# Interaction with the surrounding water ...

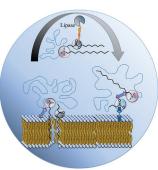




... was shown to play a crucial role in determining the aggregation propensity of proteins. In their Communication on page 3961 ff., S.-H. Chong and S. Ham shown that the overall protein hydrophobicity, defined by the hydration free energy of the protein, is the predominant determinant of protein aggregation propensity in aqueous solutions. This result paves the way for the design of aggregation-resistant proteins as biotherapeutics.

#### **Antimicrobial Polymers**

The antibacterial activity of a polymer can be controlled by a bio-cleavable satellite group. In their Communication on page 3830 ff. J. C. Tiller et al., report that a antimicrobial polymer can be deactivated by a lipase-catalyzed hydrolysis of an ester group.

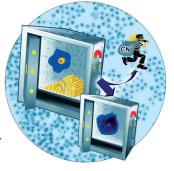


# Wireless Electrodeposition In their Communication

In their Communication on page 4001 ff., A. Kuhn, D. Bradshaw, et al. describe a high-spatial-control synthesis of Janus metal-organic frameworks without the need for a physical connection between the modified object and the electrode.

# Prussian Blue Nanoparticles

A new method for the synthesis of core-shell gold@Prussian blue analogue nanoparticles that exhibit plasmonic and magnetic properties is described by Y. Guari and co-workers in their Communication on page 3872 ff.



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"... The impressive investment by the country's founding members led to the remarkable outcomes that we admire today, to what is often referred to as 'The Start-up Nation' with its impressive numbers of recent chemistry Nobel

Nevertheless, despite this history and notable recent accomplishments, the esteem for the science of chemistry has diminished to an alarming degree in the eyes of the Israeli public ..."

Read more in the Editorial by Ilan Marek.

# **Editorial**

I. Marek\* \_\_\_\_\_\_ 3754 – 3755

Chemistry in Israel—at a Crossroads?

# Service

Spotlight on Angewandte's Sister Journals

*3770 – 3773* 



"My favorite saying is 'Where there's a will, there's a way'. My favorite drink is green tea. ..."

This and more about Wen-Jing Xiao can be found on page 3774.

**Author Profile** 

Wen-Jing Xiao \_\_\_\_\_\_\_ **3774** 

# **Books**

Self-Healing Polymers Wolfgang H. Binder

reviewed by M. W. Urban \_\_\_\_\_ 3775



# Highlights

#### **Ras Inhibitors**

J. Rudolph,\* D. Stokoe \_\_\_\_\_ 3777 - 3779

Selective Inhibition of Mutant Ras Protein through Covalent Binding

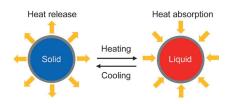
One of the first oncogenes to be discovered and one of the most prevalently mutated tumor genes is *Ras*. Shokat et al. and Gray et al. have succeeded in discovering allosteric inhibitors and inhibitory nucleotide analogues, respectively, of K-Ras proteins (see scheme) that covalently and selectively bind G12C-mutant K-Ras. These strategies of specifically targeting a mutant form of Ras may offer an opportunity for cancer—selective therapies that spare normal tissue.

# Reviews

#### **Phase-Change Materials**

D. C. Hyun, N. S. Levinson, U. Jeong, Y. Xia\* \_\_\_\_\_\_ 3780 – 3795

Emerging Applications of Phase-Change Materials (PCMs): Teaching an Old Dog New Tricks PCMs on the rise: As a result of their sharp melting points and large heats of fusion during phase transition, phase-change materials (PCMs) have already found commercial use in thermal management. The vast potential of this class of fascinating materials has recently been tapped in a diverse array of high-tech applications such as controlled release, information storage, sensing/detection, and barcoding.

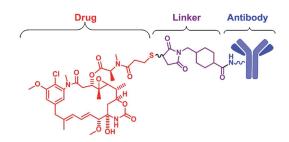


Phase change of PCM

#### Targeted Cancer Therapy

R. V. J. Chari,\* M. L. Miller, W. C. Widdison \_\_\_\_\_\_ **3796 – 3827** 

Antibody-Drug Conjugates: An Emerging Concept in Cancer Therapy



Fight together: Antibody-drug conjugates (ADCs) are an emerging new class of targeted cancer therapeutics, with validation provided by the recent marketing approvals of the ADCs brentuximab vedotin and ado-trastuzumab emtansine.

Key considerations in the design of ADCs, pre-clinical and clinical data of various ADCs in development, along with the current status and emerging advances are reviewed.

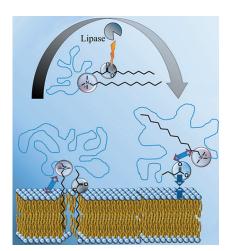
#### For the USA and Canada:

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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.





Biocides are widely used for preventing the spread of microbial infections and the fouling of materials. Since their application can build up microbial resistance and cause unpredictable long-term environmental problems, new biocidal agents are required. In a novel approach an antimicrobial polymer is deactivated by hydrolysis of an ester group through the action of a lipase. The crucial feature is the mutual interaction of the two endgroups of the polymer.

## **Communications**

## **Antimicrobial Polymers**



C. Krumm, S. Harmuth, M. Hijazi,

B. Neugebauer, A.-L. Kampmann,

H. Geltenpoth, A. Sickmann,

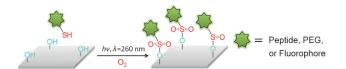
J. C. Tiller\* 3830-3834

Antimicrobial Poly (2-methyloxazoline) s with Bioswitchable Activity through Satellite Group Modification



**Frontispiece** 





When thiols meet alcohols: A method based on thiol-alcohol chemistry is used for the direct photochemical modification and patterning of hydroxy-functionalized surfaces with different thiol-containing functional molecules (see picture).

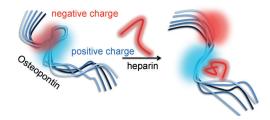
#### Photopatterning



L. Li, J. Li, X. Du, A. Welle, M. Grunze, O. Trapp, P. A. Levkin\* \_\_\_\_\_ 3835 - 3839

Direct UV-Induced Functionalization of Surface Hydroxy Groups by Thiol-Ol Chemistry





Well-balanced: The binding of heparin to the intrinsically disordered protein (IDP) osteopontin was studied by a combination of NMR and EPR spectroscopy. The results offer insight into the interplay

between structure and thermodynamics which results in low energy barriers and facilitates rapid substrate-binding and -release events in IDP interaction networks.

## Intrinsically Disordered Proteins

D. Kurzbach, T. C. Schwarz, G. Platzer,

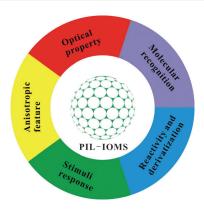
S. Höfler, D. Hinderberger,\*

R. Konrat\* \_ 3840 - 3843

Compensatory Adaptations of Structural Dynamics in an Intrinsically Disordered **Protein Complex** 



Broad spectrum: Based on the combination of the unique features of both polyionic liquids and spherical colloidal crystals, a new class of optical spheres with a series of distinct properties was fabricated. Such photonic spheres could not only be used as stimuli-responsive photonic microgels, but also serve as functional microspheres that mimic the main characteristics of small molecules, including intrinsic optical properties, specific molecular recognition, reactivity and derivatization, and anisotropy.



#### **Functional Microspheres**

Recognition Capabilities

J. Cui, W. Zhu, N. Gao, J. Li, H. Yang, Y. Jiang, P. Seidel, B. J. Ravoo,\* \_\_\_\_\_ 3844 – 3848

Inverse Opal Spheres Based on Polyionic Liquids as Functional Microspheres with Tunable Optical Properties and Molecular



3759

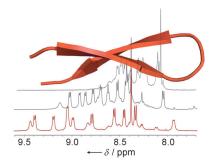


#### **Bioactive Peptides**

S. Fischer, A. Geyer\* \_\_\_\_\_ 3849-3853



Filaggrin Peptides with β-Hairpin Structure Bind Rheumatoid Arthritis Antibodies Form follows function: A filaggrin peptide in a constricted  $\beta$ -hairpin conformation binds autoantibodies against rheumatoid arthritis. The binding affinity of these peptides is comparable to those of the flexible filaggrin peptides in ELISA tests. NMR spectroscopy identifies the homogeneity of peptide folding and supports the proposed antibody-bound conformation of the epitope.

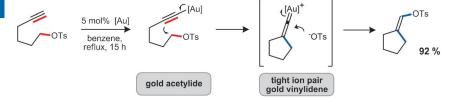




#### Gold Catalysis



Cyclization of Gold Acetylides: Synthesis of Vinyl Sulfonates via Gold Vinylidene Complexes



Gold vinylidene intermediates are generated by the cyclization of gold acetylides that carry a sulfonate leaving group. This result demonstrates for the first time that the formation of these species is not

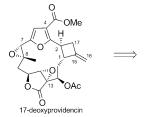
restricted to a dual activation mode. The cyclization products obtained herein contain a vinyl sulfonate moiety, which makes them useful building blocks for crosscoupling reactions.

#### **Total Synthesis**

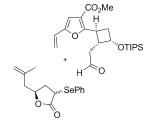
N. Toelle, H. Weinstabl, T. Gaich, J. Mulzer\* \_\_\_\_\_\_ 3859 – 3862



Light-Mediated Total Synthesis of 17-Deoxyprovidencin



Photochemistry is the key: An asymmetric synthesis of the diterpenoid 17-de-oxyprovidencin is described. Key steps include an aldol addition, a base-catalyzed Wipf-type furan formation, a Z-selective ring-closing metathesis for macrocycliza-



tion, a photoinduced Z/E isomerization to a highly strained conformationally restricted ring system, and the stereoselective formation of two epoxides on the macrocycle.

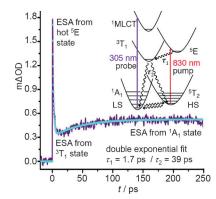


#### Ligand-Field States

A. Marino, P. Chakraborty, M. Servol, M. Lorenc, E. Collet,

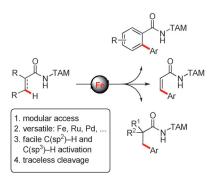
A. Hauser\* \_\_\_\_\_\_ 3863 – 3867

The Role of Ligand-Field States in the Ultrafast Photophysical Cycle of the Prototypical Iron(II) Spin-Crossover Compound [Fe(ptz)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub>



The path of LIESST resistance: Ultrafast transient absorption with an infrared pump and a UV probe allows for a detailed elucidation of the sequence of events on irradiation into the spin-allowed ligand-field transition of the high-spin species of a prototypical iron(II) spin-crossover complex, thereby identifying the lowest-energy triplet state as a short-lived intermediate state with a lifetime of 39 ps in the passage from the excited quintet to the singlet ground state.





With a little help: A versatile iron catalyst allows the arylation of C(sp2)-H and C(sp³)-H bonds in the presence of a modular and removable triazolyldimethylmethyl (TAM) auxiliary, whose structure can be varied through 1,3-dipolar azide-alkyne cycloadditions.

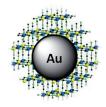
#### C-H Activation

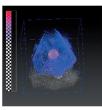
Q. Gu, H. H. Al Mamari, K. Graczyk, E. Diers, L. Ackermann\* \_\_\_ 3868 - 3871

Iron-Catalyzed C(sp<sup>2</sup>)—H and C(sp<sup>3</sup>)—H Arylation by Triazole Assistance



Prussian gold: A method for the synthesis of single- and double-layer core-shell heterostructures that are based on a welldefined gold core and shells of Prussian blue analogues has been developed. These materials feature magneto-optical properties and may be considered as multifunctional nanoobjects.





#### Prussian Blue Nanoparticles



G. Maurin-Pasturel, J. Long, Y. Guari,\* F. Godiard, M.-G. Willinger, C. Guerin,

I. Larionova \_\_\_\_\_ \_ 3872 - 3876

Nanosized Heterostructures of Au@Prussian Blue Analogues: Towards Multifunctionality at the Nanoscale







Pipe up: Alkylation of readily prepared 1,2dihydropyridines with alkyl triflates and Michael acceptors introduces quaternary carbon centers with high regio- and diastereoselectivity. Hydride or carbon nucleophile addition to the resultant iminium ion also proceeds with high diastereoselectivity. For carbon nucleophile addition, an unprecedented level of substitution is achieved to provide piperidine rings with contiguous tetrasubstituted carbon atoms.

#### Synthetic Methods

S. Duttwyler, S. Chen, C. Lu, B. Q. Mercado, R. G. Bergman,

J. A. Ellman\* \_\_\_ \_ 3877 - 3880

Regio- and Stereoselective 1,2-Dihydropyridine Alkylation/Addition Sequence for the Synthesis of Piperidines with Quaternary Centers



Quite a character: A terminal arylalumylene complex of platinum was obtained by the reaction of a dialumene-benzene adduct and [Pt(PCy<sub>3</sub>)<sub>2</sub>]. Reduction of 1,2dibromodialumanes in the presence of

Angew. Chem. Int. Ed. 2014, 53, 3757-3769

[Pt(PCy<sub>3</sub>)<sub>2</sub>] also afforded the terminal arylalumylene complexes. DFT calculations suggest that the Al-Pt bonds in the arylalumylene complexes have a significantly high electrostatic character.

#### Main-Group Ligands

K. Nagata, T. Agou, N. Tokitoh\* \_ 3881 - 3884

Syntheses and Structures of Terminal Arylalumylene Complexes



3761

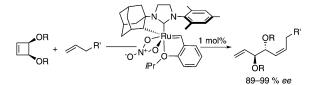


#### Asymmetric Catalysis

J. Hartung, R. H. Grubbs\* \_ 3885 - 3888



Catalytic, Enantioselective Synthesis of 1,2-anti-Diols by Asymmetric Ring-Opening/Cross-Metathesis



Rather fetching: Chiral vicinal diols are found in natural products and ligands used for asymmetric catalysis. The enantioselective ring-opening/cross-metathesis of disubstituted cyclobutenes has been carried out with an enantiopure ruthe-

nium metathesis catalyst to afford 1,2anti-diols with high enantiopurity. The synthetic versatility of the products was demonstrated in the synthesis of insect pheromone (+)-endo-brevicomin and a monosaccharide ribose.

#### Molecular Electronics

K.-C. Liao, H. J. Yoon, C. M. Bowers, F. C. Simeone,

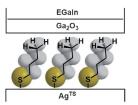
G. M. Whitesides\* \_\_\_\_\_ 3889-3893



Replacing  $Ag^{Ts}SCH_2$ -R with  $Ag^{Ts}O_2C$ -R in EGaIn-Based Tunneling Junctions Does Not Significantly Change Rates of Charge Transport



Either way: For junctions comprising thiolate- and carboxylate-anchored self-assembled monolayers (SAMs) the role of the metal—SAM interface in charge transport by tunneling was investigated and the



charge-transport rates were measured. The data suggest that Ag–SAM interfaces having either a thiolate or carboxylate anchoring group may be directly comparable.

#### **Radical Reactions**

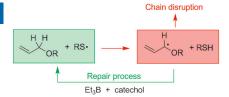
G. Povie, A.-T. Tran, D. Bonnaffé,\*

J. Habegger, Z. Hu, C. Le Narvor,

P. Renaud\* \_\_\_\_\_\_ 3894 – 3898



Repairing the Thiol-Ene Coupling Reaction



In good repair: Undesired hydrogen-atom transfers are responsible for the lack of efficiency in thiol-ene coupling reactions involving allyl glycosides. This competing reaction cannot be prevented but can be very efficiently repaired by carrying out the reaction in the presence of triethylborane and catechol.

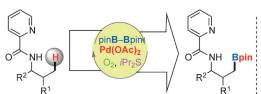
#### C-H Borylation

L.-S. Zhang, G. Chen, X. Wang, Q.-Y. Guo, X.-S. Zhang, F. Pan, K. Chen,

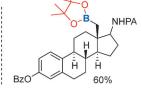
Z.-J. Shi\* \_\_\_\_\_\_ 3899 – 3903



Direct Borylation of Primary C—H Bonds in Functionalized Molecules by Palladium Catalysis



Crucial additives: A simple palladiumbased system catalyzes the conversion of primary C(sp³)—H bonds in complex organic molecules into alkyl boronate esters. Amino acids, amino alcohols, alkyl amines, and a series of bioactive mole-



cules that are modified with readily available directing groups are functionalized in the presence of commercially available additives, simple ligands, and oxygen as the terminal oxidant.



Strategic play: A direct functionalization of the title carbamates with a wide range of nucleophiles has been developed. The reaction proceeds efficiently at low temperature using Ph<sub>3</sub>CClO<sub>4</sub> as an oxidant.

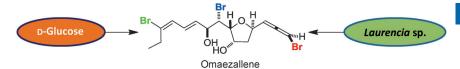
Sensitive functional groups are tolerated, thus allowing applications in natural product synthesis, the construction of chemical libraries, and the discovery of potential anticancer targets.

#### Synthetic Methods

Z. Xie, L. Liu,\* W. Chen, H. Zheng, Q. Xu, H. Yuan, H. Lou\* \_ \_ 3904 - 3908

Practical Metal-Free C(sp³)-H Functionalization: Construction of Structurally Diverse α-Substituted N-Benzyl and N-Allyl Carbamates





Omaezallene, a new brominated antifouling natural product isolated from the red alga Laurencia sp., was synthesized and its structure elucidated through NMR

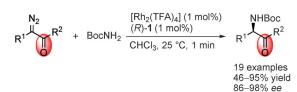
experiments. The antifouling activities of omaezallene and its isomers against the cypris larvae of the barnacle Amphibalanus amphitrite were also evaluated.

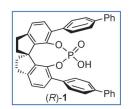
#### **Natural Products**

- T. Umezawa, Y. Oguri, H. Matsuura,
- S. Yamazaki, M. Suzuki, E. Yoshimura,
- T. Furuta, Y. Nogata, Y. Serisawa,
- K. Matsuyama-Serisawa, T. Abe,
- F. Matsuda,\* M. Suzuki,
- T. Okino\* \_\_ 3909 - 3912

Omaezallene from Red Alga Laurencia sp.: Structure Elucidation, Total Synthesis, and Antifouling Activity







Asymmetric Catalysis

B. Xu, S.-F. Zhu, \* X.-D. Zuo, Z.-C. Zhang, Q.-L. Zhou\* \_\_\_\_\_ 3913 - 3916

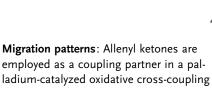
Enantioselective N-H Insertion Reaction of  $\alpha$ -Aryl  $\alpha$ -Diazoketones: An Efficient Route to Chiral  $\alpha$ -Aminoketones



Spiro inspiration: A highly enantioselective N-H insertion reaction of  $\alpha$ -diazoketones was developed by using cooperative catalysis by dirhodium(II) carboxylates and chiral spiro phosphoric acids. The insertion reaction provides a new access

route to diverse chiral  $\alpha$ -aminoketones, which are versatile building blocks in the organic synthesis, with fast reaction rates, good yields and high enantioselectivity under mild and neutral conditions.





reaction with organoboronic acids. This

reaction constitutes an efficient method-

ology for the synthesis of highly substituted furan derivatives. Palladium-carbene migratory insertion is proposed as the key step in this transformation. BQ = 1,4-benzoquinone.

#### Synthetic Methods

Y. Xia, Y. Xia, R. Ge, Z. Liu, Q. Xiao, Y. Zhang, J. Wang\* \_\_\_\_\_ 3917 - 3921

Oxidative Cross-Coupling of Allenyl Ketones and Organoboronic Acids: Expeditious Synthesis of Highly Substituted Furans



3763



#### Natural Products Synthesis

Y. Yang, C. W. Haskins, W. Zhang, P. L. Low, M. Dai\* \_\_\_\_\_\_ **3922 – 3925** 



Divergent Total Syntheses of Lyconadins A and C

**Like-a-podium**: Divergent total syntheses of the two *Lycopodium* alkaloids lyconadins A and C were developed from the intermediate 1. The synthesis of lyconadin A features a highly efficient ketal removal/formal aza-[4+2] cyclization to

form the core structure. A ketal removal/ Mannich reaction was used to construct the core structure of lyconadin C. The concise and flexible synthetic route offers a platform for the development of antineurodegenerative agents.

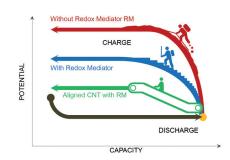


#### Lithium-Oxygen Battery

H.-D. Lim, H. Song, J. Kim, H. Gwon, Y. Bae, K.-Y. Park, J. Hong, H. Kim, T. Kim, Y. H. Kim, X. Lepró, R. Ovalle-Robles, R. H. Baughman, K. Kang\* 3926–3931



Superior Rechargeability and Efficiency of Lithium-Oxygen Batteries: Hierarchical Air Electrode Architecture Combined with a Soluble Catalyst Outstanding storage performance: A lithium—oxygen battery that uses a soluble catalyst combined with a hierarchical nanoporous air electrode shows high reversibility and good energy efficiency. Through the porous three-dimensional network of the air electrode, not only lithium ions and oxygen but also soluble catalysts can be rapidly transported, enabling significantly enhanced catalytic activity (CNT = carbon nanotube).

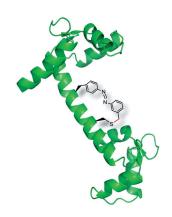


#### **Protein Engineering**

C. Hoppmann, V. K. Lacey, G. V. Louie, J. Wei, J. P. Noel, L. Wang\* **3932 – 3936** 



Genetically Encoding Photoswitchable Click Amino Acids in *Escherichia coli* and Mammalian Cells Click and switch: Photoswitchable click amino acids (PSCaas) contain a photoisomerizable azobenzene and an additional click functional group. After being incorporated into proteins, the PSCaa spontaneously generates a protein bridge with a nearby cysteine residue through proximity-enabled bioreactivity. The bridge isomerizes in response to light, thereby altering protein conformation. These PSCaas may enable optogenetic control of proteins in situ.



#### Homogeneous Catalysis

M. Jouffroy, R. Gramage-Doria, D. Armspach,\* D. Sémeril,

W. Oberhauser, D. Matt,\*

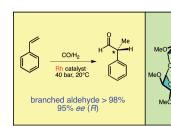
L. Toupet \_\_\_\_\_\_ 3937 - 3940



Confining Phosphanes Derived from Cyclodextrins for Efficient Regio- and Enantioselective Hydroformylation



Inside Cover

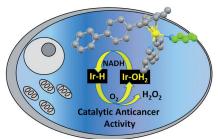


Rhodium in confinement:  $\alpha$ - and  $\beta$ -cyclodextrin derivatives bearing introverted P<sup>III</sup> donor atoms readily form monophosphane complexes in which the cyclodextrin cavity tightly wraps around the metal

center. When used as ligands in the rhodium-catalyzed hydroformylation of styrene, they lead to both high isoselectivity and enantioselectivity.



Protective pyridine: A novel half-sandwich organoiridium(III) complex with a pyridine ligand is more potent than both its chloride analogue and cisplatin towards a wide range of cancer cells. The pyridine ligand protects the iridium complex from rapid reactions with glutathione, and its potency correlates with a substantial increase in the amount of reactive oxygen species in the cancer cells.



#### Iridium Anticancer Drugs



Z. Liu, I. Romero-Canelón, B. Qamar,

J. M. Hearn, A. Habtemariam,

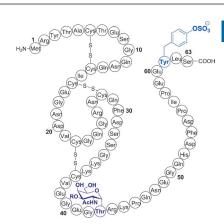
N. P. E. Barry, A. M. Pizarro,

G. J. Clarkson, P. J. Sadler\* 3941 - 3946

The Potent Oxidant Anticancer Activity of Organoiridium Catalysts



Modifications matter: Hirudin P6 is a leech-derived anti-thrombotic protein that is natively O-glycosylated and sulfated on tyrosine. Ligation chemistry was employed to assemble a library of homogeneously modified hirudin P6 proteins with variation in glycosylation at Thr-43 and sulfation at Tyr-61. The type of posttranslational modification present was shown to have a dramatic effect on inhibitory activity against both the fibrinogenolytic and amidolytic activities of thrombin.



#### Protein Synthesis

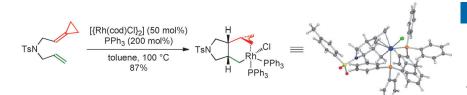
Y. S. Y. Hsieh, L. C. Wijeyewickrema,

B. L. Wilkinson, R. N. Pike,

R. J. Payne\* \_ 3947 - 3951

Total Synthesis of Homogeneous Variants of Hirudin P6: A Post-Translationally Modified Anti-Thrombotic Leech-Derived Protein





A rhodacycle intermediate implicated in rhodium-catalyzed reactions of alkylidenecyclopropanes (ACPs) was isolated and characterized. The structure of the metallacycle, which was unambiguously determined by X-ray crystallography, is catalytically competent in the rhodium-catalyzed carbocyclization and ene-cycloisomerization reactions of ACPs.

#### Metallacycles

P. A. Inglesby, J. Bacsa, D. E. Negru, P. A. Evans\* \_\_\_ \_\_\_\_ 3952 - 3956

The Isolation and Characterization of a Rhodacycle Intermediate Implicated in Metal-Catalyzed Reactions of Alkylidenecyclopropanes



Precipitation Preoxidation Carbonization An advanced templating method Nitrogen-enriched All-organic nanoporous carbon hairy nanoparticle

Nanocarbons from all-organic hairy nanoparticles: A versatile ATRP-based templating method has been developed to prepare nitrogen-enriched nanoporous carbon materials using all-organic hairy xPMMA-g-PAN nanoparticles as covalently fixed building blocks. Such materials are characterized by well-defined templated mesoporosity, high surface area, and an abundance of nitrogen-containing functional groups.

#### **Porous Materials**

D. Wu,\* Z. Li, M. J. Zhong,

T. Kowalewski,\*

K. Matyjaszewski\* -\_ 3957 - 3960

Templated Synthesis of Nitrogen-Enriched Nanoporous Carbon Materials from Porogenic Organic Precursors Prepared by ATRP







#### Protein Aggregation

S.-H. Chong, S. Ham\* \_\_\_\_ 3961 - 3964

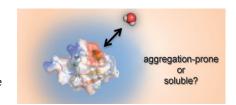


Interaction with the Surrounding Water Plays a Key Role in Determining the Aggregation Propensity of Proteins



#### Front Cover

Water, water, everywhere: Understanding the causes of protein aggregation is a central issue for understanding and preventing protein-aggregation diseases. Most studies to date have focused on the protein sequences without fully addressing the role of the surrounding water molecules. In fact, the interaction of a protein with the water surrounding it was found to play a pivotal role in determining its hydrophobicity and thus its aggregation propensity.



#### **Biocatalysis**

S. Singh,\* J. Zhang, T. D. Huber, M. Sunkara, K. Hurley, R. D. Goff,

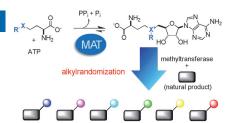
G. Wang, W. Zhang, C. Liu, J. Rohr,

S. G. Van Lanen, A. J. Morris,

J. S. Thorson\* \_\_\_\_\_\_ **3965 – 3969** 



Facile Chemoenzymatic Strategies for the Synthesis and Utilization of S-Adenosyl-L-Methionine Analogues



Mix and MATch: Methionine adenosyltransferase (MAT) was used to synthesize S-adenosylmethionine (SAM) analogues in a method directly compatible with downstream SAM-utilizing enzymes. As a proof of concept for the feasibility of natural product "alkylrandomization" by using this method, a coupled strategy in which MAT was applied in conjunction with the methyltransferase RebM was used to generate a small set of indolocarbazole analogues.

#### **Hybrid Materials**

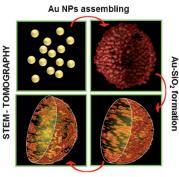
P. Kundu,\* H. Heidari, S. Bals,

N. Ravishankar,

G. Van Tendeloo \_\_\_\_\_\_ 3970 – 3974



Formation and Thermal Stability of Gold-Silica Nanohybrids: Insight into the Mechanism and Morphology by Electron Tomography



Thermal stability

A simple approach to synthesize gold nanoparticles (AuNPs) decorated on  $\mathrm{SiO}_2$  spheres is demonstrated and a rationale is discussed for the formation mechanism. Electron tomography is used to understand the morphology of and changes upon heating the hybrid (see picture). The hybrid nanoparticles show excellent thermal stability appropriate for several applications.

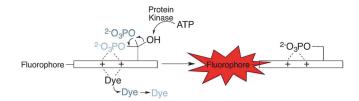
## Fluorescent Probes

N. P. Oien, L. T. Nguyen, F. E. Jernigan, M. A. Priestman,

D. S. Lawrence\* \_\_\_\_\_ 3975 - 3978



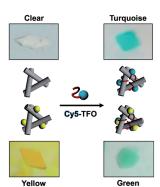
Long-Wavelength Fluorescent Reporters for Monitoring Protein Kinase Activity



Searching far and near: Fluorescent reporters for protein kinase activity were developed. The probing wavelength is preprogrammed by using readily available fluorophores, thereby enabling detection within the optical window of tissue,

specifically in the far-red and near-IR region. These agents were used to monitor endogenous cAMP-dependent protein kinase activity 1) in erythrocyte lysates and 2) in intact erythrocytes when using a light-activatable reporter.





Not so crystal clear: A macroscopic DNA crystal is presented based on the 3-fold symmetrical tensegrity triangle that has been functionalized with a triplex-forming oligonucleotide at each of its doublehelical edges. Attachment of a fluorescent dye to the oligonucleotide led to its incorporation within the asymmetric unit cell of the crystal and yielded colored DNA crystals.

#### **DNA** Objects

D. A. Rusling,\* A. R. Chandrasekaran, Y. P. Ohayon, T. Brown, K. R. Fox, R. Sha, C. Mao, N. C. Seeman\* \_\_\_\_\_ **3979 – 3982** 



Functionalizing Designer DNA Crystals with a Triple-Helical Veneer



Chain of command: A longstanding challenge in the chemical synthesis of human insulin has been solved by incorporating isoacyl dipeptide segments into the A and B chains to address the hydrophobicity-

associated issues. This route affords human insulin with a yield of 68% based on the starting A chain and represents the most efficient chemical insulin synthesis reported to date.

#### Protein Synthesis

F. Liu,\* E. Y. Luo, D. B. Flora, A. R. Mezo \_\_\_\_\_\_\_ **3983 – 3987** 

A Synthetic Route to Human Insulin Using Isoacyl Peptides



At a critical juncture: Well-defined fluorescent microarrays with various patterns were fabricated in a controlled manner by a rapid and straightforward microfluidic spinning technique. By the use of appropriately doped components, the intersections of the multidimensional microarrays served as microreactors for environmentally friendly chemical reactions to form fluorescent nanocrystals.



#### Microreactor Arrays

L. L. Xu, C. F. Wang, S. Chen\* \_\_\_\_\_\_ **3988 – 3992** 

Microarrays Formed by Microfluidic Spinning as Multidimensional Microreactors





Active detection: NADH and NADPH are critical components of cellular energy metabolism and operate as electron carriers. A novel fluorescent ubiquinonerhodol derivative (UQ-Rh) was developed

as a probe for NAD(P)H. By using the artificial promoter [ $(\eta^s-C_sMe_s)$ Ir(phen)- $(H_2O)$ ]<sup>2+</sup>, intracellular activation and imaging of NAD(P)H were successfully demonstrated.

# **Imaging Agents**

H. Komatsu,\* Y. Shindo, K. Oka, J. P. Hill, K. Ariga\* \_\_\_\_\_\_ **3993 – 3995** 

Ubiquinone-Rhodol (UQ-Rh) for Fluorescence Imaging of NAD(P)H through Intracellular Activation



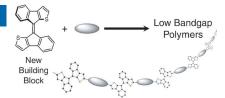


#### **Organic Solar Cells**

C.-Y. Chiu, H. Wang, F. G. Brunetti, F. Wudl, C. J. Hawker\* \_\_\_\_\_ 3996 - 4000



Twisted but Conjugated: Building Blocks for Low Bandgap Polymers



A simplified synthetic approach provided novel building blocks for conjugated polymers featuring a non-planar repeat unit and a distorted double bond. The resulting copolymers are characterized by a broad absorption profile and show promising results in solar cells.

#### Wireless Electrodeposition

- S. Yadnum, J. Roche, E. Lebraud,
- P. Négrier, P. Garrigue, D. Bradshaw,\*
- C. Warakulwit, J. Limtrakul,
- A. Kuhn\* \_ 4001 - 4005

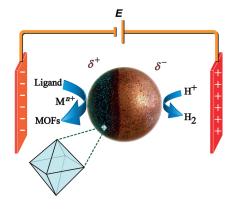


Site-Selective Synthesis of Janus-type Metal-Organic Framework Composites



#### Inside Back Cover

Two-faced MOF: The site-selective in situ synthesis of metal-organic framework (MOF) structures can be accomplished through bipolar electrochemistry, allowing the deposit to be confined to a defined area of a substrate without using masks or templates. This method can generate hybrid particles that have different combined functionalities on the same particle.





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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# Angewandte Corrigendum



Synthetic Studies on Chartelline C: Stereoselective Construction of the Core Skeleton

K. Iwasaki, R. Kanno, T. Morimoto,

T. Yamashita, S. Yokoshima,

T. Fukuyama\* \_\_\_\_ \_\_ 9160-9163

Angew. Chem. Int. Ed. 2012, 51

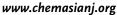
DOI: 10.1002/anie.201204726

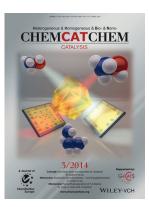
Some of the NMR spectra shown in the Supporting Information of this manuscript have not been properly processed. Copies of the correct spectra are available as Supporting Information for this Corrigendum.



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