Contents

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:

X. Lang, H. Ji, C. Chen, W. Ma, J. Zhao**
Selective Formation of Imines by Aerobic Photocatalytic Oxidation of Amines on TiO_2

*R. P. Sonawane, V. Jheengut, C. Rabalakos, R. Larouche-Gauthier, H. K. Scott, V. K. Aggarwal**
Enantioselective Construction of Quaternary Stereogenic Centers from Tertiary Boronic Esters: Methodology and Applications

*K. Nakano, S. Hashimoto, M. Nakamura, T. Kamada, K. Nozaki**
Synthesis of Stereogradient Poly(propylene carbonate) by Stereo- and Enantioselective Copolymerization of Propylene Oxide with Carbon Dioxide

*K. Ohmori, T. Shono, Y. Hatakoshi, T. Yano, K. Suzuki**
An Integrated Synthetic Strategy for Higher Catechin Oligomers

L. Aboshyan-Sorgho, C. Besnard, P. Pattison, K. R. Kittilstved, A. Aebischer, J.-C. Bünzli, A. Hauser, C. Piguet**
Molecular Near-Infrared to Visible Light Upconversion in a Trinuclear d–f–d Complex

A. Donazzi, D. Livio, M. Maestri, E. Tronconi, A. Beretta, G. Groppi, P. Forzatti*
Synergy of Homogenous and Heterogeneous Processes Probed by In Situ Spatially Resolved Measurements of Temperature and Composition

*C. A. Naini, S. Franzka, S. Frost, M. Ulbricht, N. Hartmann**
Probing the Intrinsic Switching Kinetics of Ultrathin Thermoresponsive Polymer Brushes

*X. Wurzenberger, H. Piotrowski, P. Klüfers**
A Stable Square-Planar High-Spin-d^6 Molecular $Fe^{II}O_4$ Chromophore From Rare Iron(II) Minerals

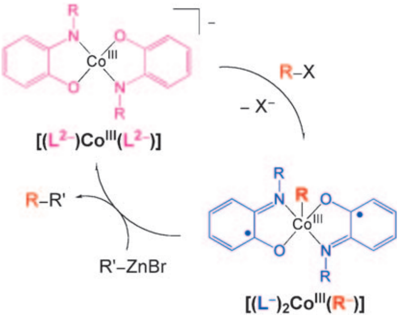
Author Profile

"My favorite subject at school was mathematics. The biggest problem that scientists face is to realize that the purpose of science is to predominantly serve people, not the other way around …"
This and more about Helmuth Möhwald can be found on page 3350.

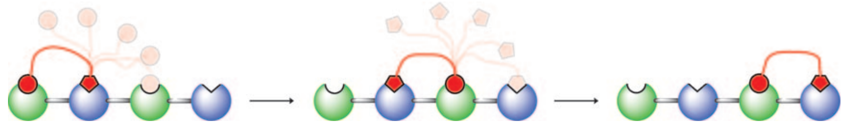
Obituaries

Highlights

Homogeneous Catalysis



Electron(ic) banking: First-row transition metals can be given a noble character by redox-active ligands, thus enabling two-electron oxidative addition and reductive elimination steps (see scheme). A recently reported cobalt-mediated Negishi-type cross-coupling reaction provides an illustrative example of this concept and reveals its potential to develop new catalytic reactions with cheap, abundant metals.



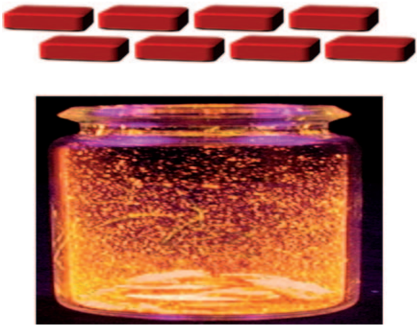
Standing on their own two feet! Inspired by naturally occurring molecular motors such as kinesins, dyneins, and myosins, a series of small-molecule walker systems have been synthesized (see picture). These artificial molecular motors are capable of moving directionally along their associated tracks, and show most of the features of their natural counterparts.

Minireviews

Let the molecule do the talking: If C–H bonds could talk, they would tell stories of inductive effects, conjugation, hyperconjugation, steric hindrance, and strain release. These stories are told from the perspective of synthetic planning and draw from the immense body of literature on the topic.

Reviews

After more than 75 years since their discovery, J-aggregates are continuing to be of great interest. This Review provides an overview on J-aggregates of various classes of dyes, including cyanines, porphyrins, phthalocyanines, and perylene bisimides, with specific emphasis on supramolecular construction principles, optical properties, and perspectives for applications.



For the USA and Canada:
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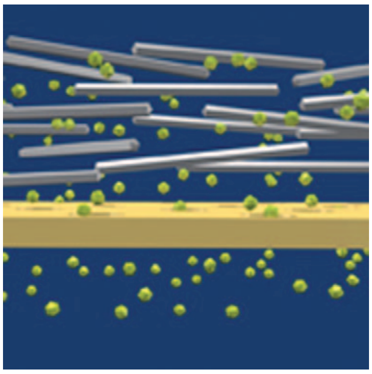
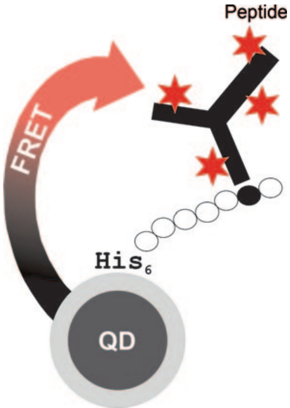
Communications

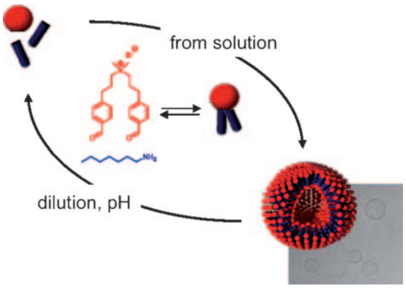
Separating the wheat from the chaff: Cross-flow filtration is shown to be an effective method to remove particle by-products from, for example, silver nanowires. To quantify the effect of purification, number- and weight-average aspect ratios and a polydispersity index are defined, which borrow concepts of molecular weight distributions from polymer science.

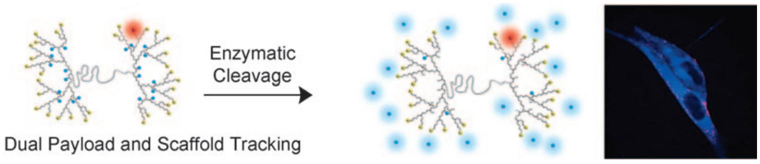


Straightforward and label-free: A simple method for the detection of histone-modifying enzymes is based on quantum dot (QD) Förster resonance energy transfer (FRET) donors. Histone acetyltransferase activity can be measured via the enzyme-dependent assembly of a quantum dot/peptide immunocomplex (see picture; His = histidine), which can be conducted in a homogeneous reaction without the need for complicated surface derivatization procedures.



Breaking bilayers: Incorporation of dynamic covalent bonds in vesicle-forming surfactants leads to the formation of responsive vesicles, which can be switched back and forth between the bilayer state and the isotropic solution using either dilution or a change in the pH value as external stimuli.



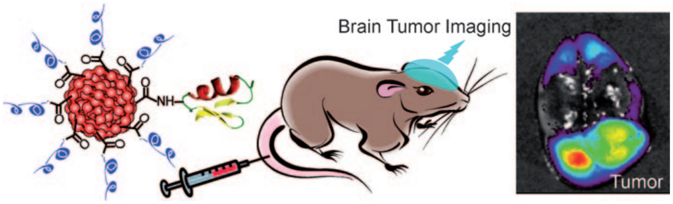


Dual action: Trackable multifunctional dendritic scaffolds with high internal loading capacity were synthesized based on a PEG core. Orthogonal functionalization of chain-end and internal groups allowed the dendrimers to be both labeled and loaded with releasable dyes for simultaneous monitoring of the dendritic carrier and release of the dye payload inside living cells (see picture).

In Vivo Probes

C. Wu, S. J. Hansen, Q. Hou, J. Yu,
M. Zeigler, Y. Jin, D. R. Burnham,
J. D. McNeill, J. M. Olson,
D. T. Chiu* ______ **3430 – 3434**

Design of Highly Emissive Polymer Dot Bioconjugates for In Vivo Tumor Targeting



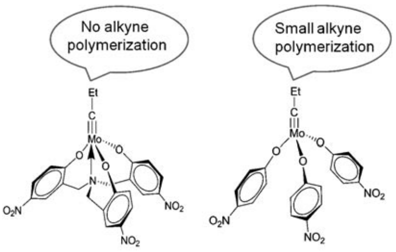
Lighting up brain tumors: Highly fluorescent nanodots that consist of semiconducting polymer blends were attached to the peptide ligand chlorotoxin. The nanodot–chlorotoxin conjugates were specifically targeted to malignant brain tumors in a transgenic mouse model, thus proving their potential as in vivo probes for clinical cancer diagnostics (see picture).

Alkyne Metathesis

K. Jyothish, W. Zhang* ______ **3435 – 3438**

Introducing A Podand Motif to Alkyne Metathesis Catalyst Design:
A Highly Active Multidentate Molybdenum(VI) Catalyst that Resists Alkyne Polymerization

Podand prevents polymers: The molybdenum(VI) propylidyne catalyst **1** with a podand triphenolamine ligand shows high activity in the metathesis of a variety of alkyne substrates, including heterocycles that contain donor moieties. With one substrate-binding site blocked by the multidentate ligand, the undesired polymerization of small alkynes that occurs with non-podand-ligand complex **2** is completely inhibited.



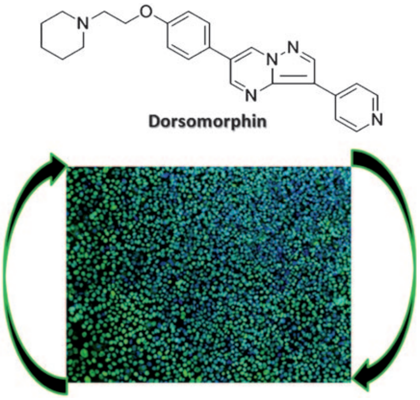
1 **2**

Stem Cells

R. Gonzalez, J. W. Lee, E. Y. Snyder,
P. G. Schultz* ______ **3439 – 3441**

Dorsomorphin Promotes Human Embryonic Stem Cell Self-Renewal

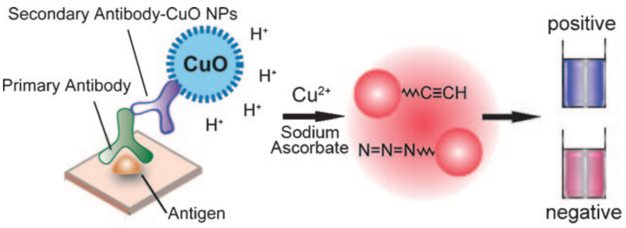
Self-renewal promoter: Using a high-throughput screening assay, the small molecule dorsomorphin (see scheme) was identified as a positive regulator of human embryonic stem cell (hESC) self-renewal. It is shown that dorsomorphin promotes hESC self-renewal by antagonizing autocrine BMP signaling.



Click Chemistry

W. Qu, Y. Liu, D. Liu, Z. Wang,*
X. Jiang* ______ **3442 – 3445**

Copper-Mediated Amplification Allows Readout of Immunoassays by the Naked Eye



An eye for color: Antibodies modified by CuO nanoparticles (NPs) are subjected to immunoreaction with the release of Cu^{II}, which can be detected by click chemistry. The Cu acts as a catalyst that induces aggregation of Au NPs functionalized with azide and alkyne groups, which can be seen as a color change (see picture). The detection of HIV in blood serum of infected patients is demonstrated.

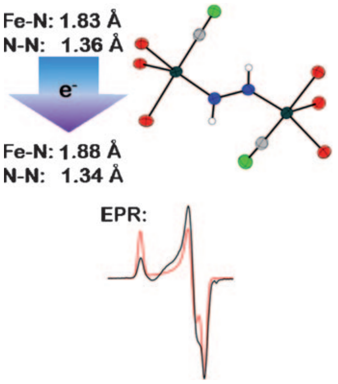
Contents

Iron-Mediated N_2 Fixation

C. T. Saouma, R. A. Kinney,
B. M. Hoffman,*
J. C. Peters* 3446–3449

Transformation of an $[Fe(\eta^2\text{-}N_2H_3)]^+$ Species to π-Delocalized $[Fe_2(\mu\text{-}N_2H_2)]^{2+/+}$ Complexes

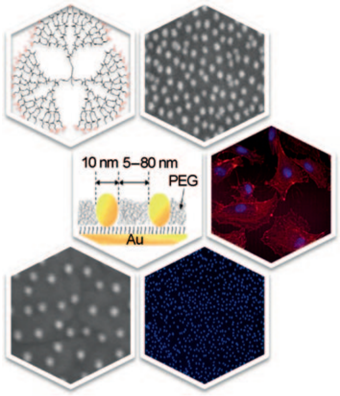
Diiron diazenes: A monomeric $Fe(\eta^2\text{-}N_2H_3)$ species has been prepared, and exposure to oxygen yields a diiron complex that features five-coordinate iron centers and an activated bridging diazene ligand (see picture; C gray, N blue, Fe black, P red, O green). Structural, theoretical, and spectroscopic data for the redox pair $[Fe_2(\mu\text{-}N_2H_2)]^{2+/+}$ are consistent with 4-center, 4-electron π-delocalized bonding across the Fe-NH-NH-Fe core that finds analogy in butadiene and the butadiene anion.



Nanopatterning

A. Lundgren, Y. Hed, K. Öberg,
A. Sellborn, H. Fink, P. Löwenhielm,
J. Kelly, M. Malkoch,*
M. Berglin* 3450–3453

Self-Assembled Arrays of Dendrimer–Gold-Nanoparticle Hybrids for Functional Cell Studies

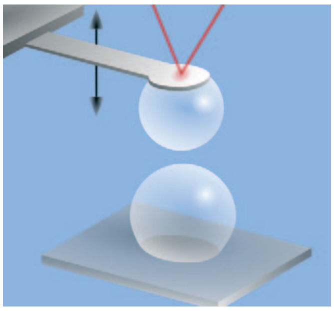


Dendrimer-controlled cell growth: A dendrimer–gold-nanoparticle hybrid array (see picture; PEG = polyethylene glycol), which can control the apparent dendrimer surface density, was used to investigate cell adhesion. The effect of the macromolecular architecture on the attachment and the morphological development of endothelial cells was studied. The dendrimer outperformed a linear counterpart, most likely modulated by the different interactions between the dendrimer and the proteins in the cell media.

Bubble Coalescence

R. F. Tabor, D. Y. C. Chan, F. Grieser,
R. R. Dagastine* 3454–3456

Anomalous Stability of Carbon Dioxide in pH-Controlled Bubble Coalescence



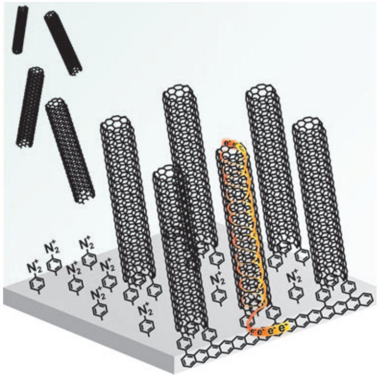
A new piece of the puzzle: Bubbles represent one of the simplest and most pervasive entities in the world around us, occurring in almost all liquid systems. The controlled collision between two microbubbles in water was investigated (see experimental setup) to understand the effect of gas type and solution pH on their stability, using ubiquitous gases—pure CO_2, air, nitrogen, and argon.

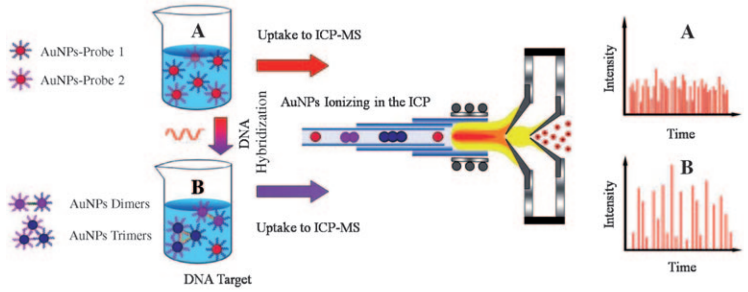
Carbon Nanotubes

O. Arias de Fuentes, T. Ferri,*
M. Frasconi,* V. Paolini,
R. Santucci 3457–3461

Highly-Ordered Covalent Anchoring of Carbon Nanotubes on Electrode Surfaces by Diazonium Salt Reactions

Tubes in file: Single-walled carbon nanotubes (SWNTs) were covalently anchored on different substrates by diazonium salt reactions (see picture). This unprecedented approach is highly versatile and leads to stable and well-organized SWCNT assemblies with potential for practical applications.





Staying single: A DNA hybridization assay employs gold-nanoparticle (AuNP) probes and single-particle inductively coupled plasma spectrometry (ICP-MS; see picture). The degree of aggregation of AuNPs is characterized by simultaneous measurement of decreased concentrations of the AuNP population and increased individual sizes.

DNA Assay

G. Han, Z. Xing, Y. Dong, S. Zhang, X. Zhang* ———— **3462 – 3465**

One-Step Homogeneous DNA Assay with Single-Nanoparticle Detection

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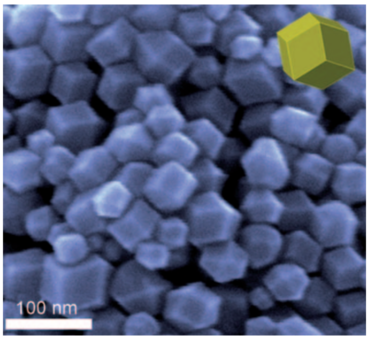

{110}-faceted alloy nanocrystals: Rhombic dodecahedral Au–Pd alloy nanocrystals (NCs) enclosed exclusively by 12 {110} facets were prepared by a simple one-pot aqueous synthetic method. The picture shows an SEM image of the NCs (inset: ideal RD structure). The NCs exhibit higher surface-enhanced Raman scattering and electrocatalytic activities than {111}-faceted nanoparticles.

Bimetallic Nanocrystals

Y. W. Lee, M. Kim, S. W. Kang, S. W. Han* ———— **3466 – 3470**

Polyhedral Bimetallic Alloy Nanocrystals Exclusively Bound by {110} Facets: Au–Pd Rhombic Dodecahedra

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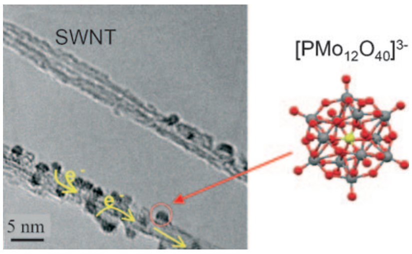

Charging clusters: A hybrid of polyoxometalate (POM) molecules individually adsorbed onto the surfaces of single-wall carbon nanotubes (SWNTs) can be used as a cathode-active material in rechargeable lithium batteries. This POM/SWNT battery exhibited a very high capacity (> 300 Ah kg^{-1}) with a short charging/discharging time (< 2 h).

Nanohybridization

N. Kawasaki, H. Wang, R. Nakanishi, S. Hamanaka, R. Kitaura, H. Shinohara, T. Yokoyama, H. Yoshikawa,* K. Awaga* ———— **3471 – 3474**

Nanohybridization of Polyoxometalate Clusters and Single-Wall Carbon Nanotubes: Applications in Molecular Cluster Batteries

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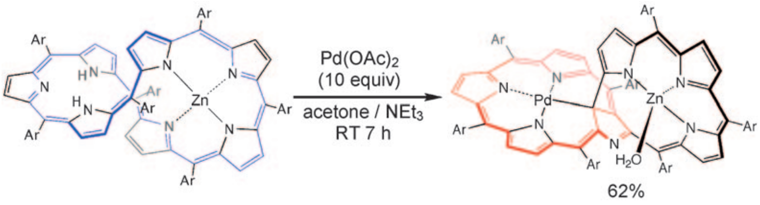


More confused: Metalation reactions of [32]heptaphyrins(1.1.1.1.1.1.1) with Pd^{II} ions result in a rearrangement to form Pd^{II} complexes that contain an N-confused-porphyrin (NCP) framework (see scheme). This rearrangement was also demonstrated for a monozinc(II) heptaphyrin complex with a figure-eight conformation. The occurrence of these transformations shows that NCPs can now be considered a member of the expanded porphyrin family.

Porphyrinoids

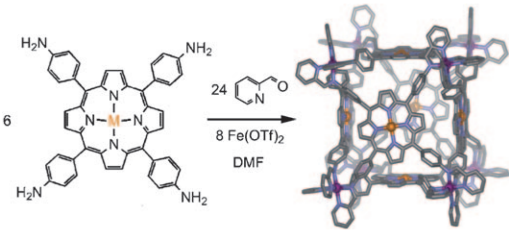
T. Yoneda, S. Saito, H. Yorimitsu, A. Osuka* ———— **3475 – 3478**

Palladium(II)-Triggered Rearrangement of Heptaphyrins to N-Confused Porphyrins

Container Molecules

W. Meng, B. Breiner, K. Rissanen,
J. D. Thoburn, J. K. Clegg,
J. R. Nitschke* ______ 3479–3483

A Self-Assembled M_8L_6 Cubic Cage that Selectively Encapsulates Large Aromatic Guests

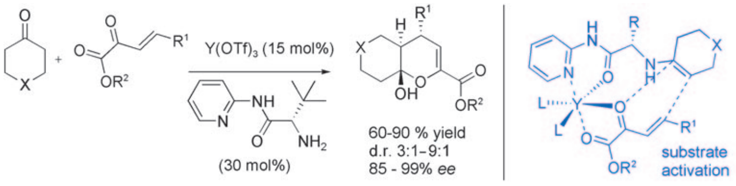


Porphyrins cubed: A series of self-assembled M_8L_6 cubic cages that enclose a volume in excess of 1300 Å^3 were synthesized (see scheme). The porphyrinic walls of the cubes provide favorable sites for π–π interactions, leading to selectivity between large and chemically similar aromatic guests: three molecules of coronene are incorporated and the higher fullerenes C_{70}–C_{84} are selectively bound in the presence of excess C_{60}.

Asymmetric Catalysis

Z. Xu, L. Liu, K. Wheeler,
H. Wang* ______ 3484–3488

Asymmetric Inverse-Electron-Demand Hetero-Diels–Alder Reaction of Six-membered Cyclic Ketones: An Enamine/Metal Lewis Acid Bifunctional Approach

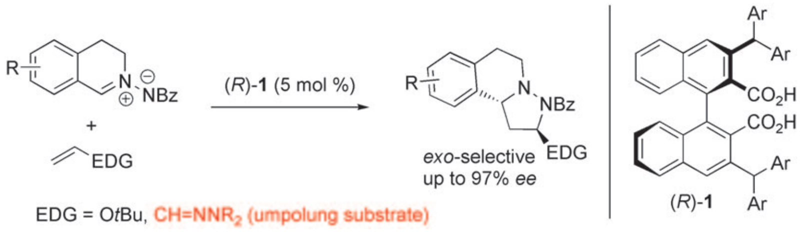


On demand: The first example of the title reaction involving cyclic ketones and β,γ-unsaturated α-ketoesters has been achieved using the novel enamine/metal Lewis acid bifunctional catalysis (see scheme; Tf = trifluoromethanesulfonyl). Enones with both electron-withdrawing and electron-donating groups at the γ position reacted smoothly with cyclohexanone affording the products in excellent chemo- and enantioselectivity.

Organocatalysis

T. Hashimoto, M. Omote,
K. Maruoka* ______ 3489–3492

Asymmetric Inverse-Electron-Demand 1,3-Dipolar Cycloaddition of C,N-Cyclic Azomethine Imines: An Umpolung Strategy

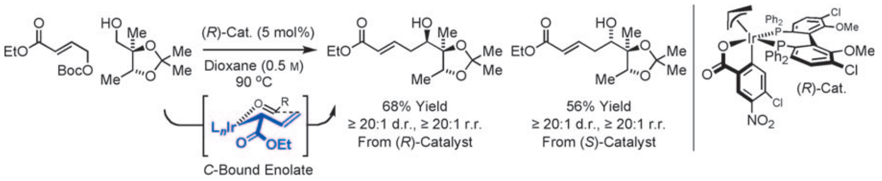


Oompa loompa: The title reaction has been accomplished with high stereoselectivity by use of an axially chiral dicarboxylic acid (see scheme). Employment of vinylogous aza-enamines as novel dipolarophiles was also implemented to establish a new concept of the inverse-electron-demand umpolung 1,3-dipolar cycloaddition. Bz = benzoyl, EDG = electron-donating group.

Synthetic Methods

A. Hassan, J. R. Zbieg,
M. J. Krische* ______ 3493–3496

Enantioselective Iridium-Catalyzed Vinylogous Reformatsky-Aldol Reaction from the Alcohol Oxidation Level: Linear Regioselectivity by Way of Carbon-Bound Enolates

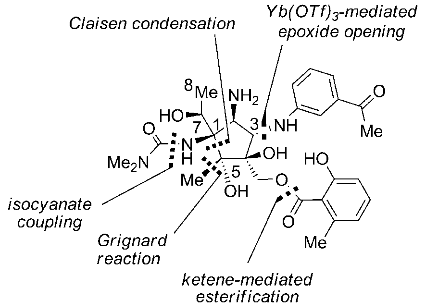


Reformatsky reinvented: Highly enantioselective vinylogous Reformatsky-type addition has been achieved from the alcohol oxidation level with linear regioselectivity through carbon-bound enolates (see scheme; Boc = *tert*-butoxycarbonyl). Complete levels of catalyst-directed diastereoselectivity are observed in the reaction of an α-chiral alcohol.

Natural Product Synthesis

S. Hanessian,* R. R. Vakiti, S. Dorich,
S. Banerjee, F. Lecomte, J. R. DelValle,
J. Zhang,
B. Deschênes-Simard ______ **3497 – 3500**

Total Synthesis of Pactamycin

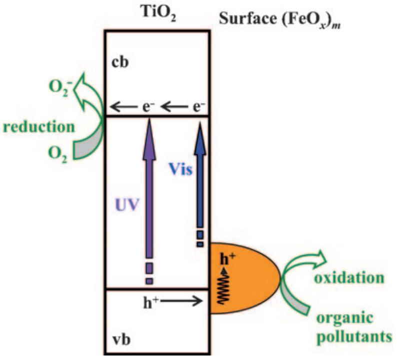


Lest we forget: 50 years after pactamycin was first isolated from a fermentation broth of *Streptomyces pactum* var *pactum*, this highly functionalized aminocyclopentitol natural product has finally succumbed to total synthesis. The modular and stereocontrolled introduction of functional groups should lead to the synthesis of less toxic congeners that maintain the antibacterial and cytotoxic activities.

Photocatalysis

H. Tada,* Q. Jin, H. Nishijima,
H. Yamamoto, M. Fujishima, S.-i. Okuoka,
T. Hattori, Y. Sumida,
H. Kobayashi ____________ **3501 – 3505**

Titanium(IV) Dioxide Surface-Modified with Iron Oxide as a Visible Light Photocatalyst

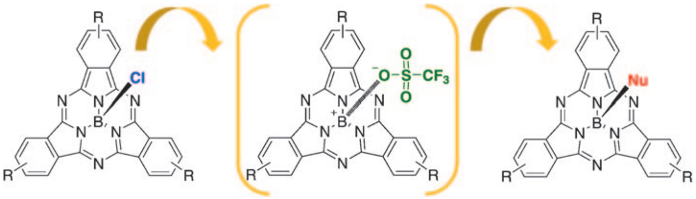


The light fandango: Anatase and anatase–rutile composite TiO_2 has been modified electronically with highly dispersed surface iron oxide species. The chemisorption–calcination cycle technique was used with $[Fe(acac)_3]$ as a precursor (acac = acetylacetonate), leading to pronounced visible-light activity and a concomitant increase in activity under illumination with UV light (cb = conduction band, vb = valence band).

Aromatic Macrocycles

J. Guilleme, D. González-Rodríguez,*
T. Torres* ____________ **3506 – 3509**

Triflate-Subphthalocyanines: Versatile, Reactive Intermediates for Axial Functionalization at the Boron Atom

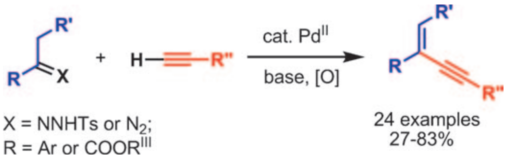


On the leave: Easily generated triflate boron subphthalocyanines are highly activated universal substrates for efficient axial substitution reactions with oxygen, sulfur, nitrogen, and carbon nucleophiles (see picture).

C–C Coupling

L. Zhou, F. Ye, J. Ma, Y. Zhang,
J. Wang* ____________ **3510 – 3514**

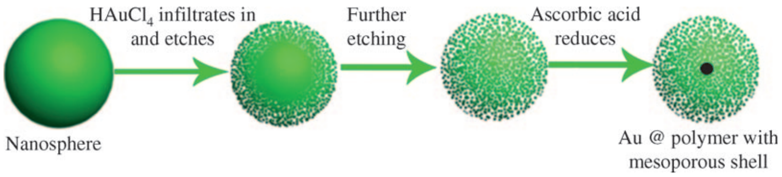
Palladium-Catalyzed Oxidative Cross-Coupling of *N*-Tosylhydrazones or Diazoesters with Terminal Alkynes: A Route to Conjugated Enynes



Coming at them from another angle: In a fresh approach to the synthesis of conjugated alkynes, the palladium-catalyzed cross-coupling of *N*-tosylhydrazones or diazoesters with terminal alkynes provided the desired enyne products with excellent stereoselectivity (see scheme; Ts = *p*-toluenesulfonyl). The reaction is proposed to involve an unprecedented alkynyl migratory insertion of a palladium carbene complex.

Contents

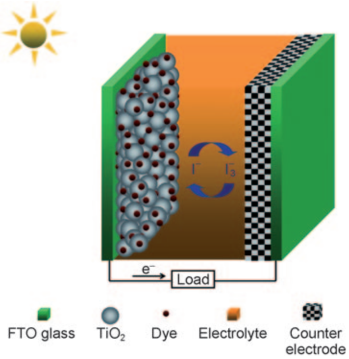
Core–Shell Structures



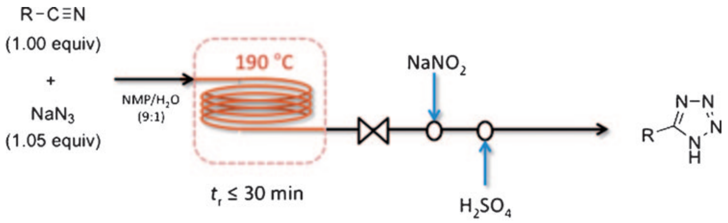
A heart of gold: Au@polymer nanostructures with hydrophobic mesoporous shells show tunable permeability and Au cores with adjustable diameters. This nanocomposite exhibits selective catalytic activity for hydrophobic molecules.

Dye-Sensitized Solar Cells

Sunny prospects for renewable energy: Molybdenum and tungsten carbides embedded in ordered nanomesoporous carbon materials as well as Mo_2C and WC are proposed as alternatives to the expensive platinum counter electrode (Pt CE). The preparation of the CEs was optimized, and the dye-sensitized solar cells (DSCs; see picture) equipped with these CEs show a higher energy conversion efficiency than those devices with a Pt CE.

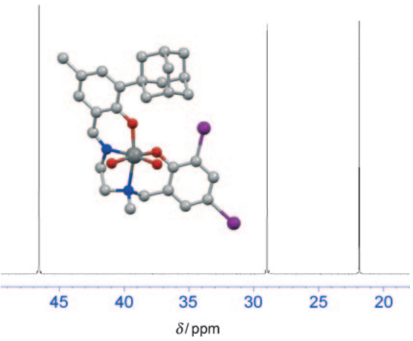


Microreactors



Safer flow: The synthesis of 5-substituted tetrazoles in flow (see scheme) is safe, efficient, scalable, requires no metal promoter, and uses a near-equimolar amount of NaN_3, yet nonetheless displays a broad substrate scope. The hazards associated with HN_3 are essentially eliminated, shock-sensitive metal azides such as $Zn(N_3)_2$ are avoided, and residual NaN_3 is quenched in-line with $NaNO_2$.

Polymerization Catalysts

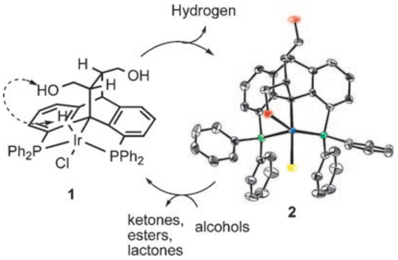


All lined up: C_1-symmetric octahedral titanium complexes (see structure, Ti dark gray, N blue, O red, I purple) whose labile positions reside in different electronic environments were designed using the readily available salalen ligands. With methylalumoxane as co-catalyst, highly active catalysts were obtained, which yielded high-molecular-weight polypropylene with ultra-high isotacticities (see ^{13}C NMR spectrum) and melting transitions.

Homogeneous Catalysis

S. Musa, I. Shaposhnikov, S. Cohen, D. Gelman* ———— 3533–3537

Ligand–Metal Cooperation in PCP Pincer Complexes: Rational Design and Catalytic Activity in Acceptorless Dehydrogenation of Alcohols



A helping hand: The dibenzobarrelene-based $PC_{sp^3}P$ pincer complex **1** was designed as a bifunctional catalyst for the acceptorless dehydrogenation of alcohols. The mechanism of the H_2 release involves interaction between the hydride ligand and the acidic sidearm in the intermediate **2** (red O, yellow Cl, green P, blue Ir). The feasibility of the complete catalytic cycle was studied using a stoichiometric model and the reaction was subsequently realized in a catalytic fashion.

Asymmetric Catalysis

G.-W. Zhang, W. Meng, H. Ma, J. Nie, W.-Q. Zhang, J.-A. Ma* ———— 3538–3542

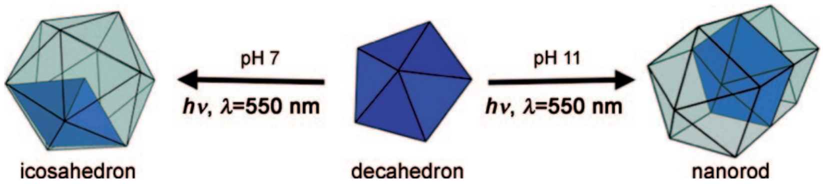
Catalytic Enantioselective Alkynylation of Trifluoromethyl Ketones: Pronounced Metal Fluoride Effects and Implications of Zinc-to-Titanium Transmetallation

Lost in transmetalation: The titanium(IV)-catalyzed title reaction, utilizing chiral cinchona alkaloids as ligands (**L1** and **L2**), was developed for the synthesis of both enantiomers of trifluoromethylated propargylic tertiary alcohols in high yield and enantioselectivity. Small amounts of BaF_2 were found to be essential for maintaining high levels of reactivity and enantioselectivity.

Heterometallic Nanostructures

M. R. Langille, J. Zhang, C. A. Mirkin* ———— 3543–3547

Plasmon-Mediated Synthesis of Heterometallic Nanorods and Icosahedra

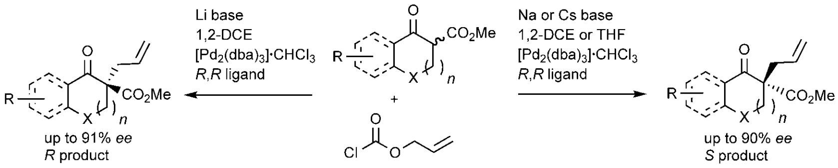


Bimetallic nanoparticles: Au–Ag core–shell heterometallic nanorods and icosahedra can be prepared from Au decahedral seed particles using plasmon-mediated synthetic methods and adjusting the pH value of the solution (see picture). This method allows for the preparation of icosahedral nanostructures with an asymmetric metal distribution.

Asymmetric Catalysis

B. M. Trost,* B. Schäffner, M. Osipov, D. A. A. Wilton ———— 3548–3551

Palladium-Catalyzed Decarboxylative Asymmetric Allylic Alkylation of β-ketoesters: An Unusual Counterion Effect

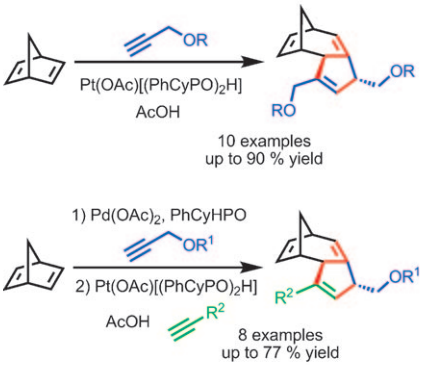


Buy one, get one free: Both enantiomers of tetralone and indanone derivatives are available in a one-pot procedure from allyl chloroformate and their β-ketoesters by using the same catalyst system (see scheme; dba = dibenzylideneacetone, 1,2-DCE = 1,2-dichloroethane, THF = tetrahydrofuran). The details of this remarkable effect were investigated by performing scavenging experiments and a variety of substrates were successfully used in the procedure.

Tandem Reactions

T. Achard, A. Lepronier, Y. Gimbert,
H. Clavier,* L. Giordano,* A. Tenaglia,*
G. Buono* ———— 3552 – 3556

A Regio- and Diastereoselective Platinum-Catalyzed Tandem [2+1]/[3+2] Cycloaddition Sequence

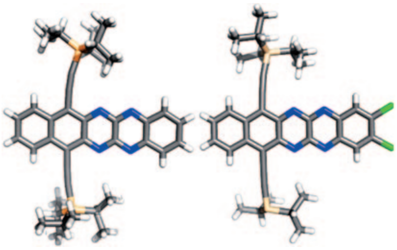


Platinum complexes bearing phosphinous acids have efficiently promoted a tandem intermolecular sequence of [2+1]/[3+2] cycloaddition reactions. This process gave access to novel tricyclic systems and the cascade reactions were regio- and diastereoselective (see scheme; Cy = cyclohexyl). The [3+2] cycloaddition reaction was investigated further and two different alkyne partners were used.

Heteroacenes

O. Tverskoy, F. Rominger, A. Peters,
H.-J. Himmel,
U. H. F. Bunz* ———— 3557 – 3560

An Efficient Synthesis of Tetraazapentacenes

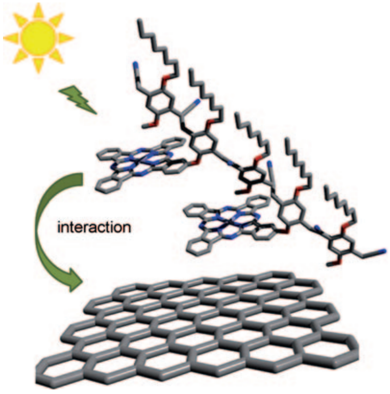


Organic electronics on demand? The palladium-catalyzed coupling of aromatic *ortho*-diamines with substituted dichloroquinoxalines furnishes *N*,*N*-dihydrotetraazaacenes, which were oxidized by MnO_2 into the corresponding tetraazapentacenes (see structures; N blue, Cl green, Si yellow). The modular synthesis of these acenes allows the introduction of any substituent by choice of the proper quinoxaline derivative.

Electronic Materials

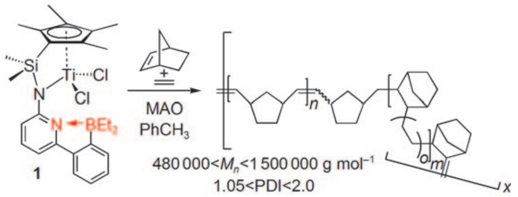
J. Malig, N. Jux, D. Kiessling, J.-J. Cid,
P. Vázquez, T. Torres,
D. M. Guldi* ———— 3561 – 3565

Towards Tunable Graphene/Phthalocyanine–PPV Hybrid Systems



Exfoliation of graphite was achieved using a zinc phthalocyanine oligomer that is also an electron donor. The resulting functionalized graphene material was investigated by Raman and electron spectroscopy and was trialed in a photoelectrochemical cell.

Designed Catalysts



Come together: Catalyst **1**, which contains a diethylboryl-protected pyridyl unit, copolymerizes ethylene and cyclic olefins such as norborn-2-ene (NBE) and *cis*-cyclooctene (COE) to give multiblock copolymers. Both vinyl insertion polymerization and ring-opening metathesis polymerization are in effect within a single polymer chain, and the respective NBE and COE blocks can be obtained in different ratios.

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

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

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