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 subject at school was certainly not sports. The three qualities that make a good scientist are curiosity, creativity, and dedication …"
This and more about Alois Fürstner can be found on page 2880.

News


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G. Bertrand


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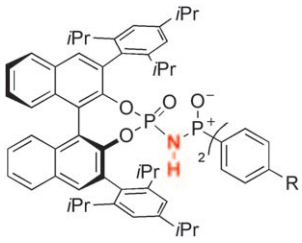
Highlights

Nitrogen enriched: The continuing quest for Brønsted acid catalysts that address unmet selectivity needs in organic synthesis has resulted in a new chiral phosphoric acid derivative. At the heart of this catalyst is a hydrogen-bond donor (N—H) that promotes an enantioselective intramolecular addition of oxygen (OH) to an azomethine (C=N). Diversity within a privileged chiral architecture invariably leads to new catalytic enantioselective chemical reactions.



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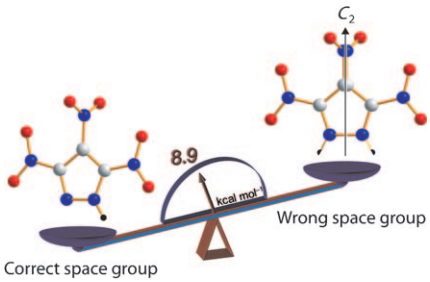
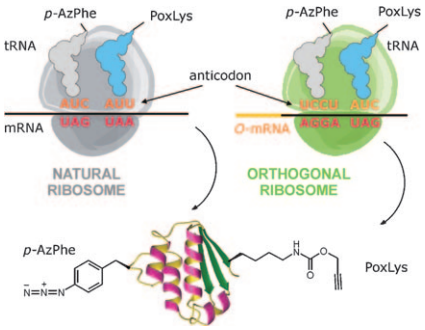


Trial and error: Topological analysis of the experimental electron density distribution of trinitropyrazole has allowed the energetic consequences of an overlooked pseudosymmetry to be quantified for the first time. This has allowed measurement of how much a small error in the assignment of a space group may cost a crystal structure; in the case of trinitropyrazole this was 8.9 kcal mol^{-1}.

Minireviews



Integration of new AA members: A pyrrolysyl-tRNA synthetase:tRNA pair can be combined with an orthogonal pair from *Methanocaldococcus jannaschii* to incorporate two chemically distinct noncanonical amino acids into a single recombinant protein. This modification was enabled by the tandem read-through of a three-base termination codon and a four-base frameshift codon at natural and orthogonal ribosomes.

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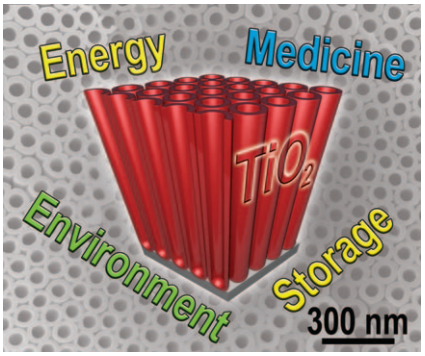
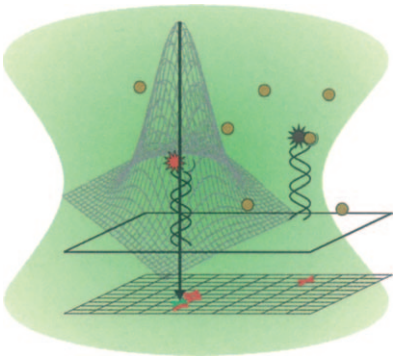
Reviews



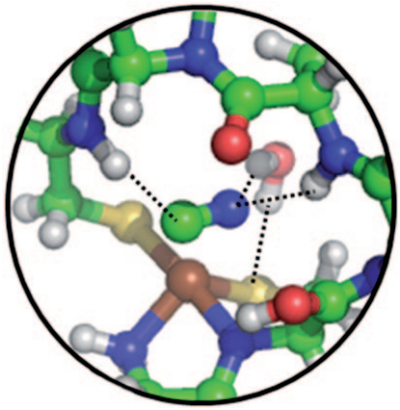
A new escapade for titania: Titanium dioxide is one of the most studied materials and has many applications, for example in photocatalysis, dye-sensitized solar cells, and biomedical devices. TiO_2 nanotubes, which have outstanding properties and have resulted in much research interest, play a particularly important part.

Communications

Revolution in resolution: Abbe's resolution limit has been overcome in fluorescence microscopy by using light-driven processes to switch the emission of fluorophores on and off. Alternatively, chemical reactions can be used, for example the coordination of Cu^{2+} ions to a fluorescent probe for the stochastic switching between spectroscopic states.



Water in site: The structure of a stable adduct of a peptide-based nickel superoxide dismutase model (NiSOD) with cyanide as substrate analogue is determined by NMR spectroscopy and optimized by DFT methods. A functional water molecule is found in the active site (see picture; Ni brown, O red/pink, C green, N blue). The role of this water molecule in the catalytic degradation of $O_2^{\bullet-}$ is discussed.



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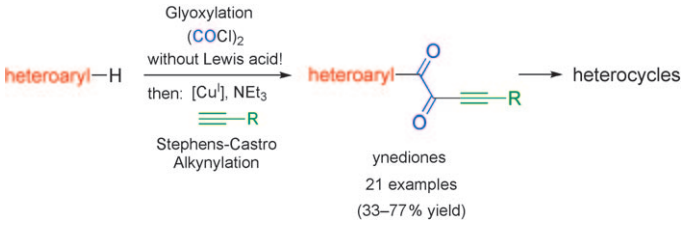
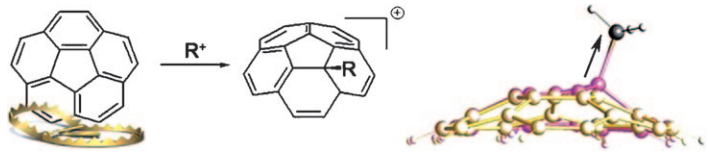


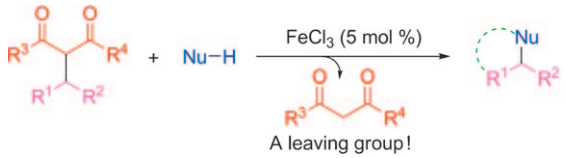
One step back, two steps forward! Starting from diverse heterocycles, the title reaction furnishes ynediones under very mild conditions in a direct and preparatively simple one-pot process. The key to avoiding decarbonylation is the Cu^{I}-catalyzed Stephens–Castro alkynylation rather than the usually more efficient Sonogashira coupling. In addition, novel highly atom-economical four-component syntheses of various heterocycles can be achieved.

Heterocycle Synthesis



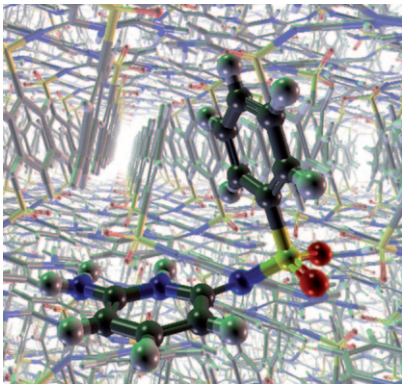
Trap for electrophiles: The reaction of corannulene with halogenated hydrocarbons in the presence of $AlCl_3$ gave the products of an electrophilic attack on the hub carbon atom of the curved aromatic surface (see picture). The X-ray diffraction characterization of a series of bowl-shaped cations illustrates structural deformations caused by the site-directed interior surface functionalization.

Carbocations



With our compliments: The 1,3-dicarbonyl unit has been shown to be a new and useful leaving group for iron-catalyzed bond cleavage (see scheme). This new strategy can complement the traditional Friedel–Crafts reaction and was applied in the synthesis of indene derivatives.

Synthetic Methods



The tale of Molecule VI: Past failures to predict the polymorphs of a sulfonimide using molecular mechanics have led to speculation that crystal-structure prediction may be of limited use owing to the kinetic nature of crystallization. An approach based on quantum mechanics now successfully predicts the three known polymorphs of this compound (molecule VI, see structure). Accurate lattice energy calculations are thus sufficient to predict the polymorphs of small organic molecules.

Crystal-Structure Prediction

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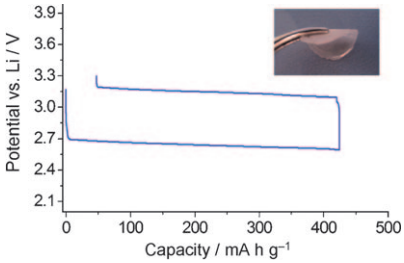
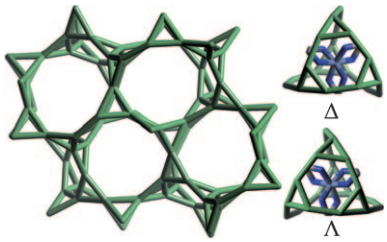


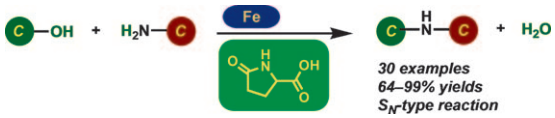
A polymer makes it possible: Use of an advanced polymer electrolyte allowed clarification of the oxygen reaction mechanism in lithium–air solid-state batteries. The related reversible processes are identified to occur at potential values that are the lowest ever reported in the absence of catalyst.

Electrochemical Cells



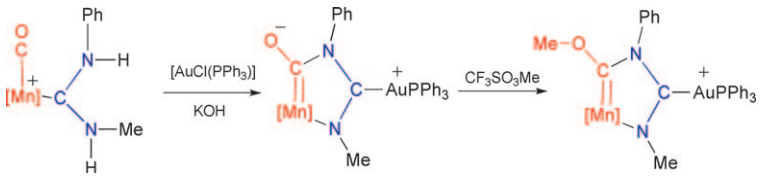
A new zeotype structure with 3D intersecting 10-ring channels is found in $[Ni(en)_3][Ga_2Ge_4O_{12}]$ (denoted GaGeO-CJ63, en = ethylenediamine). Its framework (see picture) is constructed exclusively by 3-rings, and the framework density is the second lowest among all known zeolite structures. One of the two kinds of cages in GaGeO-CJ63 is chiral and its chirality comes from the Δ and Λ enantiomers of occluded $[Ni(en)_3]^{2+}$.

Zeolite Analogues



Ironing it out: The straightforward N-alkylation using alcohols and iron/amino acid catalysis is described (see scheme). The reaction does not proceed by the conventional "borrowing hydrogen" mechanism, but appears to involve a substitution pathway (S_N) at the sp^3 carbon atom bearing the hydroxy group of the alcohol. Developing a catalyst that is effective at a near neutral pH was key to the successful N-alkylation.

N-alkylation



A Fischer carbene complex within the N-heterocyclic carbene skeleton is present in Mn^I/Au^I heterometallic compounds that were synthesized from an acyclic diaminocarbene complex, through a translocation process of metallic ions under basic conditions and subsequent alkylation with methyl triflate (see scheme; bipy = bipyridyl, [Mn] = $[Mn(CO)_2(bipy)]$).

Carbene Ligands

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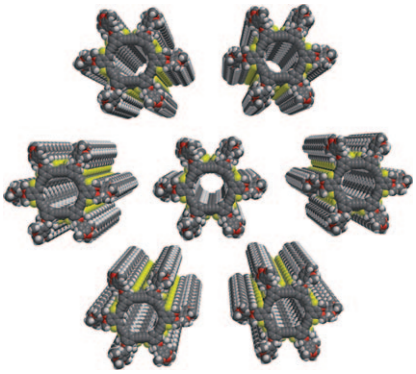
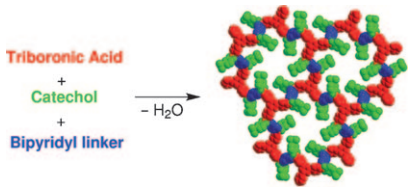
Take the tube: Self-organization of shape-persistent macrocycles in the liquid-crystalline phase by π–π stacking leads to empty nanochannels that have an inner diameter above one nanometer and either tight or more permeable walls (see picture). Solid-state NMR spectroscopy was used to confirm that the channels do not contain solvent molecules or alkyl chains.



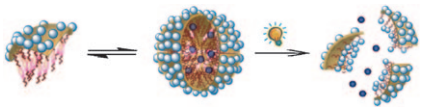
Macrocycles

The BN connection: Crystalline and soft molecular networks can be constructed using dative B–N bonds (see picture). The networks are obtained in a one-step, three-component reaction involving a triboronic acid, a catechol, and a bipyridyl linker.

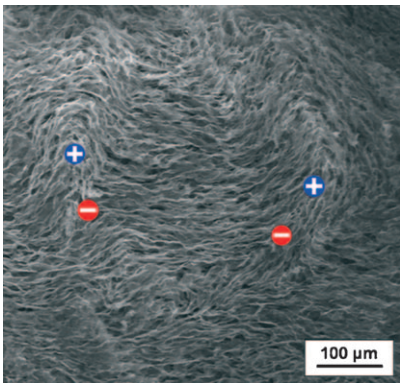


Supramolecular Chemistry

Supramolecular disassembly: Phototriggered release of noncovalently sequestered lipophilic guest molecules from dendritic supramolecular assemblies has been demonstrated. Facially amphiphilic dendrimers have been shown to provide a unique opportunity to fine-tune the release kinetics of the guest molecules in response to light (see picture).



Dendritic Micelles



Crystal clear: The liquid crystallinity of graphene oxide platelets in aqueous dispersion is demonstrated. Graphene oxide sheets are arranged around liquid-crystal disclinations (see picture). The orientation of the liquid crystals can be manipulated by a magnetic field or mechanical deformation.

Liquid Crystals

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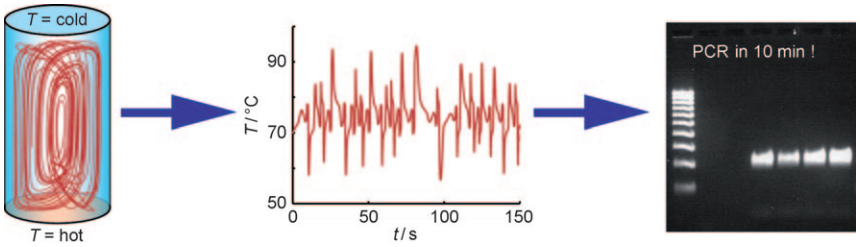
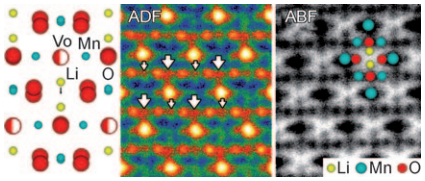
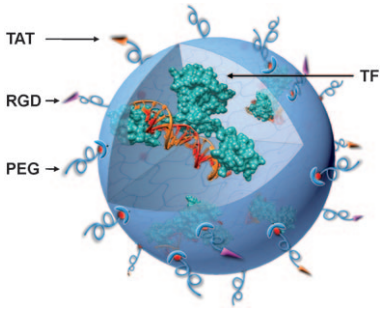


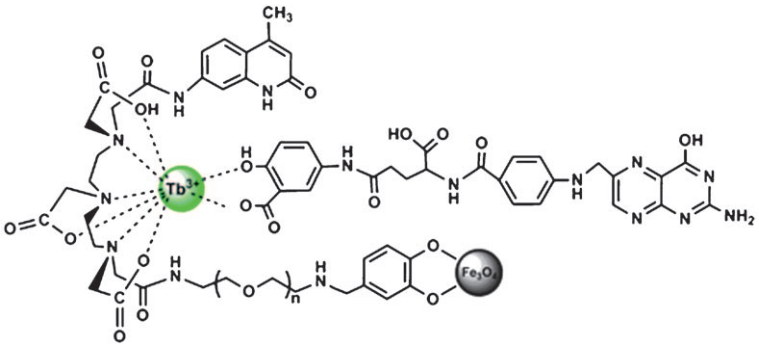
Going with the flow: DNA replication by the polymerase chain reaction (PCR) can proceed at a greatly accelerated rate when performed in the presence of a chaotic flow induced by microscale thermal convection (see picture). The consequences of these effects sharply contradict established design rules for chemistry involving coupled flow and reaction.



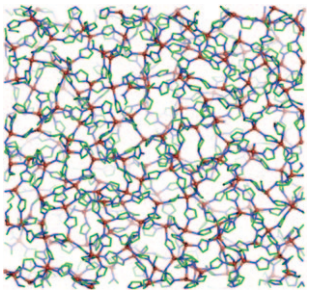
Direct observation of light elements (Li and O) in oxygen-deficient lithium manganese spinel by spherical aberration-corrected scanning transmission electron microscopy is reported. A previously unknown ordered structure was revealed by annular dark-field (ADF) imaging of oxygen columns, while Li ions are visualized successfully by annular bright-field (ABF) imaging (see picture).



Special delivery: A supramolecular nanoparticle provides a facile and modular protein delivery system (see picture, TAT enables cell membrane penetration, RGD targeting, and PEG passivation) for highly efficient transduction of intact (unmodified) transcription factors (TF). Such a TF delivery approach provides a powerful method for manipulating cellular behavior.

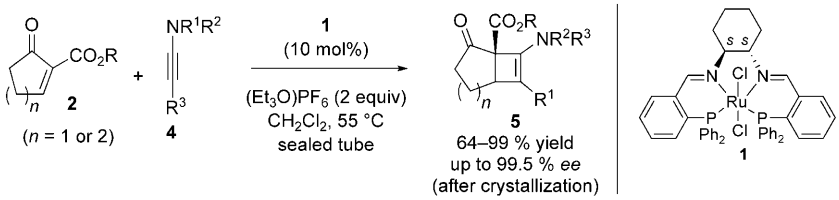


Dual imaging agent: A fluorescent Tb^{III} complex coupled to Fe_3O_4 nanoparticles and bearing a folic acid residue (see picture) shows superparamagnetism, low cytotoxicity, and high cell uptake, and thus can be used for in vitro fluorescence and magnetic resonance imaging of cells that overexpress the folate receptor, such as HeLa cells.



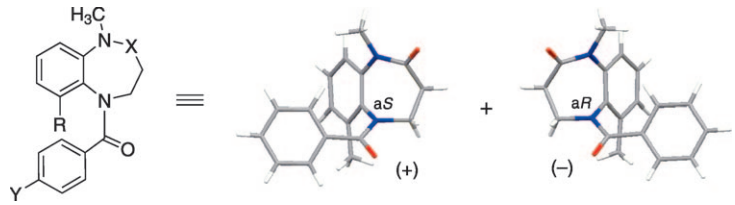
Each the same: A stable, recoverable, amorphous phase (see topology model) was produced by heating each of four different zeolitic imidazolate frameworks ZIF-1, -3, -4, and Co-ZIF-4. By comparing nanoindentation results, density measurements, and X-ray total scattering results, it is concluded that the structure of the amorphous phase is equivalent in each case. Amorphization was only observed in ZIFs encompassing unsubstituted imidazolate ligands.

Metal–Organic Frameworks



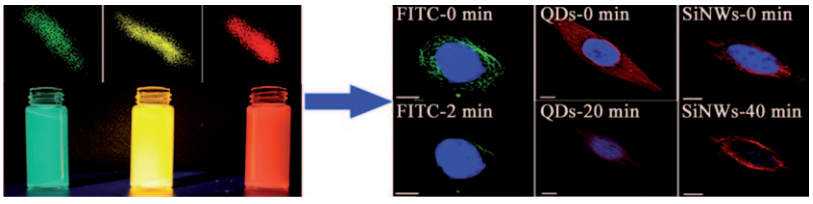
Chiral cyclobuteneamides made easy: Double chloride abstraction from the ruthenium/PNNP complex **1** in the presence of unsaturated β-keto esters **2** gives the dicationic adducts [Ru(**2**)(PNNP)]$^{2+}$ (**3**) that catalyze the [2+2] cycloaddition of a variety of ynamides **4** to produce cyclobuteneamides **5** with high yield and enantioselectivity (see scheme).

Asymmetric Catalysis



Latent chirality: Atropisomerism in the vaptan class of vasopressin receptor ligands with *N*-benzoyl benzo-fused seven-membered-ring nitrogen heterocycles was investigated by freezing the axis by *ortho* substitution. The a*S*/a*R* atropisomers caused by the Ar–N(=CO) axis were separated to reveal that the vasopressin receptor recognizes the *cis*,a*S* conformation (see picture; R = CH_3, X = –CO–, Y = H) when it binds to the ligand.

Atropisomerism



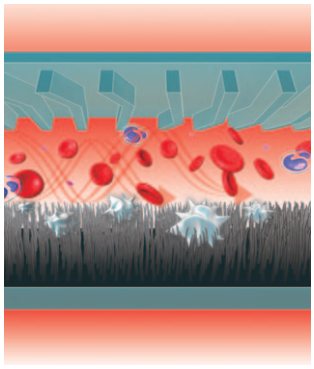
All aglow: Multicolored fluorescent quantum-dot (QD)-decorated silicon nanowires (SiNWs) are easily prepared by a one-pot microwave-assisted synthesis. The as-prepared SiNWs are highly luminescent (see picture, left) and are well-suited to long-term immunofluorescent cellular imaging (see stability comparison, right).

Fluorescent Probes

Contents

Cell Capture

Finding a needle in a haystack: A new technology is demonstrated to enrich circulating tumor cells (CTCs) with high efficiency by integrating an antibody-coated silicon nanopillar (SiNP, see picture; gray) substrate with an overlaid polydimethylsiloxane (PDMS) microfluidic chaotic mixer (turquoise). It shows significantly improved sensitivity in detecting rare CTCs from whole blood, thus providing an alternative for monitoring cancer progression.



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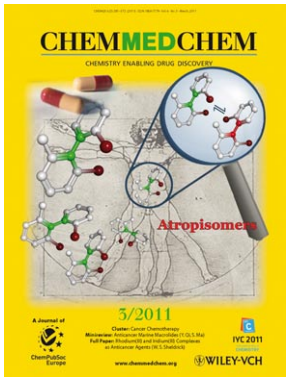

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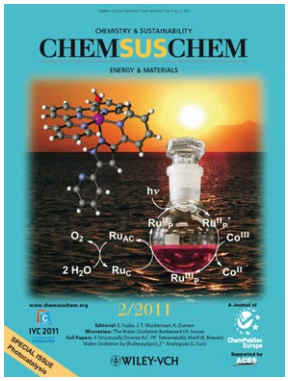

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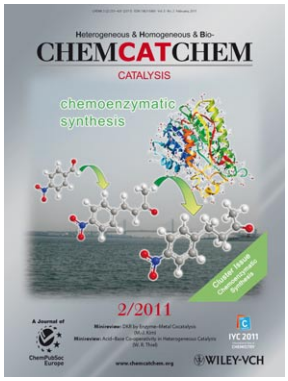

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