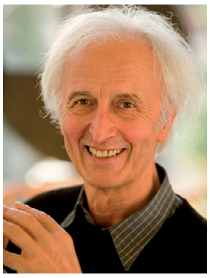
VIP *The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:*

*C. D. N. Gomes, O. Jacquet, C. Villiers, P. Thuéry, M. Ephritikhine, T. Cantat**
A Diagonal Approach to Chemical Recycling of Carbon Dioxide: New Organocatalytic Transformation for the Reductive Functionalization of CO_2

*X. Zhang, T. J. Emge, K. C. Hultzsch**
A Chiral Phenoxyamine Magnesium Catalyst for the Enantioselective Hydroamination/Cyclization of Aminoalkenes and Intermolecular Hydroamination of Vinyl Arenes

Editorial



Author Profile

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P. F. Leadlay

A. D. Hamilton

A. Fürstner

M. S. Sanford

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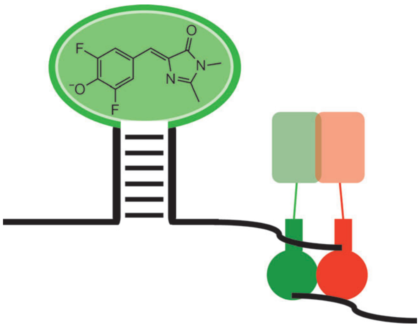
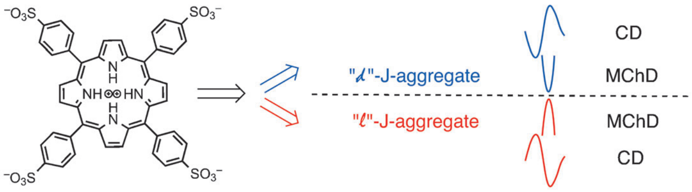
Highlights

RNA Aptamers



Retooling RNA: RNA aptamers are high-affinity ligands that can be assembled with other structures to yield multivalent molecules. These properties have been addressed in two recent studies: One describes a GFP-like RNA reporter used to study the dynamics of endogenous RNA; the other study reports on an aptamer-templated assembly of multi-enzyme complexes in bacteria for the controlled production of secondary molecules (see picture).

Chirality



The detection of magnetochiral dichroism (MChD; CD: circular dichroism) in a suspension of J-aggregate particles of an achiral amphiphilic nonmetalated porphyrin renews the interest for porphyrins in supramolecular chemistry and reinforces the concept that novel advanced materials can be obtained through self-assembly and auto-organization processes (see picture).

Essays

Fast DNA Sequencing

At warp speed: The speed and cost of sequencing DNA has undergone tremendous improvement based on Solexa sequencing. This technique arose from basic curiosity-driven research and unexpected outcomes, rather than from ideas that were strategically driven. The whole-genome sequencing of individuals now possible may one day transform the way medical disorders are classified, diagnosed, and treated.

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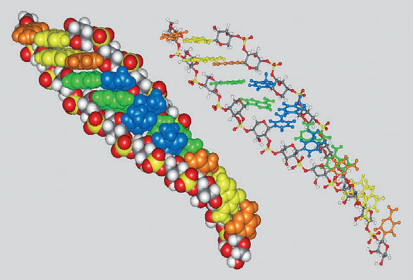
Reviews

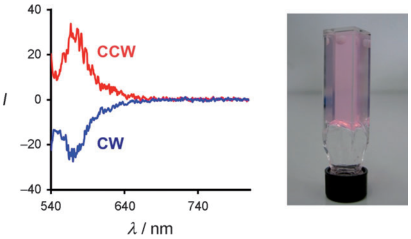
Biogenesis



The quest for the etiology of a biomolecular structure acquires special significance when the questions asked refer to molecules, the existence of which are fundamental to life, and in particular to the origin of life. In a search for the chemistry of the emergence of life, one needs to pay strict heed to molecular guides—nucleic acids, proteins, cofactors—that all carry a message, which is our job to decipher.

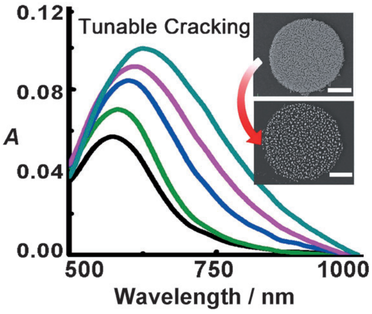
Communications

Chirality



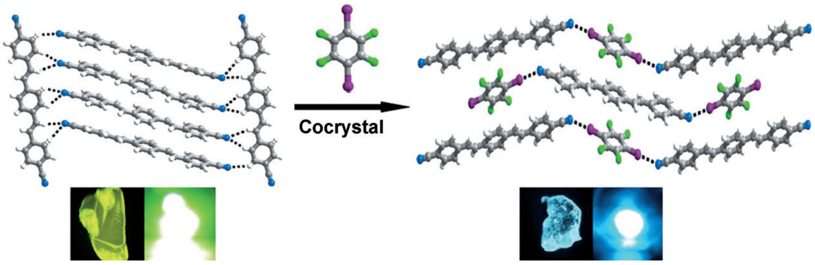
Sucked into the vortex: Hydrogels with embedded Rhodamine B dye showed stir-induced circularly polarized luminescence (CPL; see picture), the sense of which can be controlled by switching the stir direction from clockwise (CW) to counterclockwise (CCW) with slow cooling from the sol to gel states. The chiral alignment of the dye was erased by heating the sample above the gel–sol transition temperature.

Nanofabrication



You crack me up: A topographically patterned PDMS stamp was coated with thin metal film and swelled under organic vapor to induce the tunable cracking of the brittle film into metallic nanostructures (see SEM images, scale bars 1 μm). UV/Vis spectra, OLED efficiency, and SERS spectra demonstrate the fine controllability of the metallic nanostructures, the well-ordered and highly regulable surface plasmons, and the facile fabrication process.

Luminescent Materials



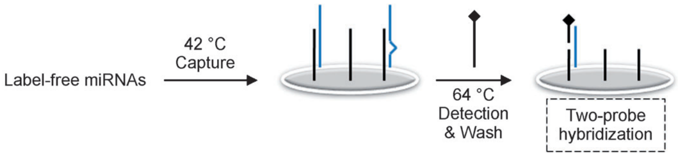
The one- and two-photon luminescence of stilbene-type solid-state materials can be tuned and controlled from blue to yellow color by a supramolecular cocrystal method.

Contents

Biosensors

J. M. Lee, Y. Jung* ______ **12487 – 12490**

Two-Temperature Hybridization for Microarray Detection of Label-Free MicroRNAs with Attomole Detection and Superior Specificity

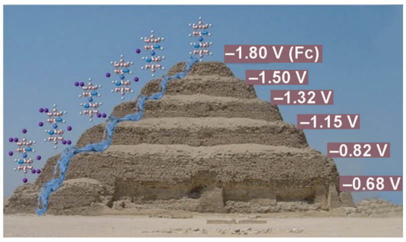


Two is better than one: Two short locked nucleic acid based probes were used to collectively capture and detect microRNAs by a simple two-temperature hybridization process. Intact microRNAs were directly measured down to attomolar concentrations with a high specificity and nearly four orders of magnitude of dynamic range. Single base mismatches in the microRNAs were potently discriminated from the perfectly matched targets.

Conducting Materials

A. Pepiol, F. Teixidor, R. Sillanpää,
M. Lupu, C. Viñas* ______ **12491 – 12495**

Stepwise Sequential Redox Potential Modulation Possible on a Single Platform



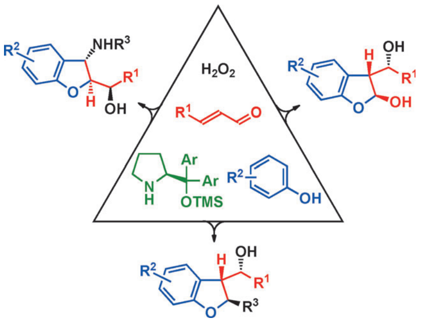
Step by step: The cluster [3,3′-Co(1,2-$C_2B_9H_{11})_2]^-$ is an excellent platform for making a stepwise tunable redox potential system by dehydroiodination. With the addition of up to eight iodine substituents (purple; see picture), there is a fall in the $E_{1/2}(Co^{III}/Co^{II})$ value from −1.80 V to −0.68 V (vs. Fc^+/Fc; Fc = ferrocene). A practical application of this tunability has been observed in the growth of polypyrrole.

Asymmetric Catalysis

Ł. Albrecht, L. K. Ransborg, V. Lauridsen,
M. Overgaard, T. Zweifel,
K. A. Jørgensen* ______ **12496 – 12500**

Taming the Friedel–Crafts Reaction: Organocatalytic Approach to Optically Active 2,3-Dihydrobenzofurans

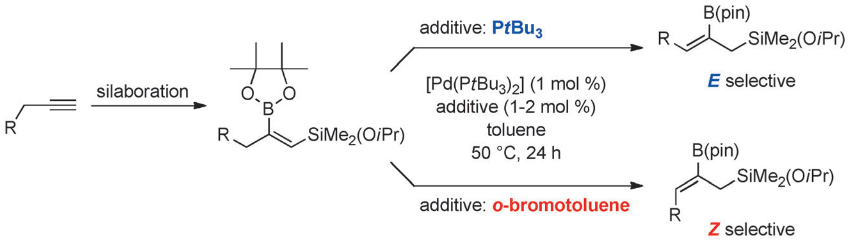
Fine-tuning: Three types of optically active *trans*-2,3-disubstituted-2,3-dihydrobenzofurans having three contiguous stereogenic centers can be efficiently accessed by one-pot reaction cascades (see scheme; TMS = trimethylsilyl). High substitution diversity of the final products can be achieved from the same common precursors by fine-tuning of their reactivity through simple structural modifications.



Olefin Isomerization

T. Ohmura,* K. Oshima,
M. Suginome* ______ **12501 – 12504**

(*E*)- and (*Z*)-β-Borylallylsilanes by Alkyne Silaboration Followed by Regio- and Stereoselective Double-Bond Migration

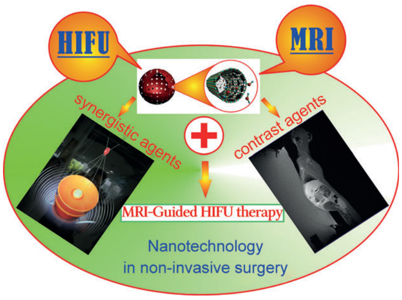


Double take: β-Borylallylsilanes have been synthesized by the regioselective silaboration of terminal alkynes followed by palladium-catalyzed double-bond migration of the resulting β-borylalkenylsilanes (see scheme). The stereoselectivity of the double-bond migration can be controlled by additives, thus leading to the stereocomplementary synthesis of (*E*)- and (*Z*)-β-borylallylsilanes.

Bionanotechnology

Y. Chen, H. Chen,* Y. Sun, Y. Zheng, D. Zeng, F. Li, S. Zhang, X. Wang, K. Zhang, M. Ma, Q. He, L. Zhang, J. Shi* ———— 12505 – 12509

Multifunctional Mesoporous Composite Nanocapsules for Highly Efficient MRI-Guided High-Intensity Focused Ultrasound Cancer Surgery

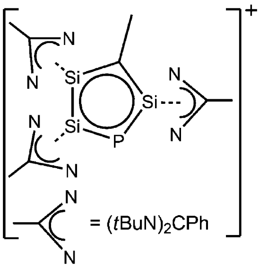


Bloodless surgical knife: Nano-biotechnology has been introduced into imaging-guided high-intensity focused ultrasound (HIFU) cancer surgery by adopting engineered multifunctional manganese-based mesoporous composite nanocapsules as the contrast agents for T_1-weighted magnetic resonance imaging (MRI) and simultaneously as synergistic agents for MRI-guided HIFU cancer surgery.

Silicon Chemistry

S. S. Sen, J. Hey, M. Eckhardt, R. Herbst-Irmer, E. Maedl, R. A. Mata,* H. W. Roesky,* M. Scheer,* D. Stalke* ———— 12510 – 12513

A Stable Cation of a CSi_3P Five-Membered Ring with a Weakly Coordinating Chloride Anion



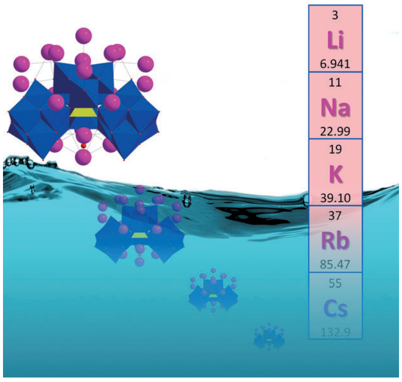
1

Don't count on counterions: The cyclic five-membered CSi_3P cation **1** is synthesized in the reaction of benzamidinato-stabilized chlorosilylene and methyl phosphaalkyne. The presence of four π electrons in **1** means it can be considered as a formal, heavier analogue of the cyclopentadienyl cation. Surprisingly the small counteranion (Cl^-) does not contribute to the ring stability.

Heteropolyniobates

Y. Hou, M. Nyman,* M. A. Rodriguez ———— 12514 – 12517

Soluble Heteropolyniobates from the Bottom of Group IA

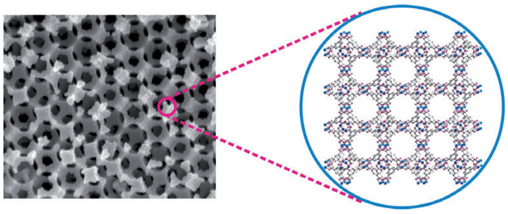


Surprising solubility: While it is already well known that $[Nb_6O_{19}]^{8-}$ salts exhibit an unusual solubility trend, that is, Cs > Rb > K > Na > Li, the heteropolyniobates of Cs and Rb had not yet been crystallized. These very soluble entities have now been obtained from solution by a simple and universal process. New polyoxoniobate geometries are thus unveiled, and the $[SiNb_{12}O_{40}]^{16-}$ Keggin ion is characterized in solution for the first time.

Metal–Organic Frameworks

Y. Wu, F. Li,* W. Zhu, J. Cui, C. Tao, C. Lin, P. M. Hannam, G. Li* ———— 12518 – 12522

Metal–Organic Frameworks with a Three-Dimensional Ordered Macroporous Structure: Dynamic Photonic Materials

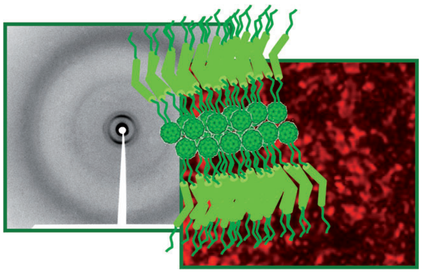


Tuning MOFs: When a metal–organic framework (MOF) with an ordered three-dimensional macroporous structure is integrated into a film, the resulting materials have an additional optical element, which can be used as a general and effective signal transducer. This, in combination with the hierarchical pore structure, makes these films interesting dynamic photonic materials with potential applications in sensors.

Supramolecular Chemistry

J. Vergara, J. Barberá, J. L. Serrano,
M. B. Ros,* N. Sebastián, R. de la Fuente,
D. O. López, G. Fernández, L. Sánchez,
N. Martín ______________ **12523 – 12528**

Liquid-Crystalline Hybrid Materials Based on [60]Fullerene and Bent-Core Structures

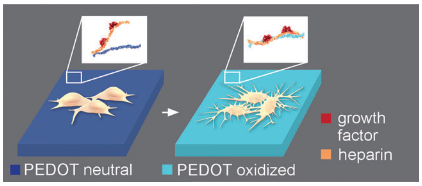


What a core-ker! By the appropriate combination of promesogenic bent-core structures and the C_{60} unit, lamellar polar liquid-crystal phases were induced (see scheme). The supramolecular organization of the functional fullerene-based assemblies, the temperature range of the soft phase, the stabilization of the mesophase-like order at room temperature, and the molecular switching under an electric field can be tuned, depending on the molecular structure.

Organic Bioelectronics

A. Herland,* K. M. Persson, V. Lundin,
M. Fahlman, M. Berggren, E. W. H. Jager,
A. I. Teixeira* ______________ **12529 – 12533**

Electrochemical Control of Growth Factor Presentation To Steer Neural Stem Cell Differentiation

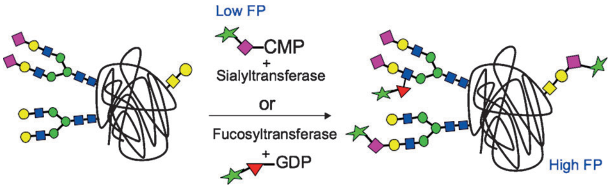


Let it grow: The conjugated polymer poly(3,4-ethylenedioxythiophene) (PEDOT) was synthesized with heparin as the counterion to form a cell culture substrate. The surface of PEDOT:heparin in the neutral state associated biologically active growth factors (see picture). Electrochemical in situ oxidation of PEDOT during live cell culture decreased the bioavailability of the growth factor and created an exact onset of neural stem cell differentiation.

Glycosyltransferase Inhibitors

C. D. Rillahan, S. J. Brown, A. C. Register,
H. Rosen, J. C. Paulson* **12534 – 12537**

High-Throughput Screening for Inhibitors of Sialyl- and Fucosyltransferases

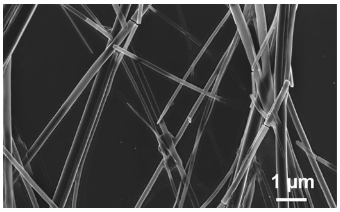


Sweet screens: A high-throughput screening platform for identification of inhibitors of sialyl- and fucosyltransferases based on fluorescence polarization (FP) has been developed. An analogue of the natural donor substrate carrying a fluorescent label (green star) is transferred to a glycoprotein acceptor, which results in robust FP (see picture). The screening of 16000 compounds against different glycosyltransferases has identified various interesting inhibitors.

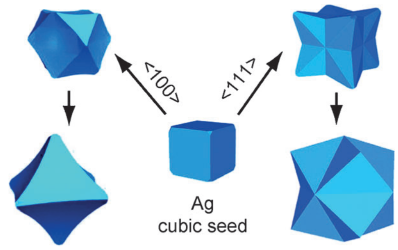
Proton Transport

H. Wang, X. Xu, N. M. Johnson,
N. K. R. Dandala,
H.-F. Ji* ______________ **12538 – 12541**

High Proton Conductivity of Water Channels in a Highly Ordered Nanowire



A proton-conductive material based on a crystalline assembly of trimesic acid and melamine (TMA·M, see picture) is reported. Because of the ordered structure of the assembly, the water-saturated proton conductivity for the TMA·M assembly is 5.5 $S\,cm^{-1}$, which is the highest proton conductivity measured to date. This exceptionally high conductivity and low-cost fabrication of the material make applications feasible for fuel-cell devices.

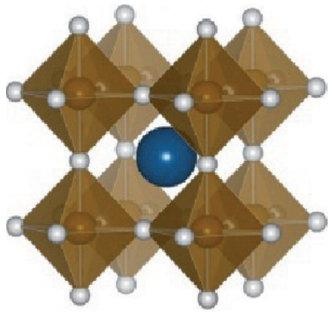


Shaped and dimpled: Silver nanocrystals enclosed by concave surfaces and thus high-index facets have been prepared by simply controlling the growth habit of Ag cubic seeds. Four types of concave nanocrystals, including octahedron, cube, octapod, and trisoctahedron, were obtained (see picture).

Concave Nanoparticles

X. Xia, J. Zeng, B. McDearmon, Y. Zheng, Q. Li, Y. Xia* ______ **12542 – 12546**

Silver Nanocrystals with Concave Surfaces and Their Optical and Surface-Enhanced Raman Scattering Properties



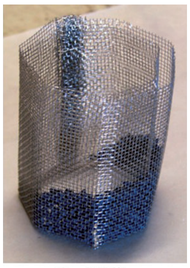
Magnetic attraction: The cubic perovskite $BaFeO_3$ (see picture, Ba blue, Fe brown, O white), which is obtained by a low-temperature reaction using ozone as an oxidant, exhibits ferromagnetism with a fairly large moment of 3.5 μ_B per Fe ion above a small critical field of approximately 0.3 T. This specific ferromagnetism is attributed to the enhancement of $O \rightarrow Fe$ charge transfer that arises from deepening of the Fe^{4+} d levels.

Perovskite Phases

N. Hayashi,* T. Yamamoto, H. Kageyama, M. Nishi, Y. Watanabe, T. Kawakami, Y. Matsushita, A. Fujimori, M. Takano ______ **12547 – 12550**

$BaFeO_3$: A Ferromagnetic Iron Oxide

AURO*lite*, consisting of gold supported on titania (picture shows extrudates in a steel net cage), is a robust catalyst for the production of catalyst-free $HCOOH/NEt_3$ adducts from H_2, CO_2, and neat NEt_3. Pure HCOOH is freed from the adducts by amine exchange.

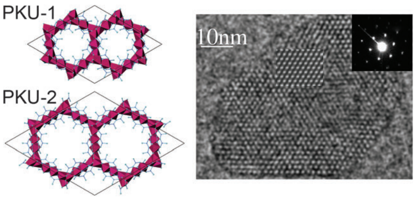


Au/TiO_2

CO_2 Hydrogenation

D. Preti, C. Resta, S. Squarcialupi, G. Fachinetti* ______ **12551 – 12554**

Carbon Dioxide Hydrogenation to Formic Acid by Using a Heterogeneous Gold Catalyst



Channel zapping: PKU-1 and newly synthesized PKU-2 ($Al_2B_5O_9(OH)_3 \cdot n H_2O$; see picture) possess microporous structures with 18-ring and 24-ring channels, respectively. They show high reactivity and size selectivity in the cyanosilylation of aldehydes as heterogeneous Lewis acid catalysts. The different channel sizes determine the substrate selectivity. These examples demonstrate the potential of octahedron-based aluminoborate channels in catalysis.

Microporous Catalysts

T. Yang, A. Bartoszewicz, J. Ju, J. Sun, Z. Liu, X. Zou, Y. Wang, G. Li, F. Liao, B. Martín-Matute,* J. Lin* ______ **12555 – 12558**

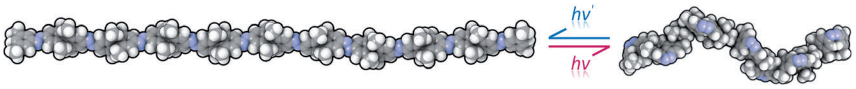
Microporous Aluminoborates with Large Channels: Structural and Catalytic Properties

Contents

Smart Polymers

D. Bléger,* T. Liebig, R. Thiermann,
M. Maskos,* J. P. Rabe,*
S. Hecht* ______ **12559 – 12563**

Light-Orchestrated Macromolecular "Accordions": Reversible Photoinduced Shrinking of Rigid-Rod Polymers



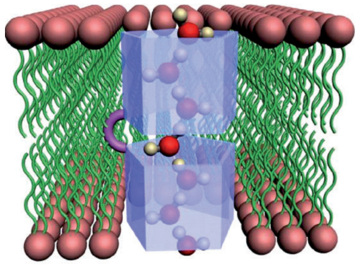
Light can play: Irradiation causes dramatic changes in the shape of rigid-rod polymers incorporating azobenzene photochromes in the main chain. The embedded photoswitches act as hinges, which upon light-induced isomerization lead to reversible shrinking and stretching of the polymer backbone (see scheme), resembling light-orchestrated macromolecular accordions.

Artificial Channels

W. Si, L. Chen, X.-B. Hu, G. Tang, Z. Chen,
J.-L. Hou,* Z.-T. Li ______ **12564 – 12568**

Selective Artificial Transmembrane Channels for Protons by Formation of Water Wires

Lined up water molecules: Artificial transmembrane channels from pillar[5]-arene monomeric and dimeric derivatives have been prepared. Single-channel conductance measurements and isotope-effect experiments under acidic conditions showed selective proton transport through the channels, which were mediated by water wires formed in the pillar[5]arene backbones (see picture).

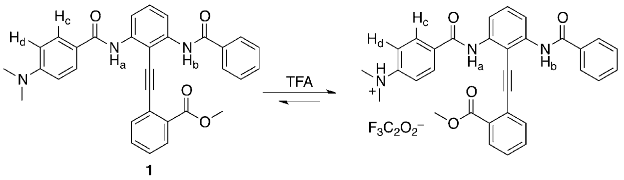


Artificial Transmembrane
Proton Channel

Molecular Switches

I. M. Jones, H. Lingard,
A. D. Hamilton* ______ **12569 – 12571**

pH-Dependent Conformational Switching in 2,6-Benzamidodiphenylacetylenes

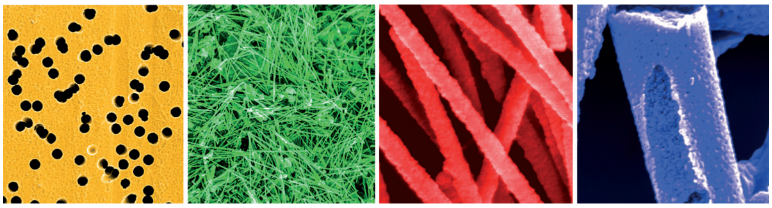


The conformational equilibrium of a pH-dependent switch based on an intramolecularly H-bonded diphenylacetylene can be predictably biased by using electron-donating or -withdrawing groups (see scheme). Furthermore, protonation of the electron-donating dimethylamino group converts it into an electron-withdrawing dimethylammonium cation with a concomitant switch in conformation.

Crystal Growth

Y.-Y. Kim, N. B. J. Hetherington,
E. H. Noel, R. Kröger, J. M. Charnock,
H. K. Christenson,
F. C. Meldrum* ______ **12572 – 12577**

Capillarity Creates Single-Crystal Calcite Nanowires from Amorphous Calcium Carbonate

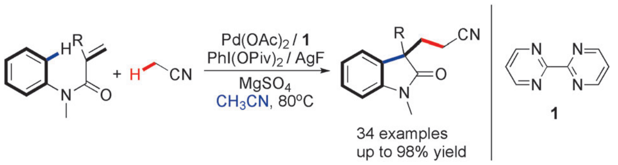


Single-crystal calcite nanowires are formed by crystallization of morphologically equivalent amorphous calcium carbonate (ACC) particles within the pores of track etch membranes. The polyaspartic acid stabilized ACC is drawn into the membrane pores by capillary action, and the single-crystal nature of the nanowires is attributed to the limited contact of the intramembrane ACC particle with the bulk solution. The reaction environment then supports transformation to a single-crystal product.

Synthetic Methods

T. Wu, X. Mu, G. Liu* ____ 12578 – 12581

Palladium-Catalyzed Oxidative Arylalkylation of Activated Alkenes: Dual C–H Bond Cleavage of an Arene and Acetonitrile



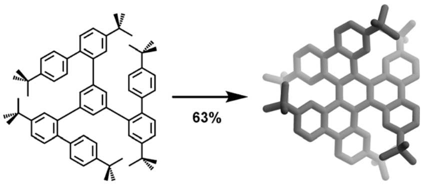
Not one but two: The title reaction proceeds through the dual C–H bond cleavage of both aniline and acetonitrile (see scheme). The reaction affords a variety of cyano-bearing indolinones in excellent yield. Mechanistic studies demonstrate that this reaction involves a fast arylation of the olefin and a rate-determining C–H activation of the acetonitrile.

Synthetic Methods

A. Pradhan, P. Dechambenoit, H. Bock, F. Durola* ____ 12582 – 12585

Highly Twisted Arenes by Scholl Cyclizations with Unexpected Regioselectivity

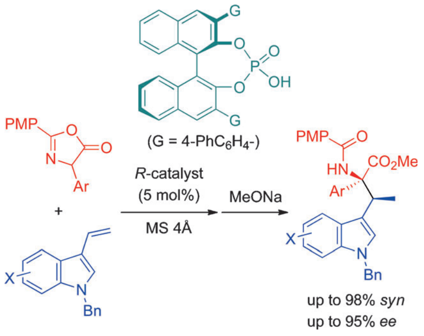
Let's twist! The Scholl reaction with quinquephenyl derivatives has been shown to have an unexpectedly strong preference for forming twisted, helicene aromatic polycycles, instead of their flat counterparts. This tendency is so strong that it will overcome even severe steric hindrance, and the procedure can be used in the efficient synthesis of hexa-*tert*-butylhexabenzotriphenylene from a simple biaryl starting material (see scheme).



Organocatalysis

M. Terada,* K. Moriya, K. Kanomata, K. Sorimachi ____ 12586 – 12590

Chiral Brønsted Acid Catalyzed Stereoselective Addition of Azlactones to 3-Vinylindoles for Facile Access to Enantioenriched Tryptophan Derivatives

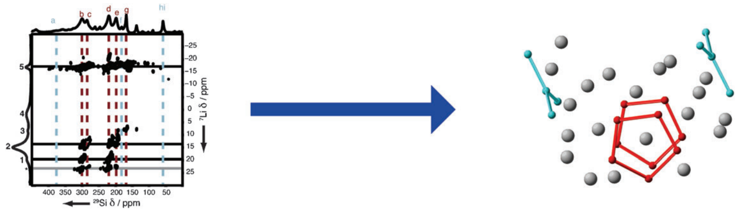


Syn-gled out: The *syn* diastereo- and enantioselective addition of azlactones to 3-vinylindoles was accomplished by using a chiral, binapthol-derived, Brønsted acid catalyst (see scheme). This method enables facile access to tryptophan derivatives with adjacent quaternary and tertiary stereogenic centers, which are potentially useful for the synthesis of peptidomimetics.

Silicon Clusters

T. K.-J. Köster, E. Salager, A. J. Morris, B. Key, V. Seznec, M. Morcrette, C. J. Pickard, C. P. Grey* 12591 – 12594

Resolving the Different Silicon Clusters in Li$_{12}$Si$_7$ by ^{29}Si and ^{6,7}Li Solid-State NMR Spectroscopy

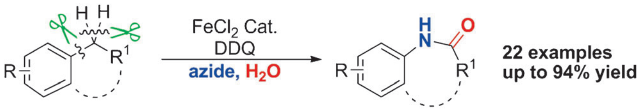


Structural signatures: The analysis of Si–Si and Si–Li connectivities by solid-state NMR spectroscopy allows the different types of silicon clusters to be discriminated in the model lithium silicide compound Li$_{12}$Si$_7$ (see picture, Si clusters red and blue, Li ions gray). The results provide new NMR spectroscopic strategies with which to differentiate and study the structures formed in silicon-based electrode materials.

Synthetic Methods

C. Qin, W. Zhou, F. Chen, Y. Ou,
N. Jiao* ______________ **12595 – 12599**

Iron-Catalyzed C−H and C−C Bond Cleavage: A Direct Approach to Amides from Simple Hydrocarbons

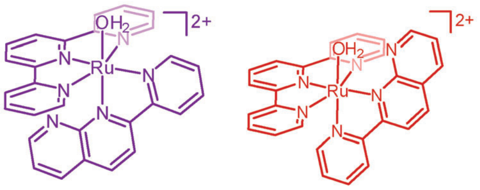


Something functional: The title reaction proceeds in the presence of azide and water to deliver amides in high yields, and it can be used in a ring-expansion strategy to generate lactams. A mechanism is proposed based on experimental results. This reaction offers a new approach to functionalizing simple and readily available hydrocarbons. DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

Water Oxidation

J. L. Boyer, D. E. Polyansky, D. J. Szalda,
R. Zong, R. P. Thummel,*
E. Fujita* ______________ **12600 – 12604**

Effects of a Proximal Base on Water Oxidation and Proton Reduction Catalyzed by Geometric Isomers of $[Ru(tpy)(pynap)(OH_2)]^{2+}$

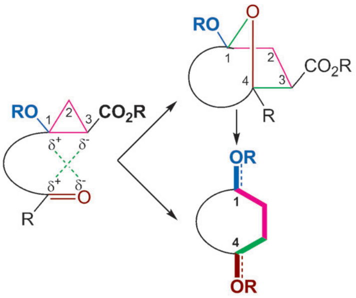


Basic difference: The importance of a pendent base in promoting proton-coupled electron-transfer reactions with low activation barriers has been discussed for H^+ reduction or H_2 oxidation in acetonitrile. Investigation of the interaction between a base positioned in the second coordination sphere of a complex and a water ligand in water oxidation reactions using geometric isomers of $[Ru(tpy)(pynap)(OH_2)]^{2+}$ (see picture) gave intriguing results.

Cycloaddition

S. Xing, Y. Li, Z. Li, C. Liu, J. Ren,
Z. Wang* ______________ **12605 – 12609**

Lewis Acid Catalyzed Intramolecular [3+2] Cross-Cycloaddition of Donor–Acceptor Cyclopropanes with Carbonyls: A General Strategy for the Construction of Acetal[*n*.2.1] Skeletons

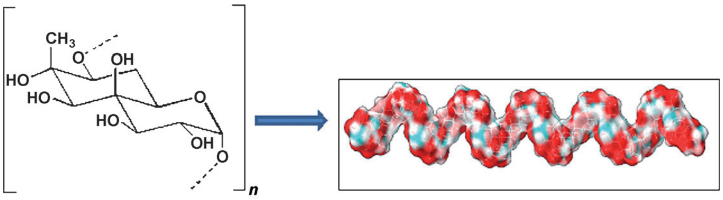


Build a bridge: The first catalytic intramolecular [3+2] cycloaddition of mono-donor–monoacceptor cyclopropanes (see scheme) provides a general and efficient strategy for construction of structurally diverse acetal[*n*.2.1] and 1,4-dioxygen-substituted cyclic skeletons, which are widely distributed in biologically important natural products.

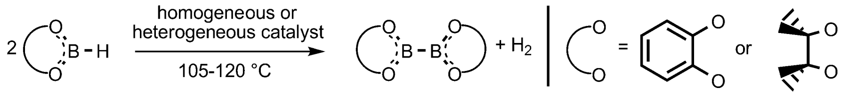
Carbohydrates

A. Silipo, M. R. Leone, G. Erbs,
R. Lanzetta, M. Parrilli, W.-S. Chang,
M.-A. Newman,
A. Molinaro* ______________ **12610 – 12612**

A Unique Bicyclic Monosaccharide from the *Bradyrhizobium* Lipopolysaccharide and Its Role in the Molecular Interaction with Plants



Sugar coat: The nitrogen-fixing soil bacterium *Bradyrhizobium* sp. BTAi1 is coated with a unique lipopolysaccharide that does not induce innate immune responses in its host plant *Aeschynomene indica* or in different plant families. The chemical nature of the monosaccharide forming the polymer (see picture) is unprecedented in nature, which helps to avoid “harmful” recognition by its symbiotic host.



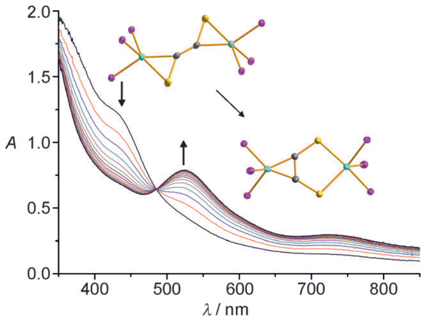
The diboranes(4) bis(catecholato)diborane (B_2Cat_2) and bis(pinacolato)diborane (B_2Pin_2) are important precursors for organoboronic esters, which are versatile reagents for the formation of carbon–carbon bonds. A new catalytic synthesis for these compounds starts from catecholborane or pinacolborane and gives the dehydrocoupling products B_2Cat_2 and B_2Pin_2 with turnover numbers of up to 11 600 (see scheme).

Dehydrocoupling of Boranes

H. Braunschweig,*
F. Guethlein ________ **12613 – 12616**

Transition-Metal-Catalyzed Synthesis of Diboranes(4)

Swing bridge: The triplet species ethenedithione has been generated within the coordination sphere of cobalt, leading to a dinuclear μ-η^2-η^2-C_2S_2 complex (see picture: C gray, Co blue, P purple, S yellow). Depending on the solvent, the C_2S_2 moiety displays a transoid or a cisoid geometry. This isomerization step changes the sign of the magnetic coupling between the cobalt centers.



Small-Molecule Stabilization

W. W. Seidel,* M. J. Meel, S. R. Hughes,
F. Hupka, A. Villinger ____ **12617 – 12620**

Ethenedithione (S=C=C=S): Trapping and Isomerization in a Cobalt Complex

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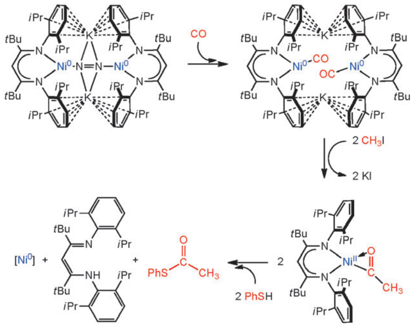
When three become one: Within one nickel-based model system, the three reactants CO, MeI, and PhSH have been assembled to yield an acetyl thioester. The reactivity is of relevance for the functioning of the acetyl coenzyme A synthase active site and provides insights into possible binding sequences.



Enzyme Models

B. Horn, C. Limberg,* C. Herwig,
S. Mebs ________ **12621 – 12625**

The Conversion of Nickel-Bound CO into an Acetyl Thioester: Organometallic Chemistry Relevant to the Acetyl Coenzyme A Synthase Active Site

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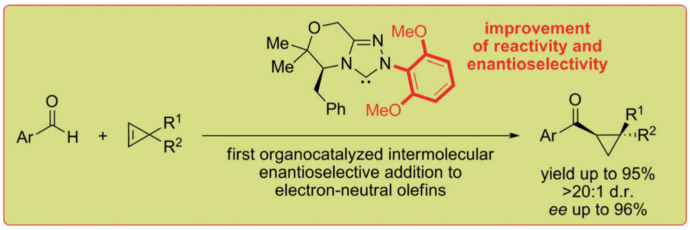


Faster, higher, stronger! The N-heterocyclic carbene (NHC) catalyzed diastereo- and enantioselective hydroacylation of cyclopropenes affords structurally valuable acylcyclopropanes. A new family of electron-rich, 2,6-dimethoxyphenyl-substituted NHCs induces excellent reactivity and enantioselectivity. Preliminary kinetic studies unambiguously demonstrated the superiority of this family of catalysts over known NHCs in this challenging transformation.

Asymmetric Organocatalysis

F. Liu, X. Bugaut, M. Schedler, R. Fröhlich,
F. Glorius* ________ **12626 – 12630**

Designing N-Heterocyclic Carbenes: Simultaneous Enhancement of Reactivity and Enantioselectivity in the Asymmetric Hydroacylation of Cyclopropenes

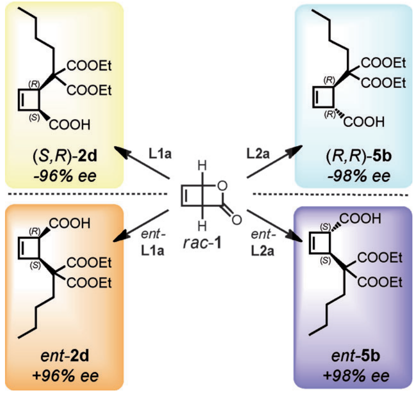
Contents

Asymmetric Catalysis

M. Luparia, M. T. Oliveira, D. Audisio,
F. Frébault, R. Goddard,
N. Maulide* ________ **12631 – 12635**

Catalytic Asymmetric Diastereodivergent Deracemization

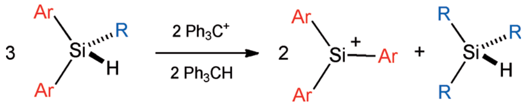
Your wish is my command: Deracemization is a powerful strategy wherein a racemate is converted into a 100% yield of a single enantiopure product. A new concept in catalytic deracemization is presented, in which a racemate with *n* stereogenic elements can be selectively converted into each one of 2^m (m = number of chiral centers of the product) different enantiopure products, by simple tuning of the reaction conditions.



Silylium Ions

A. Schäfer, M. Reißmann, A. Schäfer,
W. Saak, D. Haase,
T. Müller* ________ **12636 – 12638**

A New Synthesis of Triarylsilylium Ions and Their Application in Dihydrogen Activation



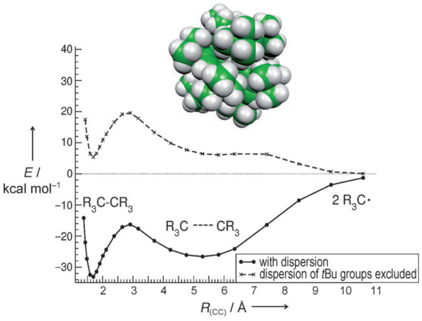
Well-shuffled: An unexpected substituent distribution reaction via alkyldiarylsilylium ions leads to a distribution of substituents. Starting from alkyldiaryl silanes, this reaction provides a facile synthetic approach to sterically highly hindered triarylsilylium ions. These silylium ions can be applied in dihydrogen activation reactions.

Dispersion Interactions

S. Grimme,*
P. R. Schreiner* ________ **12639 – 12642**

Steric Crowding Can Stabilize a Labile Molecule: Solving the Hexaphenylethane Riddle

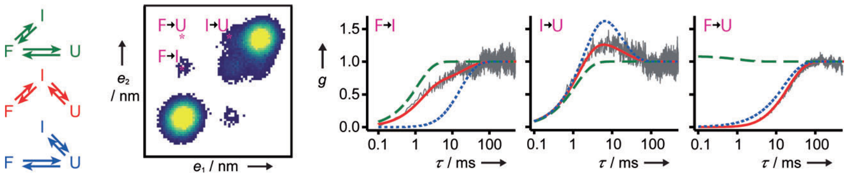
12 not so angry men: Hexaphenylethane is unstable, a phenomenon traditionally attributed to steric repulsion between the six phenyl rings. However, adding 12 bulky *tert*-butyl groups, one to each of the 12 *meta* positions, gives a stabile ethane derivative (see space-filling model and potential energy curve for the dissociation of the central C–C bond). This unexpected stabilization is shown to result from attractive dispersion interactions between the substituents.



Single-Molecule Kinetics

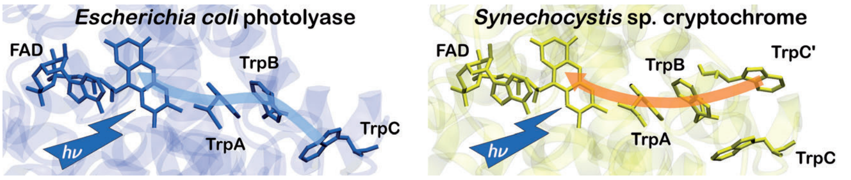
A. Hoffmann,
M. T. Woodside* ________ **12643 – 12646**

Signal-Pair Correlation Analysis of Single-Molecule Trajectories



There you go: How to get kinetic information from trajectories of single biomolecules? A method based on correlating signal ranges (here for a three-state DNA hairpin with F = folded, I = intermediate, and U = unfolded state) is reported and shows how to get the kinetic scheme and the corresponding rates, even for states with low occupancy or very short lifetime, states which overlap because of noise, and systems with very similar or very different rates.

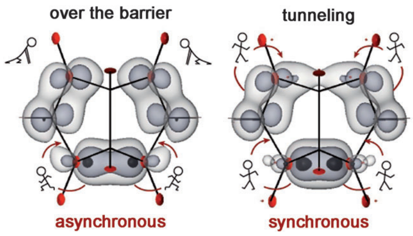
Photoinduced Electron Transfer



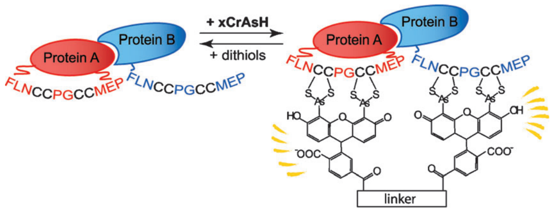
Subtle differences in the local sequence and conformation of amino acids can result in diversity and specificity in electron transfer (ET) in proteins, despite structural conservation of the redox partners. For individual ET steps, distance is not necessarily the decisive parameter; orientation and solvent accessibility of the ET partners, and thus the stabilization of the charge-separated states, contribute substantially.

Pericyclic Reactions

One at a time or all at once? Electronic fluxes during a pericyclic reaction in the electronic ground state—exemplified for the degenerate Cope rearrangement of semibullvalene—may proceed either synchronously or asynchronously. Quantum simulations show that the mechanism is determined by the preparation of the reactants, for example, synchronous at cryogenic temperatures (tunneling) but asynchronous when induced by selective laser pulses (with energy over the barrier).



Protein Cross-Linking



As you like it: xCrAsH, a dimeric derivative of the arsenical compound FlAsH, enables the highly specific, covalent cross-linking of two proteins containing a 12 amino acid peptide tag. This inducible and (by addition of dithiols) reversible system can be used to detect and manipulate protein–protein interactions both in vitro and in living cells (see picture).

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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