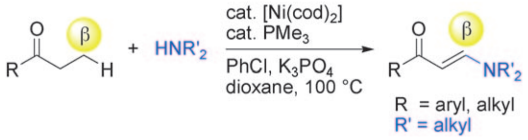

zero power low power high power

Beam me up, Scotty! Laser irradiation of Langmuir monolayers of gold nanoparticles (NPs) and elaidic acid led to dramatic reorganization that was dependent on the laser power (see picture, scale bar = 100 μm). Variable-temperature experiments indicate that localized surface heating in an extremely small temperature range, induced by the laser beam, causes ordering of the NPs.

Synthetic Methods

S. Ueno,* R. Shimizu,
R. Kuwano* — **4543 – 4545**

Nickel-Catalyzed Formation of a Carbon–Nitrogen Bond at the β Position of Saturated Ketones

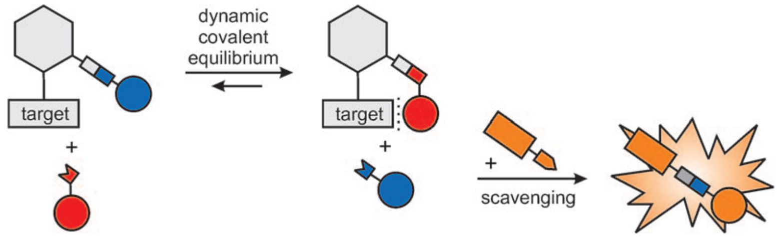


Gone fishing: When propiophenone and related ethyl ketones are treated with morpholine in the presence of K$_3$PO$_4$, chlorobenzene, and [Ni(cod)$_2$]/PMe$_3$ catalyst, a carbon–nitrogen bond is formed selectively at the β position (see scheme; cod = cycloocta-1,5-diene). Secondary amines were employed as substrates to give the corresponding β-enaminones.

Systems Chemistry

G. Gasparini, F. Bettin, P. Scrimin,
L. J. Prins* — **4546 – 4550**

Indirect Optical Analysis of a Dynamic Chemical System

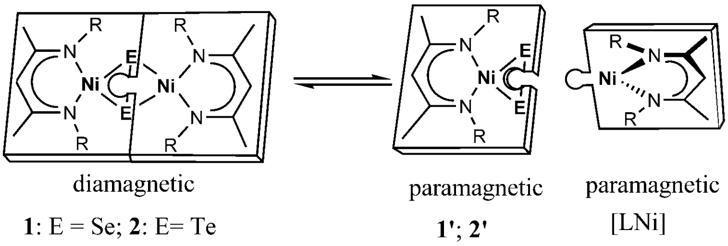


Hide and seek: The composition of a dynamic covalent equilibrium reaction is determined by measuring the 'left-over' concentration of a reference compound (blue object, see picture). Reaction of the reference compound with a scavenger generates a characteristic UV/Vis signal that is independent of the molecular structure of the target.

Nickel Chalcogenides

S. Yao, Y. Xiong, X. Zhang, M. Schlangen, H. Schwarz, C. Milsmann, M. Driess* ______ 4551–4554

Facile Dissociation of $[(LNi^{II})_2E_2]$ Dichalcogenides: Evidence for $[LNi^{II}E_2]$ Superselenides and Supertellurides in Solution

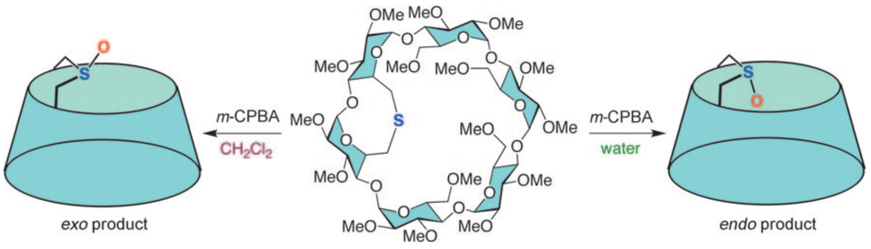


Easy breakage to open-shells: The diamagnetic butterfly-like dichalcogen complexes **1** (E = Se) and **2** (E = Te) with a $\{Ni^{II}_2E_2\}$ core, undergo facile dissociation in solution via spin crossover to give the unprecedented mononuclear paramagnetic superselenide and supertelluride species **1′** and **2′**, respectively, along with the nickel(I) fragment $[LNi^{I}]$; R = 2,6-diisopropylphenyl.

Supramolecular Chemistry

D. Armspach,* D. Matt,* L. Toupet ______ 4555–4558

Self-Mediated Stereoselective Oxidation of Thia-Capped Cyclodextrins

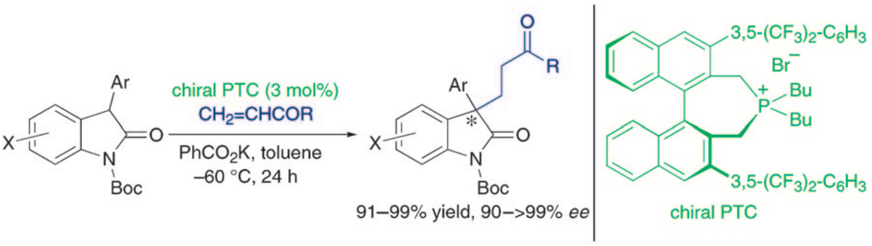


Self-control: *endo*-Sulfoxide products can be synthesized selectively by the oxidation of thia-capped cyclodextrins using *m*-chloroperoxybenzoic acid (*m*-CPBA) in water. The reaction occurs by the formation of an oxidant–cyclodextrin inclusion complex. Operating in organic media preferentially leads to *exo*-sulfoxide products.

Phase-Transfer Catalysis

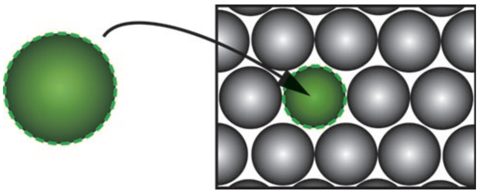
R. He, C. Ding, K. Maruoka* 4559–4561

Phosphonium Salts as Chiral Phase-Transfer Catalysts: Asymmetric Michael and Mannich Reactions of 3-Aryloxindoles



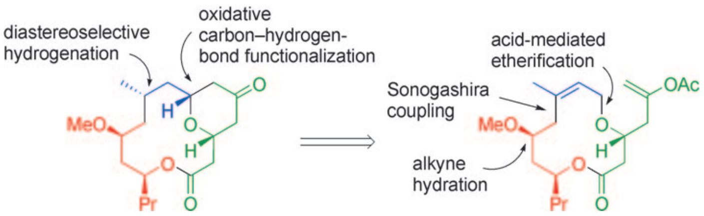
It's a PTC: A highly efficient reaction of 3-aryloxindoles in an asymmetric Michael addition was achieved by using a quaternary tetraalkylphosphonium salt as a chiral phase-transfer catalyst (PTC). The products were obtained in quantitative yields high *ee* values. The reaction of 3-aryloxindoles in an asymmetric Mannich reaction using the same catalyst also proved to be feasible.

Dynamic Materials



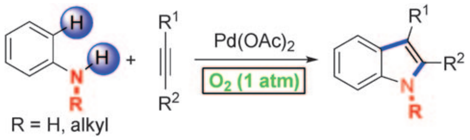
Healing hands: A complex interplay between colloidal and polymeric energetics in microgel self-assembly behavior results in soft colloidal assemblies with self-healing properties. Repulsive soft spheres can adopt highly compressed conformations in colloidal crystalline lattices without directly contacting the nearest neighbors (see picture). This distant action is directly responsible for the self-healing of the assemblies.

C–H Functionalization



Macrocyclic oxocarbenium ions can be formed from macrolactones that contain benzylic or allylic ether groups through oxidative carbon–hydrogen-bond activation mediated by 2,3-dichloro-4,5-dicyanoquinone (DDQ). The applicability of this efficient reaction to complex-molecule synthesis was demonstrated by its use in a brief formal synthesis of neopeltolide (see retrosynthetic scheme) to form the tetrahydropyrone ring.

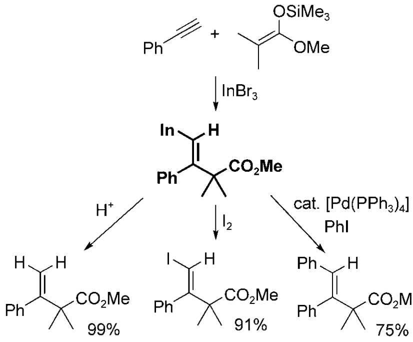
C–H Activation



Pd doles it out: A palladium-catalyzed approach to indoles using the title reaction was achieved (see scheme). The oxidant used in this catalytic cycle was O_2. Both N-nonsubstituted and N-alkyl monosubstituted anilines can be successfully transformed into the corresponding indoles by this method.

Synthetic Methods

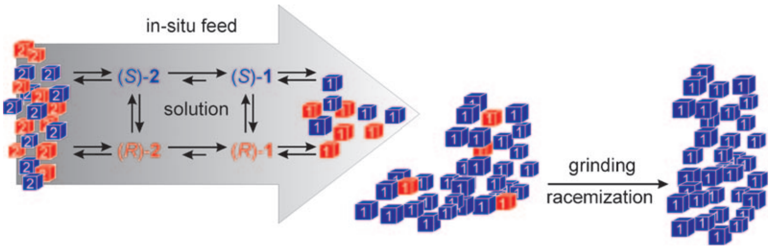
$InBr_3$ promotes the addition of ketene silyl acetals to monosubstituted alkynes to afford 2,2-disubstituted alkenylindium compounds in high regio- and stereoselectivity (see scheme). In addition, the alkenylindium derivatives have been subsequently coupled with iodobenzene in the presence of a palladium catalyst.



Chiral Resolution

W. L. Noorduin, B. Kaptein,* H. Meekes,
W. J. P. van Enckevort, R. M. Kellogg,
E. Vlieg ______ **4581 – 4583**

Fast Attrition-Enhanced Deracemization of Naproxen by a Gradual In Situ Feed

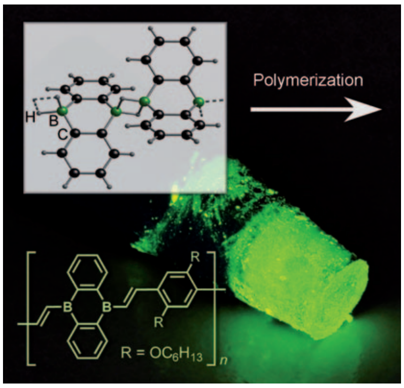


Grind and cure: Using the nonsteroidal anti-inflammatory drug naproxen, a novel concept is demonstrated to dramatically enhance the rate of the recently discovered process of deracemization using abrasive grinding. The process relies on a gradual feed of the racemic target material by an in situ conversion.

Luminescent Materials

A. Lorbach, M. Bolte, H. Li, H.-W. Lerner,
M. C. Holthausen,* F. Jäkle,*
M. Wagner* ______ **4584 – 4588**

9,10-Dihydro-9,10-diboraanthracene: Supramolecular Structure and Use as a Building Block for Luminescent Conjugated Polymers



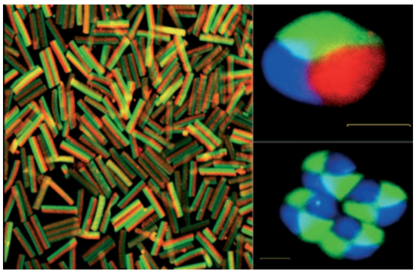
Building bridges: The title compound forms an unprecedented polymeric structure with bridging B–H–B three-center two-electron bonds in the solid state. This organoborane serves as an efficient precursor for the preparation of boron-doped π-conjugated polymers by hydroboration polymerization with a functionalized 1,4-diethynylbenzene (see picture). These polymers form thin films that show intense green luminescence.

Microstructured Materials

S. Bhaskar, J. Hitt, S. L. Chang,
J. Lahann* ______ **4589 – 4593**

Multicompartmental Microcylinders

Colorful columns: A simple yet scalable method that yields multicompartmental microcylinders with controllable internal architectures, aspect ratios, and controlled surface modification uses electrohydrodynamic co-spinning followed by microsectioning. Compartments are discriminated by different colored dyes (see CLSM images; scale bars = 10.0 μm).



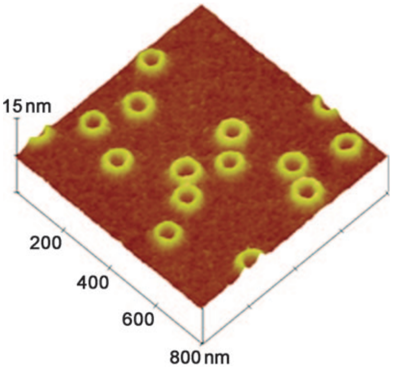
Toroidal Micelles

VIP

H. Huang, B. Chung, J. Jung, H.-W. Park,
T. Chang* ______ **4594 – 4597**

Toroidal Micelles of Uniform Size from Diblock Copolymers

Uniform nanodonuts: Stable toroidal micelles that have a highly uniform size and shape spontaneously self-assemble from a selective THF/ethanol solvent mixture (see 3D AFM image). The donut-shaped micelles can be used as a template to grow gold nanoparticles, which form along the ring surface.

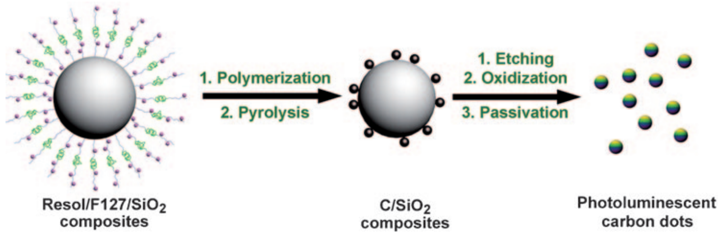


Contents

Fluorescent Nanoparticles

R. Liu,* D. Wu, S. Liu, K. Koynov, W. Knoll, Q. Li* ________ **4598–4601**

An Aqueous Route to Multicolor Photoluminescent Carbon Dots Using Silica Spheres as Carriers



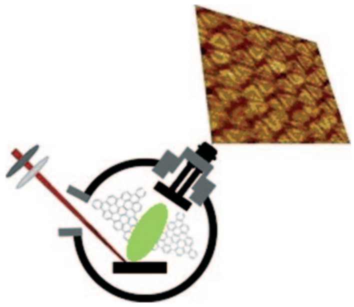
Carbon lights up: A facile chemical method yields multicolor photoluminescent carbon dots derived from polymer/silica nanocomposites, which were prepared using surfactant-modified silica spheres as carriers and resols (phenol/formaldehyde resins) as carbon precursor (see picture). The surface-passivated carbon dots show good biocompatibility as potential bioimaging agents offering nanometer-scale resolution.

Aromatic Polycycles

A. Rouhanipour, M. Roy, X. L. Feng, H. J. Räder,* K. Müllen* ________ **4602–4604**

Subliming the Unsublimable: How to Deposit Nanographenes

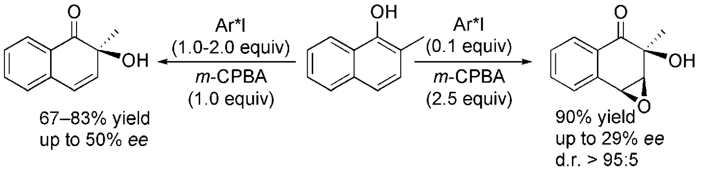
Quite sublime: Thin-layer fabrication of unsublimable large polycyclic aromatic hydrocarbons (PAHs) by pulsed laser deposition was used to prepare samples for scanning tunneling microscopy. Giant PAHs with up to 222 carbon atoms can be visualized—a size that was previously not possible because of the lack of suitable deposition methods.



Asymmetric Synthesis

S. Quideau,* G. Lyvinec, M. Marguerit, K. Bathany, A. Ozanne-Beaudenon, T. Buffeteau, D. Cavagnat, A. Chénedé ________ **4605–4609**

Asymmetric Hydroxylative Phenol Dearomatization through In Situ Generation of Iodanes from Chiral Iodoarenes and *m*-CPBA



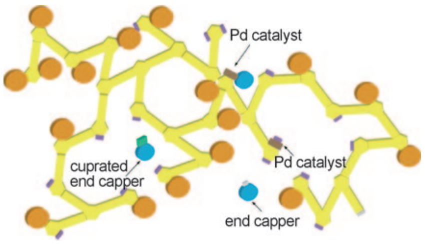
'I' is all the hype: A twofold excess of iodoarene in the title reaction leads to *ortho*-quinols in good yields, whereas organocatalytic versions of this reaction enable subsequent epoxidation in a regio- and diastereoselective fashion. Chiral iodobiarenes led to enantioselectivities up to 50% *ee*. *m*-CPBA = *meta*-chloroperoxybenzoic acid.

VIP

Polymer Synthesis

J. Tolosa, C. Kub, U. H. F. Bunz* ________ **4610–4612**

Hyperbranched: A Universal Conjugated Polymer Platform

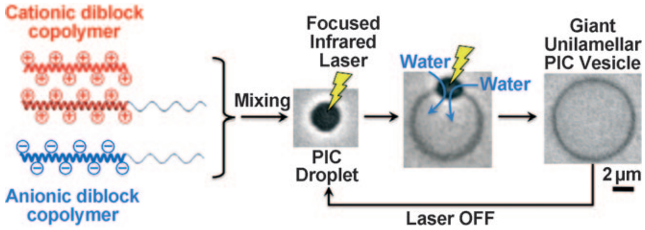


Out on a limb: Sonogashira coupling of a suitable AB$_2$ monomer containing two iodine and one alkyne group forms a hyperbranched conjugated polymer that is studded with iodine end groups (see picture: I purple). These iodine groups are a perfect handle for convenient, efficient, and high-yielding post-functionalization to access hyperbranched, fluorescent poly(phenyleneethynylene)s.

Polymeric Vesicles

H. Oana,* A. Kishimura,* K. Yonehara, Y. Yamasaki, M. Washizu, K. Kataoka ______ 4613 – 4616

Spontaneous Formation of Giant Unilamellar Vesicles from Microdroplets of a Polyion Complex by Thermally Induced Phase Separation

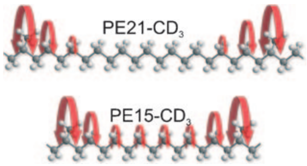


Water pump: Polyion complex (PIC) vesicles are spontaneously formed from PIC microdroplets, which are formed by mixing cationic and anionic polymers (see picture). The formation process can be reversibly controlled by local heating with a focused infrared laser that triggers microphase separation and subsequent water influx. The size of the resulting giant unilamellar vesicles is determined by the initial size of the PIC droplets.

Polymer Branching

Y. Wei, R. Graf, J. C. Sworen, C.-Y. Cheng, C. R. Bowers, K. B. Wagener,* H. W. Spiess* ______ 4617 – 4620

Local and Collective Motions in Precise Polyolefins with Alkyl Branches: A Combination of ^{2}H and ^{13}C Solid-State NMR Spectroscopy

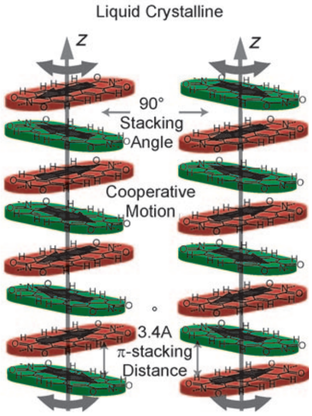


Branching out: The mobility of linear polymers changes upon branching, which has a pronounced effect on processability and drawability. Regularly branched model polyolefins were studied by advanced solid-state NMR spectroscopy, and twist defects around the branches in the crystalline regions are identified. For lower branch content, the twisting motions are decoupled; for higher content, collective motion is found (see picture).

Cooperative Motion

M. R. Hansen, T. Schnitzler, W. Pisula, R. Graf, K. Müllen, H. W. Spiess* ______ 4621 – 4624

Cooperative Molecular Motion within a Self-Assembled Liquid-Crystalline Molecular Wire: The Case of a TEG-Substituted Perylenediimide Disc

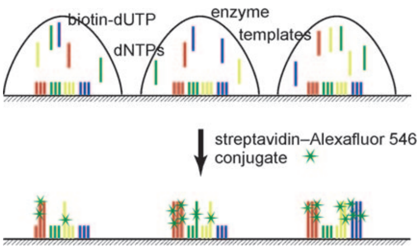


Always on the move: Molecular dynamics of perylene cores in columnar structures influences the processability and self-healing of these materials. A combination of X-ray scattering and advanced solid-state NMR methods show that these systems have restricted angular mobility of the cores even in the frozen phase, and a cooperative spiral type of motion in the liquid crystalline phase (see picture).

Protein Engineering

R. Kranaster, A. Marx* ______ 4625 – 4628

Taking Fingerprints of DNA Polymerases: Multiplex Enzyme Profiling on DNA Arrays

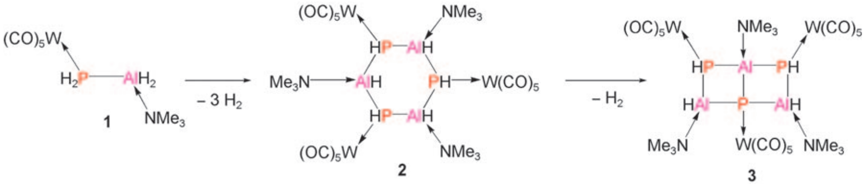


A novel screening approach based on an oligonucleotide-addressing enzyme assay enables multiplexed simultaneous profiling of DNA polymerases in nanoliter volumes in terms of their different properties. This approach was used to identify enzymes with altered properties out of a library of protein mutants.

P–Al Compounds

M. Bodensteiner, U. Vogel,
A. Y. Timoshkin, M. Scheer* **4629 – 4633**

Controlled Oligomerization of Lewis Acid/Base-Stabilized Phosphanylalanes

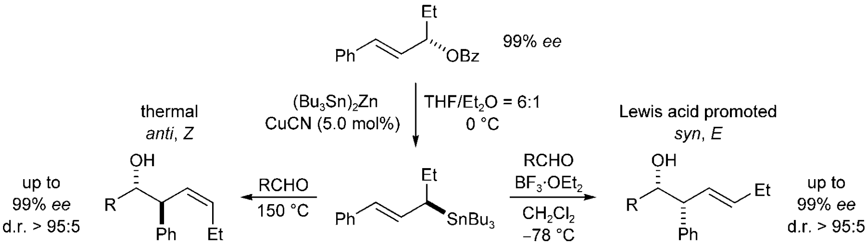


PAls should stick together: The *cyclo*-trimer **2** is obtained by H_2 elimination of Lewis acid/base-stabilized parent compound of the phosphanylalanes **1**. The elimination is controlled by fine tuning the temperature and solvent conditions. A subsequent H_2 elimination produces the ladder compound **3**. Compounds **2** and **3** are the first of a new class of Group 13/15 compounds which show no additionally donor–acceptor bonds within the framework.

Stereoselective Synthesis

E. S. Schmidtmann,
M. Oestreich* **4634 – 4638**

Enantiospecific Synthesis and Allylation of All-Carbon-Substituted α-Chiral Allylic Stannanes



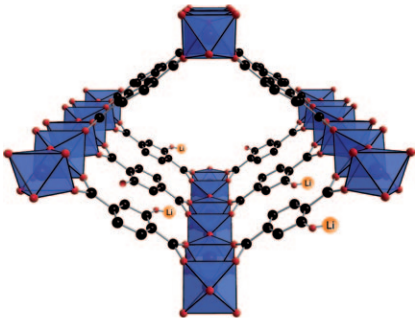
Once difficult to obtain, the title compounds can be prepared in virtually enantiomerically pure form with a bis(triorganostannyl) zinc reagent (see scheme). Subsequent diastereoselective thermal (left) and Lewis acid promoted reactions (right) illustrate the synthetic potential of these compounds.

Metal–Organic Frameworks

D. Himsl, D. Wallacher,
M. Hartmann* **4639 – 4642**

Improving the Hydrogen-Adsorption Properties of a Hydroxy-Modified MIL-53(Al) Structural Analogue by Lithium Doping

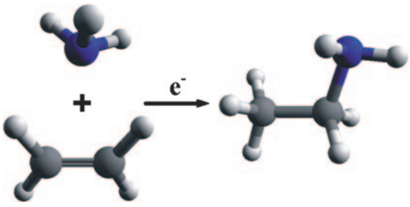
Lithium makes the difference: A simple strategy for the synthesis of lithium-doped porous metal–organic frameworks (MOFs) is developed (see structure; C black, O red, AlO_6 blue octahedra), thus paving the way for the facile preparation of lithium-doped MOFs. Moreover, the significant increase in hydrogen adsorption predicted by theoretical calculations is observed.



Electron-Induced Hydroamination

T. Hamann, E. Böhler,
P. Swiderek* **4643 – 4645**

Low-Energy-Electron-Induced Hydroamination of an Alkene

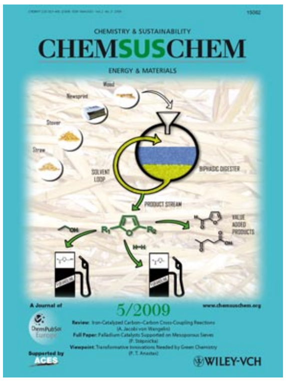


The smallest catalyst: A new strategy to control chemical synthesis by exposure to low-energy electrons relies on the electrostatic attraction caused by the soft ionization of one of the reaction partners. This approach was used to induce a reaction between C_2H_4 and NH_3 yielding aminoethane. The reaction resembles a hydroamination except that the electron beam replaces the catalyst used in the organic synthesis.

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

In this communication the name of a co-author was misspelled. The correct name is Xiaoming Zhao.

Iridium-Catalyzed Reactions of Trifluoromethylated Compounds with Alkenes: A C_{sp^3}–H Bond Activation α to the Trifluoromethyl Group

Y. Guo, X. Zhao, D. Zhang, S.-I. Murahashi* **2047–2049**

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