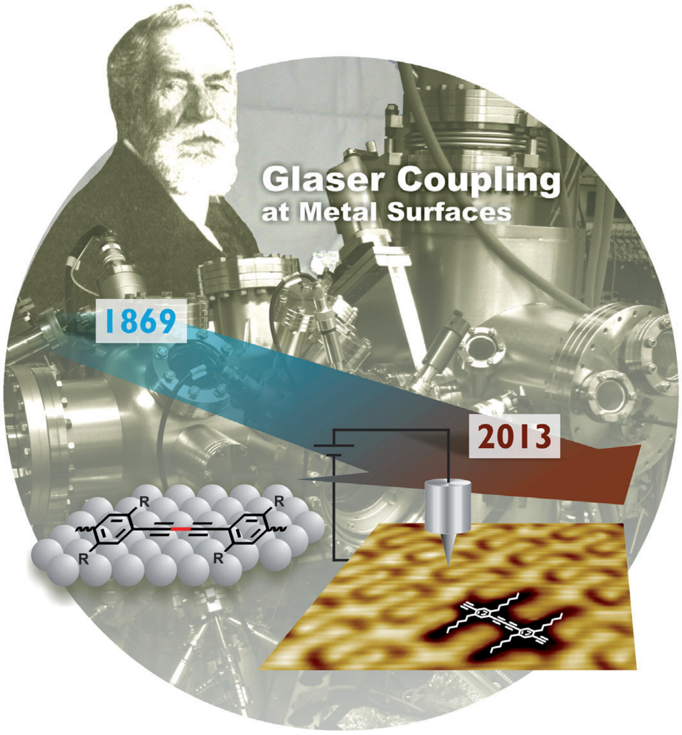
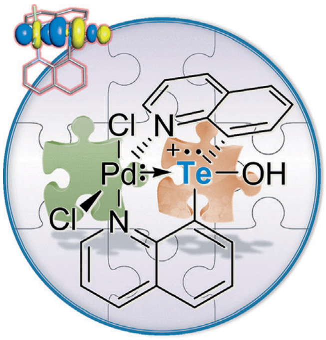
On-surface synthesis …

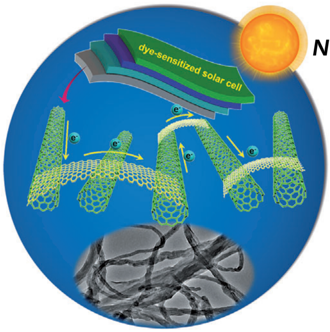


… enables the construction of defined nanostructures directly at surfaces through the covalent coupling of suitable organic precursors. These processes are carried out under ultrahigh-vacuum conditions and are monitored by scanning tunneling microscopy. In their Communication on page 4024 ff., A. Studer, H. Fuchs, and co-workers present a systematic study of the homocoupling of alkynes (Glaser coupling) as a versatile strategy for the construction of conjugated polymers at various metal surfaces.

Coordination Chemistry

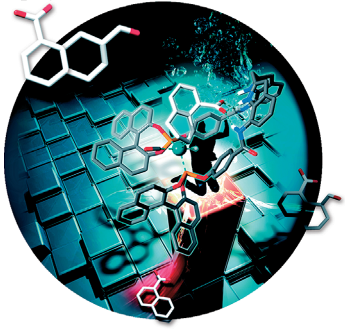
In their Communication on page 3864 ff., F. P. Gabbaï and T.-P. Lin report the successful installation of a telluronium cation, which acts as a Z-ligand, into the coordination sphere of a palladium(II) complex.





Nanomaterials

T. Liu, H. Peng, and co-workers describe the use of a unique counter electrode made of multiwalled carbon nanotubes that have been partially unzipped to produce bridging nanoribbons in their Communication on page 3996 ff.



Homogeneous Catalysis

J. N. H. Reek and P. Dydio report a rationally designed regioselective hydroformylation catalyst in their Communication on page 3878 ff. Noncovalent ligand–substrate interactions allow control of the selectivity, and allows access to usually unfavored products.

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Editorial

"... While a publication can be read again and again, a presentation is over immediately. Therefore, the rules for writing a publication differ from those for preparing a presentation. The best presentation is—like the best measurement—the one that has the highest signal-to-noise ratio ..."
Read more in the Editorial by Craig J. Hawker.

Service

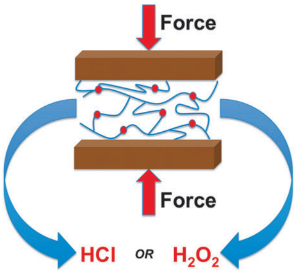
Author Profile

"My favorite saying is "be persistent and never give up". I admire anyone who inspires others and creates new ways of thinking. ..."
This and more about Sukbok Chang can be found on page 3804.

Books

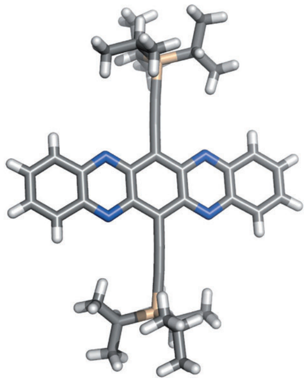
Highlights

Pressed for results: Mechanical forces can be used to generate reactive small molecules, such as mineral acids and hydrogen peroxide, from appropriately designed polymeric materials. These novel mechanically responsive scaffolds set the foundation for using mechanochemistry to access new classes of self-healing materials and to drive small-scale synthetic reactions.

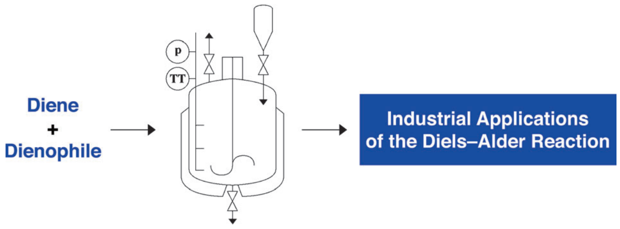


Minireviews

Electron-transporting alternatives to pentacene? Since 2010, several research groups have succeeded in synthesizing substituted diaza- and tetraazapentacenes as well as structurally similar tetraaza- and hexaazahexacenes. The symmetrical tetraazapentacene (see structure; C gray, H white, N blue, Si tan) has been investigated as an electron-transporting material in thin-film transistors.



Reviews



Diels–Alder reactions on a kg scale: The Diels–Alder reaction counts as one of the most popular transformations for the efficient synthesis of complex molecules, but its application in the industrial synthesis of pharmacologically active ingredients and agrochemicals as well as flavors and fragrances is less known. This Review gives examples of large-scale applications (> 1 kg) from a process research and development perspective.

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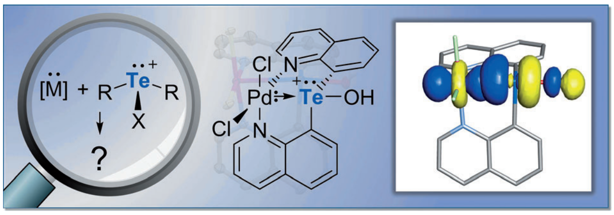
Communications

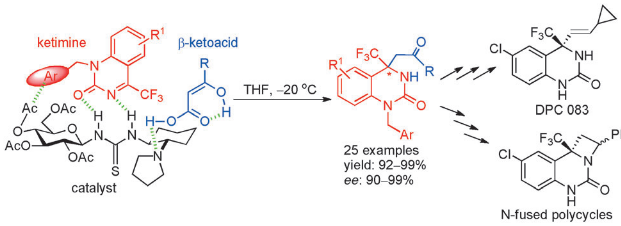
Coordination Chemistry

Frontispiece



A duel between lone pairs: A telluronium cation has been successfully installed in the coordination sphere of a palladium(II) complex. Despite the presence of a lone pair centered on the Group 16 element, the telluronium ion acts as a Z-ligand and accepts a d-electron pair from the palladium atom.

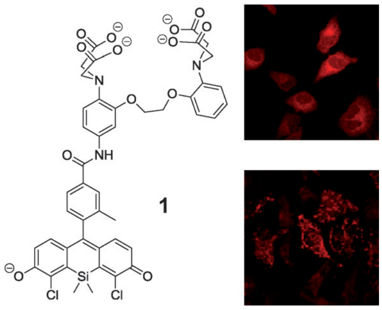
Organocatalysis



Key to success: The title reaction provides facile access to enantioenriched 3,4-dihydroquinazolin-2(1*H*)-ones containing a quaternary stereogenic center in high yields with excellent enantioselectivities. Subsequent transformations lead to the convenient preparation of the anti-HIV drug DPC 083 and N-fused polycyclic compounds without loss of enantiomeric excess.

Molecular Probes

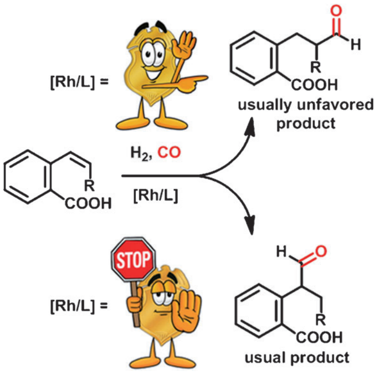
We see red (and yellow and green): Probe **1** was developed for the visualization of cytoplasmic Ca^{2+}, a pivotal second messenger in many biological responses. The new probe is suitable for multicolor imaging for the simultaneous detection of metal ions or proteins and is superior to the existing red fluorescent probe Rhod-2 for the monitoring of cytoplasmic Ca^{2+} oscillation in cultured cells (see fluorescence images of cells with **1** (top) and Rhod-2 (bottom)).



1

Homogeneous Catalysis

Back Cover

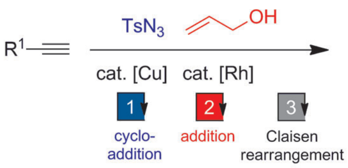


Go against the flow! A rationally designed regioselective hydroformylation catalyst, [Rh/L], in which noncovalent ligand–substrate interactions allow the unprecedented reversal of selectivity from the typical α-aldehyde to the otherwise unfavored product β-aldehyde, is reported. This catalytic system opens up novel and sustainable synthetic pathways to important intermediates for the fine-chemicals industry.

Multifunctional Reactions

T. Miura,* T. Tanaka, T. Biyajima, A. Yada,
M. Murakami* ——— 3883 – 3886

One-Pot Procedure for the Introduction of Three Different Bonds onto Terminal Alkynes through *N*-Sulfonyl-1,2,3-Triazole Intermediates



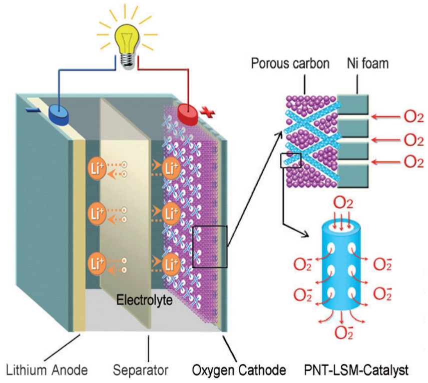
Triple strike: Copper(I) and rhodium(II) complexes can cooperate to facilely convert terminal alkynes into α-allyl-α-amino ketones through triazole intermediates. This synthetic process achieves the regioselective multifunctionalization of terminal alkynes with the formation of C–C, C–O, and C–N bonds in one pot.

Lithium–Oxygen Batteries

J. J. Xu, D. Xu, Z. L. Wang, H. G. Wang,
L. L. Zhang, X. B. Zhang* ——— 3887 – 3890

Synthesis of Perovskite-Based Porous $La_{0.75}Sr_{0.25}MnO_3$ Nanotubes as a Highly Efficient Electrocatalyst for Rechargeable Lithium–Oxygen Batteries

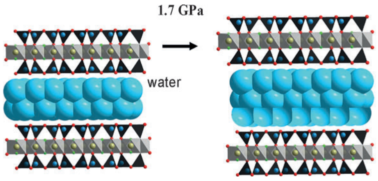
Tailoring an electrocatalyst: The synergistic effect of the high catalytic activity and the unique hollow channel structure of the perovskite-based porous $La_{0.75}Sr_{0.25}MnO_3$ nanotube electrocatalyst endows the Li-O_2 battery with a high specific capacity, superior rate capability, and good cycle stability (see picture).



High-Pressure Chemistry

S. You, D. Kunz, M. Stöter, H. Kalo,
B. Putz, J. Breu,*
A. V. Talyzin* ——— 3891 – 3895

Pressure-Induced Water Insertion in Synthetic Clays

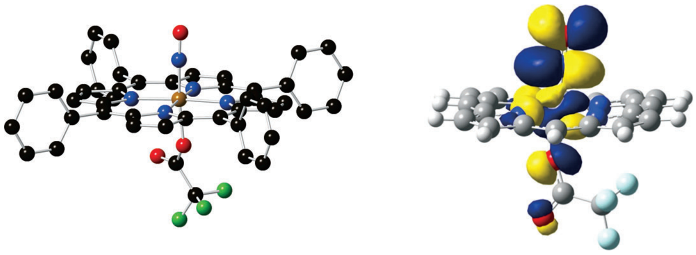


A high-pressure study of a synthetic smectite (Na-fluorohectorite) immersed in liquid media was performed using in situ synchrotron X-ray diffraction in a diamond anvil cell. A reversible phase transition because of the insertion of an additional water layer was observed for this material at 1.7 GPa. No similar transition was found when methanol was used as a pressure medium (see picture).

Crystal Nitrosylation

N. Xu,* L. E. Goodrich, N. Lehnert,*
D. R. Powell,
G. B. Richter-Addo* ——— 3896 – 3900

Preparation of the Elusive [(por)Fe(NO)(O-ligand)] Complex by Diffusion of Nitric Oxide into a Crystal of the Precursor



A crystal-gas method was used to prepare neutral [(por)Fe(NO)(O-ligand)] complexes. [(por)Fe(NO)(OC(=O)CF_3)] has an almost linear Fe–NO moiety. Porphyrin molecules move dramatically in the crystal upon NO diffusion into the lattice and binding to Fe. DFT calculations on this and related complexes provide insight into the *trans* effects of axial ligands on the Fe–NO angle.

The Mukaiyama Aldol Reaction

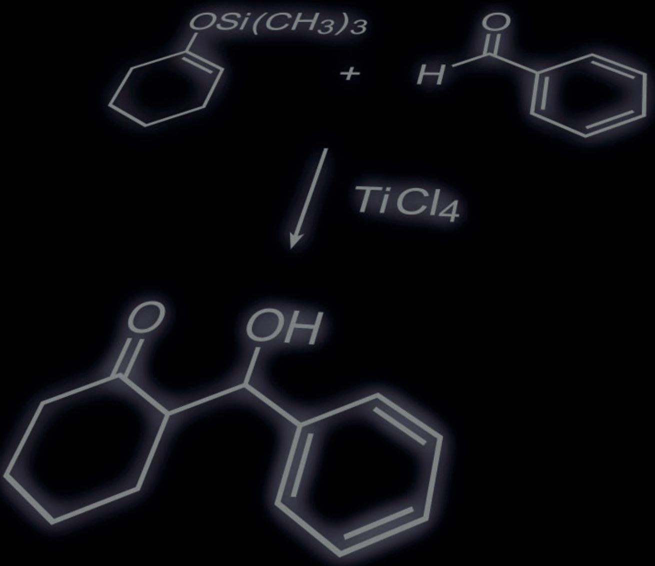
向山アルドール反応

40 Anniversary

One-Day Symposium at Hyatt Regency Tokyo, Shinjuku
August 31 (Saturday), 2013
www.banyu-zaidan.or.jp/banyu_symp/symp/mukaiyama
E-mail : mukaiyama-aldol@rs.tus.ac.jp

Speakers

Ryoji Noyori	*RIKEN and Nagoya University*
Manfred T. Reetz	*Philipps-University Marburg*
Ari M. P. Koskinen	*Aalto University*
Shinji Murai	*Nara Institute of Science and Technology*
Hisashi Yamamoto	*Chubu University*
Takeshi Kitahara	*Teikyo Heisei University*
Masakatsu Shibasaki	*Institute of Microbial Chemistry*
Katsuhiko Inomata	*Kanazawa University*
Nobuharu Iwasawa	*Tokyo Institute of Technology*
Masahiro Murakami	*Kyoto University*



Backup

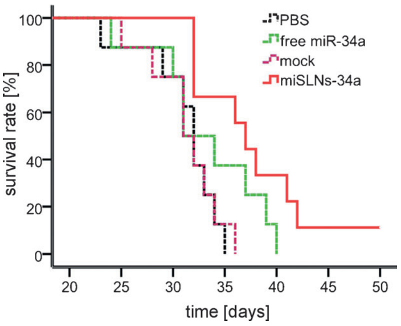
Banyu Life Science Foundation International, The Chemical Society of Japan, The Society of Synthetic Organic Chemistry, Japan, The Pharmaceutical Society of Japan, Japan Society for Bioscience, Biotechnology, and Agrochemistry

Drug Delivery

S. J. Shi, L. Han, T. Gong, Z. R. Zhang, X. Sun* ______ **3901 – 3905**

Systemic Delivery of microRNA-34a for Cancer Stem Cell Therapy

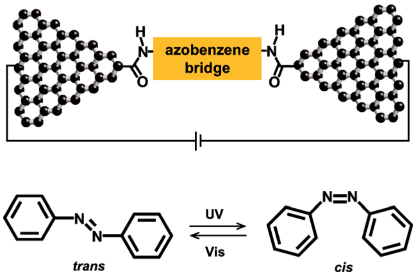
Delivered: A solid lipid nanoparticle (SLN) system was developed to deliver microRNA-34a (miR-34a) relevant for cancer stem cell (CSC) therapy into lung tissues. In miR-34a-containing SLNs (miSLNs-34a), miR-34a is protected from degradation in the serum and its cellular-transfection efficiency in vitro is increased. Thus, treatment with miSLNs-34a results in a higher probability of survival of CSC-bearing mice (see picture).



Molecular Switches

Y. Cao, S. Dong, S. Liu, Z. Liu, X. Guo* ______ **3906 – 3910**

Toward Functional Molecular Devices Based on Graphene–Molecule Junctions

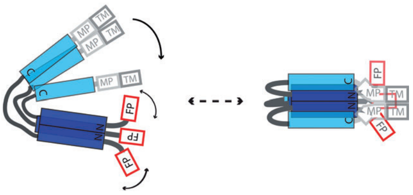


Building bridges: Molecular functionalities can be installed into electronic devices having graphene–molecule junctions generated by the dash-line lithographic (DLL) method. When a sulfonic acid modified azobenzene unit served as the bridge, the conductance could be switched reversibly by irradiation with light of different wavelengths and by exposure to solutions of different pH. Other molecular transport junctions were generated by metal-ion coordination.

Membrane Proteins

N. A. Lakomek, J. D. Kaufman, S. J. Stahl, J. M. Louis, A. Grishaev, P. T. Wingfield, A. Bax* ______ **3911 – 3915**

Internal Dynamics of the Homotrimeric HIV-1 Viral Coat Protein gp41 on Multiple Time Scales

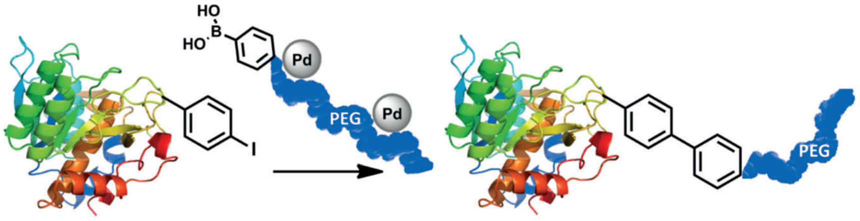


Always on the move: Solution NMR spectroscopy revealed a high degree of intrinsic mobility for the homotrimeric viral coat protein gp41: a prehairpin intermediate (left) may sample a range of relative orientations of the C-terminal and N-terminal heptad repeats, possibly in exchange with a low population of the late-fusion six-helical bundle (right; FP: fusion peptide, TM: transmembrane helix).

Protein PEGylation

A. Dumas, C. D. Spicer, Z. Gao, T. Takehana, Y. A. Lin, T. Yasukohchi, B. G. Davis* ______ **3916 – 3921**

Self-Liganded Suzuki–Miyaura Coupling for Site-Selective Protein PEGylation

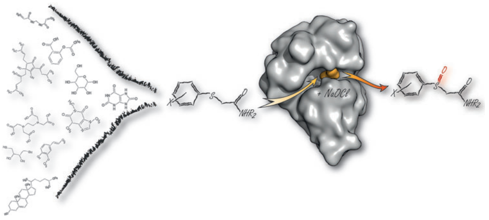


Building with PEGs: PEG–boronic acids, in the presence of simple Pd sources, are capable of acting as direct and effective Suzuki reagents in 70–98 % yield. When combined with non-natural amino acids, they allow efficient and direct, site-selective PEGylation of proteins at predetermined positions under biologically compatible conditions without the need for exogenous ligands.

Artificial Metalloenzyme

C. Esmieu, M. V. Cherrier, P. Amara,
E. Girgenti, C. Marchi-Delapierre,
F. Oddon, M. Iannello, A. Jorge-Robin,
C. Cavazza,* S. Ménage* **3922 – 3925**

An Artificial Oxygenase Built from Scratch: Substrate Binding Site Identified Using a Docking Approach

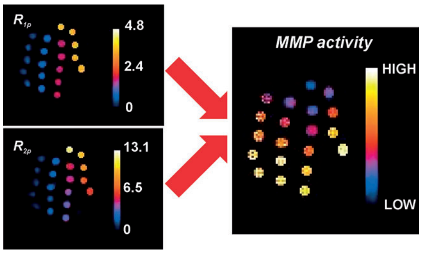


The substrate for an artificial iron monooxygenase was selected by using docking calculations. The high catalytic efficiency of the reported enzyme for sulfide oxidation was directly correlated to the predicted substrate binding mode in the protein cavity, thus illustrating the synergetic effect of the substrate binding site, protein scaffold, and catalytic site.

Molecular Imaging

V. Catanzaro, C. V. Gringeri, V. Menchise,
S. Padovan, C. Boffa, W. Dastrù,
L. Chaabane, G. Digilio,*
S. Aime* **3926 – 3930**

A R_{2p}/R_{1p} Ratiometric Procedure to Assess Matrix Metalloproteinase-2 Activity by Magnetic Resonance Imaging

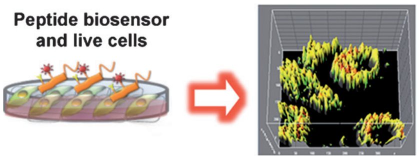


Parametric MRI: A paramagnetic gadolinium-loaded liposome for the MRI assessment of the activity of matrix metalloproteinase-2 (MMP-2) is described. The assessment relies on a procedure that involves the ratio R_{2p}/R_{1p} between the transverse and longitudinal paramagnetic contributions to the water proton relaxation rate. This method is independent of the total gadolinium concentration.

FLIM Biosensor

N. P. Damayanti, L. L. Parker,*
J. M. K. Irudayaraj* **3931 – 3934**

Fluorescence Lifetime Imaging of Biosensor Peptide Phosphorylation in Single Live Cells

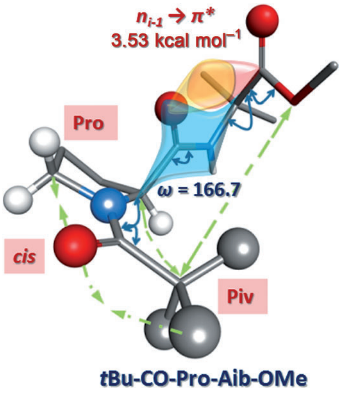


Better living through biochemistry: Phosphorylation of a Cy5-labeled Abl kinase peptide biosensor resulted in an extension of fluorescence lifetime in live cells. Time-correlated single photon counting fluorescence lifetime imaging (FLIM) enabled excellent signal-to-noise to visualize the subcellular patterns of this sensor (see picture). This strategy should be generalizable to other peptide-based kinase substrates for imaging of kinase activity in single cells.

Peptide Conformational Analysis

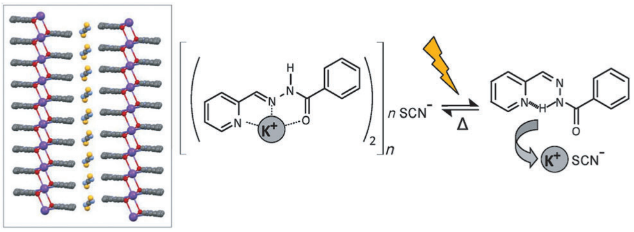
D. N. Reddy, G. George,
E. N. Prabhakaran* **3935 – 3939**

Crystal-Structure Analysis of *cis*-X-Pro-Containing Peptidomimetics: Understanding the Steric Interactions at *cis* X-Pro Amide Bonds



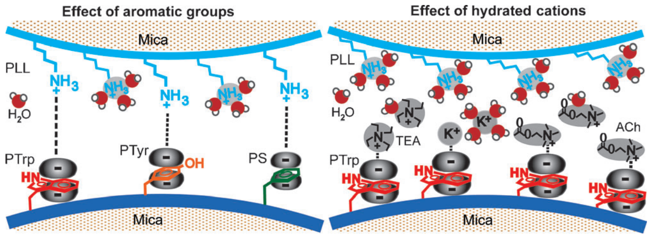
Catch the twist: The *cis* Piv-Pro conformer (Piv = pivaloyl) of peptides is no longer inaccessible. Any *cis* X-Pro tertiary-amide-bond conformer can be stabilized in crystals of peptides by accommodating the unavoidable distortion of the dihedral angle of the peptide bond to the carbonyl group of the Pro residue (see picture), in this case through $n_{i-1} \rightarrow \pi_i^*$ interactions. Steric clashes were not observed in the *cis* Piv-Pro rotamers studied.

Photoresponsive Materials



Freed at the flick of a photoswitch: An acyl hydrazone forms supramolecular assemblies upon the binding of specific salts, such as potassium thiocyanate. This process presents cation and anion selectivity as well as thermo- and photoreversibility (see scheme). In particular, the system displays photorelease of potassium cations and undergoes dynamic component exchange in the acyl hydrazone.

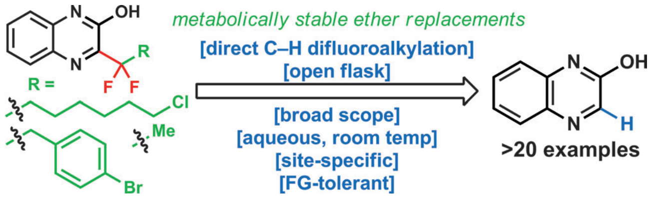
Noncovalent Interactions



The first direct probing of the nanomechanics of cation–π interactions in aqueous media was accomplished by using a surface forces apparatus with complementary theoretical simulations. The tetraethylammonium (TEA) ion breaks the adhesion between poly-L-tryptophan (PTrp) and poly-L-lysine (PLL) with a 100 times higher sensitivity relative to the K+ ion (PS = polystyrene, PTyr = poly-L-tyrosine, and ACh = acetylcholine).

VIP

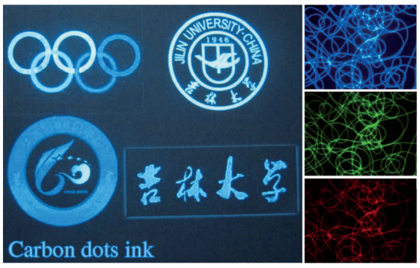
Bioisosteres



(Bioiso)steering in a new direction: A modular synthesis of reagents (e.g. sodium difluoroethylsulfinate) that can be used for the direct incorporation of difluoroalkyl groups onto heterocycles is reported. The scope and generality of the incorporation of difluoroalkyl groups is exemplified with the difluoroethyl group and a proof of principle is shown for a general synthesis of fluorinated heteroarylether bioisosteres.

Carbon Dots

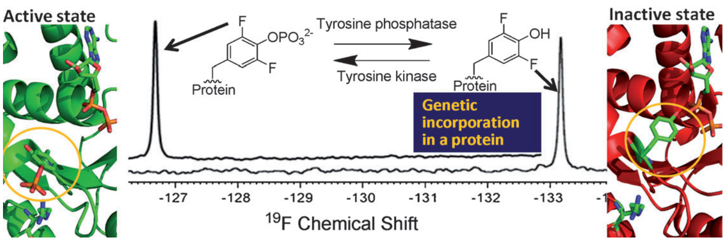
Shine on you crazy dots: A rapid and high-output strategy allows the fabrication of polymer-like carbon dots (CDs) with quantum yields as high as ca. 80%. This value is the highest reported to date for fluorescent carbon-based materials, and gives promise for their application in multicolor-patterning and biosensors.



Protein–Protein Interactions

F. H. Li, P. Shi, J. S. Li, F. Yang, T. Y. Wang, W. Zhang, F. Gao, W. Ding, D. Li, J. Li, Y. Xiong, J. P. Sun, W. M. Gong,* C. L. Tian,* J. Y. Wang* ____ **3958 – 3962**

A Genetically Encoded ^{19}F NMR Probe for Tyrosine Phosphorylation



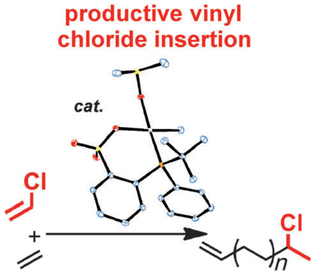
Simple and selective: Tyrosine phosphorylation is a pivotal post-translational modification which regulates the enzymatic activity, protein conformation, and protein–protein interactions. The highly efficient genetic incorporation of 3,5-difluorotyrosine (F2Y) in *E. coli* and the use of F2Y as a ^{19}F NMR probe for the tyrosine phosphorylation are reported (see picture).

Copolymerization

H. Leicht, I. Göttker-Schnetmann, S. Mecking* ____ **3963 – 3966**

Incorporation of Vinyl Chloride in Insertion Polymerization

Inside Cover

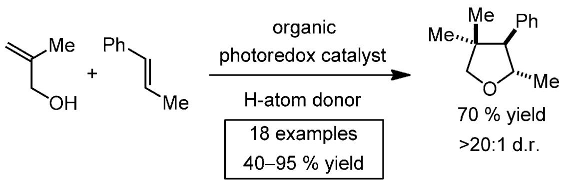


A palladium-catalyzed insertion copolymerization of vinyl chloride (VC) and ethylene gave chlorinated polyethylene with $CH_3CHCl(CH_2)_n$ units (see scheme; C blue, O red, Pd orange, S yellow). The CH_3CHCl end groups form by 2,1-insertion of VC into palladium hydride complexes, as revealed by detailed labeling studies. This first example of VC incorporation (up to 0.4 mol %) clearly shows that insertion (co)polymerization of VC is in principle feasible.

Photoinduced Electron Transfer

J.-M. M. Grandjean, D. A. Nicewicz* ____ **3967 – 3971**

Synthesis of Highly Substituted Tetrahydrofurans by Catalytic Polar-Radical-Crossover Cycloadditions of Alkenes and Alkenols

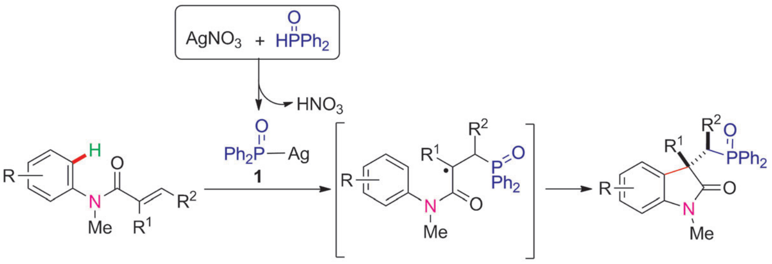


Light up my ring: The title reaction is catalyzed by an acridinium/phenylmalononitrile photoredox system. A variety of readily available olefins and unsaturated alcohols can be employed to furnish tetrahydrofuran adducts with complete regiocontrol and up to four contiguous stereogenic centers.

C–H Functionalization

Y. Li, M. Sun, H. Wang, Q. Tian, S. Yang* ____ **3972 – 3976**

Direct Annulations toward Phosphorylated Oxindoles: Silver-Catalyzed Carbon-Phosphorus Functionalization of Alkenes

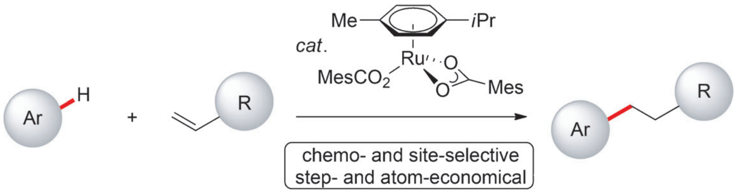


Silver screen: The $AgNO_3$-catalyzed carbon phosphorylation of alkenes occurs by an alkene addition/cyclization cascade. Ag^+ reacts with $Ph_2P(O)H$ to form the crucial active intermediate **1**, which promotes the reaction. This method requires a cheap, nontoxic silver salt as the catalyst and substrates for the transformation are simple and readily accessible.

C–H Activation

M. Schinkel, I. Marek,
L. Ackermann* ________ **3977 – 3980**

Carboxylate-Assisted Ruthenium(II)-Catalyzed Hydroarylations of Unactivated Alkenes through C–H Cleavage

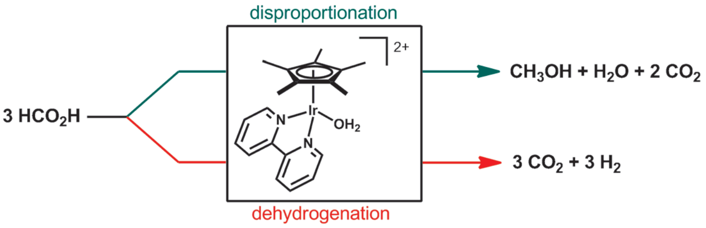


Catalytic: Ruthenium(II)biscarboxylate complexes enabled highly effective hydroarylations of unactivated alkenes through C–H bond activation. This method has a broad substrate scope and allowed for versatile functionalizations of highly fluorinated alkenes.

Homogeneous Catalysis

A. J. M. Miller,* D. M. Heinekey,
J. M. Mayer, K. I. Goldberg* **3981 – 3984**

Catalytic Disproportionation of Formic Acid to Generate Methanol

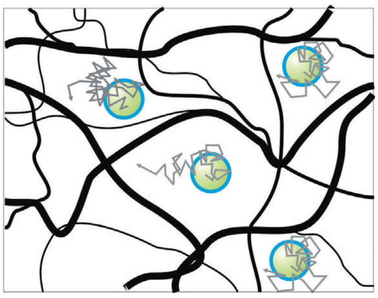


The homogeneously catalyzed disproportionation of formic acid to methanol, water, and carbon dioxide is accomplished by only 10 ppm of a readily accessible iridium catalyst, [Cp*Ir(bpy)(H$_2$O)]$^{2+}$ (Cp* = pentamethylcyclopentadienyl, bpy = 2,2′-bipyridine). Methanol is produced under mild, aqueous conditions, without the use of any organic solvents or hydrogen gas.

DNA Nanoparticles

A. J. Kim, N. J. Boylan, J. S. Suk,
M. Hwangbo, T. Yu, B. S. Schuster,
L. Cebotaru, W. G. Lesniak, J. S. Oh,
P. Adstamongkonkul, A. Y. Choi,
R. M. Kannan, J. Hanes* __ **3985 – 3988**

Use of Single-Site-Functionalized PEG Dendrons To Prepare Gene Vectors that Penetrate Human Mucus Barriers

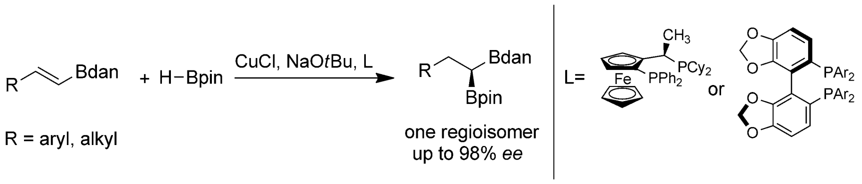


Mucus-penetrating DNA nanoparticles: A novel synthetic strategy was used to achieve a dense PEG coating on the surface of cationic polymer-based DNA nanoparticles. The dense PEG coating (blue in scheme) endows the nanoparticles with a muco-inert surface, which enables their rapid mucus penetration (trajectory indicated by gray line) and provides efficient gene transfer in various cell types.

Asymmetric Catalysis

X. Feng, H. Jeon, J. Yun* __ **3989 – 3992**

Regio- and Enantioselective Copper(I)-Catalyzed Hydroboration of Borylalkenes: Asymmetric Synthesis of 1,1-Diborylalkanes

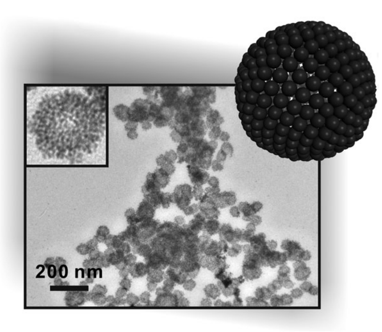


A bisphosphine/copper catalyst was used for the asymmetric hydroboration of 1,8-naphthalenediaminatoboryl (Bdan) substituted alkenes (see scheme; pin = pinacolato). Simple alkyl-substituted borylalkenes and styrene derivatives were hydroborated with high regio- and enantioselectivity. The electronic and steric properties of the Bdan group significantly affected the reactivity and regioselectivity of hydroboration.

Nanoparticle Assembly

C. Song, Y. Wang,
N. L. Rosi* ——— **3993 – 3995**

Peptide-Directed Synthesis and Assembly of Hollow Spherical CoPt Nanoparticle Superstructures



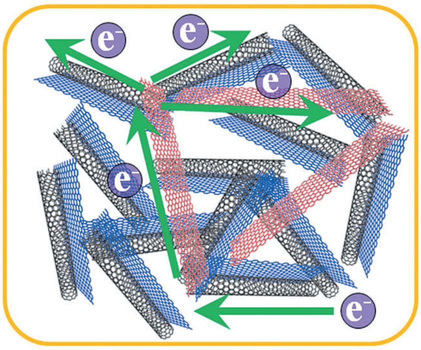
From “nano” to “super”: Peptide conjugates that consist of cobalt-binding peptides terminated with tails of biphenyl units were used to direct the synthesis and assembly of hollow spherical superstructures of CoPt nanoparticles (see picture). These magnetically separable superstructures exhibit electrocatalytic activity for methanol oxidation.

Nanomaterials

Z. Yang, M. Liu, C. Zhang, W. W. Tjiu,
T. Liu,* H. Peng* ——— **3996 – 3999**

Carbon Nanotubes Bridged with Graphene Nanoribbons and Their Use in High-Efficiency Dye-Sensitized Solar Cells

Inside Back Cover

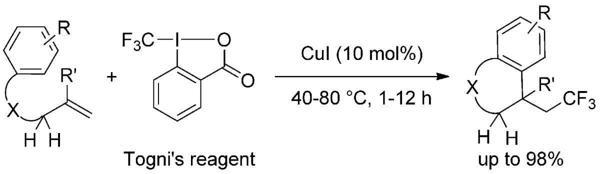


Tie a ribbon on it: Multiwalled carbon nanotubes were partially unzipped to produce nanoribbons that bridged the nanotubes. The unique structure favors rapid charge transport when used as counter electrodes in dye-sensitized solar cells, resulting in a maximum energy conversion efficiency of 8.23 % versus 7.61 % for a conventional platinum electrode.

Trifluoromethylation

H. Egami, R. Shimizu, S. Kawamura,
M. Sodeoka* ——— **4000 – 4003**

Alkene Trifluoromethylation Coupled with C–C Bond Formation: Construction of Trifluoromethylated Carbocycles and Heterocycles

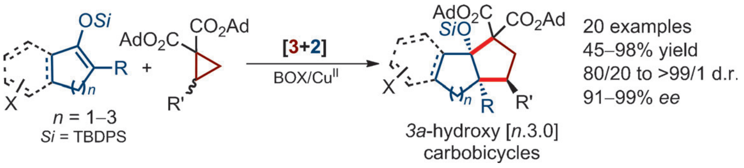


The combo pack: Copper-catalyzed trifluoromethylation of alkenes bearing an allylic proton combined with C–C bond formation affords the title compounds in good to high yields (see scheme). The reactions are faster than allylic trifluoromethylation, especially in 1,4-dioxane. A unique 1,6-oxytrifluoromethylation occurred instead of an anticipated seven-membered ring forming carbotrifluoromethylation reaction.

Asymmetric Catalysis

H. Xu, J. P. Qu, S. Liao, H. Xiong,
Y. Tang* ——— **4004 – 4007**

Highly Enantioselective [3+2] Annulation of Cyclic Enol Silyl Ethers with Donor–Acceptor Cyclopropanes: Accessing 3*a*-Hydroxy [*n*.3.0]Carbobicycles

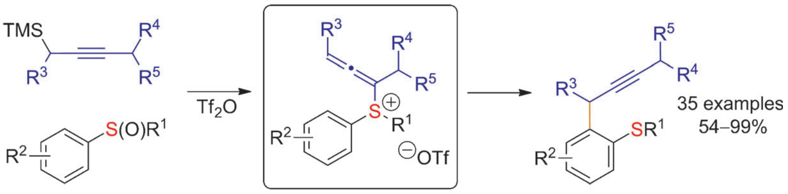


A new fuse: The title reaction was realized using a new bisoxazoline (BOX)/Cu^{II} catalyst. This reaction works well with cyclic enol silyl ethers of different sizes, and can be extended to dienol and benzene-fused substrates, thus providing an effective and general access to a range of 3*a*-hydroxy [*n*.3.0]carbobicycles which are found as a core structure in many natural products. TBDPS = *tert*-butyldiphenylsilyl.

Synthetic Methodology

A. J. Eberhart, D. J. Procter* **4008 – 4011**

Nucleophilic *ortho*-Propargylation of Aryl Sulfoxides: An Interrupted Pummerer/Allenyl Thio-Claisen Rearrangement Sequence



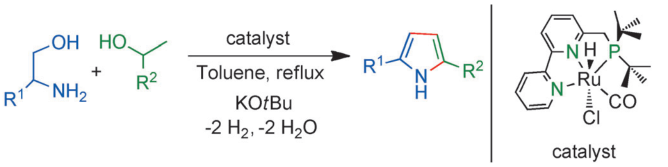
interrupted Pummerer reaction / allenyl thio-Claisen rearrangement; C–S bond formation facilitating C–C bond formation

A new direction: The nucleophilic *ortho*-propargylation of aryl sulfoxides exploits intermolecular delivery of the nucleophile to sulfur followed by an intramolecular relay to carbon (see scheme). The simple, metal-free procedure is general, regiospecific with regard to the propargyl nucleophile, and completely selective for products of *ortho*-propargylation over allenylation.

Homogeneous Catalysis

D. Srimani, Y. Ben-David, D. Milstein* **4012 – 4015**

Direct Synthesis of Pyrroles by Dehydrogenative Coupling of β-Aminoalcohols with Secondary Alcohols Catalyzed by Ruthenium Pincer Complexes

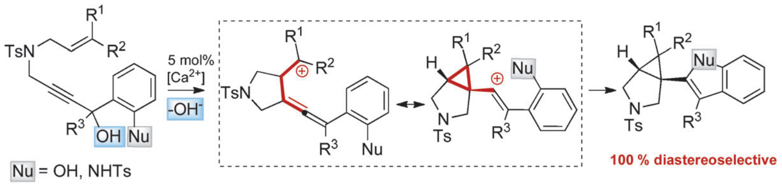


Pyrroles were synthesized in one step by using the acceptorless dehydrogenative coupling of amino alcohols with secondary alcohols (equivalent amounts), catalyzed by ruthenium pincer complexes (0.5 mol%) and a base (less than stoichiometric amounts) through selective C–N and C–C bond formation. This atom-economical, environmentally friendly methodology offers easy access to a range of substituted pyrroles in moderate to good yields.

Calcium Catalysis

T. Haven, G. Kubik, S. Haubenreisser, M. Niggemann* **4016 – 4019**

Calcium-Catalyzed Cyclopropanation



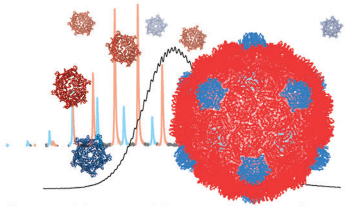
No transition metal needed: A calcium-catalyzed cycloisomerization yields highly substituted cyclopropanes with excellent diastereoselectivity (see scheme; Nu = nucleophile, Ts = *p*-toluenesulfonyl). The reaction is based on the equilibrium of a homoallenyl cation with its cyclopropane congener, which is known for gold-catalyzed reactions. According to mechanistic analysis the carbocation cascade is concerted asynchronous, and hence biomimetic.

Mass Spectrometry of Proteins

J. Snijder, R. J. Rose, D. Veesler, J. E. Johnson, A. J. R. Heck* **4020 – 4023**

Studying 18 MDa Virus Assemblies with Native Mass Spectrometry

Setting records: Native mass spectrometry was used to study the assembly of the 18 MDa capsid of bacteriophage HK97. The previous record for the analysis of capsids by this method was around 10 MDa. The results indicate that the efficiency of desolvation is the main priority in improving native MS instrumentation.



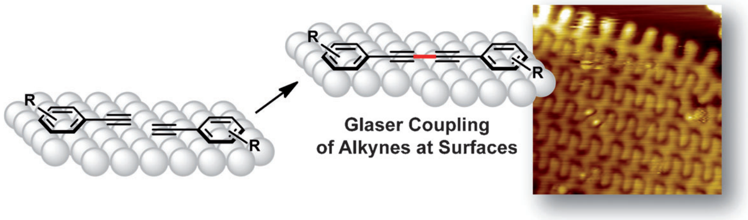
$C_{774900}H_{1235640}N_{215040}O_{218400}S_{5040}$

Surface Chemistry

H.-Y. Gao, H. Wagner, D. Zhong,
J.-H. Franke, A. Studer,*
H. Fuchs* ________ **4024 – 4028**

Glaser Coupling at Metal Surfaces

Front Cover

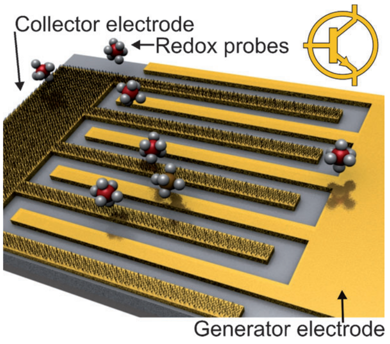


On-surface synthesis is a promising approach for constructing covalently bound nanostructures. However, the number of reliable chemical reactions suitable for on-surface chemistry is very limited. Arylalkynes can be coupled at various surfaces in a novel 2D Glaser coupling (see picture). This approach can be used for constructing conjugated materials directly on surfaces.

Redox Electronics

Y. Liu, B. Wolfrum, M. Hüske,
A. Offenhäusser, E. Wang,
D. Mayer* ________ **4029 – 4032**

Transistor Functions Based on Electrochemical Rectification

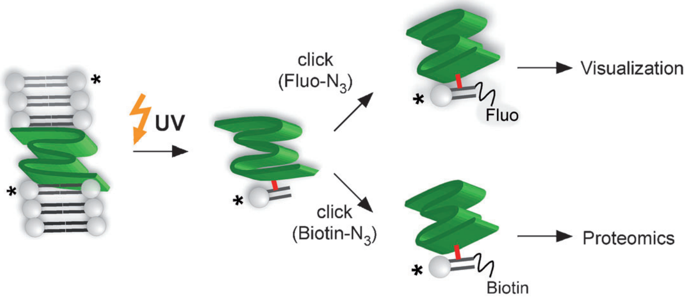


Golden transistor: A chip-based molecular transistor concept is based on an electrochemical rectifier. The device can perform transistor-like functions with opposite current directions depending on the redox inputs. The unidirectional current recorded at a chemically modified collector electrode can be tuned by the potential applied to an independent generator electrode, which allows switching of the output current and information encoding.

Protein–Lipid Interactions

P. Haberkant,* R. Raijmakers,
M. Wildwater, T. Sachsenheimer,
B. Brügger, K. Maeda, M. Houweling,
A.-C. Gavin, C. Schultz, G. van Meer,
A. J. R. Heck,
J. C. M. Holthuis ________ **4033 – 4038**

In Vivo Profiling and Visualization of Cellular Protein–Lipid Interactions Using Bifunctional Fatty Acids



Bifunctional lipid technology: Cells convert externally added photoactivatable and “clickable” fatty acids into a variety of bifunctional phospholipids that can be covalently linked to their protein-binding partners by irradiation with UV light. Derivatization of the clickable group with a reporter molecule makes it possible to identify and image the lipid-bound proteins in situ (see scheme).

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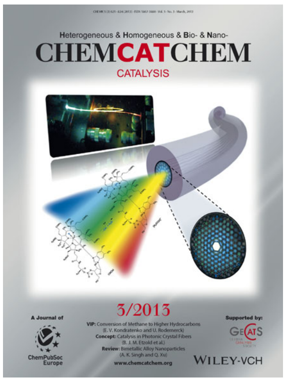
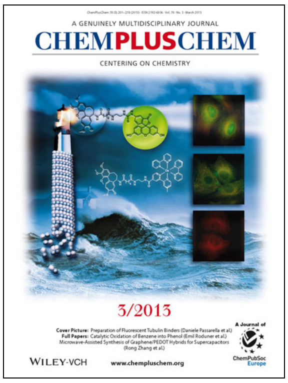
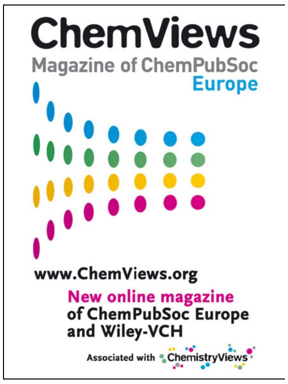
This article is accompanied by a cover picture (front or back cover, and inside or outside).







Angewandte Corrigendum

Electron-Induced Spin Crossover of Single Molecules in a Bilayer on Gold

T. G. Gopakumar,* F. Matino,
H. Naggert, A. Bannwarth, F. Tuczek,
R. Berndt **6262–6266**

Angew. Chem. Int. Ed. **2012**, *51*

DOI: 10.1002/anie.201201203

In this Communication, the preparation conditions of the molecular films were described incorrectly. During the deposition of [Fe(bpz)$_2$phen], the Au(111) substrate temperature was kept at about 100 °C. This correction does not affect the conclusions of the original Communication.