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:

M. J. D. Bosdet, W. E. Piers, T. S. Sorensen, M. Parvez*
10a-Aza-10b-borapyrenes: Heterocyclic Analogues of Pyrene with Internalized BN Moieties

M. Lingenfelder, G. Tomba, G. Costantini, L. C. Ciacchi, A. De Vita, K. Kern*
Tracking the Chiral Recognition of Adsorbed Dipeptides at the Single-Molecule Level

*H. Miyamura, R. Matsubara, Y. Miyazaki, S. Kobayashi**
Aerobic Oxidation of Alcohols at Room Temperature under Atmospheric Conditions Catalyzed by Reusable Gold Nanoclusters Stabilized by Benzene Rings of Polystyrene Derivatives

*A. Müller, R. Stürmer, B. Hauer, B. Rosche**
Stereospecific Alkyne Reduction: Novel Activity of Old Yellow Enzymes

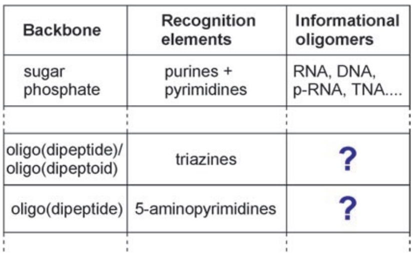
*A. Wakamiya, K. Mori, S. Yamaguchi**
3-Boryl-2,2'-bithiophene as a Versatile Core Skeleton for Full-Color Highly Emissive Organic Solids

*C. Defieber, M. A. Ariger, P. Moriel, E. M. Carreira**
Iridium-Catalyzed Synthesis of Primary Allylic Amines from Allylic Alcohols: Sulfamic Acid as an Ammonia Equivalent

News

Books

Highlights

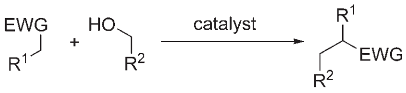


Backbone	Recognition elements	Informational oligomers
sugar phosphate	purines + pyrimidines	RNA, DNA, p-RNA, TNA....
oligo(dipeptide)/ oligo(dipeptoid)	triazines	?
oligo(dipeptide)	5-aminopyrimidines	?

A world of difference: The search for processes in which organic matter may be brought to life through self-organization is key in prebiotic chemistry. An experimental exploration of potentially primordial information-carrying oligomers differing from nucleic acids in both backbone and recognition elements is highlighted.

Prebiotic Chemistry

Minireviews



EWG = COR, CN, CO_2R, $CONR_2$, NO_2, CHOHR

... something new, something borrowed: The hydrogen autotransfer (borrowing) process involves a hydrogen abstraction/C–C coupling/hydrogen capture sequence for the alkylation of nucleophiles using primary alcohols as the source of electrophile (see scheme). The sequence proceeds with high chemical yields and atom efficiencies, with water as the only formal waste material produced.

Synthetic Methods

Contents

Reviews

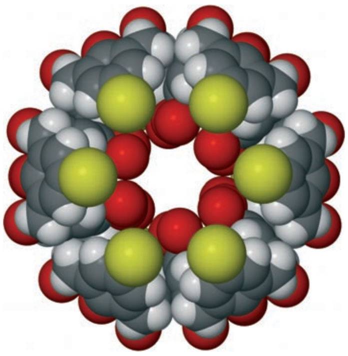
Molecular Recognition

Caught in the act: Supramolecular chemistry in aqueous media is not as violent as depicted in the scheme. However, as in natural aggregation processes, strongly bonded artificial host–guest complexes are formed in the presence of competing, polar solvents. There are numerous examples that illustrate the principles involved in the formation of the complex and the self-assembly events.

Communications

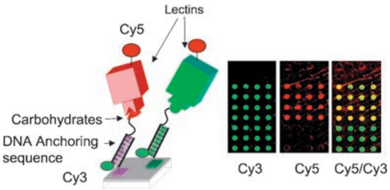
Calixarenes

Mmm, doughnuts! Six calix[4]arene molecules self-assemble into a large hexameric torus-shaped structure through hydrogen bonds (see picture; Br yellow, O red, C gray, H white). The doughnut assembly shows a noteworthy structural similarity to cucurbit[6]uril in the solid state and therefore may be viewed as a noncovalent analogue.



Carbohydrate Microarrays

When the chips are down: A glycoarray consisting of oligonucleotide/carbohydrate conjugates hybridized onto a DNA chip can be used for the immobilization of oligosaccharides at extremely low concentrations (1 µM). With lectin, the lower detection limit of the device was 2–20 nM. The relative surface density of the conjugates was monitored by Cy3 fluorescence.



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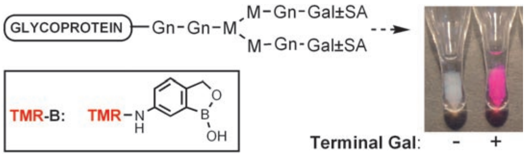

Lookin' for Gals: Treatment of a glycoprotein with β-galactosidase releases terminal galactose (Gal) that is captured on hydroxylaminated glass beads. The novel red fluorescent reagent TMR-B binds to the immobilized Gal rendering the beads bright red with the color intensity in proportion to the amount of captured Gal. Gln: GlcNAc, M: Man, SA: sialic acid, TMR: tetramethylrhodamine.

Glycosylation Analysis

M. D. Sørensen, R. Martins,
O. Hindsgaul* ———— 2403 – 2407

Assessing the Terminal Glycosylation of a Glycoprotein by the Naked Eye

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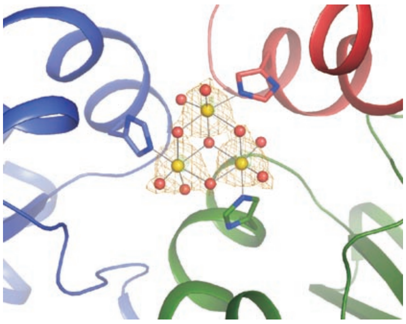


Create and protect: The cavity shell of a molybdenum/tungsten-storage protein acts as a polytopic host for several types of polyoxotungstate guests, which occur as individual clusters (one shown: yellow W, red O, ribbons protein) that are noncovalently or weakly bonded to the host. The formation of the guests is templated by the specific functionalities of the protein pockets.

Metal-Storage Proteins

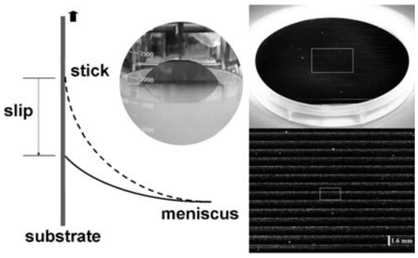
VIP

J. Schemberg, K. Schneider, U. Demmer,
E. Warkentin, A. Müller,*
U. Ermler* ———— 2408 – 2413

Towards Biological Supramolecular Chemistry: A Variety of Pocket-Templated, Individual Metal Oxide Cluster Nucleations in the Cavity of a Mo/W-Storage Protein

---

Dip, stick, slip: Dip coating, a widely used industrial process for making thin films, is used to align and position nanowires by means of the stick–slip motion of the solvent meniscus. Nanowire arrays with predefined spacing can be readily "printed" on a large substrate with tunable wire density (see picture), thus providing a facile method for producing nanowire-based devices.



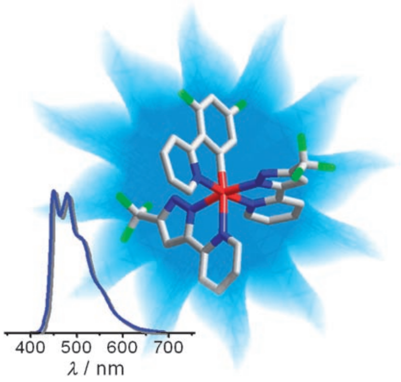
Patterning Techniques

J. Huang, R. Fan, S. Connor,
P. Yang* ———— 2414 – 2417

One-Step Patterning of Aligned Nanowire Arrays by Programmed Dip Coating

---

Dyed-in-the-wool true blue: True-blue phosphorescent organic light-emitting diodes are fabricated by using an Ir^{III} dopant (see picture; gray C; blue N; red Ir; green F). The Ir complex has an enhanced metal-to-ligand charge-transfer contribution, hence a shortened radiative lifetime in the excited state. The maximum external quantum efficiency of the fabricated device is 8.5 % and the main emission is around 450 nm.

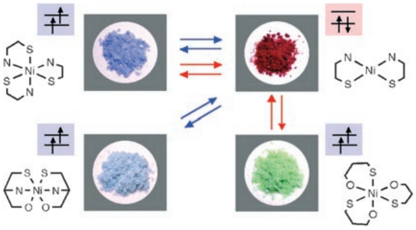


Luminescence

C.-H. Yang, Y.-M. Cheng, Y. Chi,* C.-J. Hsu,
F.-C. Fang, K.-T. Wong, P.-T. Chou,*
C.-H. Chang, M.-H. Tsai,
C.-C. Wu* ———— 2418 – 2421

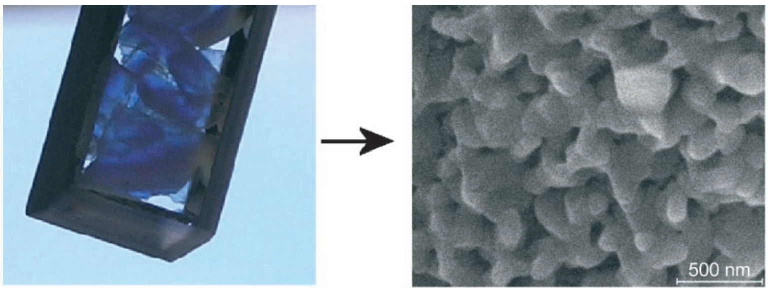
Blue-Emitting Heteroleptic Iridium(III) Complexes Suitable for High-Efficiency Phosphorescent OLEDs

Coordination Modes



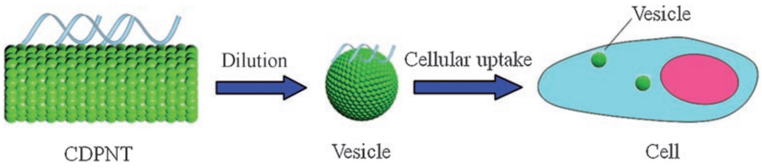
Red, blue, and green: A red Ni^{II}Au^{I} complex with a low-spin square-planar NiN_2S_2 configuration can be converted into a green high-spin octahedral NiO_3S_3 complex by lowering the pH (see scheme; pH change: red arrows). Increasing the Ni/Au ratio (Ni/Au change: blue arrows) gives a light blue octahedral $NiN_2O_2S_2$ complex; increasing the pH or decreasing the Ni/Au ratio gives a blue octahedral NiN_3S_3 configuration.

Organometallic Amphiphiles



A new kind of amphiphiles containing an organometallic headgroup, an alkyl zinc alkoxide, self-assembles to form [MeZnOPEG$_n$] gel (PEG: polyethylene glycol; $n = 400$; see picture, left), which in turn serves as a precursor to afford nanoporous ZnO (right).

Bionanotechnology

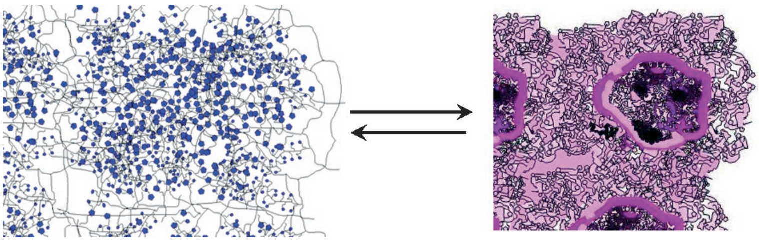


Password?—Vesicle! A cationic dipeptide can self-assemble into nanotubes at physiological pH values. Such self-assembled cationic dipeptide nanotubes (CDPNTs) are able to convert into vesicles spontaneously upon dispersion dilution and thus carry single-stranded DNA into HeLa cells across the biomembrane (see picture).

Helical Structures

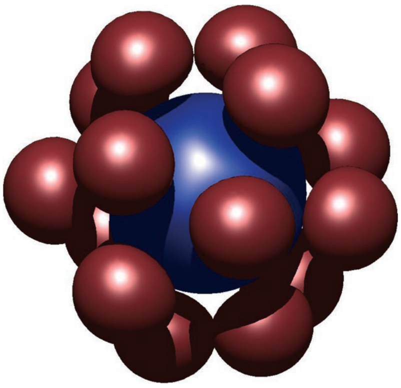
An unexpected twist: Three chiral amidine-functionalized strands and two benzenetricarboxylic acid molecules self-assemble into a 3:2 cylindrical complex with controlled helicity through amidinium–carboxylate salt-bridge formation. A related 4:2 cylindrical complex composed of two zinc porphyrin units and four chiral strands twists into one direction upon encapsulation of 4,4′-bipyridine through coordination to the zinc centers (see picture).

Porous Materials



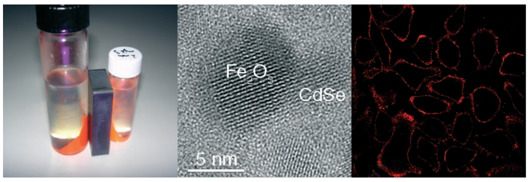
An open and closed case: Polymerization of microemulsions stabilized by surfactants based on ionic liquids leads to cross-linked polymer gels which can be transformed into porous polymers by anion exchange of the ionic liquid moiety. These porous polymers can be converted back into polymer gels by immersion in organic solvents. Subsequent immersion of these gels in water then affords the porous polymers once more (see scheme).

Coordination in the Gas Phase



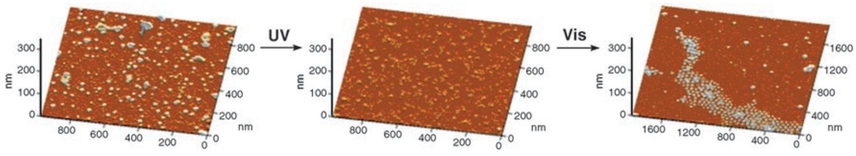
The Gregory–Newton problem of kissing hard spheres transferred to chemistry can be formulated as: what is the highest possible coordination number for an atom? First-principles quantum chemical simulations of the Pb^{2+}–He interactions revealed a remarkably stable $PbHe_{15}^{2+}$ with all He atoms in the first coordination sphere. The picture shows the HOMO of this ion.

Nanocomposites



Bifunctional nanocomposites comprising semiconductor and magnetic nanoparticles are of interest in biological applications for biolabeling, bioimaging, and cell separation. To this end, a nanocomposite system that consists of Fe_2O_3 magnetic nanoparticles and CdSe quantum dots and which exhibits superparamagnetism and tunable emission properties was prepared and used to label different live cell membranes (see picture).

Polymeric Micelles



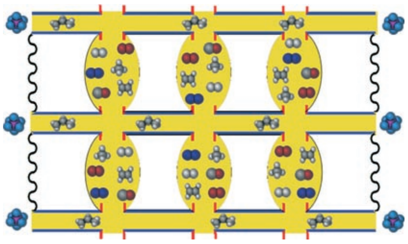
Reversible disruption and regeneration of block-copolymer micelles has been achieved by UV and visible-light irradiation and studied by atomic force microscopy (see picture). A hydrophobic dye encapsulated in the original polymeric micelles was released after UV irradiation. Remarkably, some of the released hydrophobic dye was re-encapsulated on regeneration of the micelles by irradiation with visible light.

Microporous Materials

S. Ma, D. Sun, X.-S. Wang,
H.-C. Zhou* ______ 2458–2462

A Mesh-Adjustable Molecular Sieve for General Use in Gas Separation

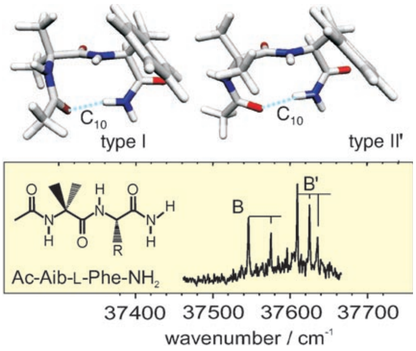
Storage space: A mesh-adjustable molecular sieve (MAMS), based on a graphitic metal–organic framework obtained by the packing of trilayers, has been prepared and characterized. The MAMS can separate any two or more gases with kinetic diameters between 2.9 and 5.0 Å through temperature-controlled molecular gating to hydrophobic gas-storage chambers (see picture).



Conformational Analysis

V. Brenner, F. Piuzzi, I. Dimicoli,
B. Tardivel, M. Mons* ______ 2463–2466

Chirality-Controlled Formation of β-Turn Secondary Structures in Short Peptide Chains: Gas-Phase Experiment versus Quantum Chemistry

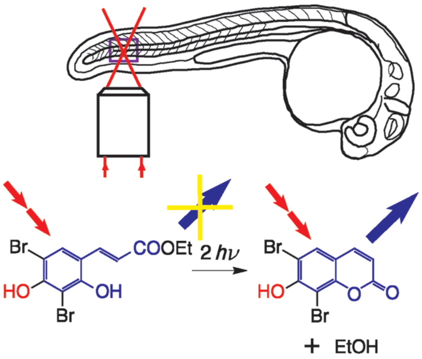


Spontaneous formation of secondary structures (i.e., β-turns) by isolated capped dipeptides in the gas phase was investigated by laser spectroscopy following supersonic expansion, and by quantum chemical calculations. The two most stable calculated β-turn structures I and II′ of one of the dipeptides were related to species B and B′, respectively, identified in the near-UV spectrum (see figure).

Caged Compounds

N. Gagey, P. Neveu,
L. Jullien* ______ 2467–2469

Two-Photon Uncaging with the Efficient 3,5-Dibromo-2,4-dihydroxycinnamic Caging Group

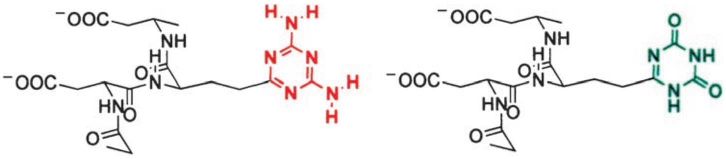


An optical syringe for targeted delivery of a substrate in vivo has been developed on the basis of the 3,5-dibromo-2,4-dihydroxycinnamic caging group. Two-photon excitation of the caged compound uncages the substrate (ethanol in the scheme) and forms a coumarin whose fluorescence allows the concentration of released substrate to be quantified. Single-cell release can be achieved with a focused laser (shown schematically for a zebrafish embryo).

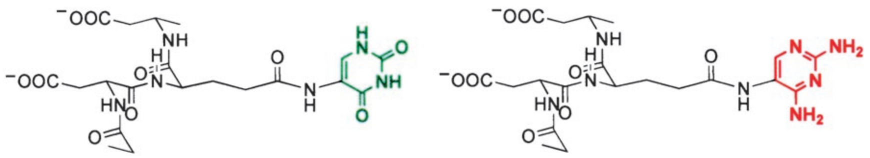
Base Pairing

G. K. Mittapalli, K. R. Reddy, H. Xiong,
O. Munoz, B. Han, F. De Riccardis,
R. Krishnamurthy,*
A. Eschenmoser* ______ 2470–2477

Mapping the Landscape of Potentially Primordial Informational Oligomers: Oligodipeptides and Oligodipeptoids Tagged with Triazines as Recognition Elements



Pairing up: Oligodipeptide, oligodeoxydipeptide, or oligodipeptoid backbones tagged with the 2,4-diaminotriazine nucleus pair strongly with complementary DNA and RNA. This is in sharp contrast with the behavior of the 2,4-dioxotriazine nucleus, which does not act as a nucleobase in these systems.



Bit different: 2,4-Dioxo- and 2,4-diamino-5-aminopyrimidine nuclei attached to an oligodipeptide backbone display a disparity in their base-pairing strength which is opposite to that shown by corresponding triazines. This behavior points to a remarkable correlation between pairing strength and ΔpK_a values of pairs of complementary bases.

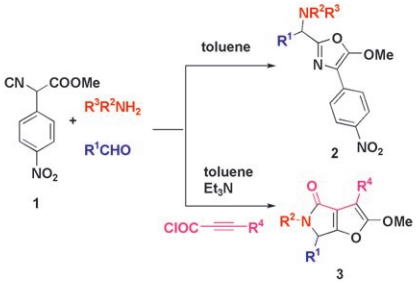
Base Pairing

G. K. Mittapalli, Y. M. Osornio, M. A. Guerrero, K. R. Reddy, R. Krishnamurthy,* A. Eschenmoser* ________ **2478 – 2484**

Mapping the Landscape of Potentially Primordial Informational Oligomers: Oligodipeptides Tagged with 2,4-Disubstituted 5-Aminopyrimidines as Recognition Elements

---

A simple approach to complexity: The reactivity pattern of α-isocyanoacetates can be tuned by modulating the acidity of the α C−H bond(s) against the nucleophilicity of the conjugate base. The unique reactivity of the α-(*p*-nitrophenyl)-α-isocyanoacetate **1** was exploited in a three-component synthesis of 5-methoxyoxazoles **2** and four-component synthesis of furopyrrolones **3**. R^1,R^2,R^3 = alkyl, aryl, benzyl; R^4 = aryl.



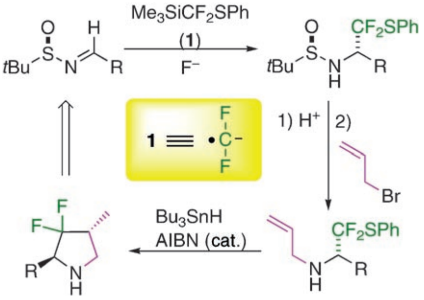
Synthetic Methods

D. Bonne, M. Dekhane, J. Zhu* ________ **2485 – 2488**

Modulating the Reactivity of α-Isocyanoacetates: Multicomponent Synthesis of 5-Methoxyoxazoles and Furopyrrolones

---

A radical synthon: Nucleophilic (phenylthio)difluoromethylation of (*R*)-*N*-(*tert*-butylsulfinyl)imines with **1**, a difluoromethylene radical anion equivalent, afforded the corresponding products in good yields and with high diastereoselectivity (d.r. ≥ 98:2). The resulting $PhSCF_2$-containing sulfinamides can be further transformed into chiral 2,4-*trans*-disubstituted 3,3-difluoropyrrolidines through an intramolecular radical cyclization methodology.



Difluoromethylenation

Y. Li, J. Hu* ________ **2489 – 2492**

Stereoselective Difluoromethylenation Using Me_3SiCF_2SPh: Synthesis of Chiral 2,4-Disubstituted 3,3-Difluoropyrrolidines

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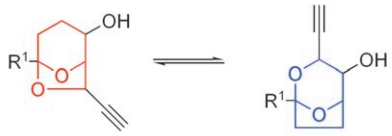


A clue from nature: Can the bicyclic acetal framework, which is present in many structurally diverse biologically active natural products, be considered a privileged scaffold? Scaffolds with this framework were synthesized and elaborated to give a collection of small-molecule derivatives as potential orally bioavailable lead compounds, and preliminary biological tests gave encouraging results.

Drug Design

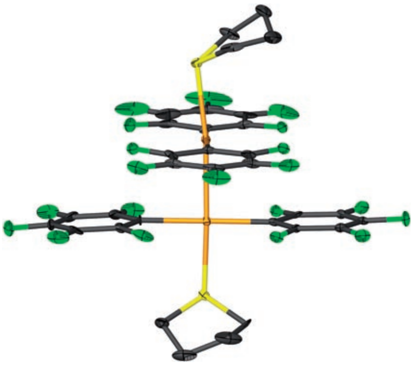
L.-G. Milroy, G. Zinzalla, G. Prencipe, P. Michel, S. V. Ley,* M. Gunaratnam, M. Beltran, S. Neidle ________ **2493 – 2496**

Chemical Variation of Natural-Product-Like Scaffolds: Design, Synthesis, and Biological Activity of Fused Bicyclic Acetal Derivatives

Gold Compounds

J. Coetzee, W. F. Gabrielli, K. Coetzee, O. Schuster, S. D. Nogai, S. Cronje, H. G. Raubenheimer* ______ **2497 – 2500**

Structural Studies of Gold(I, II, and III) Compounds with Pentafluorophenyl and Tetrahydrothiophene Ligands



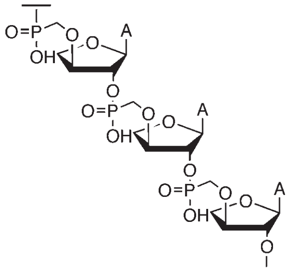
A golden opportunity was seized to prepare an unbridged, dinucleur gold(II) compound, $[Au_2(C_6F_5)_4(tht)_2]$ (tht = tetrahydrothiophene), without any stabilizing chelating ligands (see picture; Au orange, S yellow, F green, C black) and to crystallographically characterize the gold(I) and gold(III) complexes participating in this conversion. A unique ligand scrambling of the latter gold(III) compound occurs in solution.

Synthetic Biology

M. Renders, G. Emmerechts, J. Rozenski, M. Krecmerová, A. Holý, P. Herdewijn* ______ **2501 – 2504**

Enzymatic Synthesis of Phosphonomethyl Oligonucleotides by Therminator Polymerase

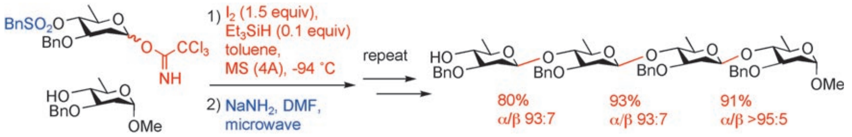
Therminator is the hero when it comes to the enzymatic production of phosphonomethyl–threosyl oligonucleotides with a non-natural 3′–2′ linkage (see scheme). The ability of Therminator polymerase to catalyze the condensation of diphosphate derivatives of nucleosides to give modified oligomers promises to be quite general. Such oligonucleotides are useful tools in synthetic biology because of the innate stability of the phosphonate linkage.



Oligosaccharides

H. Tanaka,* A. Yoshizawa, T. Takahashi* ______ **2505 – 2507**

Direct and Stereoselective Synthesis of β-Linked 2,6-Deoxyoligosaccharides



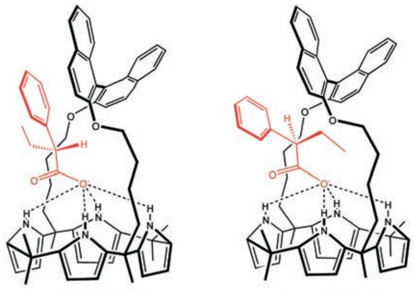
Short and sweet: Glycosidation of 2-deoxyglycosyl imidates with I_2 as shown in the scheme (Bn = benzyl, Bz = benzoyl, MS = molecular sieves) proceeds smoothly to provide the corresponding β-linked 2-deoxyglycosides in excellent yields and selectivity. This coupling method has been shown to be adaptable to the synthesis of various β-linked oligosaccharides containing 2,6-dideoxy- and 2,3,6-trideoxyglycosides.

Enantioselective Anion Binding

H. Miyaji, S.-J. Hong, S.-D. Jeong, D.-W. Yoon, H.-K. Na, J. Hong, S. Ham, J. L. Sessler, C.-H. Lee* ____ **2508 – 2511**

A Binol-Strapped Calix[4]pyrrole as a Model Chirogenic Receptor for the Enantioselective Recognition of Carboxylate Anions

Binding straps: Chiral calix[4]pyrroles **1** bearing an (*R*)- or (*S*)-binol-derived strap on one side of the tetrapyrrolic core (see picture) were synthesized and characterized. The resulting systems bind selected chiral carboxylate anions (shown in red) with high affinity in acetonitrile while at the same time exhibiting enantiomeric discrimination. PB = 2-phenylbutyrate.



(*S*)-**1**•(*S*)-PB favored

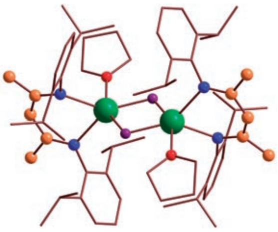
(*S*)-**1**•(*R*)-PB

Calcium Compounds

S. Nembenna, H. W. Roesky,*
S. Nagendran, A. Hofmeister, J. Magull,
P.-J. Wilbrandt, M. Hahn ___ **2512 – 2514**

A Well-Defined Hydrocarbon-Soluble Calcium Monofluoride, [{LCaF(thf)}$_2$]: The Application of Soluble Calcium Derivatives for Surface Coating

See-through coats: A hydrocarbon-soluble dimeric calcium monofluoride is prepared (see structure; green Ca, purple F, red O, blue N, orange C). This compound is a precursor for the preparation of thin layers of transparent CaF$_2$ at room temperature by dip-coating.

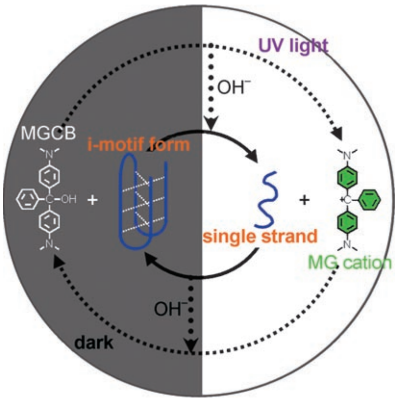


DNA Conformational Switch

H. Liu, Y. Xu, F. Li, Y. Yang, W. Wang,
Y. Song, D. Liu* ___ **2515 – 2517**

Light-Driven Conformational Switch of i-Motif DNA

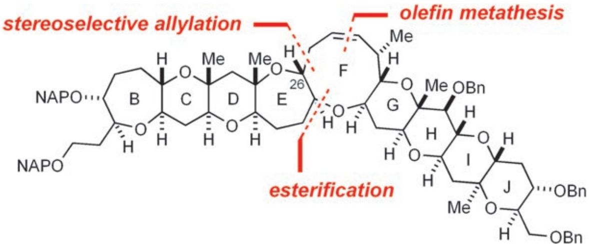
Making the switch: A photoinduced DNA conformational switch between the i-motif and random-coil structures has been achieved by combination with a reversible photoirradiated pH-jump system (see picture; MGCB: malachite green carbinol base, MG: malachite green). Multiple cycling of this switch has also been demonstrated.



Natural Products Synthesis

K. Sato, M. Sasaki* ___ **2518 – 2522**

Studies toward the Total Synthesis of Gambieric Acids A and C: Convergent Assembly of the Nonacyclic Polyether Skeleton



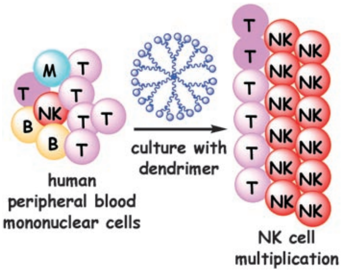
A solid approach to ethereal rings: Key features of a convergent synthesis of the nonacyclic polyether skeleton of gambieric acids A and C include the connection of the BCD and GHIJ ring systems by esterification, the construction of the E ring in the form of a lactone, a stereoselective allylation to establish the C26 stereocenter, and the formation of the F ring by ring-closing metathesis (see scheme; Bn = benzyl, NAP = 2-naphthylmethyl).

Cell Multiplication

L. Griffe, M. Poupot, P. Marchand,
A. Maraval, C.-O. Turrin, O. Rolland,
P. Métivier, G. Bacquet, J.-J. Fournié
A.-M. Caminade,* R. Poupot,*
J.-P. Majoral* ___ **2523 – 2526**

Multiplication of Human Natural Killer Cells by Nanosized Phosphonate-Capped Dendrimers

Non-natural born killers: The addition of phosphorus-containing dendrimers capped with phosphonate end groups to cultures of human peripheral blood mononuclear cells (white blood cells) strongly stimulates the selective multiplication of functional natural killer (NK) cells (see picture), which play a key role in anticancer immunity. Both the generation of the dendrimer and the type of end groups are important criteria for the activity.

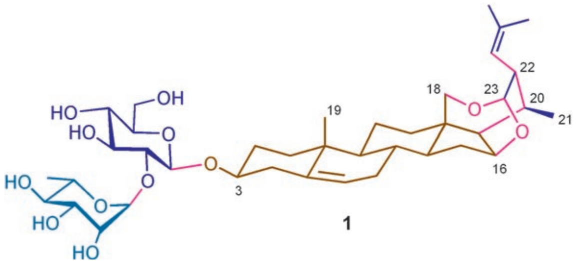


Contents

Natural Products Synthesis

P. Tang, B. Yu* ———— **2527 – 2530**

Total Synthesis of Candicanoside A, a Potent Antitumor Saponin with a Rearranged Steroid Side Chain



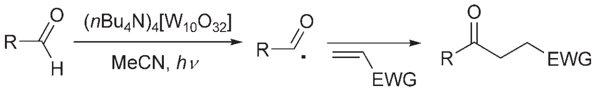
1

The fused-ring scaffold of candicanoside A (**1**), a potent antitumor agent with a unique differential pattern, has now been synthesized from inexpensive starting materials. Compound **1** has the potential to act as a lead compound for the synthesis of antitumor agents with a novel mode of action.

Synthetic Methods

S. Esposti, D. Dondi, M. Fagnoni,*
A. Albini ———— **2531 – 2534**

Acylation of Electrophilic Olefins through Decatungstate-Photocatalyzed Activation of Aldehydes



With tungsten and lamp: Ketones were prepared by the photocatalytic generation of acyl radicals from aldehydes and trapping them with equimolar amounts of electrophilic alkenes. Photocatalysis with tetrabutylammonium decatungstate is effective also at low temperatures (−20 to −50 °C), thus minimizing radical decarbonylation and allowing acylation by highly substituted aldehydes. EWG = electron-withdrawing group.

Cross-Coupling

Z. Liu, R. C. Larock* ———— **2535 – 2538**

Palladium-Catalyzed, Sequential, Three-Component Cross-Coupling of Aryl Halides, Alkynes, and Arynes

Three's a crowd? Polycyclic aromatic hydrocarbons can be synthesized efficiently and in high yield using the first palladium-catalyzed, sequential, three-component coupling of alkynes and arynes with aryl halides (see scheme). This process appears to involve the catalytic, stepwise carbopalladation of an alkyne and an aryne to generate the three-component products.

Supporting information is available on the WWW (see article for access details).

A video clip is available as Supporting Information on the WWW (see article for access details).

Service

Corrigenda

Total Synthesis of Tubulysin U and V

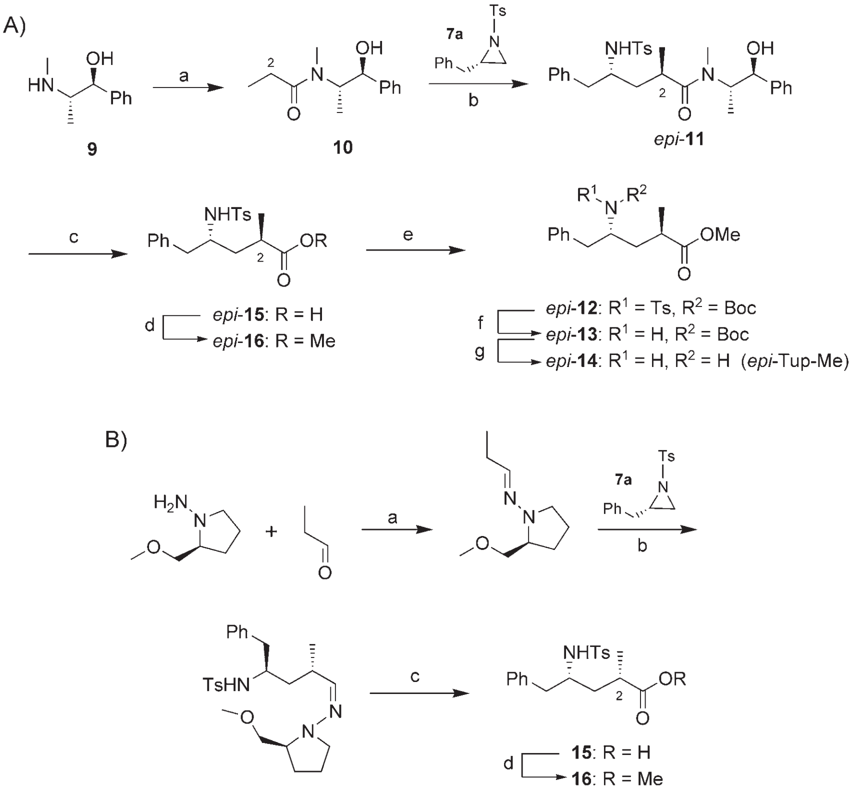
A. Dömling,* B. Beck, U. Eichelberger, S. Sakamuri, S. Menon, Q.-Z. Chen, Y. Lu, L. A. Wessjohann* ________ **7235–7239**

Angew. Chem. Int. Ed. **2006**, *45*

DOI 10.1002/anie.200601259

A recent evaluation of the biological activity of the tubulysin U and V diastereomers, shown in the Experimental Section and Supporting Information of our recent Communication, suggest that the wrong diastereomers were selected for data presentation. Re-evaluation of the other diastereomers obtained confirmed that the assignment of the tubuvaline spectra shown in the Supporting Information therein need to be inverted. More importantly, it appears that the synthesis of the first building block, tubuphenylalanine (Tup), shown in Scheme 2 therein and in line with the procedure and assignment reported by Vicario et al.,[1] does not give the diastereomer shown but rather its C2 epimer as the major product (see revised Scheme 2 below, part A). Careful repetitions of the synthesis of Tup using the original unmodified procedure of Vicario et al. or our variation and also using different batches of the auxiliary to exclude mislabeled reagents always led to production of the wrong C2 diastereomers *epi*-**11**–*epi*-**16** as the major components, with only some of the correct diastereomers (**11**–**16**) formed.

To be absolutely sure that the obtained stereochemistry is different from that expected from the report of Vicario et al.,[1] we also synthesized **15** and **16** again through a different pathway, using Enders' SAMP as auxiliary. This approach gave the correct diastereomer of the common intermediate **15** in four steps (Scheme 2 B).[2] In the meantime the syntheses by the groups of Ellman[3] and Zanda[4] also emanated, and comparison of the specific rotation values of **14** and *epi*-**14** with those reported by Zanda



Schema 2. A) Synthesis of the methyl ester of *epi*-tubuphenylalanine (*epi*-Tup) as the major product by the pseudoephedrine route. Reagents and conditions: a) Propionic anhydride, Et$_3$N, CH$_2$Cl$_2$; b) 1. LDA, LiCl, THF, −78 °C; 2. (*S*)-(+)-2-benzyl-1-(toluene-4-sulfonyl)aziridine, THF, −20 °C (Tup is only formed as a minor isomer in step b); c) 4 M H$_2$SO$_4$/dioxane, reflux; d) MeOH, conc. HCl, reflux; e) Boc$_2$O, DMAP, CH$_3$CN; f) Mg (powder), MeOH, ultrasound; g) 4 N HCl in dioxane. B) Synthesis of Tup derivatives **15** and **16** using Enders' SAMP auxiliary to give the correct diastereomer as the major product. Reagents and conditions: a) neat, 99%; b) 1. LDA, 0 °C; 2. (*S*)-(+)-2-benzyl-1-(toluene-4-sulfonyl)aziridine, THF, −100 °C→RT, 85% major isomer (separated and processed further); c) 1. O$_3$, acetone, −78 °C; 2. Jones reagent, −78 °C→RT, 55%; d) CH$_2$N$_2$, Et$_2$O/MeOH, 100%. Ts: toluene-4-sulfonyl, Boc: *tert*-butyloxycarbonyl, SAMP: (*S*)-(−)-1-amino-2-methoxymethylpyrrolidine, LDA: lithium diisopropylamide, Jones reagent: chromic acid in acetone.

and co-workers confirmed our findings. It appears that NMR spectroscopy is not ideal to determine the stereochemistry of Tup. Tup and its C2 epimer can display almost identical behavior and spectra, depending considerably on the conditions used. The same is true for the Tuv and Tup diastereomers and the final products, most of which often behave very similarly with respect to NMR spectroscopy and chromatography. Spectra of both Tup epimers and a mixed spectrum are provided in the Supporting Information herein. Vicario et al. used NMR spectroscopy, including nOe studies on a cyclized five-membered ring derivative, for their assignment. Specific rotation and X-ray analyses are more conclusive, but the relevant data were not known at the time of our first synthesis, which was based on analogy and the assignments in reference [1]. More details will be discussed in an upcoming full paper.

Experimental data for the correct diastereomers are hereby provided in the revised Supporting Information. The previously reported diastereomers also have been updated with the corrected names, stereochemical descriptors, and formulas. Finally, in Table 1, column 1, G should read H.

We thank Prof. G. Höfle and Dr. F. Sasse for the biological evaluation of the tubulysins, Prof. M. Zanda for providing reference spectra prior to publication of his manuscript[4] to additionally verify the correct diastereomers, and Dr. Simon Dörner and Gisela Schmidt (IPB) for experimental support. We apologize for any inconvenience caused by our misassignment.

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[1] J. L. Vicario, D. Badia, L. Carrillo, *J. Org. Chem.* **2001**, *66*, 5801–5807.
[2] D. Enders, C. F. Janeck, G. Raabe, *Eur. J. Org. Chem.* **2000**, 3337–3345.
[3] H. M. Peltier, J. P. McMahon, A. W. Patterson, J. A. Ellman, *J. Am. Chem. Soc.* **2006**, *128*, 16018–16019.
[4] M. Sani, G. Fossati, F. Huguenot, M. Zanda, *Angew. Chem.* **2007**, DOI: 10.1002/ange.200604557; *Angew. Chem. Int. Ed.* **2007**, DOI: 10.1002/anie.200604557.

A Highly Regio- and Stereoselective Vinylogous Horner–Wadsworth–Emmons Route to Densely Substituted 1,3-Butadienes

S. M. Date, S. K. Ghosh* ____ **386–388**

Angew. Chem. Int. Ed. **2007**, *46*

DOI 10.1002/anie.200604013

Since publication of their Communication, the authors have noticed a couple of errors. In Table 2, entry 10, the R group should read 3-pyridyl, while reference [20] should refer the readers to reference [8h] therein. The authors apologize for their oversight.