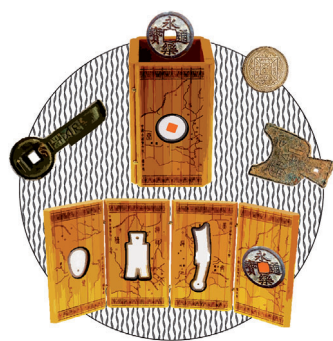
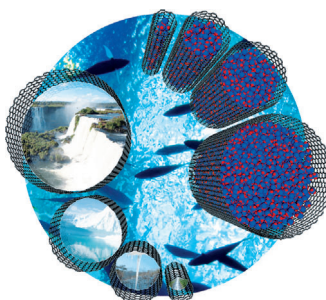




... such as Teflon and hydrophilic polymer surfaces can prevent protein adhesion to generate protein-resistant surfaces. The Review by R. Haag et al. on page 8004 ff. describes methods and recent advances in the field of protein interactions on polymeric materials. The cover picture illustrates the adsorption of proteins (egg white) to material surfaces as exemplified by the egg in the pan. (Graphic designed by Achim Wiedekind with a background picture by Ruben Haag.)

Hydrogen Bonds

In his Communication on page 8032 ff., T. Ohba describes the anomalous structure of water in carbon nanotubes. In nanotubes with diameters of 2 and 3 nm, water forms clusters because of prolific hydrogen bonding.

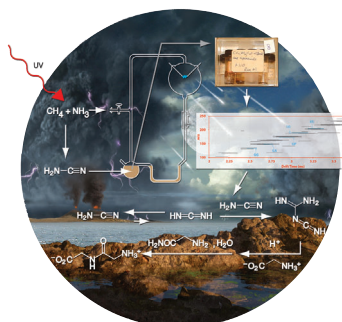


DNA Origami Nanostructures

In their Communication on page 8137 ff., M. Endo, H. Sugiyama, H. Mao et al. report DNA origami nanostructures that were used as expanded platforms for multiplex mechanochemical sensing.

Prebiotic Chemistry

From an analysis of archived samples from Stanley Miller's previously unreported 1958 cyanamide experiment, F. M. Fernández, J. L. Bada et al. show in their Communication on page 8132 ff. that cyanamide enhances amino acid polymerization under prebiotic conditions.



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Service

Spotlight on Angewandte's Sister Journals

7980 – 7983

Author Profile



"My greatest achievement is hopefully still to come from an unexpected observation.

I lose track of time whenever I'm playing Bach ..."

This and more about Nuno Maulide can be found on page 7984.

Nuno Maulide _____ 7984

News



T. W. Ebbesen



S. W. Hell



J. B. Pendry



S. I. Stupp



C.-S. Hsu

Kavli Prize in Nanoscience:

T. W. Ebbesen, S. W. Hell,
J. B. Pendry _____ 7985

SPSJ International Awards:

S. I. Stupp and C.-S. Hsu _____ 7985

Books

Microwaves in Nanoparticle Synthesis

Satoshi Horikoshi, Nick Serpone

reviewed by P.-X. Gao _____ 7986

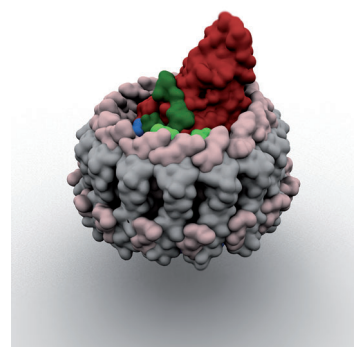
Highlights

Photosynthesis

O. Einsle* ————— 7988 – 7990

Connecting Photosynthetic Light
Harvesting and Charge Separation at
Higher Detail

Beside the unique reaction center, efficient organismic photosynthesis requires additional arrays of chromophores to harvest photons and direct them by resonance energy transfer to the interspersed sites of charge separation. A crystal structure of the complex of a bacterial reaction center with light-harvesting complex I now reveals new details on how the storage ring interacts with and connects to the site of charge separation.



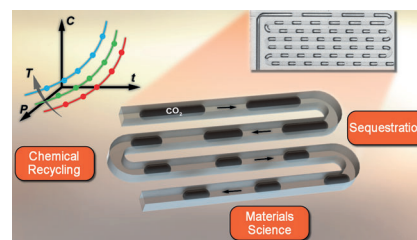
Minireviews

Segmented-Flow Microfluidics

M. Abolhasani, A. Günther,
E. Kumacheva* ————— 7992 – 8002

Microfluidic Studies of Carbon Dioxide

Utilizing greenhouse gas: Microfluidics offers numerous advantages in studies of CO₂-related processes, including physical and chemical capturing of CO₂ and its recycling into valuable products. This Minireview highlights recent progress in this area.

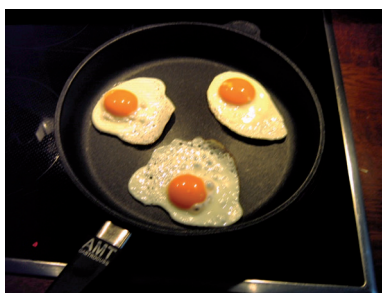


Reviews

Protein-Resistant Surfaces

Q. Wei, T. Becherer, S. Angioletti-Uberti,
J. Dzubiella, C. Wischke, A. T. Neffe,
A. Lendlein, M. Ballauff,
R. Haag* ————— 8004 – 8031

Protein Interactions with Polymer
Coatings and Biomaterials



The prevention of protein interactions plays a major role in everyday life, for example on common Teflon surfaces. This review focuses on recent developments in analytical, biochemical, and theoretical techniques that lead to a better understanding of polymeric biomaterials for applications as bioinert and biospecific surface coating materials in biomedical systems.



Front Cover

For the USA and Canada:

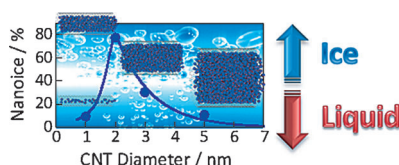
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electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

Communications

Ice-like water clusters: Water in carbon nanotubes with a diameter of 1 nm had fewer hydrogen bonds than bulk water under ambient conditions. In carbon nanotubes with diameters of 2 and 3 nm, water formed cluster structures even under ambient conditions, because of prolific hydrogen bonding. The critical cluster size is 0.8–3.4 nm; that is, the fundamental size of a cluster is 0.8 nm.

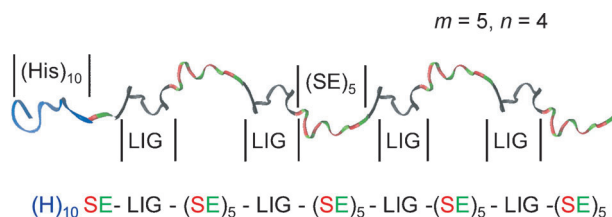


Water

T. Ohba* _____ 8032–8036

Size-Dependent Water Structures in Carbon Nanotubes

Frontispiece



Quantity and spacing: A protein-engineering approach was designed to develop monodisperse polyvalent molecules based on tandem-repeat polypeptide scaffolds. This approach allowed for

precise control over ligand spacing and valency of the polyvalent molecules. This approach was applied to develop potent inhibitors of anthrax lethal toxin.

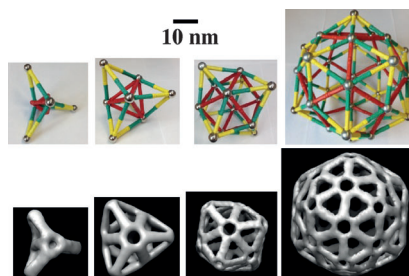
Polyvalent Inhibitors

S. Patke, M. Boggara, R. Maheshwari, S. K. Srivastava, M. Arha, M. Douaisi, J. T. Martin, I. B. Harvey, M. Brier, T. Rosen, J. Mogridge, R. S. Kane* _____ 8037–8040

Design of Monodisperse and Well-Defined Polypeptide-Based Polyvalent Inhibitors of Anthrax Toxin



(Versa)tile DNA: In a directed DNA self-assembly strategy, directing tiles (yellow) and assembly tiles (red/green) were employed to control the assembly pathway of DNA nanostructures. This approach enables the rational design and assembly of a range of complex DNA nanocages, including bipyramids and Kleitopes of polyhedra. The structures produced were thoroughly characterized by gel electrophoresis and cryogenic electron microscopy.



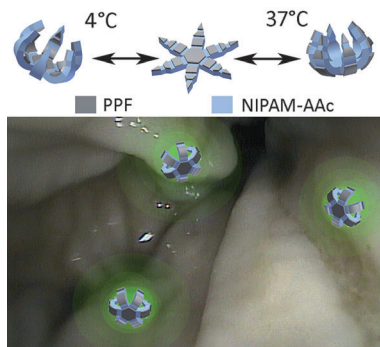
Nanostructures

C. Tian, X. Li, Z. Liu, W. Jiang, G. Wang,* C. Mao* _____ 8041–8044

Directed Self-Assembly of DNA Tiles into Complex Nanocages



Thermoresponsive polymeric grippers for controlled drug release (“theragrippers”) close spontaneously above 32 °C and grip onto tissue. They were loaded with drugs mesalamine and doxorubicin, which eluted for up to 7 days. Theragrippers show improved site-specific delivery and offer a novel strategy for sustained release with immediate applicability in the gastrointestinal tract.



Drug Delivery

K. Malachowski, J. Breger, H. R. Kwag, M. O. Wang, J. P. Fisher, F. M. Selaru, D. H. Gracias* _____ 8045–8049

Stimuli-Responsive Theragrippers for Chemomechanical Controlled Release

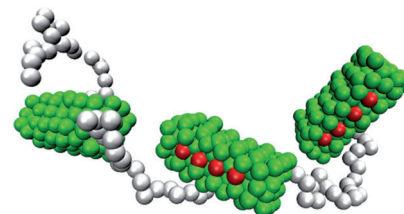




Macroscopic Objects

S. Averick, O. Karácsy, J. Mohin,
X. Yong, N. M. Moellers, B. F. Woodman,
W. Zhu, R. A. Mehl, A. C. Balazs,*
T. Kowalewski,*
K. Matyjaszewski* ————— **8050–8055**

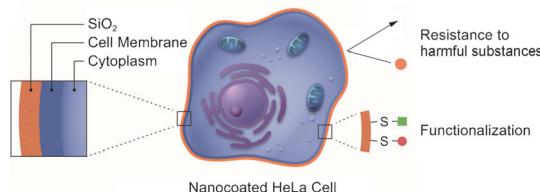
Protein oligomers, prepared from diazido GFP (green fluorescent protein) and dialkyne PEO (poly(ethylene oxide)), self-assemble into micrometer scale objects. The dynamics of protein assembly were elucidated and the driving force for fiber formation is the discrete interactions of hydrophobic residues on GFP.



Cooperative, Reversible Self-Assembly of
Covalently Pre-Linked Proteins into Giant
Fibrous Structures

Cell Coating

J. Lee, J. Choi, J. H. Park, M.-H. Kim,
D. Hong, H. Cho, S. H. Yang,*
I. S. Choi* ————— **8056–8059**

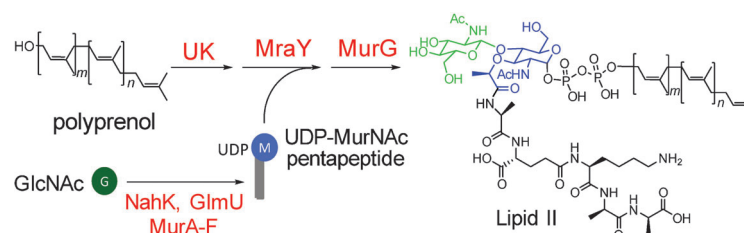


Safety glass: Several types of mammalian cells, namely HeLa cells, NIH 3T3 fibroblasts, and Jurkat cells, are individually coated with silica through bioinspired silicification. The fabrication processes

are highly cytocompatible, thus leading to minimal loss of viability, and the silica coating confers protection against harmful substances, such as trypsin and poly-(allylamine hydrochloride).

Synthetic Methods

L.-Y. Huang, S.-H. Huang, Y.-C. Chang,
W.-C. Cheng, T.-J. R. Cheng,*
C.-H. Wong* ————— **8060–8065**



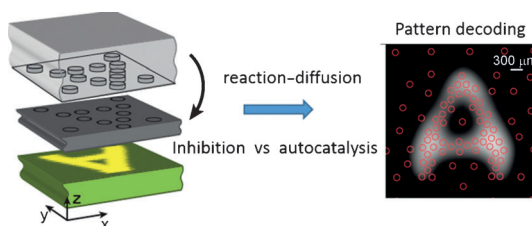
Hum with activity: Described in this study is a practical enzymatic method for the synthesis of lipid II, coupled with cofactor regeneration, to give the product in 50–

70% yield. This method was further applied to the synthesis of lipid II analogues, the activities of which were evaluated for bacterial transglycolase.



Biochemical Networks

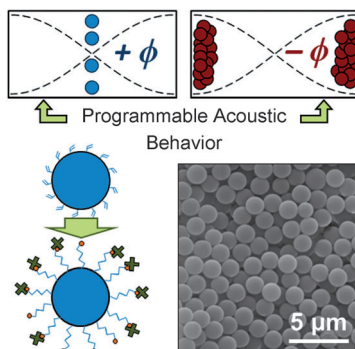
S. N. Semenov, A. J. Markvoort,
T. F. A. de Greef,
W. T. S. Huck* ————— **8066–8069**



Mixed signals: A wet stamping method was used to precisely control the concentrations of enzymes and inhibitors in place and time inside layered gels. By coupling diffusion from spatially well-

defined sources and enzymatic reactions such as autocatalysis and inhibition inside a hydrogel, a complex biochemical network that is capable of threshold sensing was constructed.

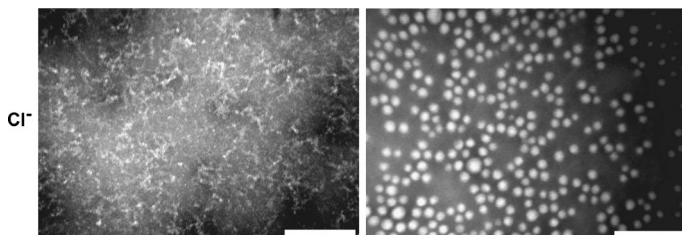
Hear ye, hear ye! A class of functional, monodisperse, and acoustically programmable (FMAP) particles produced by nucleation and growth bulk synthesis is presented. This approach for synthesizing silicone gel particles enables direct programmability of properties for versatile control in acoustofluidic systems for bio-sensing and sorting applications.



Elastomeric Particles

C. W. Shields IV, D. Sun, K. A. Johnson, K. A. Duval, A. V. Rodriguez, L. Gao, P. A. Dayton, G. P. López* — 8070–8073

Nucleation and Growth Synthesis of Siloxane Gels to Form Functional, Monodisperse, and Acoustically Programmable Particles



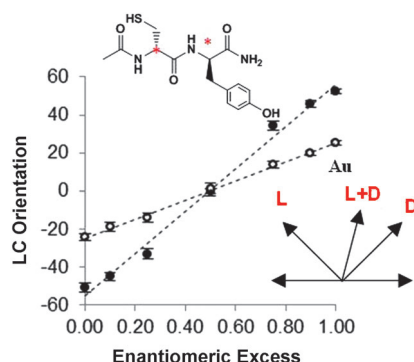
Unexpected: The micellization of protonated polymers at low pH values is surprisingly induced by chaotropic (ClO_4^-) instead of kosmotropic (Cl^-) anions. This

behavior follows an anti-Hofmeister trend, as it is contrary to the effects of these anions in protein solubilization.

Micellization

Y. Li, Y. Wang, G. Huang, X. Ma, K. Zhou, J. Gao* — 8074–8078

Chaotropic-Anion-Induced Supramolecular Self-Assembly of Ionic Polymeric Micelles



The orientations of liquid crystals (LCs) anchored on monolayers formed from mixtures of chiral versus achiral molecules were compared. Changes in the enantiomeric excess of mixed monolayers of chiral dipeptides gave rise to continuous changes in the orientations of nematic LCs, allowing arbitrary tuning of their azimuthal orientations. In contrast, the same LCs exhibited discontinuous changes in orientation on surfaces presenting mixtures of achiral molecules.

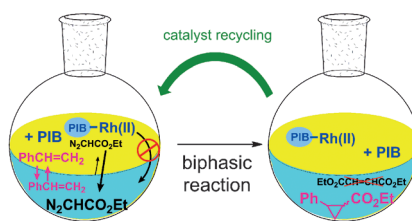
Chirality and Surfaces

Y. Bai, R. Abbasi, C. Wang, N. L. Abbott* — 8079–8083

Liquid Crystals Anchored on Mixed Monolayers of Chiral versus Achiral Molecules: Continuous Change in Orientation as a Function of Enantiomeric Excess



Suppression of by-product: In biphasic heptane/ CH_3CN mixtures, heptane-soluble polyisobutylene (PIB)-bound Rh^{II} cyclopropanation and O–H insertion catalysts form only modest amounts of the undesired carbene dimer. It was shown that the phase isolation of these catalysts is enhanced by the addition of a polyolefin oligomer cosolvent, which acts as anti-leaching agent and minimizes the leaching of the PIB-bound species into the polar phase in liquid/liquid separations.



Polymers as Antileaching Agents

Y. Liang, M. L. Harrell, D. E. Bergbreiter* — 8084–8087

Using Soluble Polymers to Enforce Catalyst-Phase-Selective Solubility and as Antileaching Agents to Facilitate Homogeneous Catalysis

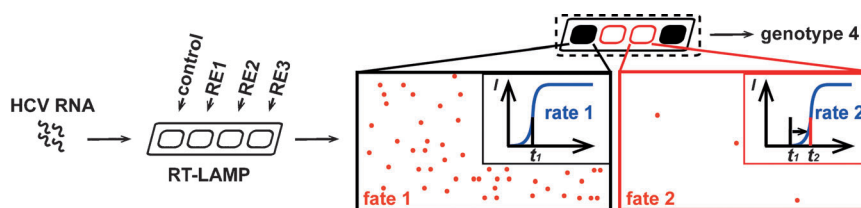


Genotyping

B. Sun, J. Rodriguez-Manzano,
D. A. Selck, E. Khorosheva,
M. A. Karymov,
R. F. Ismagilov* — 8088 – 8092



Measuring Fate and Rate of Single-Molecule Competition of Amplification and Restriction Digestion, and Its Use for Rapid Genotyping Tested with Hepatitis C Viral RNA



Rate or fate? Competition among reverse transcription, exponential amplification, and linear degradation was monitored at the single-molecule level and used for rapid genotyping of the hepatitis C virus. End-point digital measurements were

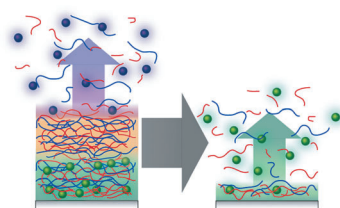
primarily sensitive to changes in “fate” of single molecules, but bulk real-time kinetic measurements were dominated by the rate of amplification of the earliest molecules.

Sequential Protein Delivery

B. B. Hsu, K. S. Jamieson,
S. R. Hagerman, E. Holler, J. Y. Ljubimova,
P. T. Hammond* — 8093 – 8098



Ordered and Kinetically Discrete Sequential Protein Release from Biodegradable Thin Films



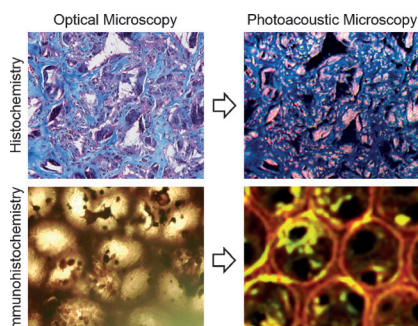
Taking turns: Inclusion of covalent and copper-free click chemistry in layer-by-layer thin films during assembly generates sequential release behavior without modification of the protein itself. Increasingly thick barrier layers deposited on protein-containing layers delay the onset of protein release, which can be harnessed to generate well-defined sequential protein release with minimal overlap.

Biomedical Imaging

Y. S. Zhang, J. Yao, C. Zhang, L. Li,
L. V. Wang,* Y. Xia* — 8099 – 8103



Optical-Resolution Photoacoustic Microscopy for Volumetric and Spectral Analysis of Histological and Immunochemical Samples



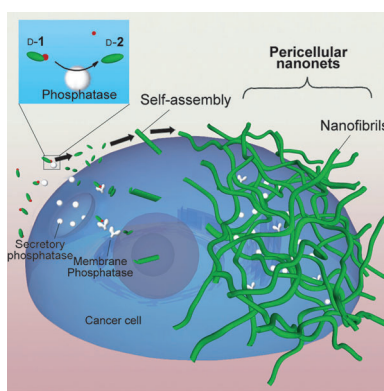
Seeing not seen before: The quantitative analysis of biological samples after (immuno)histochemical staining has been achieved by optical-resolution photoacoustic microscopy. In addition to the three-dimensional imaging capability, components with different absorption spectra could be readily separated by collecting images at different wavelengths.

Cancer Cell Apoptosis

Y. Kuang, J. Shi, J. Li, D. Yuan, K. A. Alberti,
Q. Xu, B. Xu* — 8104 – 8107



Pericellular Hydrogel/Nanonets Inhibit Cancer Cells



A small D-peptide derivative is reported to form fibrils and nanonets in the pericellular space. The pericellular nanonets encapsulate cancer cells, which not only prohibits cell adhesion but also selectively induces cancer cell apoptosis. This is the first example of synthetic peptides to achieve biological function through formation of nanonets.

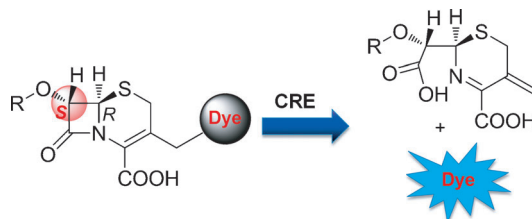


Chemistry is a language: Formal analysis confirms Lehn's analogy between chemistry and a natural language. English language patterns and the structural motifs of organic molecules follow the same statistics. The methods of computational linguistics can thus be applied to organic molecules to identify characteristic, information-rich patterns defining symmetry/repeat sub-units and bonds amenable to retrosynthetic disconnections.

Chemical Linguistics

A. Cadeddu, E. K. Wylie, J. Jurczak, M. Wampler-Doty, B. A. Grzybowski* — 8108–8112

Organic Chemistry as a Language and the Implications of Chemical Linguistics for Structural and Retrosynthetic Analyses



No more hiding: A series of fluorogenic probes based on stereochemically modified cephalosporin were developed and are specific for carbapenem-resistant *Enterobacteriaceae* (CRE). Data collected using recombinant β -lactamase enzymes

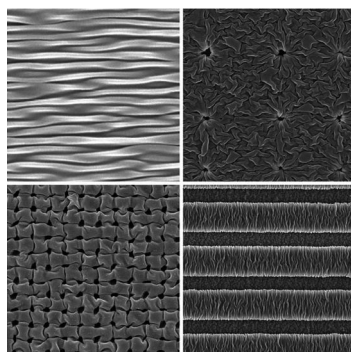
and live bacterial species show, for the first time, that these probes can be potentially used for specific detection of carbapenemases, especially metallo- β -lactamase-active bacterial pathogens.

Fluorescent Probes

H. Shi, Y. Cheng, K. H. Lee, R. F. Luo, N. Banaei, J. Rao* — 8113–8116

Engineering the Stereochemistry of Cephalosporin for Specific Detection of Pathogenic Carbapenemase-Expressing Bacteria

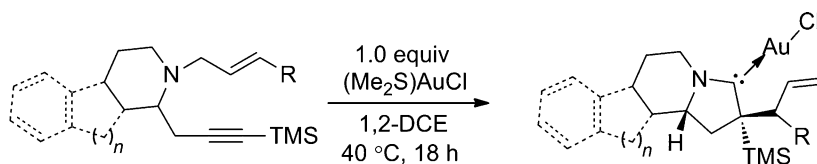
Gaining the upper hand on wrinkles: In a process to create nanowrinkles with control over their amplitude and orientation, the patterning of strain distribution in the top skin layer of a polymer substrate produced ordered structures from disordered structures. Representative types of nanotextured surfaces include (clockwise from top left) 1D nanowrinkles, directed nanowrinkles, directed nanofolds, and hierarchical directed 1D nanowrinkles.



Nanopatterns

M. D. Huntington, C. J. Engel, T. W. Odom* — 8117–8121

Controlling the Orientation of Nanowrinkles and Nanofolds by Patterning Strain in a Thin Skin Layer on a Polymer Substrate



Golden opportunities: A cyclization–rearrangement cascade of different 1,7-enynes triggered by the addition of $(\text{Me}_2\text{S})\text{AuCl}$ provides facile access to structurally unique chiral cyclic alkyl ami-

nocarbene–gold(I) complexes in high yields. These novel complexes are catalytically active and display biologic activity against cancer cell lines.

Gold Complexes

F. Kolundžić, A. Murali, P. Pérez-Galán, J. O. Bauer, C. Strohmann, K. Kumar,* H. Waldmann* — 8122–8126

A Cyclization–Rearrangement Cascade for the Synthesis of Structurally Complex Chiral Gold(I)–Aminocarbene Complexes

Antibiotic Nanoparticles

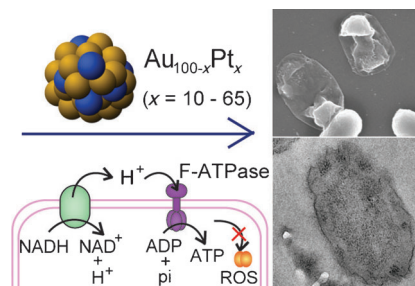


Y. Zhao, C. Ye, W. Liu, R. Chen,
X. Jiang* ————— 8127–8131



Tuning the Composition of AuPt
Bimetallic Nanoparticles for Antibacterial
Application

No side-effect: Bimetallic nanoparticles of AuPt are potent antibiotic reagents with low cytotoxicity. The antibiotic mechanism includes the rupture in the bacterial inner membrane and the increase of intracellular adenosine triphosphate levels, but does not involve the generation of reactive oxygen species (see picture).



Inside Cover

Prebiotic Chemistry

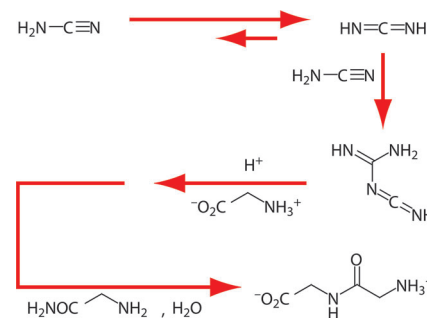


E. T. Parker, M. Zhou, A. S. Burton,
D. P. Glavin, J. P. Dworkin,
R. Krishnamurthy, F. M. Fernández,*
J. L. Bada* ————— 8132–8136



A Plausible Simultaneous Synthesis of
Amino Acids and Simple Peptides on the
Primordial Earth

Prebiotic polymerization: Archived samples from Stanley Miller's previously unreported 1958 cyanamide experiment were investigated to evaluate cyanamide-mediated amino acid polymerization under prebiotic conditions. Aqueous heating experiments indicate that in the presence of an amino acid amide, the dimerization of cyanamide under the mildly basic conditions of the spark-discharge experiment significantly enhances polymerization reactions.



Back Cover

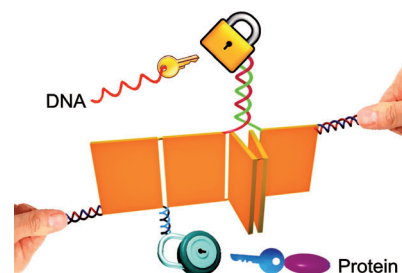
Mechanochemical Sensing Devices



D. Koirala, P. Shrestha, T. Emura,
K. Hidaka, S. Mandal, M. Endo,*
H. Sugiyama,* H. Mao* — 8137–8141

Single-Molecule Mechanochemical
Sensing Using DNA Origami
Nanostructures

DNA origami nanostructures were used as expanded platforms for multiplex mechanochemical sensing with improved throughput at the single-molecule level. Topological rearrangements of the DNA origami nanoassemblies in response to the binding of specific targets were monitored in real time by using optical tweezers.



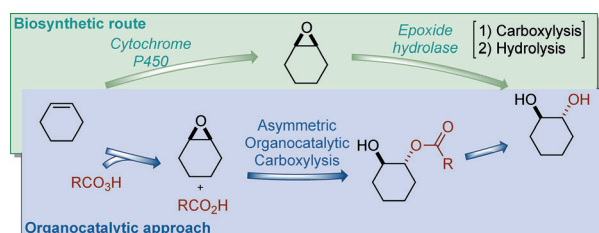
Inside Back Cover

Asymmetric Catalysis



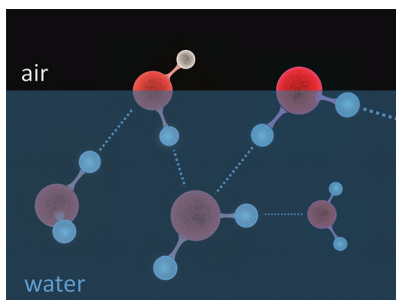
M. R. Monaco, S. Prévost,
B. List* ————— 8142–8145

Organocatalytic Asymmetric Hydrolysis of
Epoxides



The natural strategy: Carboxylic acids were activated with chiral phosphoric acid catalysts and the mechanism of epoxide hydrolase served as a model for the asymmetric hydrolysis of *meso*-epoxides.

This method was coupled with the Prilezhaev oxidation and the subsequent hydrolysis of the ester moiety to provide the first highly enantioselective *anti*-dihydroxylation of simple olefins.



Lonesome water: In contrast to bulk water, water molecules at the air/water interface are remarkably heterogeneous. Two-dimensional sum-frequency generation spectroscopy shows that weakly hydrogen-bonded water molecules at the interface are largely decoupled from the bulk.

Interfacial Heterogeneity

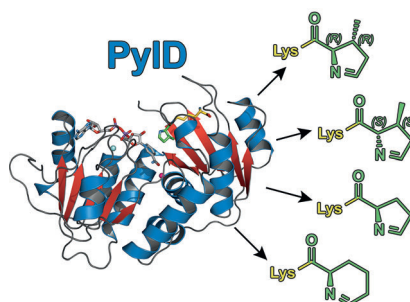


C.-S. Hsieh, M. Okuno, J. Hunger, E. H. G. Backus, Y. Nagata, M. Bonn* — 8146–8149

Aqueous Heterogeneity at the Air/Water Interface Revealed by 2D-HD-SFG Spectroscopy



PyID is the ultimate enzyme in the biosynthesis of the 22nd proteinogenic amino acid pyrrolysine. The structurally and mechanistically unique dehydrogenase exhibits broad substrate specificity, which can be exploited for the formation of pyrroline and tetrahydropyridine rings in a diverse set of amino acids. Thus, the system presents an attractive prospect for the *in vivo* incorporation of pyrrolysine analogues into defined target proteins.



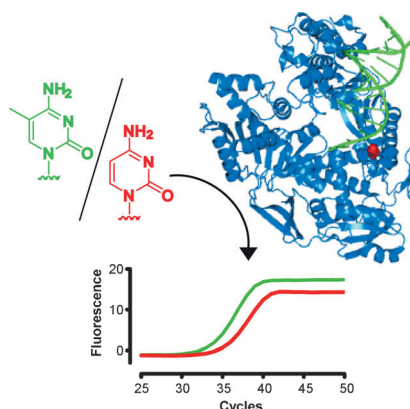
Pyrrolysine Analogues

F. Quitterer, P. Beck, A. Bacher, M. Groll* — 8150–8153

The Formation of Pyrroline and Tetrahydropyridine Rings in Amino Acids Catalyzed by Pyrrolysine Synthase (PyID)



Delicate: The thermostable DNA polymerases KlenTaq and KOD exo- were found to sense 5-methylcytosine (5mC) in primer-extension experiments from mismatched primers. On this basis, a DNA polymerase mutant with advanced 5mC-detection capabilities was generated and successfully applied in a methylation-specific PCR approach directly from untreated human genomic DNA.



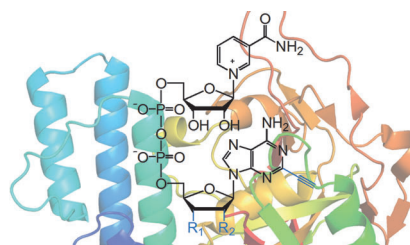
DNA Methylation

J. Aschenbrenner, M. Drum, H. Topal, M. Wieland, A. Marx* — 8154–8158

Direct Sensing of 5-Methylcytosine by Polymerase Chain Reaction



Stop and Click: Poly(ADP-ribosylation) is a complex posttranslational modification of proteins that is carried out by ADP-ribosyltransferases (ARTs) with the use of NAD⁺. In order to tackle the complexity of the modification, which often hampers subsequent analysis, we developed new NAD⁺ analogues that are substrates for wild-type ARTs but act as chain terminators and allow labeling through click chemistry.



ADP-Ribosylation

Y. Wang, D. Rösner, M. Grzywa, A. Marx* — 8159–8162

Chain-Terminating and Clickable NAD⁺ Analogues for Labeling the Target Proteins of ADP-Ribosyltransferases



C–H Amination

S. Manna, K. Matcha,
A. P. Antonchick* — 8163–8166

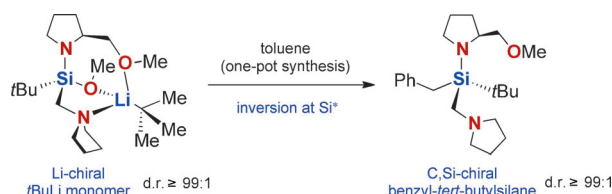


Disappearing Me: A novel selective annulation between 2-aminopyridine derivatives and arenes under metal-free conditions provides the important pyrido[1,2-*a*]benzimidazole scaffold under

mild reaction conditions. In this intermolecular reaction the methyl group of methylbenzenes serves as a traceless, non-chelating, and highly regioselective directing group.

Silicon/Lithium-Centered Chirality

J. O. Bauer, C. Strohmann* — 8167–8171

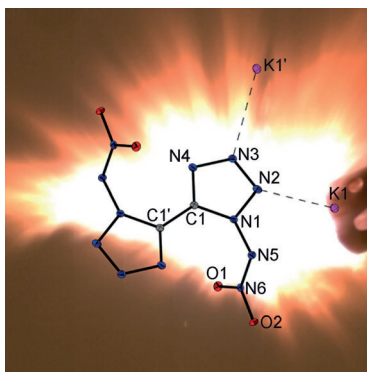


Well-balanced reactivity is shown for a silicon-chiral *tert*-butyl-substituted amino-methoxysilane possessing an additional nitrogen donor function in the geminal position to silicon. This silane transfers its

stereochemical information onto the lithium atom of a *t*BuLi molecule, forming a monomeric [methoxysilane-*t*BuLi] adduct with a tetrameric and asymmetrically coordinated lithium atom.

Energetic Materials

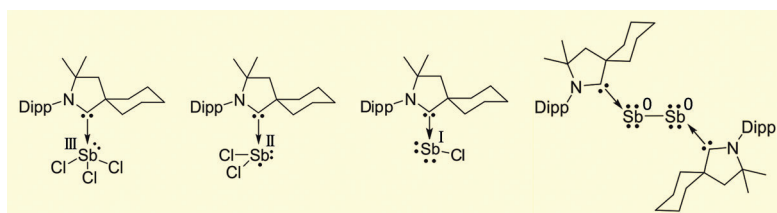
D. Fischer, T. M. Klapötke,*
J. Stierstorfer — 8172–8175



Fast and furious: The picture shows the moment of detonation of the new primary explosive potassium 1,1'-dinitramino-5,5'-bistetrazolate, which can be synthesized by a safe and sustainable procedure. It shows faster detonation with greater initiation power than lead azide while simultaneously being environmentally compatible.

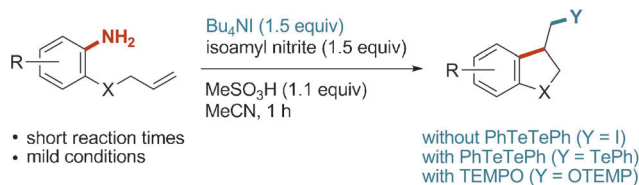
Carbene–Antimony Adducts

R. Kretschmer, D. A. Ruiz, C. E. Moore,
A. L. Rheingold,
G. Bertrand* — 8176–8179



3..2..1..0: The stepwise reduction of a cyclic alkyl(amino)carbene–SbCl₃ complex yields three different antimony species in the formal oxidation states of two, one, and zero. The one-electron reduction

delivers the first neutral antimony-centered radical in solution. The radical and the three other compounds were characterized by EPR spectroscopy and X-ray crystallography, respectively.



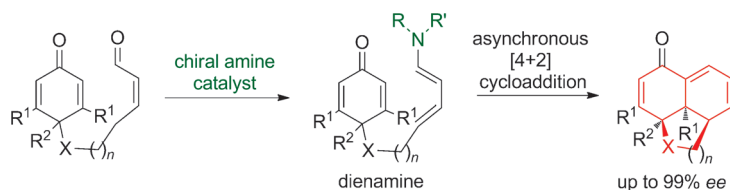
Tamed radicals: The carboiodination of anilines leads to the corresponding cyclized iodoes. The aryl diazonium salts generated in situ react with I^- ions to give the corresponding aryl radicals, which are

cyclized and trapped. When the reaction is conducted in the presence of TEMPO and PhTePh, the respective carboaminoxylated and phenyltellurated cyclized products are obtained.

Radical Cyclizations

M. Hartmann, A. Studer* — 8180–8183

Cyclizing Radical Carboiodination, Carbottelluration, and Carboaminoxylation of Aryl Amines



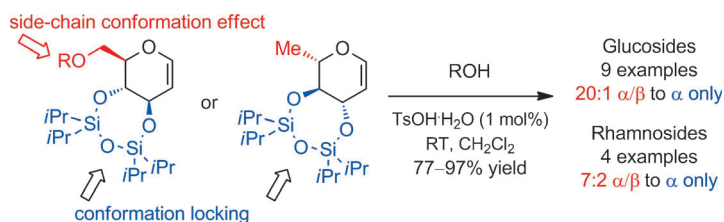
Breaking the mirror: In an asymmetric synthesis of tricyclic compounds containing a heterocyclic ring by the desymmetrization of cyclohexadienones, a large variety of substituents at different positions of the cyclohexadienone were toler-

ated, and the size of the heterocyclic ring could be varied. DFT calculations showed that the reaction proceeds through an asynchronous [4+2] cycloaddition (see scheme).

Asymmetric Synthesis

C. Martín-Santos, C. Jarava-Barrera, S. del Pozo, A. Parra S. Díaz-Tendero, R. Mas-Ballesté, S. Cabrera, J. Alemán* — 8184–8189

Highly Enantioselective Construction of Tricyclic Derivatives by the Desymmetrization of Cyclohexadienones



Locked in: Glucals and rhamnals are converted into disaccharides or glycoconjugates with high α -selectivity and yields using *p*-toluenesulfonic acid ($\text{TsOH}\cdot\text{H}_2\text{O}$) as a catalyst. The glycosylation stereoselectivity arises from confor-

mational locking of the intermediate oxacarbenium cation by a 3,4-O-disiloxane protecting group. Glucals outperform rhamnals because the C6 side-chain conformation further augments the selectivity.

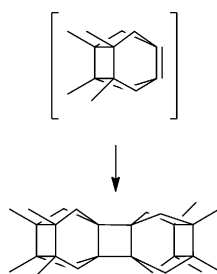
Synthetic Methods

E. I. Balmond, D. Benito-Alifonso, D. M. Coe, R. W. Alder, E. M. McGarrigle,* M. C. Galan* — 8190–8194

A 3,4-*trans*-Fused Cyclic Protecting Group Facilitates α -Selective Catalytic Synthesis of 2-Deoxyglycosides



Rock the boat: The dimerization of a highly pyramidalized alkene led to a nonacyclic compound featuring three planar cyclobutane rings, four cyclopentane rings, and four cyclohexane rings in boat conformations. In the cyclohexane rings, very short H–H and C–C distances were found between the flagpole hydrogen atoms and also between the flagpole carbon atoms.



Polycycles

M. Rey-Carrizo, M. Barniol-Xicota, M. Font-Bardia, S. Vázquez* — 8195–8199

Dimerization of Pyramidalized 3,4,8,9-Tetramethyltetracyclo [4.4.0.0^{3,9}.0^{4,8}]dec-1(6)-ene to a Hydrocarbon Featuring Four Cyclohexane Rings in Boat Conformations



Polyazides

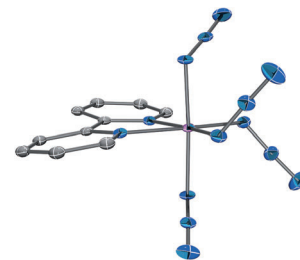
R. Haiges,* R. J. Buszek, J. A. Boatz,
K. O. Christe ——— 8200–8205



Preparation of the First Manganese(III)
and Manganese(IV) Azides

Put your differences azide:

$\text{Mn}(\text{N}_3)_3 \cdot \text{CH}_3\text{CN}$ was obtained from MnF_3 through fluoride–azide exchange with Me_3SiN_3 in CH_3CN solution. The reaction of $\text{Mn}(\text{N}_3)_3 \cdot \text{CH}_3\text{CN}$ with PPh_4N_3 or 2,2'-bipyridine (bipy) resulted in disproportionation reactions and the formation of 1:1 mixtures of $(\text{bipy})_2\text{Mn}(\text{N}_3)_2$ and $(\text{bipy})\text{Mn}(\text{N}_3)_4$ (see structure) or $[\text{PPh}_4]_2[\text{Mn}(\text{N}_3)_4]$ and $[\text{PPh}_4]_2[\text{Mn}(\text{N}_3)_6]$, respectively.



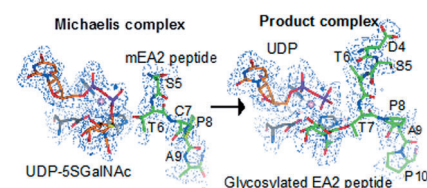
Catalytic Mechanisms

E. Lira-Navarrete, J. Iglesias-Fernández,
W. F. Zandberg, I. Compañón, Y. Kong,
F. Corzana, B. M. Pinto, H. Clausen,
J. M. Peregrina, D. J. Vocadlo, C. Rovira,*
R. Hurtado-Guerrero* ——— 8206–8210



Substrate-Guided Front-Face Reaction
Revealed by Combined Structural
Snapshots and Metadynamics for the
Polypeptide *N*-Acetylgalactosaminyl-
transferase 2

The magic of many moments: Structural snapshots of GalNAc-T2 complexes during the catalytic cycle were combined with quantum-mechanics/molecular-mechanics metadynamics to reveal an ordered bi–bi kinetic mechanism. Critical aspects of substrate recognition were identified that dictate the specificity for acceptor Thr versus Ser residues and enforce a front-face reaction in which the substrate *N*-acetyl sugar coordinates glycosyl transfer.



DOI: 10.1002/anie.201406704

Flashback: 50 Years Ago ...

Noble gas fluorides were first reported in 1962, and two years later progress in the field, including xenon difluoride, tetrafluoride, and higher fluorides, as well as krypton fluorides, were summarized in a Review by one of the protagonists, Rudolf Hoppe from the University of Giessen.

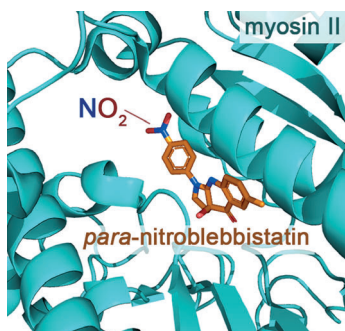
In another Review, Gottfried Schill discussed the directed synthesis of catena compounds (now more commonly known as catenanes). These interlocked ring systems were initially formed in very low yields in statistical reactions, however Schill and co-workers developed

a directed synthesis to avoid extra-annular ring closure.

Ernst Otto Fischer, who shared the 1973 Nobel Prize in Chemistry with Geoffrey Wilkinson, published a Communication on tungsten carbonyl carbene complexes. Reaction of $\text{W}(\text{CO})_6$ with LiC_6H_5 resulted in the formation of an orange crystalline compound $[\text{N}(\text{CH}_3)_4][\text{W}(\text{CO})_5\text{COC}_6\text{H}_5]$, which was protonated and methylated to give $\text{W}(\text{CO})_5(\text{COC}_6\text{H}_5)(\text{CH}_3)$ as diamagnetic orange-red crystals. $\text{W}(\text{CO})_5(\text{COCH}_3)(\text{CH}_3)$ was obtained when $\text{W}(\text{CO})_6$ was reacted with LiCH_3 in an analogous manner.

Margot Becke-Goehring reported on a pentavalent phosphorus–nitrogen compound. Reaction of aqueous methylammonium chloride with PCl_5 led to the formation of $\text{P}_4[\text{N}(\text{CH}_3)]_6\text{Cl}_8$, which was postulated to have a cage structure. Becke-Goehring was made Vice-Chancellor of the University of Heidelberg in 1966, and was the first woman appointed to such a role in a West German University.

[Read more in Issue 8/1964.](#)

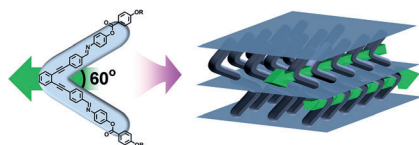


No side effects: Blebbistatin, the most popular myosin II inhibitor, is phototoxic, cytotoxic, and light sensitive. However, its C15 nitro analogue displays none of these side effects and maintains the specificity and inhibitory properties of the parent. Thus, *para*-nitroblebbistatin can replace blebbistatin both in vitro and in vivo.

Enzyme Inhibition

M. Képiró, B. H. Várkuti, L. Végner, G. Vörös, G. Hegyi, M. Varga, A. Málnási-Csizmadia* — 8211–8215

para-Nitroblebbistatin, the Non-Cytotoxic and Photostable Myosin II Inhibitor

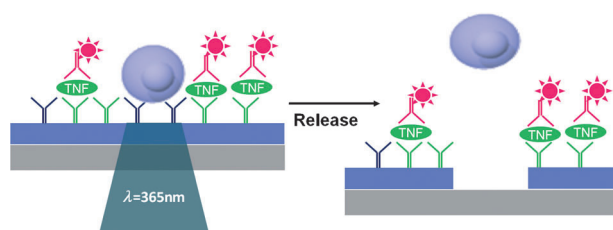


Switchable banana phases were induced by a liquid-crystal-forming molecule with a 60° angle. The molecules are effectively packed in the bent direction within the layer, irrespective of the acute shape. This system confirms the viability of ferro-switchable banana phases and also provides insights into the nature of structure–property relationships.

Liquid Crystals

E.-W. Lee, K. Takimoto, M. Tokita, J. Watanabe, S. Kang* — 8216–8220

Bent Molecules with a 60° Central Core Angle that Form B7 and B2 Phases



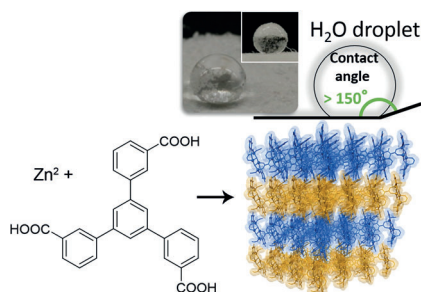
Function-based cell retrieval: The function-based sorting of live cells is enabled by a photodegradable poly(ethylene glycol) hydrogel. Hydrogel-coated substrates were used to isolate T-cells from

a heterogeneous mixture of immune cells, to analyze cytokine secretion on a cell-by-cell basis, and then to release cells that are actively producing cytokines. TNF = tumor necrosis factor.

Photodegradable Hydrogels

D.-S. Shin,* J. You, A. Rahimian, T. Vu, C. Siltanen, A. Ehsanipour, G. Stybayeva, J. Sutcliffe, A. Revzin* — 8221–8224

Photodegradable Hydrogels for Capture, Detection, and Release of Live Cells



A strong aversion to water: In an approach to water-resistant porous materials with a superhydrophobic surface without the use of alkylation or fluorination, a porous coordination polymer was synthesized with a low-symmetry nano-scale organic linker. The material exhibited superhydrophobicity (see picture) as a result of the surface corrugation created by the aromatic hydrocarbon and displayed selective uptake of organic molecules from water.

Coordination Polymers

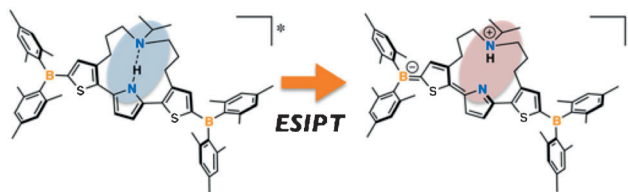
K. P. Rao, M. Higuchi, K. Sumida, S. Furukawa, J. Duan, S. Kitagawa* — 8225–8230

Design of Superhydrophobic Porous Coordination Polymers through the Introduction of External Surface Corrugation by the Use of an Aromatic Hydrocarbon Building Unit



Excited-State Design

N. Suzuki, A. Fukazawa, K. Nagura,
S. Saito, H. Kitoh-Nishioka, D. Yokogawa,
S. Irle,* S. Yamaguchi* — 8231–8235



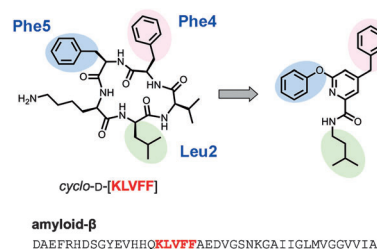
Hold on to the strap: A new type of excited-state intramolecular proton transfer (ESIPT) chromophores has been developed by incorporation of an amine-embedded alkyl strap into an emissive boryl-substituted dithienylpyrrole skele-

ton. The product's dual fluorescence covers a wide range in the visible region depending on the solvent polarity. The zwitterionic ESIPT state is efficiently stabilized by the aminoalkyl strap and the terminal boryl groups.

Amyloid Inhibitors

T. Arai, T. Araya, D. Sasaki, A. Taniguchi,
T. Sato, Y. Sohma,*
M. Kanai* — 8236–8239

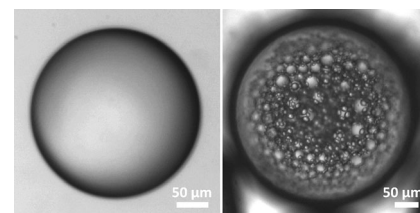
A unique pharmacophore motif for aggregation inhibitors of Alzheimer's amyloid β ($A\beta$), without the involvement of backbone amide moieties (see picture; right), was identified based on structure–activity relationship studies using *cyclo*-[KLVFF] (left). This allowed non-peptidic, small-molecule aggregation inhibitors to be designed that possess significant activity that is comparable to the parent cyclic peptides.



Emulsions

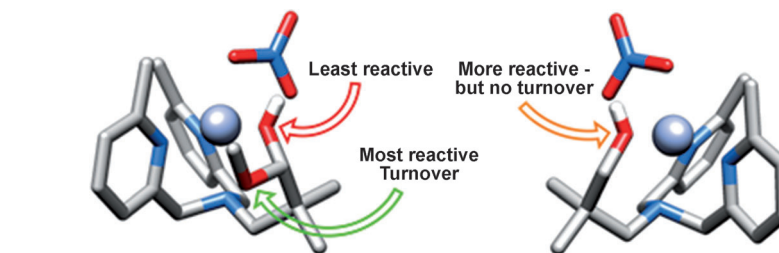
J. Bae, T. P. Russell,*
R. C. Hayward* — 8240–8245

Water-in-oil-in-water (w/o/w) double emulsions are spontaneously generated from o/w single emulsions by the osmotic pressure provided by salt species initially dispersed in the oil phase. This phenomenon provides a simple route to tailor block copolymer self-assembly, yielding multi-vesicular structures and hierarchically structured porous films after solvent evaporation.



Enzyme Models

E. Y. Tirel, Z. Bellamy, H. Adams,
V. Lebrun, F. Duarte,
N. H. Williams* — 8246–8250



Taking turns: Using an acetal as a ligand-based nucleophile generates a Zn complex capable of cleaving DNA-like phosphodiester with both turnover and unexpectedly enhanced reactivity. The pro-

posed mechanism involves a tautomer which combines a more effective Lewis acid with a more reactive nucleophile, and suggests a new strategy for creating more efficient metal-ion-based catalysts.



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



This article is accompanied by a cover picture (front or back cover, and inside or outside).



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



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The Hot Papers are articles that the Editors have chosen on the basis of the referee reports to be of particular importance for an intensely studied area of research.

Angewandte Corrigendum

In this Communication, reference compound **1-Ac** and intermediate **5-p** were used. While both compounds were reported initially in reference [12b] as cited, the detailed experimental protocols and spectroscopic data were published subsequently in reference [12c], which has to be added. The application of chiral oxaziridines for the stereoselective oxidation of phosphonates was published originally in reference [15a] as cited. The method has been applied to allyl phosphonates in another reference [15b], which has to be added.

References [12] and [15] should read as follows:

- [12] a) B. Müller, C. Schaub, R. R. Schmidt, *Angew. Chem.* **1998**, 110, 3021–3024; *Angew. Chem. Int. Ed.* **1998**, 37, 2893–2897; b) K. H. Jung, R. Schwörer, R. R. Schmidt, *Trends Glycosci. Glycotechnol.* **2003**, 15, 275–289; c) D. Skropeta, R. Schwörer, T. Haag, R. R. Schmidt, *Glycoconjugate J.* **2004**, 21, 205–219.
[15] a) D. Pogatchnik, D. Wiemer, *Tetrahedron Lett.* **1997**, 38, 3495–3498; b) D. Skropeta, R. R. Schmidt, *Tetrahedron: Asymmetry* **2003**, 14, 265–273.

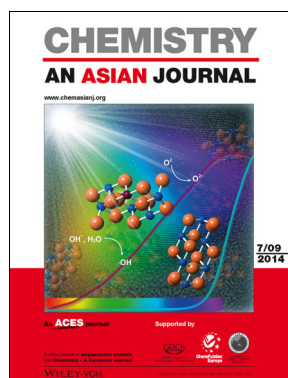
Fluorescent Mimetics of CMP-Neu5Ac Are Highly Potent, Cell-Permeable Polarization Probes of Eukaryotic and Bacterial Sialyltransferases and Inhibit Cellular Sialylation

J. J. Preidl, V. S. Gnanapragassam, M. Lisurek, J. Saupe, R. Horstkorte, J. Rademann* _____ **5700–5705**

Angew. Chem. Int. Ed. **2014**, 53

DOI: 10.1002/anie.201400394

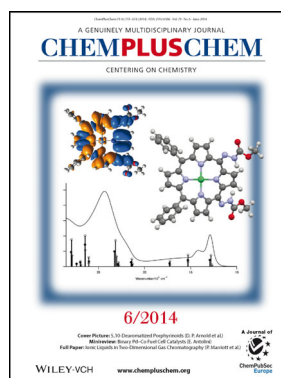
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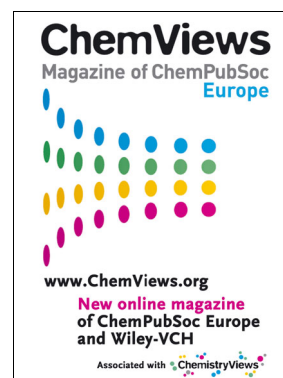
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