

## 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:

K. Fuchibe, T. Kaneko, K. Mori, T. Akiyama\*

Expedient Synthesis of N-Fused Indoles: A C-F Activation and **C-H Insertion Approach** 

A. Giannis, \* P. Heretsch, V. Sarli, A. Stößel Synthesis of Cyclopamine Using a Biomimetic and **Diastereoselective Approach** 

W. A. Chalifoux, R. McDonald, M. J. Ferguson, R. R. Tykwinski tert-Butyl Endcapped Polyynes: Crystallographic Evidence of **Reduced Bond-Length Alternation** 

S. T. Scroggins, Y. Chi, J. M. J. Fréchet\*

Polarity-Directed One-Pot Asymmetric Cascade Reactions Mediated by Two Catalysts in an Aqueous Buffer

D. C. K. Rathwell, S.-H. Yang, K. Y. Tsang, M. A. Brimble\* An Efficient Formal Synthesis of the Human Telomerase Inhibitor ( $\pm$ )- $\gamma$ -Rubromycin

C. A. Strassert,\* M. Otter, R. Q. Albuquerque, A. Höne, Y. Vida, B. Maier, L. De Cola\*

Photoactive Hybrid Nanomaterial for Targeting, Labeling, and Killing Antibiotic-Resistant Bacteria

D. Loffreda,\* F. Delbecg, F. Vigné, P. Sautet

Fast Prediction of Selectivity in Heterogeneous Catalysis from Extended Brønsted-Evans-Polanyi Relations: A Theoretical Insight

P. Eisenberger, R. O. Ayinla, J. M. P. Lauzon, L. L. Schafer\* Ta-Amidate Complexes for the Hydroaminoalkylation of Secondary Amines: Enhanced Substrate Scope and **Enantioselective Chiral Amine Synthesis** 

J. N. Payette, H. Yamamoto\*

Cationic Oxazaborolidine-Catalyzed Enantioselective Diels-Alder Reaction of  $\alpha$ , $\beta$ -Unsaturated Acetylenic Ketones



S. Bellemin-Laponnaz



J. Jiménez-Barbero



F. Caruso

## News

Catalysis:

S. Bellemin-Laponnaz Awarded \_\_\_\_ 7476

Prize for J. Jiménez-Barbero \_\_\_

Physical Chemistry:

F. Caruso Elected \_

Landmarks in Organo-Transition Metal Chemistry

Chemical Vapour Deposition

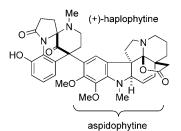
Helmut Werner

Anthony C. Jones, Michael L. Hitchman

## Books

reviewed by A. Filippou \_\_\_ \_ 7477

reviewed by G. Malandrino \_\_\_\_



Yes they can! The Fukuyama and Tokuyama research groups recently achieved the first total synthesis of haplophytine, followed soon after by the report from Nicolaou, Chen, et al. This concludes the story that began several decades ago with its isolation from a Mexican plant and its identification. These syntheses are discussed in the context of five total syntheses of aspidophytine, the lower portion of halophytine.

# Highlights

**Natural Products** 

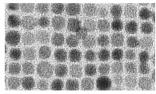
E. Doris\* \_\_\_ 7480 - 7483

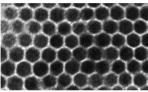
Total Syntheses of (+)-Haplophytine

#### Nanostructures

S. L. Brock\* \_\_\_\_\_\_ 7484 – 7486

All-Inorganic Nanocrystal Arrays





Snuggle up: Nanocrystals have long been known to form ordered arrays and superlattices, but traditional organic capping ligands keep the nanocrystals separated, precluding conductivity. Now researchers have used molecular metal chalcogenide caps to form 2D and 3D nanocrystal arrays (see picture) with closer packing and much improved conductivity.

## Essays

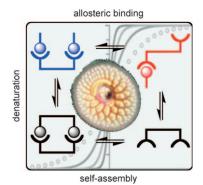
## Molecular Recognition

C. A. Hunter,\*

H. L. Anderson\* \_\_\_\_\_ 7488 - 7499



What is Cooperativity?



The lamprey holds the clue to the link between supramolecular self-assembly and allosteric ligand binding. Chelate cooperativity in self-assembled structures results in denaturation behavior that is indistinguishable from allosteric ligand binding. The chelate effect is the most common origin of positive cooperativity, yet its significance has been widely overlooked.

## **Minireviews**

## **MOFs** in Catalysis

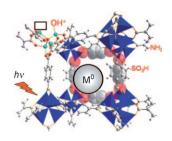
D. Farrusseng,\* S. Aguado,

C. Pinel \_\_\_\_\_\_ 7502 – 7513

Metal-Organic Frameworks: Opportunities for Catalysis

## MOFing ventured, MOFing gained:

Thanks to their multifunctional features (see picture; rectangle = Lewis center), metal-organic frameworks are of great potential value for catalysis, including photocatalysis. Their design is described in light of challenges in catalysis, and current challenges and perspectives are discussed.

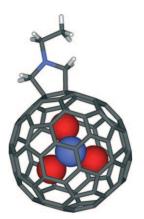


## For the USA and Canada:

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electronic / print or 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.





Guests welcome: The chemical and electrochemical properties of endohedral metallofullerenes, that is, fullerenes that encapsulate a metallic moiety in their interior, depend on the size and structure of the fullerene cage, their exohedral functionalization, as well as the type of metallic unit (see example; blue N, red Sc). The properties can be fine-tuned and offer potential applications in molecular electronics and medicine, for example.

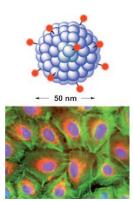
## Reviews

## Fullerene Chemistry

M. N. Chaur, F. Melin, A. L. Ortiz, L. Echegoyen\* \_\_\_\_\_\_ **7514-7538** 

Chemical, Electrochemical, and Structural Properties of Endohedral Metallofullerenes

Gels for cells: A new method to produce biocompatible polyglycerol microgel nanoparticles with controllable size (25–100 nm, see picture, top) and a readily functionalizable surface is developed. Fluorescence imaging shows clear evidence for particle uptake by cells through endocytotic pathways and localization of the particles in the perinuclear region.



## **Communications**

## **Functional Nanoparticles**

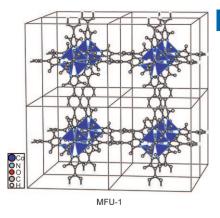
A. L. Sisson, D. Steinhilber, T. Rossow, P. Welker, K. Licha,

R. Haag\* \_\_\_\_\_ **7540 – 7545** 

Biocompatible Functionalized Polyglycerol Microgels with Cell Penetrating Properties



Structurally related to MOF-5, the cobalt(II)-containing metal—organic framework MFU-1 is stable to hydrolysis. Catalytic turnover is achieved in oxidation reactions with redox-active MFU-1, and the solid catalyst is easily recovered from the reaction mixture. Catalytic transformations have been shown to occur inside the pores of the microporous solid.



## Catalytically Active MOFs

M. Tonigold, Y. Lu, B. Bredenkötter,

B. Rieger, S. Bahnmüller, J. Hitzbleck,

G. Langstein, D. Volkmer\* \_ **7546-7550** 

Heterogeneous Catalytic Oxidation by MFU-1: A Cobalt(II)-Containing Metal-Organic Framework



# Incredibly



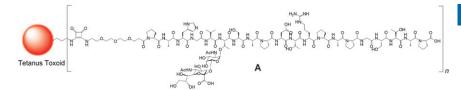
Manuscripts submitted to *Angewandte Chemie* can be published in a matter of days, and that's including meticulous peer review, careful copy-editing, and author proofing. The peer-review process requires an average of just 13 days, and 30% of all Communications are brought to readers within two months after submission of the original manuscript. The articles are not only published rapidly, they are also swiftly assimilated within the scientific community, as reflected by the extremely high Immediacy Index of *Angewandte Chemie* (2007: 2.271).



www.angewandte.org service@wiley-vch.de







An ideal combination: The vaccine A is obtained by conjugation of the synthetic tumor-associated sialyl-T<sub>N</sub>-MUC1 glycopeptide antigen to tetanus toxoid

(molecular weight > 150 000). Vaccine A induces a very strong and selective immune response against the glycopeptide structure in wild-type mice (Balb/c).

#### Antitumor Vaccines

A. Kaiser, N. Gaidzik, U. Westerlind, D. Kowalczyk, A. Hobel, E. Schmitt, H. Kunz\* \_\_ \_\_\_\_\_ 7551 – 7555

A Synthetic Vaccine Consisting of a Tumor-Associated Sialyl-T<sub>N</sub>-MUC1 Tandem-Repeat Glycopeptide and Tetanus Toxoid: Induction of a Strong and Highly Selective Immune Response

Valuable vicinal 1,2-diols can be prepared with high enantioselectivity by the asymmetric ruthenium-catalyzed hydrogenation of aryl- and alkyl-substituted  $\alpha$ -hydroxy ketones (see scheme). The ligands, which are distinguished by their modular construction, display excellent enantioface differentiation.

## Asymmetric Synthesis

R. Kadyrov,\* R. M. Koenigs, C. Brinkmann, D. Voigtlaender,

M. Rueping\* \_ 7556-7559

Efficient Enantioselective Synthesis of Optically Active Diols by Asymmetric Hydrogenation with Modular Chiral Metal Catalysts



$$\begin{array}{c|c} H_2O_3P & PO_3H_2 \\ H_2N & CH_3 \end{array}$$

More than mending bones: A simple geminal aminobisphosphonate (see picture) is the most potent selective inhibitor of the acid sphingomyelinase known to date. It can be synthesized in a one-step procedure and inhibits cell death in vitro. Since the acid sphingomyelinase is a putative drug target for inflammatory lung diseases, bisphosphonates may find application in the treatment of pulmonary diseases.

## **Enzyme Inhibitors**

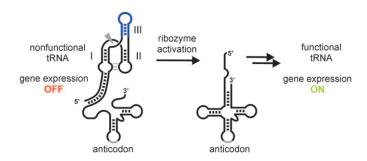
A. G. Roth, D. Drescher, Y. Yang,

S. Redmer, S. Uhlig,

C. Arenz\* \_\_

Potent and Selective Inhibition of Acid Sphingomyelinase by Bisphosphonates





External influence: Transfer RNA can be regulated by fusing a ligand-dependent ribozyme to the tRNA, resulting in disruption of the functional tRNA structure.

Upon small-molecule-dependent activation of ribozyme cleavage, the tRNA is released and can be processed to act in translation.

## RNA Technology

B. Berschneider, M. Wieland, M. Rubini, J. S. Hartig\* \_\_\_\_\_\_ **7564 – 7567** 

Small-Molecule-Dependent Regulation of Transfer RNA in Bacteria

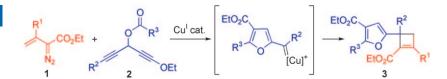


## Copper Catalysis

J. Barluenga,\* L. Riesgo, L. A. López,
 E. Rubio, M. Tomás \_\_\_\_\_\_ 7569 – 7572



Discrimination of Diazo Compounds Toward Carbenoids: Copper(I)-Catalyzed Synthesis of Substituted Cyclobutenes



With perfect exe-Cu-tion: Copper(I) catalyzes several processes in an ordered manner. First it is able to transform substrate 2 into a copper(I) furylcarbene by isomerization/cyclization, which then

reacts with 1 to produce a cyclopropyldiazo derivative, which undergoes copper(I)-catalyzed, regioselective ring enlargement to cyclobutene 3.

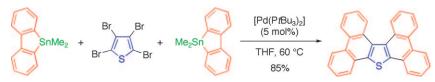
## Polycyclic Hydrocarbons

I. Nagao, M. Shimizu,\*

T. Hiyama \_\_\_\_\_\_ 7573 – 7576



9-Stannafluorenes: 1,4-Dimetal Equivalents for Aromatic Annulation by Double Cross-Coupling



**Double or nothing!** A straightforward and high-yielding approach to a variety of polycyclic aromatic hydrocarbons has been achieved through palladium-catalyzed annulation of 9,9-dimethyl-9-stan-

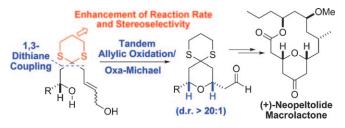
nafluorenes and dithienostannole with 1,2-dihaloarenes (see scheme). In addition, 1,1-dibromo-1-alkenes can also be applied to this annulation to produce dibenzofulvenes in excellent yields.

## Natural Product Synthesis

H. Kim, Y. Park, J. Hong\* \_\_ 7577 - 7581



Stereoselective Synthesis of 2,6-cis-Tetrahydropyrans through a Tandem Allylic Oxidation/Oxa-Michael Reaction Promoted by the gem-Disubstituent Effect: Synthesis of (+)-Neopeltolide Macrolactone



The minimal use of protecting groups is one highlight of a concise and efficient synthesis of (+)-neopeltolide macrolactone on the basis of the title tandem reaction and dithiane coupling reactions (see scheme). The *gem*-disubstituent

effect of the dithiane moiety promoted the oxa-Michael reaction following allylic oxidation to ensure the efficient synthesis of the 2,6-cis-tetrahydropyran and high diastereoselectivity.

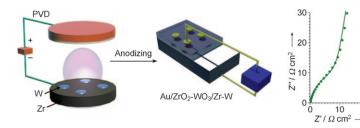
## Solid Electrolytes

D. Kowalski, Y. Aoki,

H. Habazaki\* \_\_\_\_\_\_ **7582 – 7585** 



High Proton Conductivity in Anodic  $ZrO_2/WO_3$  Nanofilms

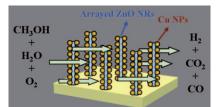


Amorphous double-oxide nanofilm  $(ZrO_2/WO_3)$  is a new class of proton-conducting electrolyte that can be simply fabricated by physical vapor deposition (PVD) and anodic oxidation of Zr/W alloy film (see

schematic). The practical area-specific resistivity of 0.2  $\Omega$  cm<sup>2</sup> is reached at a temperature as low as 100 °C for a 60 nm thick oxide film.



A microreformer that consists of arrayed zinc oxide nanorods (ZnO NRs) with copper nanoparticles (Cu NPs; see picture) is an active catalyst for the conversion of methanol into hydrogen.



## Microreformer Design

Y.-G. Lin, Y.-K. Hsu, S.-Y. Chen, Y.-K. Lin, L.-C. Chen,\* K.-H. Chen\* — **7586 – 7590** 

Nanostructured Zinc Oxide Nanorods with Copper Nanoparticles as a Microreformation Catalyst





One after the other: Triblock peptide synthesis was achieved at ambient temperature by sequential reaction of sulfonamide-protected peptidyl thioacids first with highly reactive 2,4-dinitrobenzene-sulfonamides and second with more

moderately reactive sulfonamides to produce the oligopeptides in good yields. The method is compatible with C-terminal thioesters and thus presents a new approach for native chemical ligation strategies.

## **Chemical Ligation**

D. Crich,\* I. Sharma \_\_\_\_\_ 7591 - 7594

Triblock Peptide and Peptide Thioester Synthesis With Reactivity-Differentiated Sulfonamides and Peptidyl Thioacids



Ligand = 
$$N$$

A. G. Sergeev, T. Schulz, C. Torborg,

Palladium Catalysis

A. Spannenberg, H. Neumann,
M. Beller\* \_\_\_\_\_\_ **7595 – 7599** 

Turning down the heat: The first room temperature Pd-catalyzed synthesis of phenols from aryl bromides and chlorides is presented. Stoichiometric studies of Pd-mediated hydroxylation of aryl halides employing a bulky imidazolyl-phosphine

ligand and the novel palladium precursor  $[Pd(cod)(CH_2SiMe_3)_2]$  led to development of efficient catalytic synthesis of phenols under ambient conditions (see scheme; Ad = adamantyl, cod = 1,5-cyclooctadiene).

Palladium-Catalyzed Hydroxylation of Aryl Halides under Ambient Conditions





Advancing alkaloid synthesis: (+)-Haplophytine (see structure) was the target of a total synthesis featuring a highly stereoselective intramolecular Mannich reaction, Friedel–Crafts alkylation, oxidative rearrangement, and Fischer indole synthesis.

## Natural Product Synthesis



H. Ueda, H. Satoh, K. Matsumoto, K. Sugimoto, T. Fukuyama,\*

H. Tokuyama\* \_\_\_\_\_ 7600 – 7603

Total Synthesis of (+)-Haplophytine

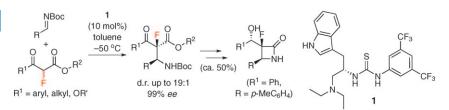


#### Asymmetric Catalysis

X. Han, J. Kwiatkowski, F. Xue, K.-W. Huang,\* Y. Lu\* \_\_\_\_\_\_ **7604 – 7607** 



Asymmetric Mannich Reaction of Fluorinated Ketoesters with a Tryptophan-Derived Bifunctional Thiourea Catalyst



Fluorinated quaternary stereocenters: A novel bifunctional catalyst 1 derived from natural tryptophan promoted the Mannich reaction of  $\alpha$ -fluoro- $\beta$ -ketoesters to afford fluorinated chiral molecules containing vicinal quaternary and tertiary

stereogenic centers with exceptional enantioselectivity. An unprecedented  $\alpha$ -fluoro- $\beta$ -lactam was also prepared by this method (see scheme; Boc = tert-butoxycarbonyl).

#### **Emissive Siloles**

Z. Zhao, Z. Wang, P. Lu, C. Y. K. Chan, D. Liu, J. W. Y. Lam, H. H. Y. Sung, I. D. Williams, Y. Ma,

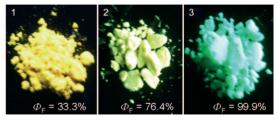
B. Z. Tang\* \_\_\_\_\_\_ 7608 - 7611



Structural Modulation of Solid-State Emission of 2,5-Bis(trialkylsilylethynyl)-3,4-diphenylsiloles



Solidarity means strength: In new silole luminogens, the solid aggregates are stronger emitters than isolated molecules. The solid-state emission is tunable by varying molecular structures of the luminogens. Increasing bulkiness of the sub-



stituents weakens intermolecular interactions and restricts intramolecular rotations, leading to a blue shift in emission color and a great increase in emission efficiency (see examples in picture).

## Palladium Catalysis

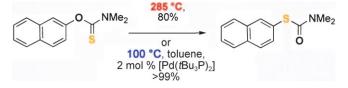
J. N. Harvey, J. Jover, G. C. Lloyd-Jones,\*

J. D. Moseley, P. Murray,

J. S. Renny \_\_\_\_\_\_ 7612-7615



The Newman–Kwart Rearrangement of O-Aryl Thiocarbamates: Substantial Reduction in Reaction Temperatures through Palladium Catalysis



**Much cooler:** The development of a catalyst for the Newman–Kwart rearrangement allows an escape from the harsh thermal conditions of the standard uncatalyzed reaction (see scheme). Mechanistic investigations, employing kinetic, isotopic labelling (<sup>2</sup>H, <sup>18</sup>O, <sup>34</sup>S)

and DFT studies, suggest that the reaction proceeds through a five-centred Pd–S coordinated oxidative addition, with intermolecular exchange of aryl and thiocarbamate moieties through dimerization of the resting state.



## **Natural Product Synthesis**

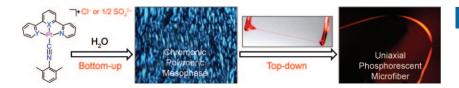
K. C. Nicolaou,\* S. M. Dalby, S. Li,
T. Suzuki, D. Y.-K. Chen\* \_\_\_\_ **7616–7620** 



Total Synthesis of (+)-Haplophytine



A problem solved: Haplophytine (1) yields to total synthesis through a convergent strategy employing modern synthetic methods. Key steps include hypervalent iodine mediated oxidative coupling, semipinacol type oxidative skeletal rearrangement, Suzuki–Miyaura coupling, and radical cyclisation.



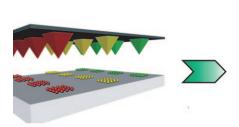
Soft matter with a hard core: Through Pt"...Pt" and hydrophobic interactions, planar organoplatinum(II) cations with chloride or sulfate as counterions selforganize themselves in water into redemissive, chromonic, and viscoelastic mesophases from which aligned films and discrete uniaxial microfibers with cofacial molecular orientations can be readily prepared.

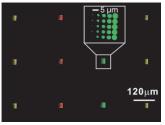
## Liquid Crystals

W. Lu, Y. Chen, V. A. L. Roy, S. S.-Y. Chui, C.-M. Che\* \_\_\_\_\_\_ 7621 – 7625

Supramolecular Polymers and Chromonic Mesophases Self-Organized from Phosphorescent Cationic Organoplatinum(II) Complexes in Water







High-end printer: A novel way of using a polymer pen lithography (PPL) array mould to localize different inks on the pens of a PPL array has been developed. This technique allows for rapid pen inking and subsequent generation of multiplexed

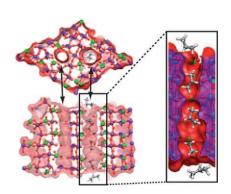
patterns of up to 150000 nano- and microscale protein features per second (see picture). It is a general approach, which in principle can be extended to any substance that can be transported by PPL.

#### **Protein Nanoarrays**

Z. Zheng, W. L. Daniel, L. R. Giam, F. Huo, A. J. Senesi, G. Zheng, C. A. Mirkin\* \_ 7626 - 7629

Multiplexed Protein Arrays Enabled by Polymer Pen Lithography: Addressing the Inking Challenge





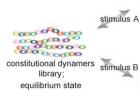
What's your occupation? The ReaxFF computational approach is used to resolve partial or mixed occupation of crystallographic sites of the Mo<sub>3</sub>VO<sub>x</sub> multimetal oxide (MMO) catalyst. It provides insight into the oxidation state and coordination environment of the metal sites. identifies donor-acceptor networks in the catalyst, and predicts selectivity for molecular diffusion into channels of the framework (see picture).

## Multimetal Oxide Catalysts

K. Chenoweth, A. C. T. van Duin, W. A. Goddard, III\* \_\_\_\_\_ 7630 - 7634

The ReaxFF Monte Carlo Reactive **Dynamics Method for Predicting** Atomistic Structures of Disordered Ceramics: Application to the Mo<sub>3</sub>VO<sub>x</sub> Catalyst





evolution of dynamer A'. new function A" 000

evolution of evolution of dynamer B', new function B"

Aptly folded: Dynamic polymer libraries were generated by polycondensation through reversible imine bonds and can undergo driven evolution under the double stimuli of donor-acceptor stacking and metal-ion binding (see picture). The specific binding modes of alkali metal ions are associated with specific constitutional changes and with different optical natures that reflect the presence and the positions of donor and acceptor units within the folded dynamer.

## Constitutional Dynamic Chemistry

S. Fujii, J.-M. Lehn\* \_\_\_\_\_ 7635 - 7638

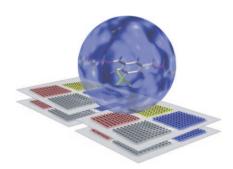
Structural and Functional Evolution of a Library of Constitutional Dynamic Polymers Driven by Alkali Metal Ion Recognition



## **Droplet Microarrays**

In Situ Assembly and Screening of Enzyme Inhibitors with Surface-Tension Microarrays

Hundreds of reactions were conducted in parallel in droplets maintained on a glass slide through differential surface tension in a new approach to submicroliter-scale synthesis. This "surface-tension microarray" was applied to the in situ assembly of thousands of derivatives of phenylboronic acid and their profiling against the NS3/4A protease of the hepatitis C virus. Several potent inhibitors of the enzyme were identified.



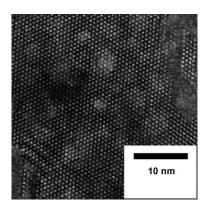
#### Zeolites

D. H. Park, S. S. Kim, H. Wang, T. J. Pinnavaia,\* M. C. Papapetrou, A. A. Lappas,

K. S. Triantafyllidis\* \_\_\_\_\_ 7645 - 7648

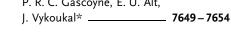


Selective Petroleum Refining Over a Zeolite Catalyst with Small Intracrystal Mesopores Cracking good cracking: Mesoporous ZSM-5 zeolite catalysts (see TEM image) made by soft templating methods show higher gas—oil cracking activity and greatly enhanced product selectivity than conventional ZSM-5. The cracking of large hydrocarbons to gasoline and diesel fuel occurs in intracrystal mesopores, while the conversion of smaller molecules into feedstock olefins occurs in framework micropores.



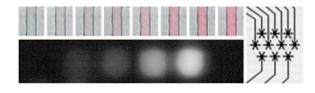
## **Analytical Methods**

D. M. Vykoukal, G. P. Stone, P. R. C. Gascoyne, E. U. Alt,





Quantitative Detection of Bioassays with a Low-Cost Image-Sensor Array for Integrated Microsystems



Portable assay systems require inexpensive detectors that can be integrated with microfluidic sample handling. Now a mass-produced digital-camera sensor has been interfaced with different lab-on-achip architectures to image nanoliter

reagent droplets and for quantitative photometry of colorimetric and bioluminescence assays (see contact images of the fluid-handling electrode array (right), and colorimetric (top) and bioluminescent samples (bottom)).

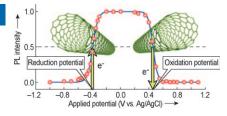


## Carbon Nanotubes

Y. Tanaka, Y. Hirana, Y. Niidome, K. Kato, S. Saito, N. Nakashima\* — 7655 – 7659

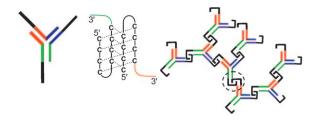


Experimentally Determined Redox Potentials of Individual (n,m) Single-Walled Carbon Nanotubes



Nanotubes reveal their potential: The fabrication of a thin film that retains isolated single-walled nanotubes (SWNTs) allows the experimental determination of the redox potentials of many individual SWNTs that have different chirality indexes (*n*,*m*). The method is simple and applicable to all individual SWNTs whose near-IR photoluminescence (PL) is detectable (see picture).





Y switch? A fast, pH-responsive DNA hydrogel (see picture; right) was prepared by a three-armed DNA nanostructure (left) assembling together through the formation of intermolecular i-motif struc-

tures (middle). The hydrogel can be switched to the non-gel state in minutes by simply using environmental pH changes.

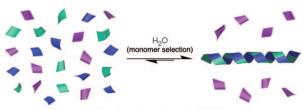
#### **DNA Nanostructures**

E. Cheng, Y. Xing, P. Chen, Y. Yang, Y. Sun, D. Zhou,\* L. Xu, Q. Fan,

D. Liu\* \_\_\_\_\_\_ 7660 – 7663

A pH-Triggered, Fast-Responding DNA Hydrogel





Random polymer formed in MeCN

**Hydrophobic selection**: Reversible polymerization and folding of amphiphilic dialdehyde and dihydrazide monomers yields nanostructured rods. The resulting dynamers are stable enough to resist the incorporation of excess dihydrazide. In

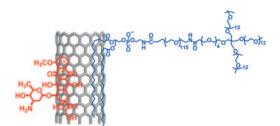
water, a more hydrophobic dihydrazide component (see picture, green) is favored over a less hydrophobic one (purple). This selectivity is lost when MeCN is added, implicating that hydrophobicity drives selectivity.

### **Dynamic Nanostructures**

J. F. Folmer-Andersen,
J.-M. Lehn\* \_\_\_\_\_\_ **7664 – 7667** 

Constitutional Adaptation of Dynamic Polymers: Hydrophobically Driven Sequence Selection in Dynamic Covalent Polyacylhydrazones





The evidence is stacking up: Many therapeutic advantages such as prolonged circulation in the blood, increased tumor drug uptake, enhanced therapeutic efficacy, and markedly reduced toxic side effects are provided by a carbon nanotube

based chemotherapeutic formulation (see picture). In this system, doxorubicin (DOX) is loaded onto the sidewalls of functionalized single-walled carbon nanotubes by supramolecular  $\pi$ – $\pi$  stacking.

## Drug Delivery

Z. Liu, A. C. Fan, K. Rakhra, S. Sherlock,
A. Goodwin, X. Chen, Q. Yang,
D. W. Felsher,\* H. Dai\* \_\_\_\_\_ 7668 – 7672

Supramolecular Stacking of Doxorubicin on Carbon Nanotubes for In Vivo Cancer Therapy



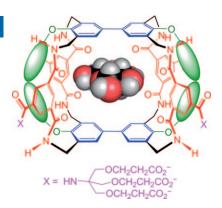
## Carbohydrate Recognition

N. P. Barwell, M. P. Crump, A. P. Davis\*

7673 - 7676



A Synthetic Lectin for β-Glucosyl



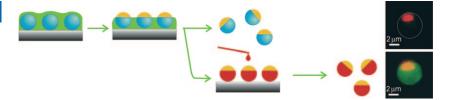
**Evolving tastes**: Addition of alkoxy groups (green; see picture) to macrotricyclic carbohydrate receptors yields improved affinities and new selectivities. Notably, the propoxy-substituted receptor shows a strong preference for β-glucosyl. Glucose is bound both in water and reconstituted blood plasma, which holds promise for applications in blood glucose monitoring.

#### Janus Particles

X. Y. Ling, I. Y. Phang, C. Acikgoz, M. D. Yilmaz, M. A. Hempenius, G. J. Vancso, J. Huskens\* \_\_ 7677 - 7682



Janus Particles with Controllable Patchiness and Their Chemical Functionalization and Supramolecular Assembly



Seeing the right face: Mono- and bifunctionalized Janus particles with controllable chemical patchiness are prepared by a general masking/unmasking technique and subsequent chemical functionalization (see picture). Supramolecular "host"- and "guest"-functionalized Janus particles were prepared, and specific noncovalent host-guest interactions were used to controllably assemble heterogeneous particles.

## Cooperative Catalysis

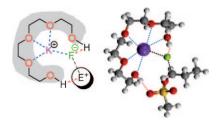
J. W. Lee, H. Yan, H. B. Jang, H. K. Kim, S.-W. Park, S. Lee,\* D. Y. Chi,\* C. E. Song\* \_\_\_\_\_\_ 7683 – 7686





Bis-Terminal Hydroxy Polyethers as All-Purpose, Multifunctional Organic Promoters: A Mechanistic Investigation and Applications

Achiral polyether derivatives have been shown to dramatically accelerate S<sub>N</sub>2 reactions by the simultaneous activation of both the nucleophile (KF) and electrophile (sulfonate; see picture). By using chiral variants as catalysts, the desilylative kinetic resolution of the silyl ethers of racemic secondary alcohols has been achieved. Density functional calculations provide detailed insight into the modes of action of this type of organic promoter.

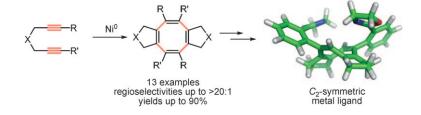


## Synthetic Methods

P. A. Wender,\* J. P. Christy, A. B. Lesser, M. T. Gieseler \_\_\_\_\_\_ 7687 – 7690



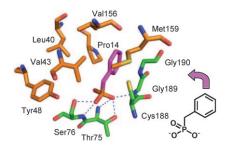
The Synthesis of Highly Substituted Cyclooctatetraene Scaffolds by Metal-Catalyzed [2+2+2+2] Cycloadditions: Studies on Regioselectivity, Dynamic Properties, and Metal Chelation



All-kynes of COTs: A Ni<sup>0</sup>-catalyzed [2+2+2+2] cycloaddition of 1,6-diynes yields highly functionalized hexa- and octa-substituted cyclooctatetraenes (COTs; see picture) along with the first example of a fully intramolecular

[2+2+2+2] cycloaddition product. The regioselectivity of this process is studied and the initial use of COT ligands is shown in the formation of a Zn<sup>II</sup> complex with a bis (oxazoline) COT.





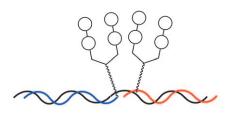
Rational enhancement: The X-ray crystal structure of an arylmalonate decarboxylase (AMDase) with a mechanism-based inhibitor bound to an active-site dioxyanion hole provides insight into the mechanism of this intriguing enzyme. The structure also guided the extension of the AMDase biocatalytic repertoire to include a wide range of  $\alpha$ -alkenyl as well as  $\alpha$ -arylmalonates.

## **Enzyme Mechanisms**

K. Okrasa, C. Levy, M. Wilding,
M. Goodall, N. Baudendistel, B. Hauer,
D. Leys,\* J. Micklefield\* \_\_\_\_\_\_ 7691 – 7694

Structure-Guided Directed Evolution of Alkenyl and Arylmalonate Decarboxylases





All under control: The programmability of hybridization has been utilized to generate a combinatorial library of structures that emulate the topologies of complex carbohydrates interacting with an antibody that shows broad-spectrum activity against HIV. This simple method involves attaching oligosaccharides tagged with peptide nucleic acids onto DNA templates in a controlled manner (see schematic picture).

## **Bioorganic Chemistry**

K. Gorska, K.-T. Huang, O. Chaloin, N. Winssinger\* \_\_\_\_\_\_ 7695 – 7700

DNA-Templated Homo- and Heterodimerization of Peptide Nucleic Acid Encoded Oligosaccharides that Mimick the Carbohydrate Epitope of HIV





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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