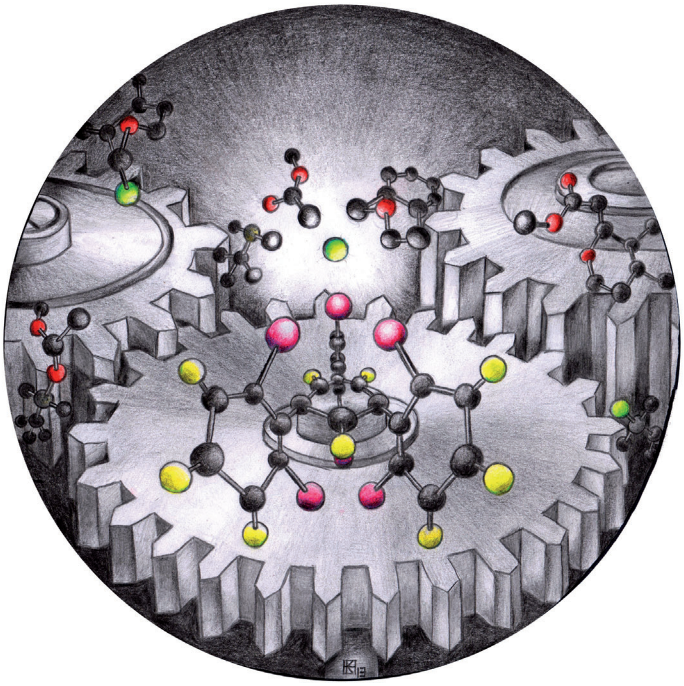
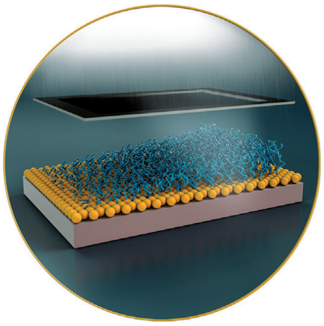
Neutral multidentate ...

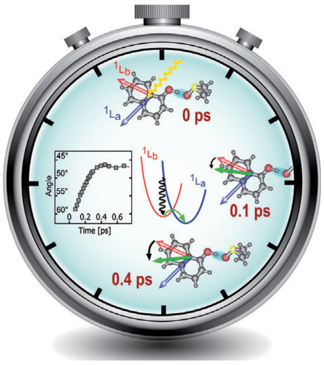


… halogen-bond donors (halogen-based Lewis acids) can be used as organocatalysts in a halide abstraction reaction. In their Communication on page 7028 ff., S. M. Huber et al. describe the halogen-bond-catalyzed reaction of 1-chloroisochroman with ketene silyl acetals. The organocatalytic activity crucially depends on the iodine substituents of the halogen-bond donors, and hidden acid catalysts can be ruled out with high probability.

Photochemistry

In their Communication on page 6844 ff., C. J. Hawker et al. present a facile approach to three-dimensional patterned polymer brushes based on visible-light-mediated controlled radical polymerization using a simple photomask.



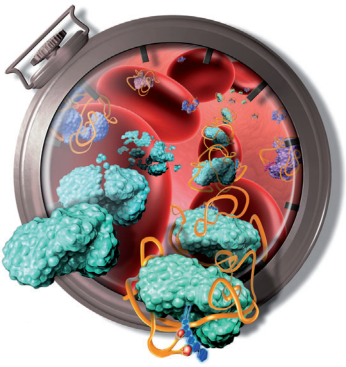


Femtochemistry

The non-adiabatic excited-state dynamics of 1-naphthol are addressed with femtosecond time resolution by E. T. J. Nibbering, M. Chergui, et al. in their Communication on page 6871 ff.

Therapeutic Proteins

The interaction between Ni-NTA (conjugated to PEG) and oligohistidine (on the protein) is used to specifically modify TRAIL proteins. In their Communication on page 6880 ff., K. C. Lee, S. Lee, et al. show this approach greatly increases the protein half-life in vivo.



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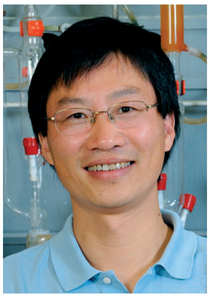
Spotlight on Angewandte's Sister Journals ***6808 – 6810***

Author Profile



"I can never resist a delicious French dessert. My biggest motivation is to learn something new every day ..."
This and more about Jieping Zhu can be found on page 6812.

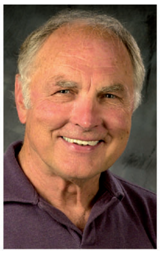
Jieping Zhu ______ **6812 – 6813**

News

K. Anseth

J. S. Francisco

M. Gruebele



G. D. Stucky

C.-M. Che

C. M. Dobson

V. Gouverneur

M. S. Islam

D. O'Hagan

G. Thornton

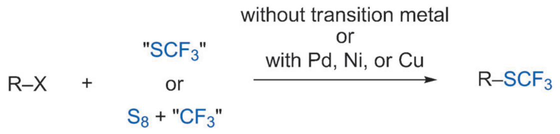
New Members of the National Academy of Sciences Royal Society Wolfson Research Merit Awards ______ **6814 – 6815**

Highlights

Trifluoromethylthiolation

A. Tlili, T. Billard* ________ **6818 – 6819**

Formation of C–SCF_3 Bonds through Direct Trifluoromethylthiolation



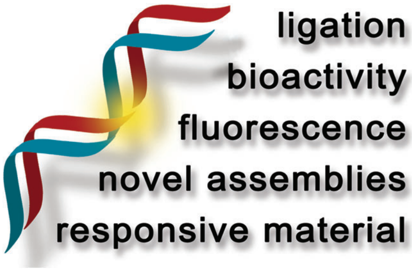
Modern chemistry with an old substituent: The introduction of the SCF_3 group into organic substrates is a challenging task because of harsh or specific synthetic methods. However, recent advances in the formation of C–SCF_3 bonds include the trifluoromethylthiolation with transition-metal-free systems or in the presence of palladium, nickel, or copper catalysts (see scheme).

Reviews

Non-natural Translation

K. Gorska, N. Winssinger* _ **6820 – 6843**

Reactions Templated by Nucleic Acids: More Ways to Translate Oligonucleotide-Based Instructions into Emerging Function



Not lost in translation: The programmability of oligonucleotide recognition offers an attractive platform to direct the assembly of reactive partners so that a functional output is achieved. Recent progress in the type of transformations and their applications (such as the translation of oligonucleotide information in functional materials and novel architectures, bioactivity, or fluorescence) are summarized.

Communications

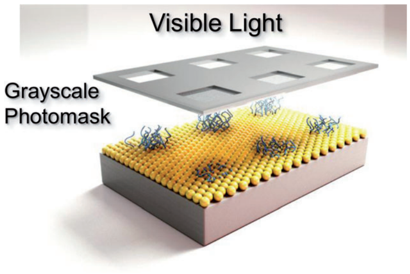
Photochemistry

J. E. Poelma, B. P. Fors, G. F. Meyers, J. W. Kramer, C. J. Hawker* _ **6844 – 6848**

Fabrication of Complex Three-Dimensional Polymer Brush Nanostructures through Light-Mediated Living Radical Polymerization

Frontispiece

A facile approach to unique 3D, patterned polymer brushes is based on visible-light-mediated controlled radical polymerization. The temporal and spatial control of the polymerization allows the patterning of polymer brushes from a uniform initiating layer using a simple photomask (see picture). Furthermore, gradient polymer brushes, patterned block copolymers, and complex 3D structures can be obtained by modulating light intensity.



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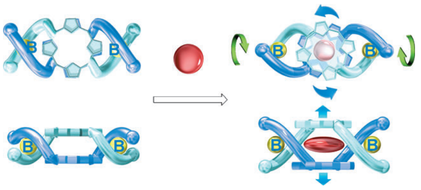
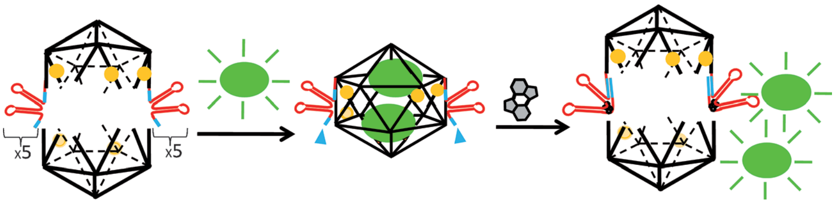


Influential guests: The intercalation of an electron-deficient aromatic guest (shown in red) between the two porphyrin rings of an optically active, porphyrin-linked double-stranded spiroborate helicate triggered rotary motion of the porphyrin rings in one direction in conjunction with a unidirectional twisting motion of the spiroborate helix. This system has potential for the development of chirality-responsive molecular machines.

Host–Guest Systems

S. Yamamoto, H. Iida,
E. Yashima* ———— **6849 – 6853**

Guest-Induced Unidirectional Dual Rotary and Twisting Motions of a Spiroborate-Based Double-Stranded Helicate Containing a Bisporphyrin Unit



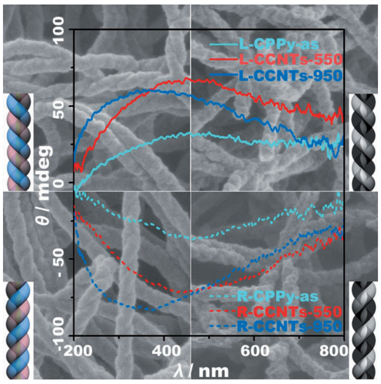
DNA Trojan horse: A DNA icosahedron (black, see scheme) held together with aptamers (red) was used to encapsulate molecular cargo such as fluorescent dextran (green). In the presence of a molecular trigger (gray hexagons), the aptamers fold back leading to opening of the icosahedron and simultaneous release of the encapsulated cargo.

DNA Nanocapsules

A. Banerjee, D. Bhatia, A. Saminathan,
S. Chakraborty, S. Kar,
Y. Krishnan* ———— **6854 – 6857**

Controlled Release of Encapsulated Cargo from a DNA Icosahedron using a Chemical Trigger

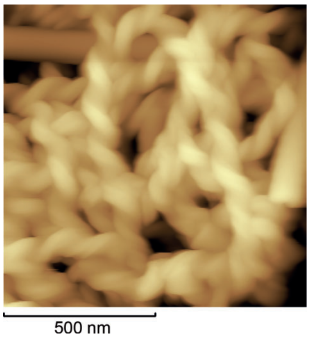
In one step, self-assembled helical polypyrrole nanotubes were carbonized to enantiopure chiral carbonaceous nanotubes with a partially graphitized nanostructure (see picture). The ordered helical arrangement of the carbon nanostructure resulted in enantiomeric materials with distinct optical activity. Moreover, their unique structure endowed them with high reversible storage capacity of lithium ions.



Nanostructures

S. Liu, Y. Duan, X. Feng, J. Yang,
S. Che* ———— **6858 – 6862**

Synthesis of Enantiopure Carbonaceous Nanotubes with Optical Activity

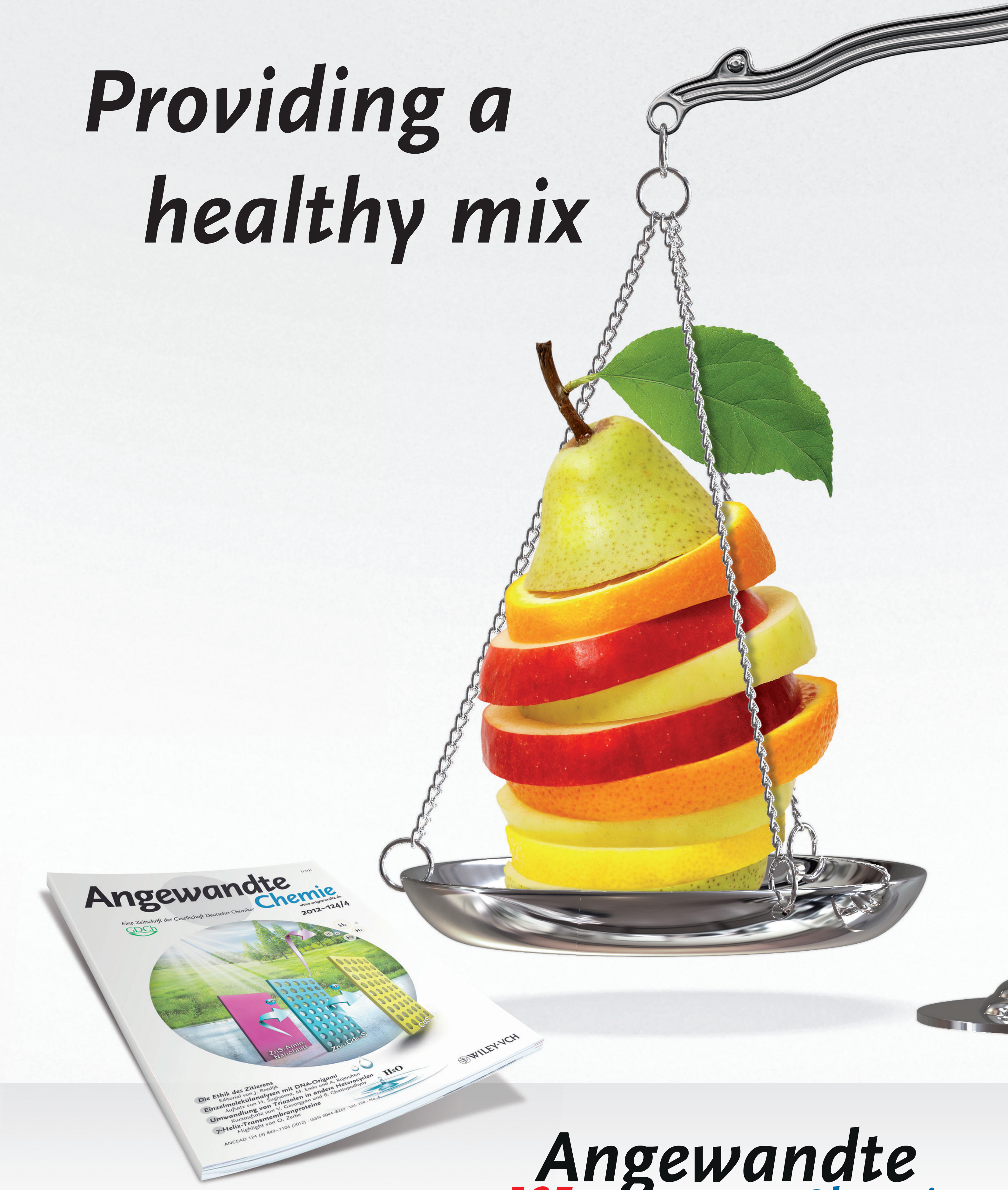


Controlling chirality: A general method to obtain homochiral helical nanofilaments (HNFs) based on a twisted nematic (TN) configuration was developed. By mixing bent-core molecules in the B4 phase with rod-like molecules in the nematic phase, the mixtures show the phase sequence of N–Bx(B4/N). Homochiral HNFs in the Bx phase were obtained from the mixtures when TN cells were cooled. The homochiral HNFs were observed by atomic force microscopy (see picture).

Liquid Crystals

T. Ueda, S. Masuko, F. Araoka,
K. Ishikawa, H. Takezoe* —— **6863 – 6866**

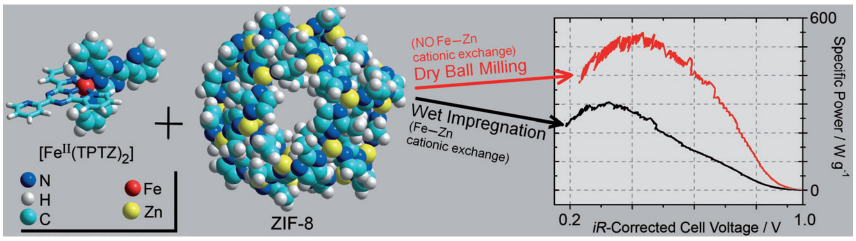
A General Method for the Enantioselective Formation of Helical Nanofilaments


Providing a healthy mix

Fuel Cells

J. Tian, A. Morozan, M. T. Sougrati,
M. Lefèvre, R. Chenitz, J.-P. Dodelet,*
D. Jones, F. Jaouen* ______ **6867–6870**

Optimized Synthesis of Fe/N/C Cathode Catalysts for PEM Fuel Cells: A Matter of Iron–Ligand Coordination Strength



It's all in the detail: Highly active Fe/N/C catalysts for the oxygen-reduction reaction in polymer-electrolyte-membrane (PEM) fuel cells can be obtained from a precursor constructed from the zeolitic imidazolate framework ZIF-8 and an iron–ligand complex if, and only if, the displacement of Zn^{II} ions from ZIF-8 by Fe^{II} ions is restricted (see picture; TPTZ = 2,4,6-tris(2-pyridyl)-*s*-triazine).

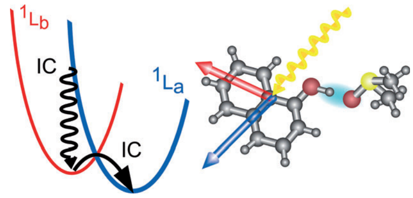
Femtochemistry

F. Messina, M. Prémont-Schwarz,
O. Braem, D. Xiao, V. S. Batista,
E. T. J. Nibbering,*
M. Chergui* ______ **6871–6875**

Ultrafast Solvent-Assisted Electronic Level Crossing in 1-Naphthol

Inside Back Cover

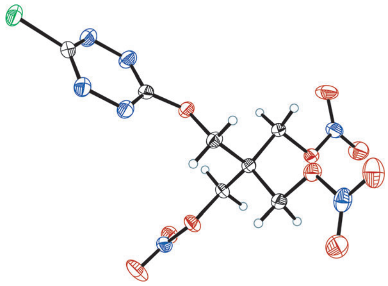
Solvent effects: The nonadiabatic inversion dynamics of the energetic order of the electronic excited states of the photoacid 1-naphthol have been revealed by ultrafast spectroscopy on a femtosecond timescale (see picture; IC = internal conversion). The energetic order of the excited states L_a and L_b of 1-naphthol is reversed in 60 fs in polar dimethyl sulfoxide solvent.



High-Nitrogen Compounds

D. E. Chavez,* S. K. Hanson,
J. M. Veauthier,
D. A. Parrish ______ **6876–6879**

Electroactive Explosives: Nitrate Ester-Functionalized 1,2,4,5-Tetrazines



Oxidation state control: The synthesis and characterization of two nitrate ester-functionalized electroactive tetrazine molecules (see example; N blue, Cl green, O red, C black) has been accomplished. The compounds are redox active and have desirable explosive properties. The reversible nature of their reduction could be utilized to control their chemical and physical properties.

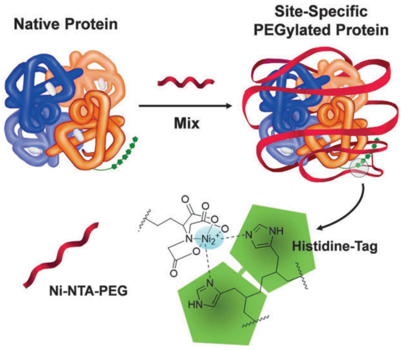
Protein Modifications

T. H. Kim, M. Swierczewska, Y. Oh, A. Kim,
D. G. Jo, J. H. Park, Y. Byun,
S. Sadegh-Nasseri, M. G. Pomper,
K. C. Lee,* S. Lee* ______ **6880–6884**

Mix to Validate: A Facile, Reversible PEGylation for Fast Screening of Potential Therapeutic Proteins In Vivo

Back Cover

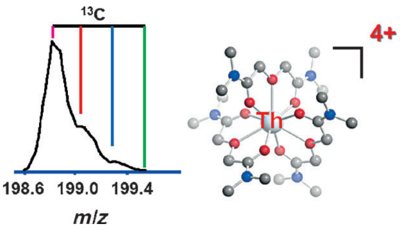
Happy TRAILs to you: PEGylation of proteins through complementary interactions between a His-tag and a Ni^{2+} complex of nitrilotriacetic acid (NTA, see picture), a well-established practice in protein research, was used to improve the half-life of therapeutic proteins in the blood following systemic administration in vivo. Animal models show that this site-specific modification improves the efficacy of modified TRAIL proteins.



Metal Polycations

Y. Gong, H.-S. Hu, G. Tian, L. Rao, J. Li,*
J. K. Gibson* ______________ **6885 – 6888**

A Tetrapositive Metal Ion in the Gas Phase: Thorium(IV) Coordinated by Neutral Tridentate Ligands



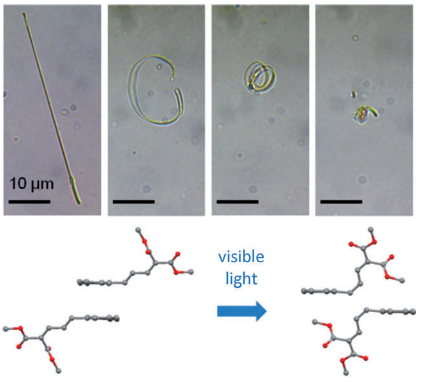
Sheltering thorium ions: A Th^{4+} ion supported by three neutral tetramethyl-3-oxaglutaramide ligands (L = TMOGA) is produced in the gas phase by electrospray ionization (see graph). The thorium in chiral $Th(L)_3^{4+}$ is coordinated by nine oxygen atoms (see picture; O red, N blue, C gray). Quantum chemical studies revealed a decrease in Th–O binding energies and bond orders and an increase in bond lengths, as the number of coordinating ligands increases.

Photoresponsive Nanowires

T. Kim, M. K. Al-Muhanna,
S. D. Al-Suwaidan, R. O. Al-Kaysi,*
C. J. Bardeen* ______________ **6889 – 6893**

Photoinduced Curling of Organic Molecular Crystal Nanowires

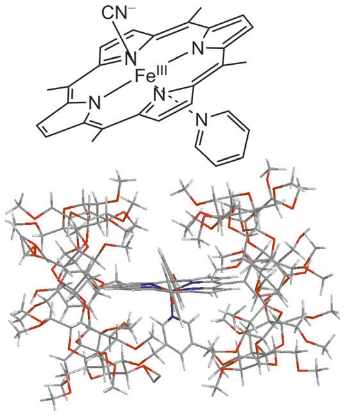
Molecular crystal nanowires composed of an anthracene-9-(1,3-butadiene) derivative exhibit a rapid transition from straight to highly coiled structures when exposed to a pulse of visible light. The curling does not depend on the direction of light illumination and occurs for nanowires composed of either the *E* or *Z* isomer. The shape change is driven by an *E*⇄*Z* photoisomerization reaction that generates a mixture of isomers within a single nanowire.



Supramolecular Medicine

K. Watanabe, H. Kitagishi,
K. Kano* ______________ **6894 – 6897**

Supramolecular Iron Porphyrin/Cyclodextrin Dimer Complex that Mimics the Functions of Hemoglobin and Methemoglobin

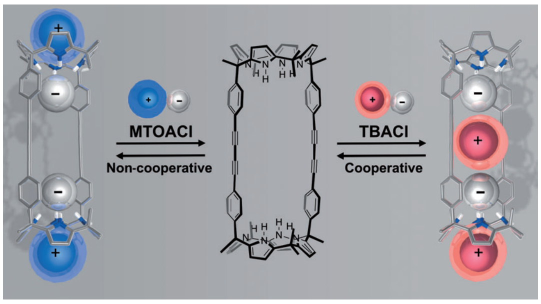


A real life saver: A supramolecule (met-hemoCD3, see scheme) was prepared by including a water-soluble porphinato iron(III) in a capsule of a cyclodextrin dimer (Py3OCD), which was synthesized in only two steps. The structure of met-hemoCD3 was determined by X-ray crystal analysis (see picture). Ferrous hemoCD3 showed functions similar to those of hemoglobin/myoglobin and also functioned as an antidote for cyanide poisoning.

Supramolecular Chemistry

V. Valderrey, E. C. Escudero-Adán,
P. Ballester* ________ 6898 – 6902

Highly Cooperative Binding of Ion-Pair Dimers and Ion Quartets by a Bis(calix[4]pyrrole) Macrotricyclic Receptor

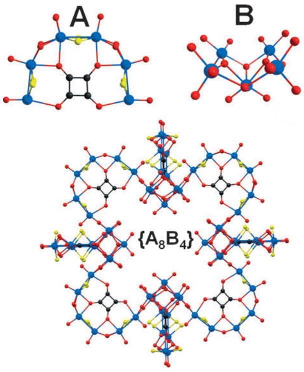


Connect four: A macrotricyclic receptor equipped with two convergent calix[4]pyrrole units features unprecedented binding properties towards two ion pairs. A highly cooperative binding process is observed for pairs of tetrabutylammonium (TBA) salts. MTOA = methyltrioctylammonium.

POMcycles

H.-Y. Zang, H. N. Miras, D.-L. Long,
B. Rausch, L. Cronin* ________ 6903 – 6906

Template-Directed Assembly of Polyoxothiometalate Scaffolds into Nanomolecular Architectures

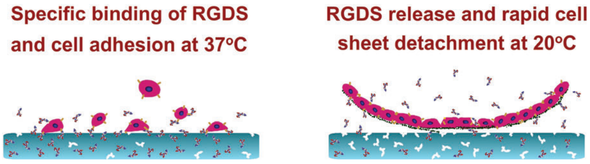


A new family of nanomolecular clusters was obtained by using the squarate anion as a template for the self-assembly of $[Mo_2O_2S_2(H_2O)_6]^{2+}$ (A) with the structure-directing anion $[Mo_5O_{18}]^{6-}$ (B) whose geometry dictates the formation of the polyoxothiometalate building blocks $[(Mo_2O_2S_2)_3(OH)_4(C_4O_4)]$ and $[(Mo_2O_2S_2)_2(OH)_2(C_4O_4)]$. A gradual evolution in both symmetry and structural completeness is observed upon traversing the generations of the POMcycle family.

Molecular Imprinting

G. Pan,* Q. Guo, Y. Ma, H. Yang,
B. Li* ________ 6907 – 6911

Thermo-Responsive Hydrogel Layers Imprinted with RGDS Peptide: A System for Harvesting Cell Sheets

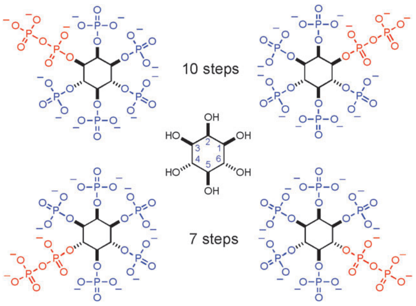


The efficient promotion of cell adhesion on a polymer surface and detachment of sheets of cells is possible with thermo-responsive cell culture substrates that are biofunctionalized through noncovalent molecular imprinting. The key is the thermo-responsive “specific binding” of the cell-adhesive peptide RGDS on the cell sheet harvest system (see picture).

Phosphorylation

S. Capolicchio, D. T. Thakor, A. Linden,
H. J. Jessen* ________ 6912 – 6916

Synthesis of Unsymmetric Diphospho-Inositol Polyphosphates

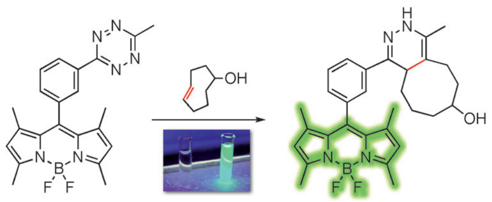


One to rule them all: A novel C_2-symmetric phosphoramidite was developed that can be used to prepare all four unsymmetric diphospho inositol pentaphosphates (PP-$InsP_5$). The target structures were synthesized in few steps and high enantiomeric ratios. With the obtained compounds, specificity of Ddp1 from yeast (a PP-$InsP_5$ phosphatase) was studied.

Fluorogenic Probes

J. C. T. Carlson, L. G. Meimetis,
S. A. Hilderbrand,
R. Weissleder* ____________ 6917 – 6920

BODIPY–Tetrazine Derivatives as Superbright Bioorthogonal Turn-on Probes

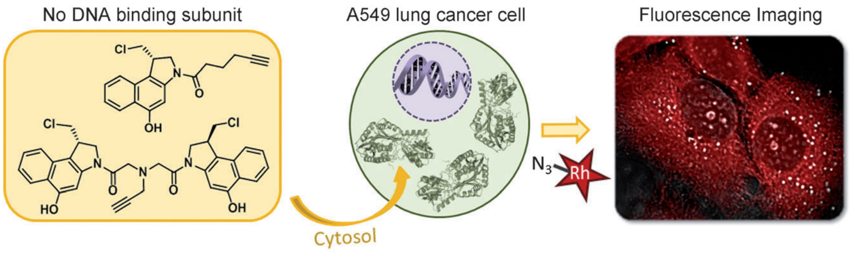


The fastest and the brightest: A new design that intimately connects tetrazine to a BODIPY fluorophore enables exceptionally efficient energy transfer and quenching. Upon reaction of the tetrazine, the brightness of the fluorophore increases more than a thousand-fold, which is a fluorogenic activation up to two orders of magnitude greater than previously described.

Antitumor Agents

T. Wirth, G. F. Pestel, V. Ganal, T. Kirmeier,
I. Schuberth, T. Rein, P. L. F. Tietze,*
P. S. A. Sieber* ____________ 6921 – 6925

The Two Faces of Potent Antitumor Duocarmycin-Based Drugs: A Structural Dissection Reveals Disparate Motifs for DNA versus Aldehyde Dehydrogenase 1 Affinity



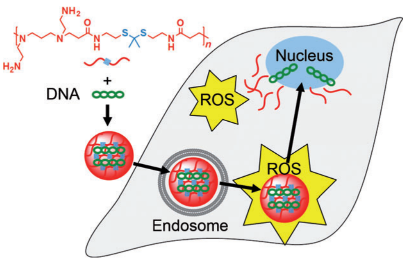
Duocarmycin-derived seco-cyclopropabenzindole (CBI) drugs have been shown to bind DNA and an aldehyde dehydrogenase (ALDH1A1) in lung cancer cells. The removal of the DNA-binding indole moiety results in a CBI compound that does not bind to DNA in whole cells but still exhibits remarkable cytotoxicity. This CBI compound has an increased affinity for ALDH1A1. Rh = rhodamine.

Targeted Delivery

M. S. Shim, Y. Xia* ____________ 6926 – 6929

A Reactive Oxygen Species (ROS)-Responsive Polymer for Safe, Efficient, and Targeted Gene Delivery in Cancer Cells

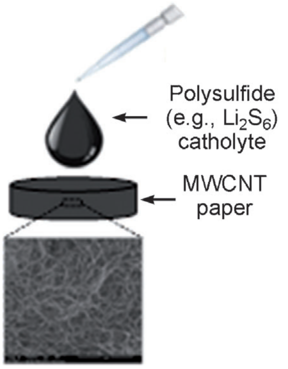
Stimuli-responsive release: The high levels of reactive oxygen species (ROS) in prostate cancer cells can be exploited to trigger cancer-targeted gene delivery. A ROS-responsive thioketal-based cationic polymer was synthesized and functionalization with a cancer-targeting peptide led to selective and enhanced gene transfection in prostate cancer cells (see scheme).



Lithium–Sulfur Batteries

Y. Fu, Y.-S. Su,
A. Manthiram* ____________ 6930 – 6935

Highly Reversible Lithium/Dissolved Polysulfide Batteries with Carbon Nanotube Electrodes

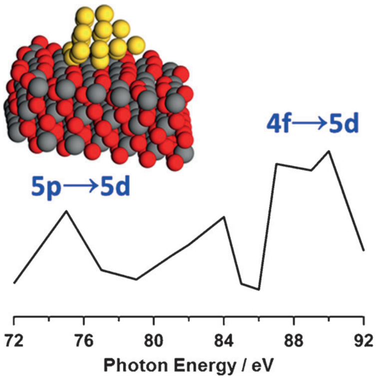


On paper: A lithium/dissolved polysulfide cell is developed utilizing a self-weaving, free-standing multiwalled carbon nanotube (MWCNT) "paper" as a host for the dissolved polysulfide active material and the reaction products. Exceptionally high capacities of 1600 mAh g^{-1} initially and 1411 mAh g^{-1} after 50 cycles (based on the mass of sulfur) are obtained at a rate of C/10.

Gold Catalysts

Y. Zhou, N. J. Lawrence, L. Wang, L. Kong, T.-S. Wu, J. Liu, Y. Gao, J. R. Brewer, V. K. Lawrence, R. F. Sabirianov, Y.-L. Soo, X. C. Zeng, P. A. Dowben, W. N. Mei, C. L. Cheung* ______ **6936 – 6939**

Resonant Photoemission Observations and DFT Study of s–d Hybridization in Catalytically Active Gold Clusters on Ceria Nanorods

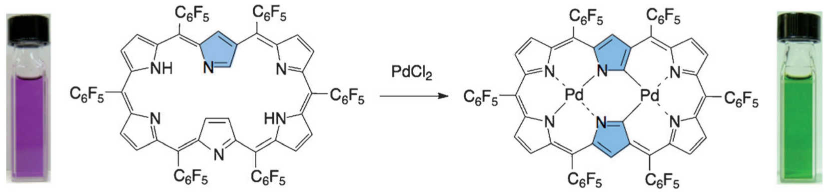


Up shift: 6s–5d hybridization and the up-shift of the 5d band to the Fermi level is demonstrated in catalytically active gold clusters on a cerium oxide nanorod support by using resonant photoemission spectroscopy and density functional theory modeling. These results help to explain the high catalytic activity of this system in CO oxidation.

Expanded Porphyrins

S. Gokulnath, K. Nishimura, M. Toganoh, S. Mori, H. Furuta* ______ **6940 – 6943**

Palladium-Induced Pyrrolic Rearrangement of a Singly to a Doubly N-Confused [26]Hexaphyrin

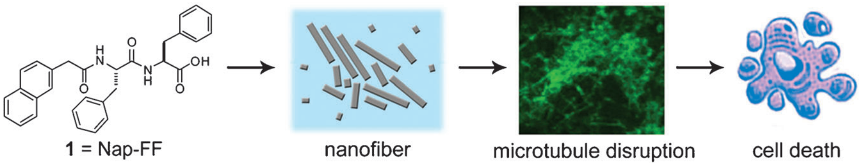


A pyrrolic rearrangement reaction of singly N-confused [26]hexaphyrin mediated by $PdCl_2$ afforded doubly N-confused [26]hexaphyrin bis(Pd^{II}) complex. The bis(Pd^{II}) complex is a rare example of an aromatic compound with definite non-degenerate HOMOs and LUMOs.

Anticancer Nanofibers

Y. Kuang, B. Xu* ______ **6944 – 6948**

Disruption of the Dynamics of Microtubules and Selective Inhibition of Glioblastoma Cells by Nanofibers of Small Hydrophobic Molecules

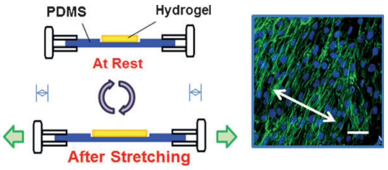


Ganging up against the bad guys: Nanofibers of **1** efficiently inhibited the growth of glioblastoma cells but exhibited little acute toxicity toward a neuronal cell line. The selective cytotoxicity probably stems from the Warburg effect of cancer cells and the existence of microtubule-stabilizing proteins in neurons. Supramolecular nanofibers that can interrupt the self-organization of proteins may have potential as nanomedicines for the treatment of cancer.

Soft Material Chemistry

C. Cha, E. Antoniadou, M. Lee, J. H. Jeong, W. W. Ahmed, T. A. Saif, S. A. Boppart, H. Kong* ______ **6949 – 6952**

Tailoring Hydrogel Adhesion to Polydimethylsiloxane Substrates Using Polysaccharide Glue

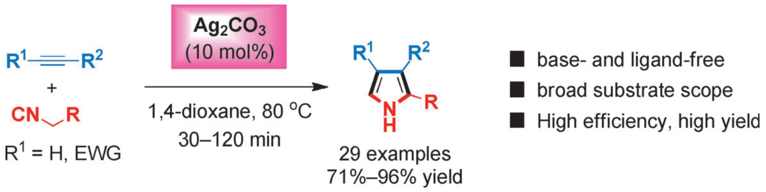


Hydrogel meets silicone: The chemical functionalization of a polydimethylsiloxane (PDMS) surface with polysaccharide “glue” induces a strong, permanent adhesion between the hydrogel and PDMS. This hydrogel-coated silicone substrate was useful for controlling cellular organization under mechanical stretching (see picture) and also in fabricating microfluidic devices filled with the gel.

Cycloaddition

J. Liu, Z. Fang, Q. Zhang,* Q. Liu, X. Bi* ——— 6953 – 6957

Silver-Catalyzed Isocyanide-Alkyne Cycloaddition: A General and Practical Method to Oligosubstituted Pyrroles

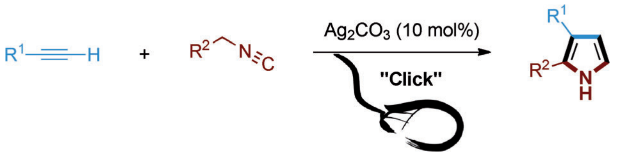


Ag$_2$CO$_3$ is the key: The transition-metal-catalyzed cycloaddition of isocyanides and unactivated terminal alkynes has been realized with Ag$_2$CO$_3$ as a unique and robust catalyst (see scheme). The protocol is highly efficient, allowing a broad range of terminal and internal alkynes to react under base- and ligand-free conditions, generating synthetically useful oligosubstituted pyrroles in high yields.

Cycloaddition

M. Gao, C. He, H. Chen, R. Bai, B. Cheng, A. Lei* ——— 6958 – 6961

Synthesis of Pyrroles by Click Reaction: Silver-Catalyzed Cycloaddition of Terminal Alkynes with Isocyanides

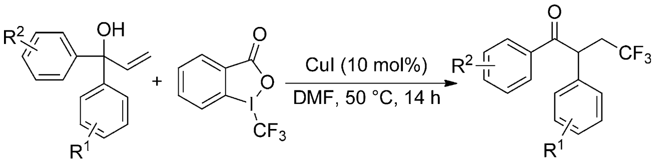


Just click with silver: Pyrroles are prepared by the co-cyclization of terminal alkynes and isocyanides in a silver-catalyzed click reaction. This route represents an extremely simple, efficient, and atom-economic approach to substituted pyrroles in good yields with high selectivity, thus complementing the click method for the rapid formation of multifunctional heterocycles.

Trifluoromethylation

X. Liu, F. Xiong, X. Huang, L. Xu, P. Li,* X. Wu* ——— 6962 – 6966

Copper-Catalyzed Trifluoromethylation-Initiated Radical 1,2-Aryl Migration in α,α-Diaryl Allylic Alcohols



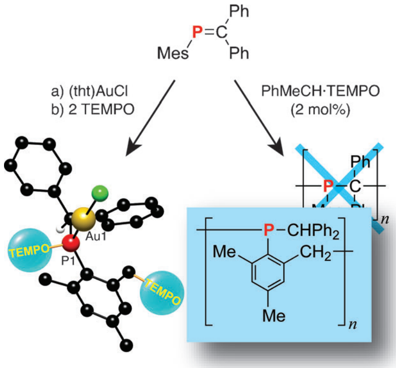
Not only symmetrical, but also unsymmetrical α,α-diaryl allylic alcohols are employed as substrates in the title reaction. A number of arenes and even heteroarenes underwent radical 1,2-aryl migration ("neophyl rearrangement") to produce α-aryl β-trifluoromethyl ketones. The preferential migration of electron-deficient aryl groups over electron-rich ones in unsymmetrical substrates supports the radical mechanism, which was further confirmed by DFT calculations.

Phosphorus Polymers

P. W. Siu, S. C. Serin, I. Krummenacher, T. W. Hey, D. P. Gates* ——— 6967 – 6970

Isomerization Polymerization of the Phosphaalkene MesP=CPh$_2$: An Alternative Microstructure for Poly(methylenephosphine)s

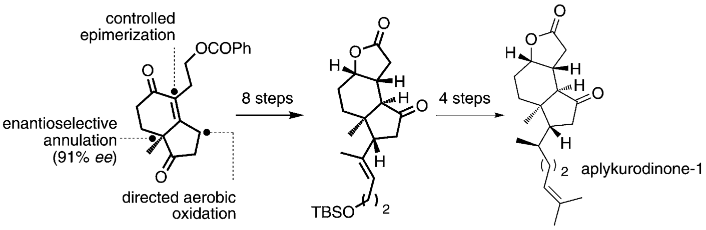
Unique pathway: The radical-initiated addition polymerization of MesP=CPh$_2$ propagates through the *ortho*-bound CH$_3$ group of the Mes moiety after C–H bond activation (see scheme, Mes = 2,4,6-trimethylphenyl, tht = tetrahydrothiophene, TEMPO = 2,2,6,6-tetramethyl-l-piperidinoxyl). This unique isomerization polymerization mechanism contrasts the previously suggested head-to-tail enchainment typically observed for olefins.



Natural Products

P. A. Peixoto, A. Jean, J. Maddaluno,
M. De Paolis* ________ **6971 – 6973**

Formal Enantioselective Synthesis of Aplykurodinone-1



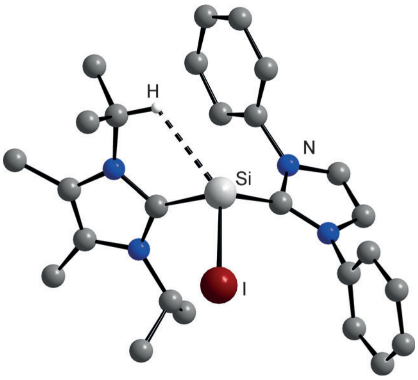
Step economy and simplicity were combined in the asymmetric formal synthesis of aplykurodinone-1 (see scheme; TBS = *tert*-butyldimethylsilyl). The key features of the strategy involve a one-pot aerobic and directed oxidation/deoxygenation and a late-stage controlled epimerization to form the chiral architecture of the molecule.

Ionic Silicon(II) Compounds

A. C. Filippou,* Y. N. Lebedev, O. Chernov,
M. Straßmann,
G. Schnakenburg ________ **6974 – 6978**

Silicon(II) Coordination Chemistry: N-Heterocyclic Carbene Complexes of Si^{2+} and SiI^{+}

Ligand swap: The exchange of N-heterocyclic carbene (NHC) ligands at Si^{II} centers is shown to provide access to a dicationic NHC complex of silicon(II), and an NHC adduct of the iodosilyliumylidene cation SiI^{+}, $[SiI(IiPr_2Me_2)(IDipp)]^{+}$ (see picture). Characterization studies led to the discovery of an unprecedented C–H···Si anagostic interaction for $[SiI(IiPr_2Me_2)(IDipp)]^{+}$.



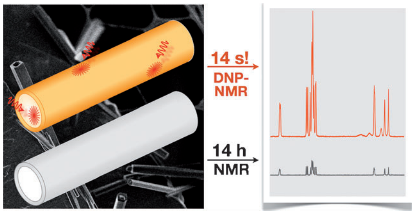
Peptide Nanoassemblies

VIP

H. Takahashi, B. Viverge, D. Lee,
P. Rannou, G. De Paëpe* ____ **6979 – 6982**

Towards Structure Determination of Self-Assembled Peptides Using Dynamic Nuclear Polarization Enhanced Solid-State NMR Spectroscopy

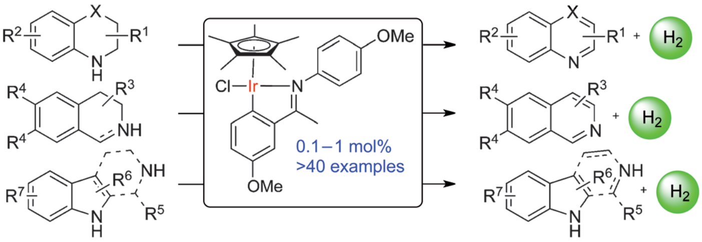
Supra-sensitivity: Dynamic nuclear polarization (DNP) enhanced solid-state NMR spectroscopy was performed on self-assembled peptide nanotubes. This approach yields significant experimental time savings (about five orders of magnitude; see picture) and was used to exemplify the feasibility of supramolecular structural studies of organic nanoassemblies at an atomic scale using DNP-enhanced solid-state NMR spectroscopy.



Synthetic Methods

J. Wu, D. Talwar, S. Johnston, M. Yan,
J. Xiao* ________ **6983 – 6987**

Acceptorless Dehydrogenation of Nitrogen Heterocycles with a Versatile Iridium Catalyst

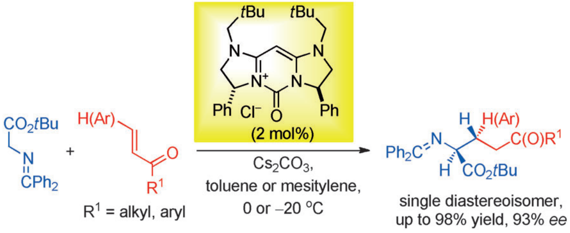


Gas up: A cyclometalated iridium complex is found to catalyze the dehydrogenation of various benzofused N-heterocycles, thus releasing H_2. Driven by as low as 0.1 mol% catalyst, the reaction affords quinolines, indoles, quinoxalines, isoquinolines, and β-carbolines in high yields.

Asymmetric Synthesis

A. E. Sheshenev, E. V. Boltukhina,
A. J. P. White, K. K. Hii* ____ **6988 – 6991**

Methylene-Bridged Bis(imidazoline)-Derived 2-Oxopyrimidinium Salts as Catalysts for Asymmetric Michael Reactions

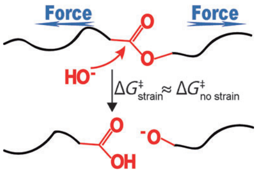


In nothing flat: The title salts, having planar nitrogen centers, were utilized successfully as phase-transfer catalysts for asymmetric Michael reactions of *tert*-butyl glycinate benzophenone Schiff base with vinyl ketone and chalcone derivatives, thus providing excellent levels of diastereo- and enantiocontrol (see scheme).

Kinetics

S. Akbulatov, Y. Tian, E. Kapustin,
R. Boulatov* ____________ **6992 – 6995**

Model Studies of the Kinetics of Ester Hydrolysis under Stretching Force



Experiments and computations are reported of how stretching a polymer containing an ester moiety affects the kinetics of its basic hydrolysis (see picture). DFT computations of complete conformational ensembles of three homologous esters suggest that a stretching force stabilizes the tetrahedral intermediate and the second transition state (TS) but has no effect on the relative energy of the first TS.

DOI: 10.1002/anie.201303901

50 Years Ago ...

Angewandte Chemie International Edition was first published in 1962, the mother journal first in 1888. In this monthly flashback, we feature some of the articles that appeared 50 years ago. This look back can open our eyes, stimulate discussion, or even raise a smile.

The first Review in the July 1963 issue was by T. Wieland and H. Determann, who summarized the developments in solution-phase peptide synthesis from 1959–1962, including protecting groups and methods of coupling. The Review was well-timed, as July 1963 marked a turning point in peptide chemistry when R. B. Merrifield published his seminal paper on solid-phase peptide synthesis and revolutionized the field.

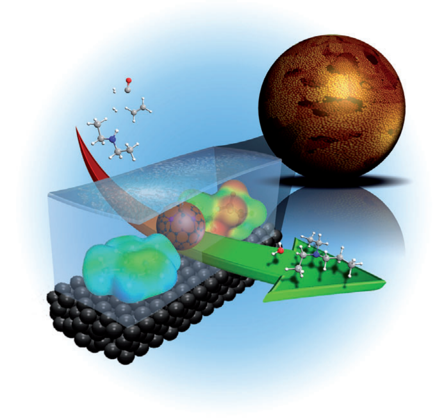
Armin Weiss and co-workers published two Communications: the first reported the isolation of pure $BaSi_2$ by melting Ba and Si followed by slow cooling. The Si atoms in $BaSi_2$ formed discrete Si_4 tetrahedra rather than forming layers, which are formed in $CaSi_2$. The second paper dealt with the structure of $Co(CN)_2$. As both the hydrated and anhydrous forms have a cubic structure, it was postulated that large cavities must be present in the anhydrous form, which can form inclusion or zeolitic compounds with a wide range of polar guests. The three-dimensional framework cannot accommodate molecules with diameters greater than 3.6 Å and thus acts as a molecular sieve.

Georg Wittig reported on the preparation of azatriptycene in a Communication. The target compound was prepared by a ring-closing reaction that took place when treating 9-*o*-chlorophenyl-9,10-dihydroacridine with KNH_2 in liquid ammonia.

The Conference Report covered some highlights from the South-West German section of the Division of Food and Forensic Chemistry of the Gesellschaft Deutscher Chemiker (GDCh; German Chemical Society). Among the topics presented were the investigation of inks in ballpoint pen samples, and the detection of sweetened, fortified, and diluted wines to confirm if so-called top-quality wines really were the real thing.

Read more in Issue 6/1963

Just SILP-ing through: Hydroaminomethylation of ethylene and diethylamine to diethylpropylamine is demonstrated as a continuous gas-phase reaction (see picture) using a supported ionic liquid phase (SILP) to immobilize the applied homogenous Rh-Xantphos catalyst. Highly selective and long-term stable (18 days) catalyst operation was obtained if the ionic liquid was of low basicity and lipophilicity combined with a porous activated carbon support.



Supported Catalysts

M. J. Schneider, M. Lijewski, R. Woelfel,
M. Haumann,
P. Wasserscheid* ________ **6996–6999**

Continuous Gas-Phase Hydroaminomethylation using Supported Ionic Liquid Phase Catalysts

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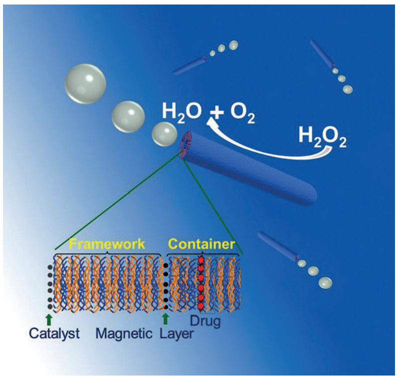
Nanotransporters: Self-assembled polymer multilayer nanorockets based on a template-assisted layer-by-layer technique can self-propel by chemical power, namely hydrogen peroxide degradation. They can perform drug loading, targeted transportation, and triggered drug release by an external physical stimuli in a controlled manner.



Autonomous Nanopropulsion

Z. Wu, Y. Wu, W. He, X. Lin, J. Sun,
Q. He* ________ **7000–7003**

Self-Propelled Polymer-Based Multilayer Nanorockets for Transportation and Drug Release

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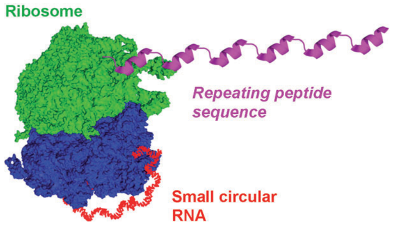
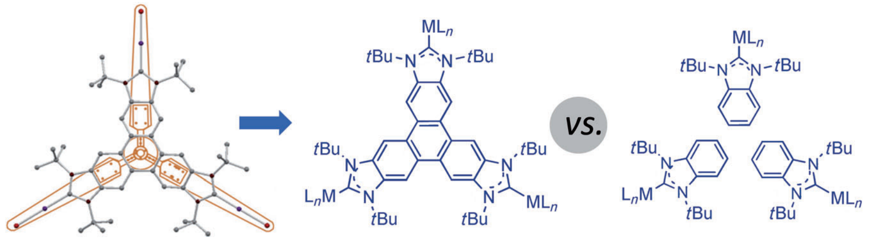


Getting the runaround: Small circular RNA molecules containing an infinite open reading frame were synthesized and tested in an *E. coli* cell-free translation system. A circular RNA 126 nucleotides in length was found to produce more product than its linear counterpart by two orders of magnitude, because a ribosome can work more effectively towards the elongation on circular RNA than it can on linear RNA in this continuous peptide synthesis.

Continuous Translation Reaction

N. Abe, M. Hiroshima, H. Maruyama,
Y. Nakashima, Y. Nakano, A. Matsuda,
Y. Sako, Y. Ito,* H. Abe* ____ **7004–7008**

Rolling Circle Amplification in a Prokaryotic Translation System Using Small Circular RNA



Triple play: A novel triphenylene-based tris(N-heterocyclic carbene) ligand with D_{3h} symmetry and a highly π-delocalized system has been prepared and coordinated to palladium and gold (see figure). The catalytic activities of the new complexes have been compared with those of related benzimidazolylidene and a triptycene-based tris(N-heterocyclic carbene) complexes in three reactions.

Homogeneous Catalysis

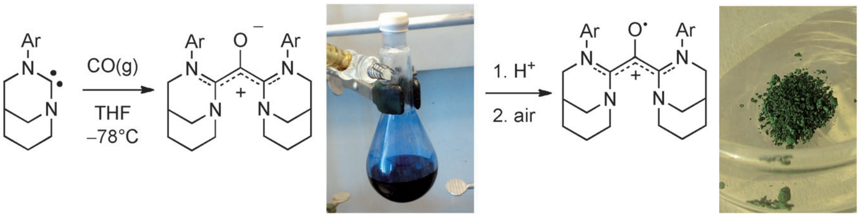
S. Gonell, M. Poyatos,
E. Peris* ________ **7009–7013**

Triphenylene-Based Tris(N-Heterocyclic Carbene) Ligand: Unexpected Catalytic Benefits

Stable Radicals

D. Martin, C. E. Moore, A. L. Rheingold,
G. Bertrand* ________ **7014–7017**

An Air-Stable Oxyallyl Radical Cation



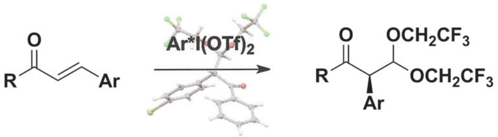
Easy does it! Simply take two carbenes, add carbon monoxide, then HCl, and open the flask to air, and an oxyallyl radical cation is formed.

Stereoselective Rearrangement

U. Farid, F. Malmedy, R. Claveau,
L. Albers, T. Wirth* ________ **7018–7022**

Stereoselective Rearrangements with Chiral Hypervalent Iodine Reagents

Inside Cover

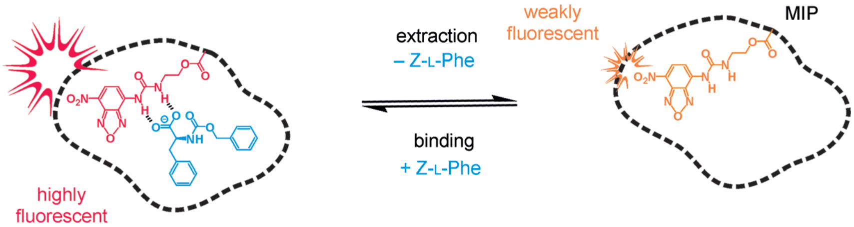


I likes rearrangements: Hypervalent iodine compounds can be used as environmentally friendly, mild, and selective reagents for highly enantioselective rearrangements of alkenes. For the first time, rearrangements to α-arylated ketones can be performed enantioselectively using lactic acid-based iodine(III) reagents.

Sensor Particles

W. Wan, M. Biyikal, R. Wagner,
B. Sellergren,* K. Rurack* __ **7023–7027**

Fluorescent Sensory Microparticles that "Light-up" Consisting of a Silica Core and a Molecularly Imprinted Polymer (MIP) Shell



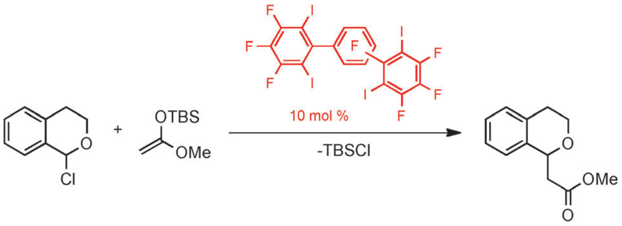
From darkness came light: Incorporation of urea-based fluorescent dyes in an anion-imprinted thin polymer shell coated onto silica microparticles leads to a unique and highly enantioselective fluorescent "light-up" response to analytes (see scheme, MIP molecularly imprinted polymer).

Halogen Bonds

F. Kniep, S. H. Jungbauer, Q. Zhang,
S. M. Walter, S. Schindler,
I. Schnapperelle, E. Herdtweck,
S. M. Huber* ________ **7028–7032**

Organocatalysis by Neutral Multidentate Halogen-Bond Donors

Front Cover

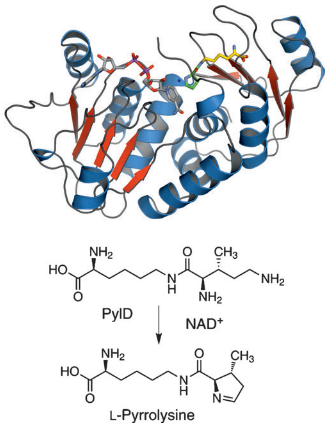


I(n)organocatalysis: Neutral multidentate halogen-bond donors (halogen-based Lewis acids) catalyze the reaction of 1-chloroisochroman with ketene silyl acetals. The organocatalytic activity is linked to the presence (and number as well as orientation) of iodine substituents. As hidden acid catalysis can be ruled out with high probability, this case constitutes strong evidence for halogen-bond based organocatalysis. TBS = *tert*-butyldimethylsilyl.

Pyrrolysine Biosynthesis

F. Quitterer, P. Beck, A. Bacher,
M. Groll* ——— **7033 – 7037**

Structure and Reaction Mechanism of Pyrrolysine Synthase (PylD)

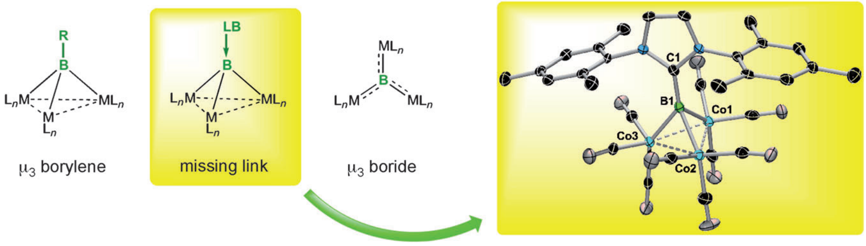


The final step in the biosynthesis of the 22nd genetically encoded amino acid, pyrrolysine, is catalyzed by PylD, a structurally and mechanistically unique dehydrogenase. This catalyzed reaction includes an induced-fit mechanism achieved by major structural rearrangements of the N-terminal helix upon substrate binding. Different steps of the reaction trajectory are visualized by complex structures of PylD with substrate and product.

Boron Ligands

P. Bissinger, H. Braunschweig,*
A. Damme, T. Kupfer,
K. Radacki ——— **7038 – 7041**

An Electron-Precise, Tetrahedral μ$_3$ Boride Complex



Boron at the top: Reaction of *I*Mes·BBr$_3$ (*I*Mes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) with Na[Co(CO)$_4$] afforded the trimetalloboride [(CO)$_9$Co$_3$(μ$_3$-B·*I*Mes)] with high selectivity. This species has a tetrahedral geometry with an electron-precise bonding situation, which is uncommon for a μ$_3$ boride complex. It can be considered the missing link between a tetrahedral μ$_3$ borylene (nonclassical) and planar μ$_3$ boride (electron-precise) complexes.

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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