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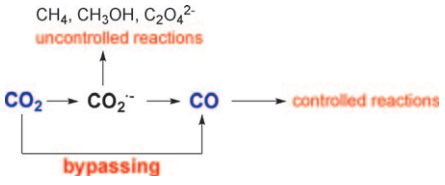
VIP *The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:*

Author Profile

"My favorite piece of research is Emil Fischer's beautiful work on the hexoses. When I was eighteen I wanted to move to and live in Spain (it just took me another 20 years to see it through) …" This and more about Kilian Muñiz can be found on page 4260.

Highlights

CO_2 Reduction



CO_2, can do: Recently, two groups independently described elegant ways for the direct two-electron reduction of CO_2 to CO, bypassing the formation of the $CO_2^{\bullet-}$ radical (see scheme). Armstrong et al. used a photoactive Ru complex and the CO_2-reducing enzyme CODH I immobilized on TiO_2 nanoparticles. Cummins et al. exploited a Nb^V nitrido complex in which the nitrido ligand reacts with CO_2 to give a carbamate species.

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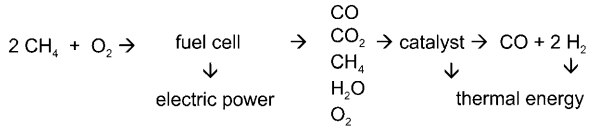
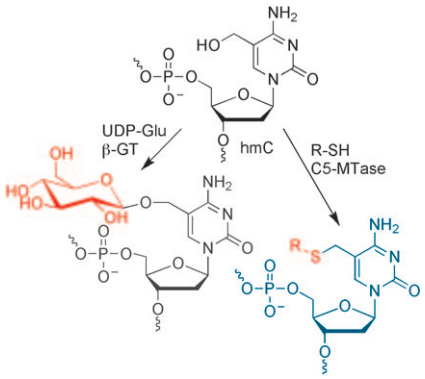


No coking is observed in a single-chamber fuel cell in which CH_4 and O_2 are converted into a mixture of H_2O, CO, H_2, CH_4, CO_2, and O_2; electric power is generated and the product gas mixture is passed over a syngas catalyst, which generates heat and forces the mixture to thermodynamic equilibrium. The advantages of this setup over the direct conversion of CH_4 and O_2 into syngas at higher temperatures are the generation of electric power and the improved reactor safety.

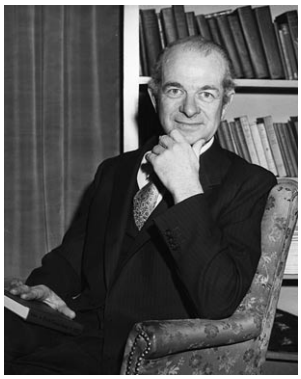
Single-Chamber Fuel Cells



New methods for the chemoenzymatic derivatization of 5-hydroxymethylcytosine (hmC) utilize bacteriophage β-glycosyltransferase (β-GT) or an unexpected activity of bacterial cytosine 5-methyltransferases (C5-MTase) to install reactive functional groups on the hydroxymethyl group for detection, quantification, affinity enrichment, and analysis of the recently discovered epigenetic hmC modification in mammalian DNA.

DNA Modification

Essays



Porphyrins may be confused, but Linus Pauling and Melvin Calvin were not! Calvin proposed "carboporphyrins" in 1943 and, unbeknownst to contemporary science, Pauling contemplated the existence and stability of such fundamental porphyrin isomers in 1944. What he called "isoporphyrins" with "extroverted pyrrole rings", nowadays called N-confused porphyrins, were discovered 50 years later in 1994 by Furuta and Latos-Grażyński et al.

Porphyrin Isomers

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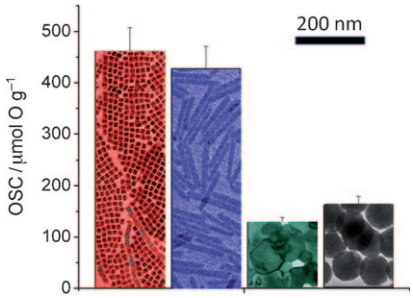
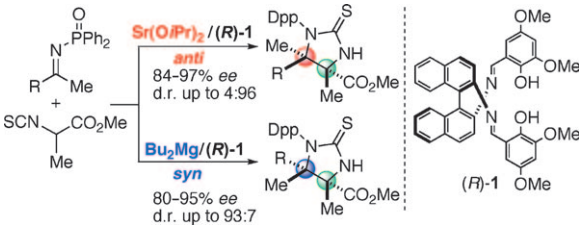
Small plate structure makes big difference: A facile synthetic method for high-quality ceria nanoplates enclosed by (100) facets involves the usage of a mineralizer. Compared to the 3D ceria nanomaterials prepared by combustion and hydrothermal treatment, the ceria nanoplates exhibit superior oxygen storage properties (see picture).

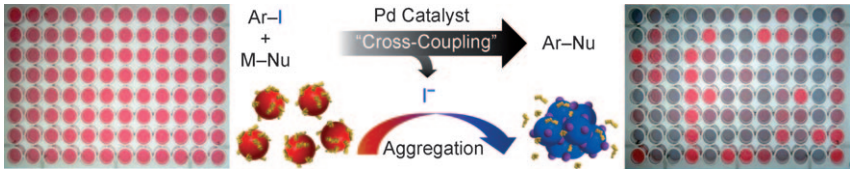


CeO_2 Nanoplates



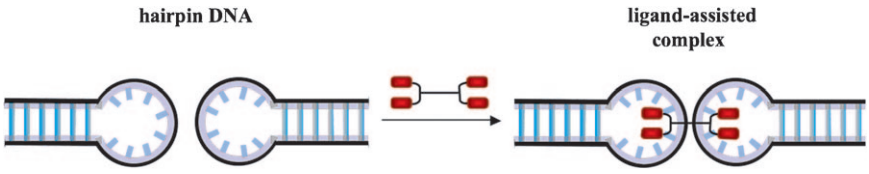
Now accessible: Sterically hindered vicinal tetrasubstituted carbon stereocenters, which are not accessible by asymmetric hydrogenation, were constructed by a catalytic asymmetric C–C bond formation (see scheme; Dpp = diphenylphosphinoyl). By changing the Group 2 metal center, stereodivergent access to α,β-tetrasubstituted α,β-diamino esters was realized.

Asymmetric Synthesis



Catching the couplings: A general and simple screening method for palladium-catalyzed coupling reactions of aryl iodides utilizes gold nanoparticles. This assay was successfully employed in several aminations, α-arylation of ketones, and decarboxylative couplings. 96 samples were screened in a few minutes.

Colorimetric Assays



All loopy: The interaction of a series of mismatch-binding molecules with hairpin DNA that contains a $d(CGG)_3$ sequence in the loop is described (see picture). Native polyacrylamide gel electrophoresis of hairpin-loop DNA shows that the newly synthesized mismatch-binding molecule, a tetrameric form of *N*-methoxycarbonyl-1,8-naphthyridine, assists the formation of a loop–loop complex of two DNA hairpin loops.

DNA Interactions

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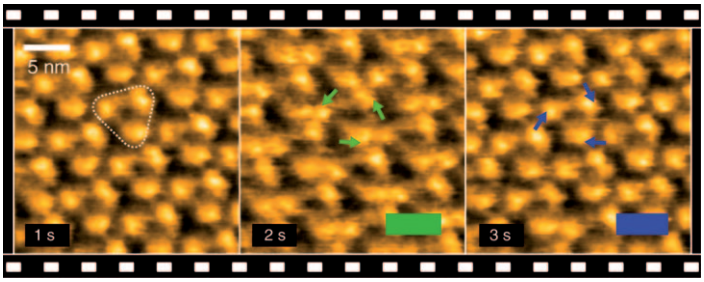
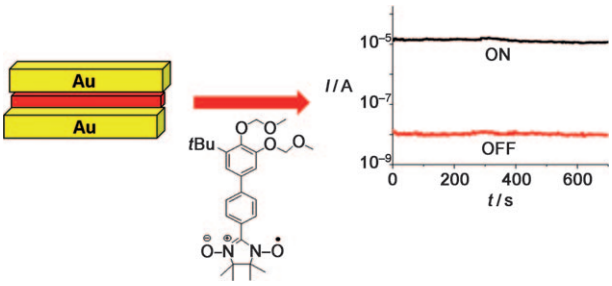


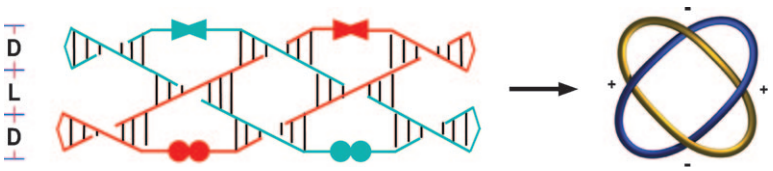
Blue light, green light: High-speed atomic force microscopy visualized light-induced structural changes of the D96N bacteriorhodopsin (bR) mutant under alternate two-color illumination. With green light, each bR molecule is displaced outward from the trimer center. This activated structure is driven back to the ground state by the subsequent blue-light illumination (see picture).

Real-Time Atomic Force Microscopy



Can't fight the SEEPR: Simultaneous electrochemical electron paramagnetic resonance reveals that a molecule containing the nitronyl nitroxide (NN) radical (structure and red layer) is redox-active, with switchability between oxidized and reduced states. An organic NN radical device utilizes the dual p- and n-type properties in a memory device.

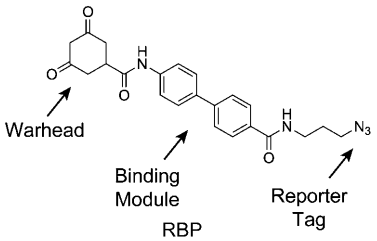
Molecular Electronics



DNA weaves a braided pattern: Two DNA single strands with mixed D- and L-nucleotides combine to weave a braided toroidal link. 5′,5′ linkages (fused circles) and 3′,3′ linkages (bow-tie structures) are needed to maintain the strand polarity. Properly placed L-nucleotides are needed to achieve the woven pattern.

DNA Nanotechnology

Three in one: The design strategy for redox-based probes (RBPs) that detect the reversible oxidation of protein tyrosine phosphatases (PTPs) includes a "warhead" that forms a covalent adduct with the oxidized active site cysteine of PTPs, a synthetic module that directs binding to the PTP active site, and a chemical reporter tag used for the identification, purification, or direct visualization of the probe-labeled proteins (see picture).



Chemoselective Redox Probes

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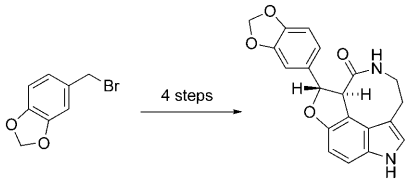
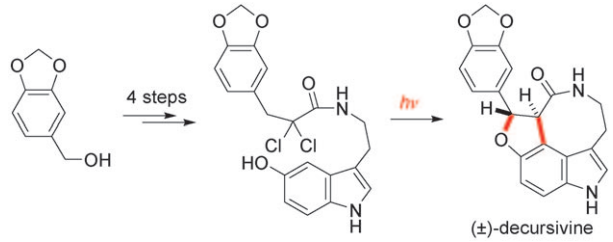
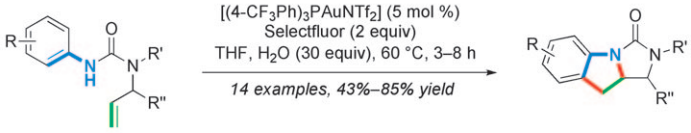


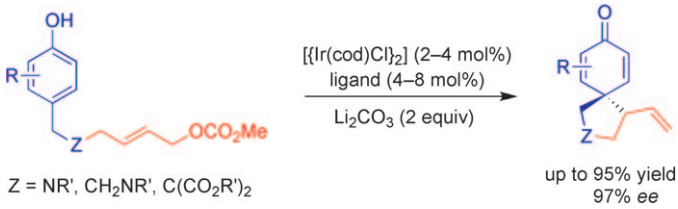
A four-step synthesis of the extracyclic, antimalarial indole natural product decursivine is described starting from commercial piperonyl bromide and serotonin (see scheme). A photoinitiated reaction cascade involving indole radical cation formation, rearrangement, radical recombination, rearomatization, elimination, and diastereoselective auto-acid-catalyzed closure of the dihydrofuran ring combine in a single step to conclude this remarkably efficient synthesis.



A photo op: The concise total syntheses of (±)-decursivine and (±)-serotobenine were achieved by using the titled cascade reaction, which is modeled on the biomimetic pathway. The synthesis of (±)-decursivine, which exhibits antimalarial activity, was carried out in five steps without using protecting groups.



Gold rush: A combination of oxidative gold(I)/gold(III) catalysis and C–H functionalization led to the first oxidative coupling between in situ generated alkyl gold reagents and C_{sp^2}–H bonds, affording tricyclic indolines through a formal [3+2] annulation between a vinyl group and an aniline moiety [see scheme; Tf = trifluoromethanesulfonyl, Selectfluor = 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate)].



Aromaticity lost: In the presence of [{Ir(cod)Cl}$_2$] and a binol-derived phosphoramidite ligand, spirocyclohexadienone derivatives were obtained with up to 97% *ee* through iridium-catalyzed intramolecular asymmetric allylic dearomatization of phenols (see scheme; cod = cycloocta-1,5-diene).

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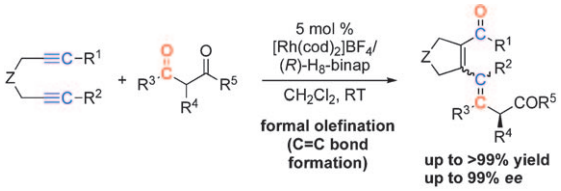
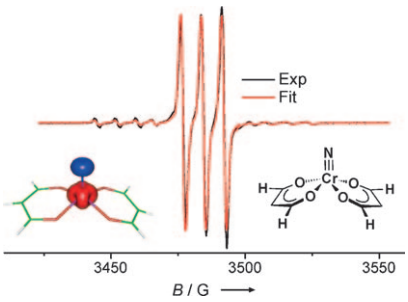


A cationic rhodium(I) complex catalyzes the title reaction of 1,6-diynes through a [2+2+2] cycloaddition and subsequent electrocyclic ring opening (see scheme; cod = 1,5-cyclooctadiene, H_8-binap = 2,2′-bis(diphenylphosphino)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl). The asymmetric intramolecular [2+2+2] cycloaddition of 1,3-dicarbonyl compounds with 1,6-enynes was also accomplished.

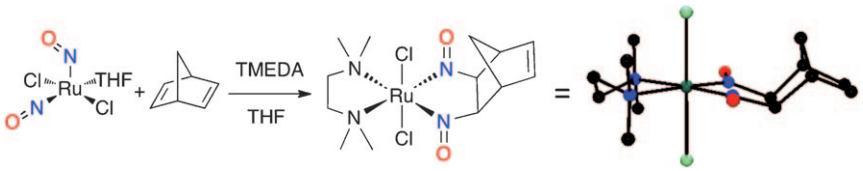
Asymmetric Catalysis

Longer, yet stronger: Terminal chromium(V) nitride complexes (see picture) react with low-valent platinum-metal complexes as well as with main-group Lewis acids to yield nitride-bridged systems. Rigorous fitting of the EPR data shows that the superhyperfine coupling of the chromium(V) center with the ^{14}N nuclear spin approximately doubles in response to the formation of a Cr–N bridge. This effect also exists in computations for the hypothetical lengthening of the Cr–N bond.



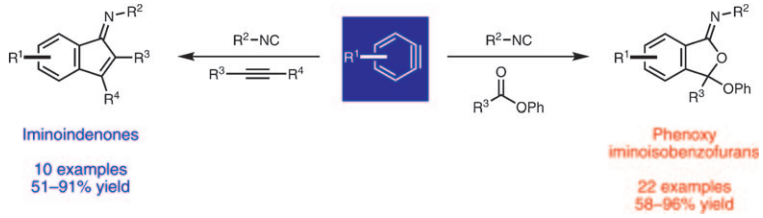
EPR Spectroscopy

Unruly NO more: The synthesis of $[RuCl_2(NO)_2(THF)]$ has been achieved by the reaction of $[\{(cymene)RuCl_2\}_2]$ with NO in THF. In the presence of a chelating L_2-type ligand $[RuCl_2(NO)_2(THF)]$ binds alkenes to its nitrosyl nitrogen atoms (see scheme).



Ligand-Based Reactivity

Triple crown: A pair of three-component coupling reactions between arynes, isocyanides, and either activated alkynes or phenyl esters generates unusual iminoindenones or phenoxy iminoisobenzofurans (see scheme), the latter of which may be advanced to *o*-ketobenzamides by performing direct hydrolysis. The synthetic utility of these compounds is demonstrated in a rapid preparation of substituted dibenzoketocaprolactams.



Multicomponent Reactions

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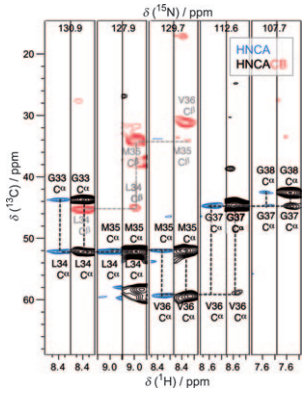
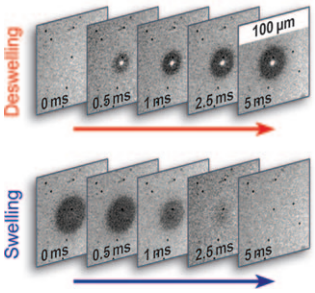


Structural characterization of insoluble proteins often relies on solid-state NMR spectroscopy. Perdeuteration and partial back-substitution of exchangeable protons, as proposed for crystalline model proteins, is now shown to lead to beneficial proton spectra for heterogeneous systems, such as fibrils formed by the Alzheimer's disease β-amyloid peptide Aβ40, the lipid reconstituted β-barrel membrane protein OmpG, and the α-helical membrane protein bacteriorhodopsin.

Protein Analysis



Laser-stimulated polymer brushes: The temperature-dependent switching kinetics of surface-grafted thermoresponsive polymer brushes were investigated by a stroboscopic micromanipulation/-characterization technique for real-time parallel measurements (see picture). Intrinsic response times range from the microsecond to the millisecond time scale; these results could lead to fabrication of nanosized polymeric actuators and sensors with unprecedented responsivities.

Stroboscopic Laser Techniques

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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