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:

*Z. Zhang, Z. Wang, R. Zhang, K. Ding**
Extremely Efficient Titanium Catalyst for the Enantioselective Cyanation of Aldehydes Using Cooperative Catalysis

*Q. Wang, M. Zhang, C. Chen, W. Ma, J. Zhao**
Photocatalytic Aerobic Oxidation of Alcohols on TiO_2: The Acceleration Effect of Brønsted Acids

Y. Fu, Q. Dai, W. Zhang, J. Ren, T. Pan, C. He**
AlkB Domain of Mammalian ABH8 Catalyzes Hydroxylation of 5-Methoxycarbonylmethyluridine at the Wobble Position of tRNA

C. Apostolidis, B. Schimmelpfennig, N. Magnani, P. Lindqvist-Reis, O. Walter, R. Sykora, A. Morgenstern, E. Colineau, R. Caciuffo, R. Klenze, R. G. Haire, J. Rebizant, F. Bruchertseifer, T. Fanghänel*
$[An(H_2O)_9](CF_3SO_3)_3$ (An=U–Cm, Cf): Exploring Their Stability, Structural Chemistry, and Magnetic Behavior by Experiment and Theory

*S. Rizzato, J. Bergès, S. A. Mason, A. Albinati, J. Kozelka**
Dispersion-Driven Hydrogen Bonding: Theoretically Predicted H–Bond between H_2O and Platinum(II) Identified by Neutron Diffraction

*D. R. Dreyer, H. Jia, C. W. Bielawski**
Graphene Oxide: A Convenient Carbocatalyst for Facilitating Oxidation and Hydration Reactions

H. Amouri, J. Moussa, A. K. Renfrew, P. J. Dyson, M. N. Rager, L.-M. Chamoreau*
Metal Complex of Diselenobenzoquinone : Discovery, Structure, and Anticancer Activity

*H. Wang, A. Pyatenko, K. Kawaguchi, X. Li, Z. Swiatkowska–Warkocka, N. Koshizaki**
Selective Pulsed Heating for the Synthesis of Semiconductor and Metal Submicrometer Spheres

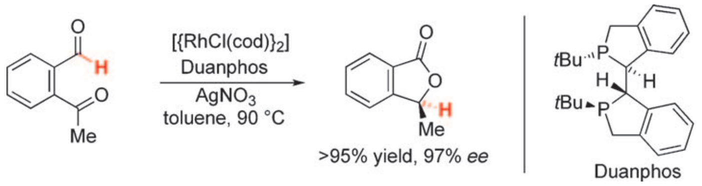
Author Profile

"My favorite subjects at school were mathematics, chemistry, and French.
The three qualities that make a good scientist are curiosity, enthusiasm, and persistence …"
This and more about Carsten Schmuck can be found on page 6024.

Books

Highlights

Phthalide Synthesis



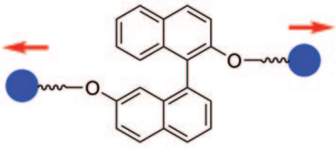
Controlling carbonyl groups: Identification of the correct ligand/counterion combination was essential to allow the efficient and selective rhodium-catalyzed conversion of a series of ketobenzaldehydes into the corresponding phthalides using the title reaction (see scheme; cod = cycloocta-l,5-diene).

Contents

Mechanochemistry

G. Cravotto,* P. Cintas* ___ **6028 – 6030**

Reconfiguration of Stereoisomers under Sonomechanical Activation



Let's twist to the music: In an unprecedented reconfiguration of thermally stable atropisomers, mechanical stress induced by ultrasound waves on a polymer-bound substrate (see structure) did effectively cause racemization facilitating enantiomer interconversion.

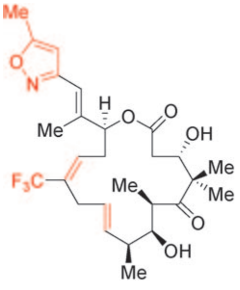
Reviews

Drug Discovery

R. M. Wilson,
S. J. Danishefsky* ___ **6032 – 6056**

On the Reach of Chemical Synthesis: Creation of a Mini-Pipeline from an Academic Laboratory

Successful journey: This retrospective Review describes investigations into the total synthesis and evaluation of biologically active small molecules (such as iso-fludelone; see structure), as well as the development of a program directed toward the chemical synthesis of therapeutically relevant larger molecules, including the glycoprotein erythropoietin.



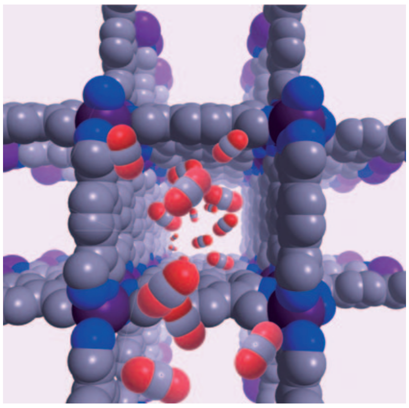
iso-fludelone

Carbon Dioxide Capture

D. M. D'Alessandro,* B. Smit,*
J. R. Long* ___ **6058 – 6082**

Carbon Dioxide Capture: Prospects for New Materials

Getting CO_2 under control: This Review highlights the challenges for carbon capture and storage technologies which have been proposed to reduce CO_2 emissions from large point sources. The most recent developments in new materials and emerging concepts for CO_2 separations by absorption, adsorption, and membranes, amongst other approaches, are discussed, with particular attention on progress in the burgeoning field of metal–organic frameworks (see example).

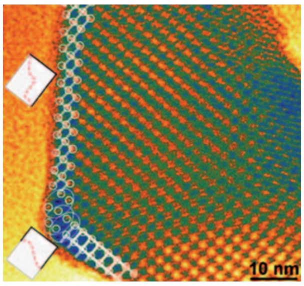


Communications

Surface Structure Elucidation

W. Zhang, A. Trunschke, R. Schlögl,
D. Su* ___ **6084 – 6089**

Real-Space Observation of Surface Termination of a Complex Metal Oxide Catalyst



Looking good: High-resolution TEM can be used to determine the surface structure of a metal oxide catalyst in real space. The picture shows HR-TEM images of one catalyst particle along ⟨001⟩ direction far from Scherzer focus. The perimeter of the particle is highlighted by the fractured structural units.

For the USA and Canada:
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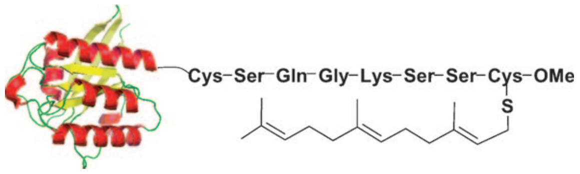
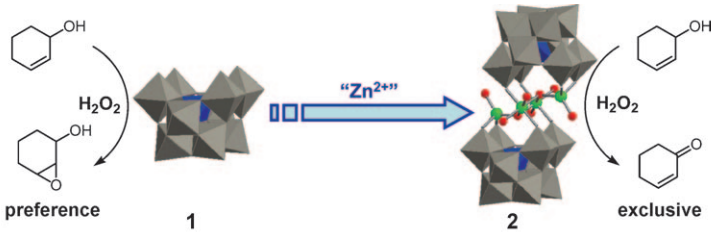
Protein Synthesis



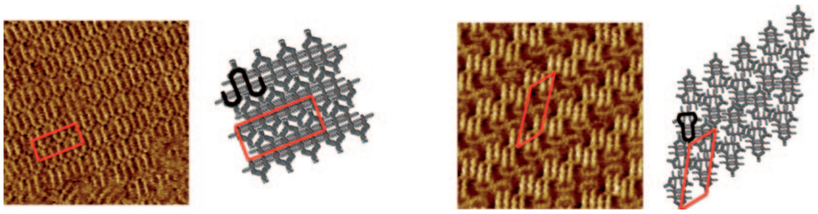
Now available! Farnesylated and carboxymethylated Rheb (see picture) and K-Ras4B GTPases were synthesized in useful amounts by a combination of expressed protein ligation and solid-phase lipopeptide synthesis. The functionality of the proteins was proven by biochemical, biophysical, and cell-based investigations.

Polyoxometalate Chemistry



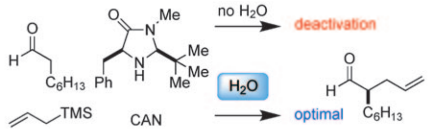
Zinc in: Polyoxometalate **1** reacts with Zn^{2+} ions in acetone to form a novel sandwich-type POM **2** in almost quantitative yield. The H_2O_2-based oxidation of secondary alcohols with **2** efficiently proceeds, with an activity and chemoselectivity that is very different from those of tungsten-based catalysts including **1** (see scheme; green Zn).

Self-Assembled Monolayers



Starting from the same bisacetylene, different reaction conditions (palladium or copper catalysis) selectively yielded cyclic or acyclic oligomers with $n=2$–6 (see picture for $n=3$) linked by freely rotating corner units. STM images of self-assembled monolayers revealed the difference in the adsorption behavior of the acyclic and cyclic oligomers.

Organocatalysis

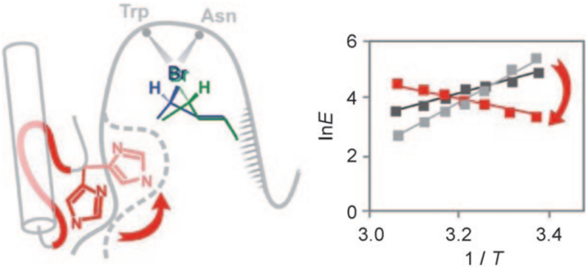


Wet chemistry: Organo-SOMO activation is an intricate process. The catalyst is deactivated in the absence of H_2O and its concentration is maintained with 2 equivalents of H_2O. The kinetic role of ceric ammonium nitrate (CAN) is masked by phase transfer and its limited solubility is enhanced by added H_2O. Mechanistic studies show that careful addition of H_2O to dried reagents greatly enhances reaction. TMS = trimethylsilyl.

Enantioselectivity

Z. Prokop, Y. Sato, J. Brezovsky, T. Mozga,
R. Chaloupkova, T. Koudelakova,
P. Jerabek, V. Stepankova, R. Natsume,
J. G. E. van Leeuwen, D. B. Janssen,
J. Florian, Y. Nagata, T. Senda,
J. Damborsky* ________ **6111–6115**

Enantioselectivity of Haloalkane Dehalogenases and its Modulation by Surface Loop Engineering



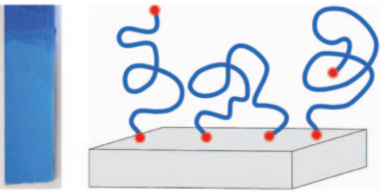
In the loop: Engineering of the surface loop in haloalkane dehalogenases affects their enantiodiscrimination behavior. The temperature dependence of the enantioselectivity (ln*E* versus 1/*T*) of β-bromoalkanes by haloalkane dehalogenases is reversed (red data points) by deletion of the surface loop; the selectivity switches back when an additional single-point mutation is made. This behavior is not observed for α-bromoesters.

Ultrathin Films

R. Gill, M. Mazhar, O. Félix,
G. Decher* ________ **6116–6119**

Covalent Layer-by-Layer Assembly and Solvent Memory of Multilayer Films from Homobifunctional Poly(dimethylsiloxane)

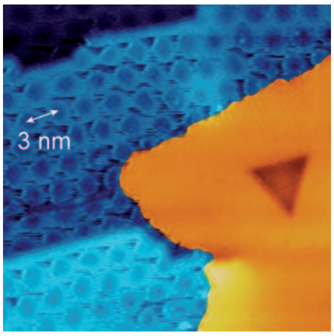
Catching the end groups: A simple procedure was used for the covalent layer-by-layer assembly of homobifunctional H_2N-poly(dimethylsiloxane)-NH_2 on SiO_2 surfaces that leads to robust layer-by-layer films of optical quality (see picture; photo on left) despite the use of non-purified commercial starting materials. The films show a solvent memory for swelling and de-swelling when immersed in the corresponding solvent for each polymer.



Monolayers

T. Brugger, H. Ma, M. Iannuzzi, S. Berner,
A. Winkler, J. Hutter, J. Osterwalder,
T. Greber* ________ **6120–6124**

Nanotexture Switching of Single-Layer Hexagonal Boron Nitride on Rhodium by Intercalation of Hydrogen Atoms

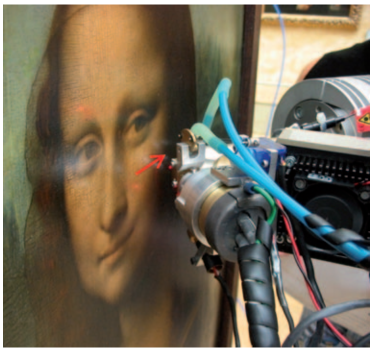


Playing nano-tectonics: The interaction of atomic hydrogen with a single layer of hexagonal boron nitride on rhodium leads to the removal of the *h*-BN surface corrugation (see picture; blue region: corrugated, orange region: flat). This change of surface texture arises from the intercalation of hydrogen atoms between the *h*-BN skin and the metal, and can be restored by annealing to about 600 K to expel the hydrogen atoms.

Analyzing Works of Art

L. de Viguerie, P. Walter,* E. Laval,
B. Mottin, V. A. Solé ________ **6125–6128**

Revealing the *sfumato* Technique of Leonardo da Vinci by X-Ray Fluorescence Spectroscopy

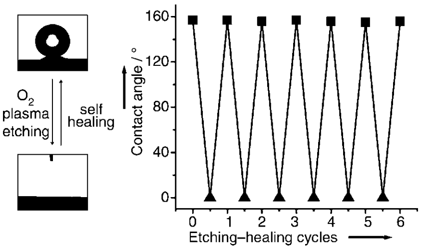


Not just a pretty face: Non-invasive X-ray fluorescence spectroscopy was used to reveal the *sfumato* paint layer stacking method that was used by Leonardo da Vinci to paint the faces in seven of his paintings. A strong diversity in his technique could clearly be seen with this method.

Superhydrophobic Coatings

Y. Li, L. Li, J. Sun* **6129 – 6133**

Bioinspired Self-Healing Superhydrophobic Coatings

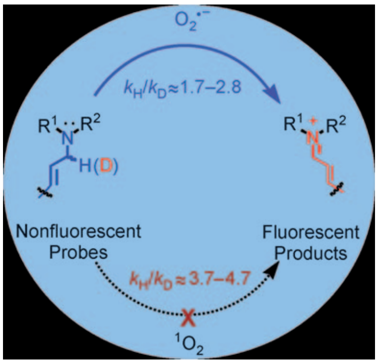


Heal thyself! Self-healing superhydrophobic coatings are fabricated by preserving healing agents of reacted fluoroalkylsilane in layered polymeric coatings that are porous and rigidly flexible. When the top layer of fluoroalkyl chains decomposes or the coatings are scratched, the healing agents migrate to the surface to restore the superhydrophobicity of the coatings (see picture).

Fluorescent Probes

K. Kundu, S. F. Knight, S. Lee, W. R. Taylor,
N. Murthy* **6134 – 6138**

A Significant Improvement of the Efficacy of Radical Oxidant Probes by the Kinetic Isotope Effect

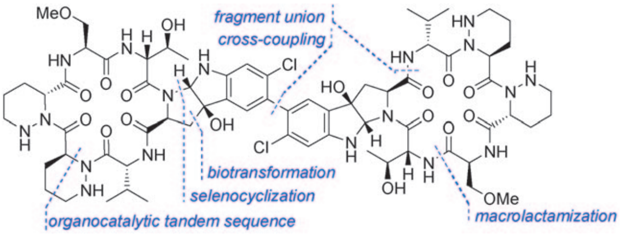


A breath of fresh air: The rate of aerial oxidation of dihydroethidium and hydrocyanine radical oxidant probes can be selectively reduced by deuteration (see picture). The reaction rate between the deuterated compounds and the superoxide radical was reduced by a much smaller factor because of mechanistic differences between the two reactions. The deuterated probes are more effective than their hydrogen analogues in vitro, in cell culture, and in vivo.

Total Synthesis

A. J. Oelke, D. J. France, T. Hofmann,
G. Wuitschik, S. V. Ley* **6139 – 6142**

Total Synthesis of Chloptosin



Two is better that one: A new organocatalytic route for the asymmetric preparation of the embedded piperazic acids and a Stille coupling of an *ortho*-chloropyrroloindole served as key steps in the total synthesis of the dimeric cyclopeptide chloptosin (see structure).

Niobium Compounds

P. J. Alonso, I. Ara, A. B. Arauzo,
M. A. García-Monforte, B. Menjón,*
C. Rillo **6143 – 6146**

σ-Organoniobium Compounds with $[NbR_4]^-$ and NbR_4 Stoichiometries

Securely nested: The first examples of σ-organoniobium compounds with $[Nb^{III}R_4]^-$ and $Nb^{IV}R_4$ stoichiometries are reported. The Nb centers within the $[Nb(C_6Cl_5)_4]^{q-}$ units ($q = 0$, 1) are located in triakis tetrahedral environments formed by the combination of inner NbC_4 (see picture; gray) and outer $NbCl_4$ (green) tetrahedra.

Contents

Total Synthesis

M. A. McGowan, C. P. Stevenson, M. A. Schiffler, E. N. Jacobsen* ______ **6147 – 6150**

An Enantioselective Total Synthesis of (+)-Peloruside A

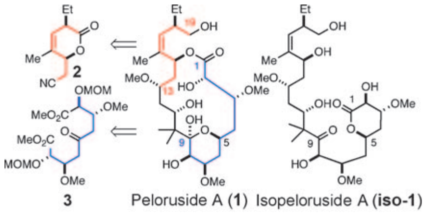
Short and sweet: Chiral epoxides, prepared using (salen)cobalt-catalyzed ring-opening reactions, and a chromium catalyst controlled hetero-Diels–Alder reaction were used to set most of the stereocenters in the total synthesis of the microtubule-stabilizing agent peloruside A. The overall highly convergent route required only 20 steps in the longest linear sequence. MOM = methoxymethyl, TBS = *tert*-butyldimethylsilyl.

Natural Products

T. R. Hoye,* J. Jeon, L. C. Kopel, T. D. Ryba, M. A. Tennakoon, Y. Wang _ **6151 – 6155**

Total Synthesis of Peloruside A through Kinetic Lactonization and Relay Ring-Closing Metathesis Cyclization Reactions

The other side: A convergent total synthesis of peloruside A (**1**) is described. The key strategic features are a diastereoselective lactonization to generate a C5–C9 valerolactone from the C_2-symmetric ketone **3**, and a relay ring-closing metathesis reaction to produce a dehydrovalerolactone **2**. A new isomer of **1**, the valerolactone isopeloruside A (**iso-1**), was identified. MOM = methoxymethyl.

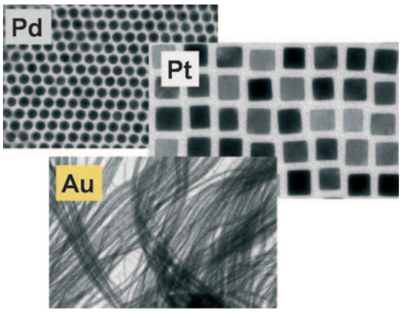


Metal Nanocrystals

Y. Kang, X. Ye, C. B. Murray* **6156 – 6159**

Size- and Shape-Selective Synthesis of Metal Nanocrystals and Nanowires Using CO as a Reducing Agent

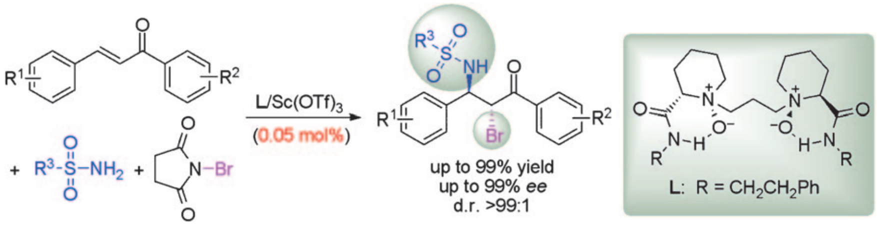
Putting the pedal to the metal: A facile strategy for the synthesis of metal nanocrystals is demonstrated that employs carbon monoxide as a reducing agent. Highly monodisperse platinum nanocubes, spherical palladium nanocrystals, and ultrathin gold nanowires can be produced within 15 minutes.



Asymmetric Catalysis

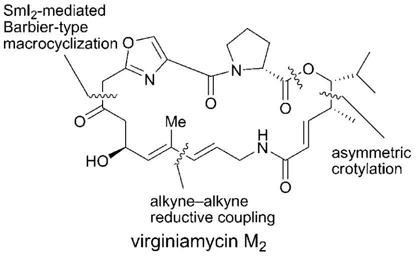
Y. F. Cai, X. H. Liu, Y. H. Hui, J. Jiang, W. T. Wang, W. L. Chen, L. L. Lin, X. M. Feng* ______ **6160 – 6164**

Catalytic Asymmetric Bromoamination of Chalcones: Highly Efficient Synthesis of Chiral α-Bromo-β-Amino Ketone Derivatives



Stand and deliver: The first highly regio- and enantioselective bromoamination of chalcones has been developed which proceeds via an unusual bromonium-based mechanism to deliver the title compounds. Excellent results were obtained using 0.05 mol% of the C_2-symmetric *N*,*N'*-dioxide/scandium(III) complex under mild conditions (see scheme).

Natural Product Synthesis

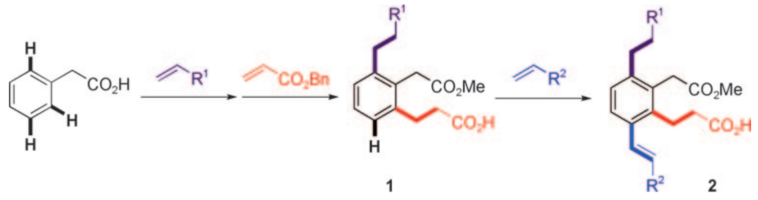


Has a nice ring to it: A concise and modular total synthesis of the naturally occurring antibiotic virginiamycin M_2 is described. A Barbier-type cyclization was used to close the 23-membered macrocycle and deliver virginiamycin M_2 in 19 steps from a chiral organosilane.

J. Wu, J. S. Panek* **6165–6168**

Total Synthesis of (−)-Virginiamycin M_2

C–H Activation



A balancing act: Complementary catalytic systems are described, in which the reactivity/selectivity balance in Pd^{II}-catalyzed *ortho*-C–H olefination can be modulated to enable sequential C–H functionalization for the rapid preparation of 1,2,3-trisubstituted arenes **1**. Additionally, a rare example of iterative C–H activation, in which a newly installed functional group directs subsequent C–H activation has been demonstrated (**2**).

K. M. Engle, D.-H. Wang, J.-Q. Yu* **6169–6173**

Constructing Multiply Substituted Arenes Using Sequential Palladium(II)-Catalyzed C–H Olefination

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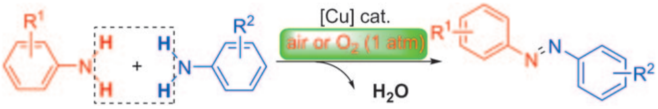
Azo Compounds



In the air tonight: A novel approach to symmetric and unsymmetric aromatic azo compounds from simple anilines catalyzed by inexpensive CuBr has been disclosed. Air (or dioxygen) was used as an oxidant under mild reaction conditions, with H_2O as the byproduct, to make this transformation environmentally benign and very easy to handle.

C. Zhang, N. Jiao* **6174–6177**

Copper-Catalyzed Aerobic Oxidative Dehydrogenative Coupling of Anilines Leading to Aromatic Azo Compounds using Dioxygen as an Oxidant

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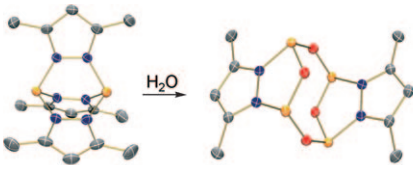
Phosphorus Chemistry

A door to new opportunities: The stepwise hydrolysis of a diphosphorus trication is an efficient method for the preparation of an unusual ligand-stabilized dication that contains a novel cationic $[P_4O_4]^{2+}$ framework (see Scheme; gray C, blue N, red O, orange P). This approach demonstrates the potential of the diphosphorus trication as a source for phosphorus building blocks to be used in the construction of novel cationic ring and cluster systems.



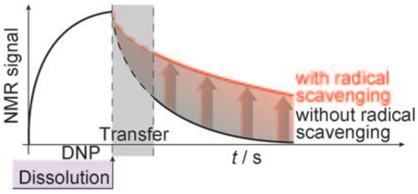
J. J. Weigand,* K.-O. Feldmann, A. K. C. Echterhoff, A. W. Ehlers, K. Lammertsma **6178–6181**

Preparation of Ligand-Stabilized $[P_4O_4]^{2+}$ by Controlled Hydrolysis of a Janus Head Type Diphosphorus Trication

NMR Spectroscopy

P. Miéville, P. Ahuja, R. Sarkar, S. Jannin,*
P. R. Vasos, S. Gerber-Lemaire,
M. Mishkovsky, A. Comment, R. Gruetter,
O. Ouari, P. Tordo,
G. Bodenhausen ______ **6182 – 6185**

Scavenging Free Radicals To Preserve Enhancement and Extend Relaxation Times in NMR using Dynamic Nuclear Polarization

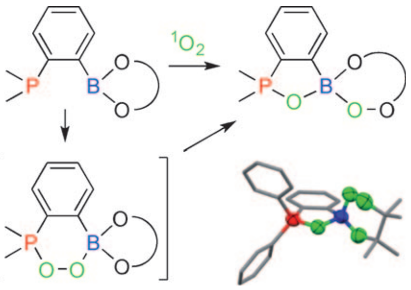


Vitamin C for longer lifetimes: *N*-oxide radicals that are widely used for dynamic nuclear polarization can be reduced by scavengers such as sodium ascorbate (vitamin C) during the dissolution process, thus diminishing losses of polarization during the transfer and extending transverse and longitudinal relaxation times in NMR spectroscopy (see picture).

Singlet Dioxygen Fixation

S. Porcel, G. Bouhadir, N. Saffon,
L. Maron, D. Bourissou* ______ **6186 – 6189**

Reaction of Singlet Dioxygen with Phosphine–Borane Derivatives: From Transient Phosphine Peroxides to Crystalline Peroxoboronates

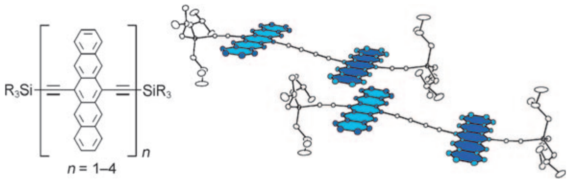


Singlet dioxygen is readily split by phosphine–boronates under mild conditions. The initially formed phosphine peroxides spontaneously rearrange by B→O migration. The resulting peroxoboronates have been structurally characterized, and their ability to undergo oxygen transfer reactions substantiated.

Conjugated Oligomers

D. Lehnherr, A. H. Murray, R. McDonald,
R. R. Tykwinski* ______ **6190 – 6194**

A Modular Synthetic Approach to Conjugated Pentacene Di-, Tri-, and Tetramers

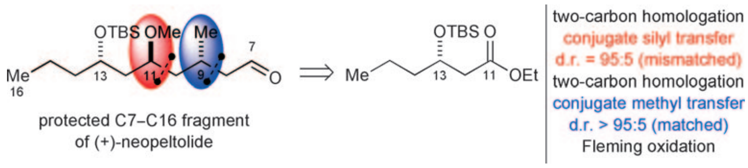


Mind the band gap: π-conjugated pentacene di-, tri-, and tetramers can be synthesized by using a versatile building block in Hay homocoupling as well as Cadiot–Chodkiewicz cross-coupling reactions. This modular approach allows the evaluation of solubility, stability, and the HOMO–LUMO gap as a function of compound length. Long-range three-dimensional π overlap occurs in the iBu$_3$Si-substituted pentacene dimer (see figure; $n=2$).

Iterative Synthesis

E. Hartmann,
M. Oestreich* ______ **6195 – 6198**

Asymmetric Conjugate Silyl Transfer in Iterative Catalytic Sequences: Synthesis of the C7–C16 Fragment of (+)-Neopeltolide

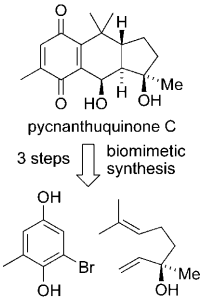


Matched or mismatched, that is not the question! The *anti,anti* configuration of the C7–C16 fragment of (+)-neopeltolide is stereoselectively installed in an iterative sequence of catalyst-controlled *Si* group and Me group transfers, even with mismatched selectivity in the former (*Si* = Me$_2$PhSi, see scheme; TBS = *tert*-butyldimethylsilyl).

Biomimetic Synthesis

F. Löbermann, P. Mayer,
D. Trauner* ———— **6199 – 6202**

Biomimetic Synthesis of (−)-Pycnanthuquinone C through the Diels–Alder Reaction of a Vinyl Quinone



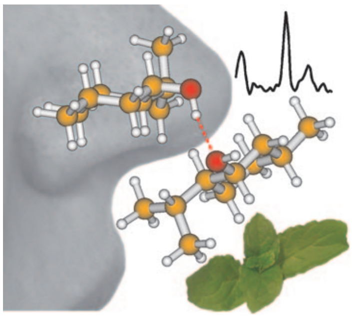
Three strikes and you're out! A concise, asymmetric synthesis of pycnanthuquinone C underscores the biosynthetic relevance of Diels–Alder reactions of vinyl quinones. The relative and absolute configuration of the natural product has been elucidated.

Vibrational Spectroscopy

M. Albrecht, J. Will,
M. A. Suhm* ———— **6203 – 6206**

Chirality Recognition in Menthol and Neomenthol: Preference for Homoconfigurational Aggregation

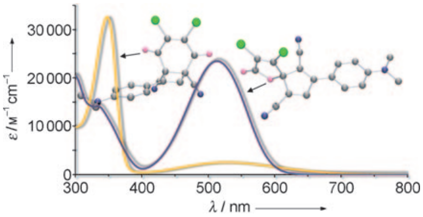
Cool chirality: L-Menthol (see ball-and-stick model), a most important fragrance, is characterized in terms of its conformation, selective aggregation, and sublimation. The data indicate a preference for homoconfigured aggregates.



Push–Pull Chromophores

S.-i. Kato, M. T. R. Beels, P. La Porta,
W. B. Schweizer, C. Boudon,
J.-P. Gisselbrecht, I. Biaggio,
F. Diederich* ———— **6207 – 6211**

Homoconjugated Push–Pull and Spiro Systems: Intramolecular Charge-Transfer Interactions and Third-Order Optical Nonlinearities

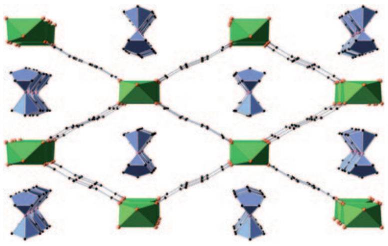


Homoconjugated push–pull chromophores are obtained by [2+2] cycloaddition of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone to anilino or ferrocene donor-substituted alkynes, and in one case a spiro compound (see picture: examples with corresponding electron adsorption spectra; C gray, Cl green, N blue, O red). Significant third-order optical nonlinearities could be measured for the first time for homoconjugated push–pull systems.

Metal–Organic Frameworks

M. Meilikhov, K. Yusenko, A. Torrisi, B. Jee,
C. Mellot-Draznieks, A. Pöppl,
R. A. Fischer* ———— **6212 – 6215**

Reduction of a Metal–Organic Framework by an Organometallic Complex: Magnetic Properties and Structure of the Inclusion Compound $[(\eta^5\text{-}C_5H_5)_2Co]_{0.5}$@MIL-47(V)



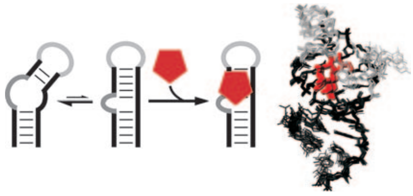
The stoichiometric reduction of the MIL-47(V) framework (see picture; green VO_6 octahedra) was performed using cobaltocene as an organometallic reducing agent. The formation of a mixed-valence compound with a V^{3+}/V^{4+} ratio of 1:1 was confirmed by magnetic susceptibility measurements. Incorporation of cobaltocene into the MIL-47(V) framework can be reversed upon treatment with water.

RNA–Ligand Interactions

E. Duchardt-Ferner, J. E. Weigand,
O. Ohlenschläger, S. R. Schmidtke,
B. Suess, J. Wöhnert* ______ **6216 – 6219**

Highly Modular Structure and Ligand Binding by Conformational Capture in a Minimalistic Riboswitch

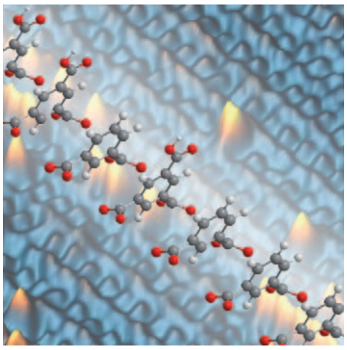
Be prepared: The structure of an synthetic neomycin riboswitch RNA (N1) is investigated by NMR spectroscopy. A largely disordered free structural ensemble also contains a compact conformation that resembles the ligand-bound state thus suggesting a binding mechanism by conformational capture (see scheme, red = ligand).



Self-Assembled Monolayers

I. Cebula, C. Shen, M. Buck* **6220 – 6223**

Isophthalic Acid: A Basis for Highly Ordered Monolayers



Standing on their own two feet: Underpotential deposition of Cu on Au(111) yields a surface onto which 1,3-benzenedicarboxylic acid (IPA) and 1,3,5-benzenetricarboxylic acid (TMA) adsorb in a bipodal configuration. Both molecules form highly crystalline isostructural monolayers, thus demonstrating the potential of the IPA moiety as tecton for self-assembled monolayers. A thin film of a Cu–TMA coordination polymer was grown on a patterned TMA monolayer.

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

Retraction

The results that are described in the article entitled “Facile Palladium-Catalyzed Arylation of Heterocycles and Nonactivated Arenes with Aryl Chlorides”, for which I am the responsible corresponding author, were criticized by a very attentive reader after appearance of the article online in Early View. Quite a few of the spectroscopic data are incorrect, and the original mass spectra cannot be located. The critical reader and his co-workers were unable to reproduce our results, and we are grateful to them for bringing this to our attention. I herewith withdraw the Communication with the consent of the co-author.

Herbert Plenio

Facile Palladium-Catalyzed Arylation of Heterocycles and Nonactivated Arenes with Aryl Chlorides

J. Pschierer, H. Plenio*

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