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 chemistry, though I was not particularly good at it at the time! My greatest achievement has been mentoring a large number of very successful young scientists …"
This and more about Anthony K. Cheetham can be found on page 3598.

News

S. W. Hell

K. Meerholz

B. M. Weckhuysen

Books

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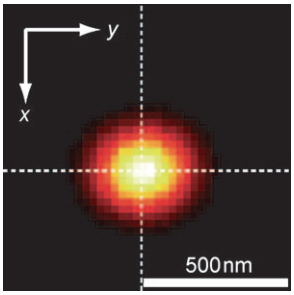
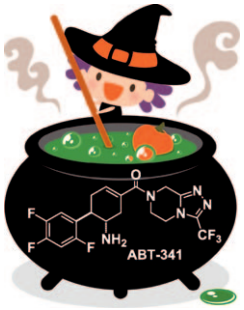
Highlights

The detection of single-molecule absorption under ambient conditions is a very challenging task, because the tiny change in transmission is difficult to discriminate against the noise from the light beam and from scattering. By pushing the detection limits of photothermal contrast imaging, single-molecule absorption has been measured by the refraction index change induced in the environment by the heat released from the molecule (see image).



All in one: A one-pot synthesis of the dipeptidylpeptidase IV selective inhibitor ABT-341 (see structure) by using an "uninterrupted sequence of reactions" has been developed. This strategy broadens the spectrum of one-pot reactions and is poised to speed up the synthesis of medicinally relevant drug compounds.



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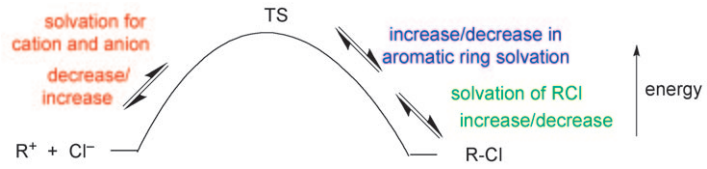

Solvent matters: Cations are reference substrates in the equation $\log k = s(E+N)$; neglect of solvent effects (see picture; TS = transition state) on their electrophilicity (E) leads to unreliable values of the nucleophilicity (N) and slope (s) parameters that characterize nucleophiles (k is the rate constant). Consequently, these parameters are not recommended for a general scale of nucleophilicity as suggested by Mayr and co-workers.

For the USA and Canada:
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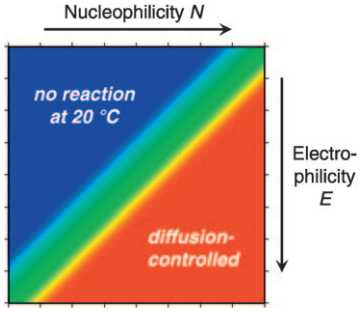
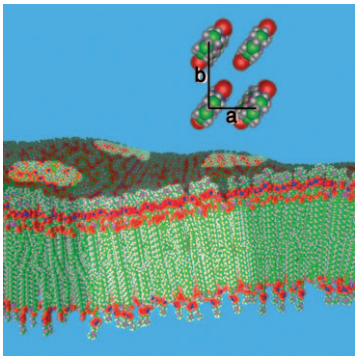
Simple and unambiguous: In the equation $\log k = s(E+N)$, the nucleophilicity N is obtained through the intercepts on the abscissa of linear $\log k$ versus E (electrophilicity) correlations. This approach places nucleophiles that differ by more than 30 orders of magnitude in reactivity on a single scale that can be used as a guide for designing organic syntheses. The equation in question is not only more practical but is also more precise than Bentley's alternatives.

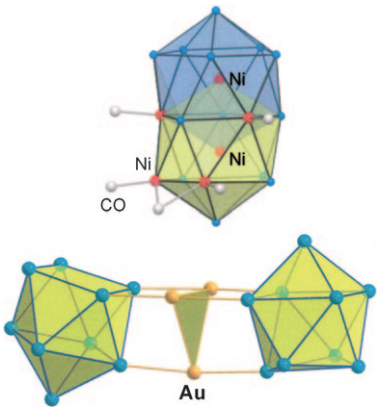


Minireviews



Are we all on the same raft? Membrane lipids segregate into domains. During the past two decades the structural organization of such lipid domains has been studied by several X-ray diffraction techniques. The correlation between crystalline lipid domains and lipid phases, and their relevance to functional domains in biological membranes are discussed in this Minireview.

Reviews



Zintl ions go intermetalloid: Zintl phases are mainly at home in solid-state chemistry, but their soluble representatives open fascinating possibilities as precursors for intermetalloid clusters and cage compounds. The recent upsurge of research activity in this field has now provided a rich plethora of new compounds, for example Zintl ions functionalized with organic groups, by oxidative coupling reactions, or by encapsulation of metal ions with the formation of endohedral clusters and intermetalloid compounds.

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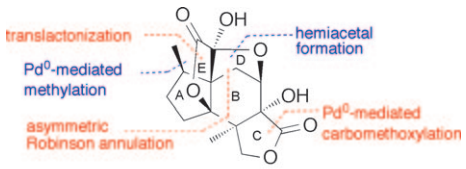
Communications

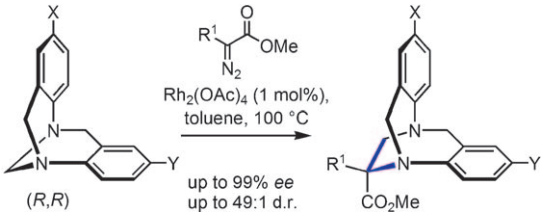
Natural Products



1: (−)-jiadifenolide

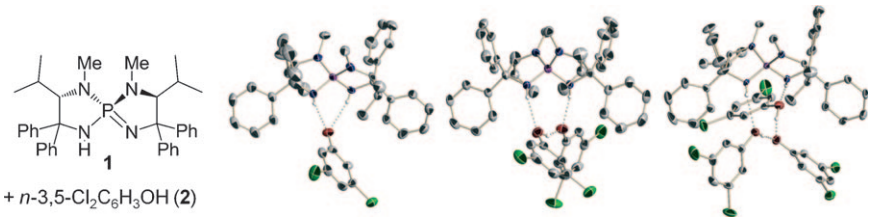
Neurofunk: Highlights of the synthesis of **1**, a potent modulator of neurotrophic factors, include construction of the B ring through an asymmetric Robinson annulation, assembly of the E ring lactone through a novel acid-induced cascade reaction, and Pd⁰-mediated carbomethoxylation and methylation reactions for the construction of the C and A rings, respectively.

Synthetic Methods



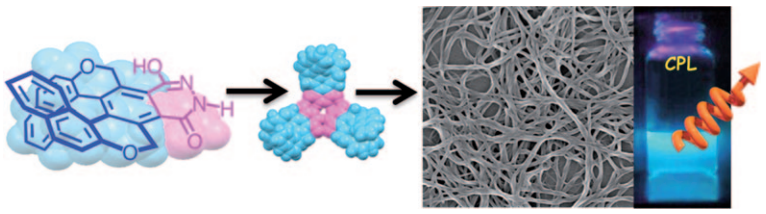
Bridging the gap: Configurationally stable ethano-bridged Tröger bases have been prepared in a single step by the direct rhodium(II)-catalyzed reaction of methano-bridged Tröger bases and diazo esters (see scheme). The process is general, enantiospecific, diastereoselective (with introduction of a new quaternary carbon center), and regioselective.

Supramolecular Catalysis

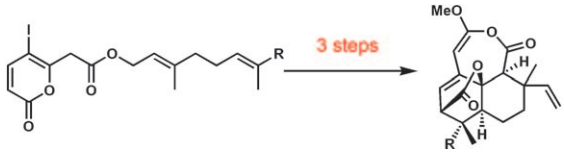


As you like it: Low-temperature ^{31}P NMR spectroscopic and X-ray crystallographic analyses have revealed that chiral *P*-spiro triaminoiminophosphorane **1** and 3,5-dichlorophenol (**2**) selectively assemble into three types of discrete molecular structures, **1**·[**2**]$_n$ (n = 1–3; see picture) depending on the stoichiometry of **2**.

Self-Assembly

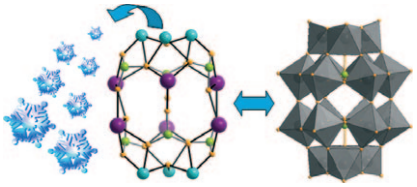


High in fiber: 1D fibrous superstructures are formed by an enantiopure phthalhydrazide-functionalized helicene in nonpolar solvents. Trimeric disks are formed by hydrogen-bonding interactions of phthalhydrazide units that are longitudinally interlocked for optimal packing (see picture). The resulting supramolecular assemblies exhibited large circularly polarized luminescence in solution.



In a flash: The total synthesis of transtaganolide and basiliolide natural products is achieved in three steps from achiral, monocyclic esters (see scheme). Featured in the syntheses are an Ireland-Claisen/Diels–Alder cascade and a novel methoxyacetylide coupling/cyclization sequence.

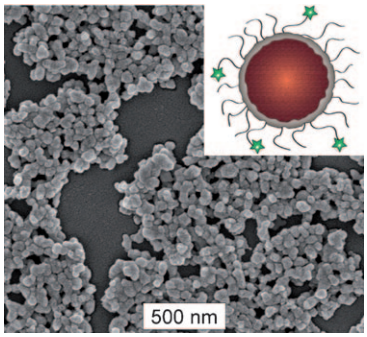
Natural Product Synthesis



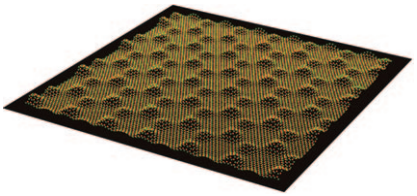
Cool stuff: The usage of phosphonates has led to formation of a family of 3d–4f heterometallic cages with a Wells–Dawson-like structure (see picture; Gd, Dy, or Y purple; Ni cyan; P green; O orange; C gray). Magnetic studies show ferromagnetic interactions within the oxo-centered nickel triangle and huge entropy change in the Gd analogue, which, in principle, can be used as an ultralow-temperature coolant.

Molecular Coolers

Seeing is believing: Phosphorescent nanoscale coordination polymers (NCPs) with unprecedentedly high dye loadings were coated with thin silica shells to tune the dye release kinetics (see picture). Further functionalization of the NCP/silica particles with poly(ethylene glycol) (PEG) and PEG-anisamide enhanced their biocompatibility and targeting ability, allowing cancer-specific imaging of human lung cancer H460 cells.



Functional Coordination Polymers



Directing films: The chemical vapor deposition of $(MeO)_3B$ on a multilayered Rh(111) substrate results in selective precursor decomposition leading to a boride-type film. This film can be oxidized into a well-ordered boron nitride monolayer (see picture with model structure), thus opening up a new approach to BN systems.

Boron Nitride Monolayers

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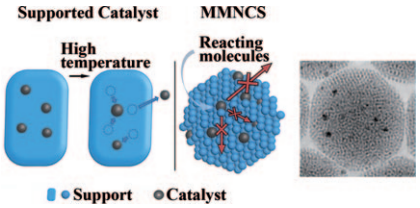
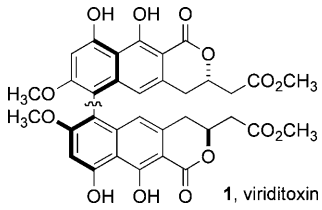
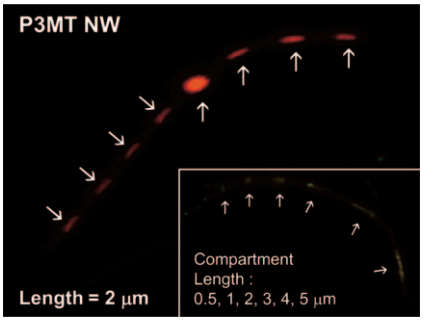


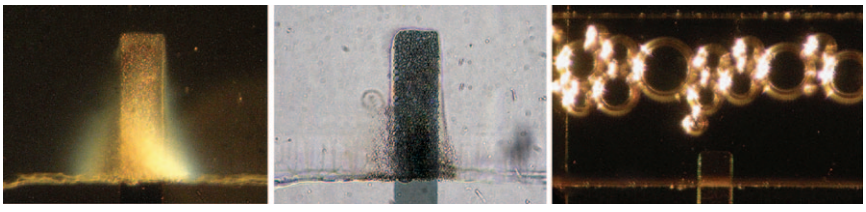
A caged catalyst: Noble-metal and oxide nanoparticles can be assembled to obtain high-temperature-stable mesoporous multicomponent nanocomposite colloidal spheres (MMNCSs; see picture). CO oxidation and cyclohexene hydroconversion were selected to examine the catalytic activity, selectivity, and thermal stability of these MMNCSs. The exhibited catalytic properties suggest that the reported MMNCSs are ideal model catalysts for high-temperature reactions.



Remote control: Vanadium catalysts provide the key to synthesizing the bacteria-fighting natural product viriditoxin. An achiral catalyst shows modest levels of remote diastereocontrol induced by the lactone stereogenic center and chiral catalysts can be used to enhance or reverse this inherent selectivity.



Let your little light shine: Light-emitting organic poly(3-methylthiophene) (P3MT) and inorganic titanium dioxide single nanowires (NWs) treated with focused electron beams have multiple 1D serial compartments (see picture) similar to superlattice NWs, which are applicable to light-emitting color barcode NWs. The structural, optical, and electrical properties of the treated NW compartments can be controlled through the irradiation conditions.



Visible to the naked eye: An interplay between microscale electrophoresis and electrochemistry was exploited to simultaneously confine macromolecular encapsulants near an electrode surface while inflating them with gases evolved from the electrochemical reactions localized there. The compacted film can be seen under ordinary white light even when samples are unlabeled thus enabling a label-free technique for the detection of a variety of macromolecules including DNA, proteins, and cyclodextrans.

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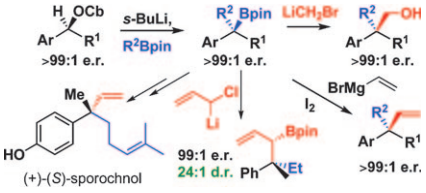
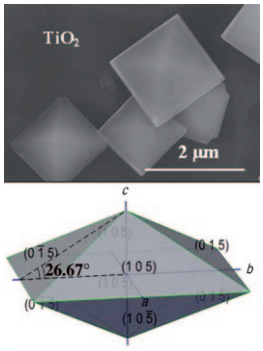


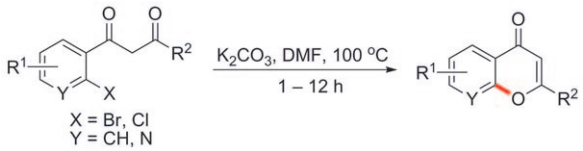
Pin it down: A range of substrates that bear versatile functional groups with quaternary stereogenic centers have been prepared with very high enantioselectivity from tertiary boronic esters (see scheme; Cb = *N*,*N*-diisopropylcarbamoyl, pin = pinacolato). The preparation of allylboronic esters bearing contiguous quaternary and tertiary stereogenic centers, and applications to natural product synthesis are also reported.

Quaternary Centers



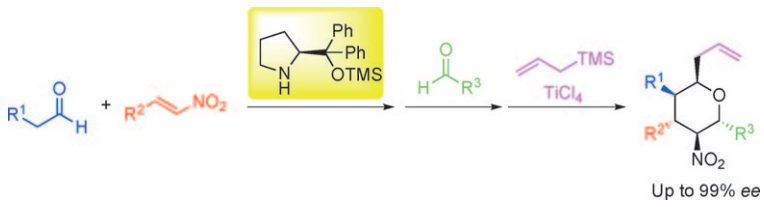
Put your best face forward: The performance of TiO_2 anatase crystals in energy and environmental applications is normally correlated with the TiO_2 crystal facets exposed, and increasing the percentage of highly reactive surfaces is extremely important. A new gas-phase oxidation process using $TiCl_4$ as precursor now yields anatase TiO_2 single crystals with primarily high-index {105} facets, which can cleave water photocatalytically.

High-Index Facets



Expect the upexpected: A transition-metal-free approach to access chromone derivatives has been developed. The intramolecular O-arylation of substituted 1-(2-haloaryl)-propane-1,3-diones in DMF in the presence of K_2CO_3 gave the corresponding target products in good to excellent yields (see scheme; DMF = *N*,*N*′-dimethylformamide).

Oxygen Heterocycles



Domino effect: The title reaction uses an asymmetric Michael/Henry reaction/acetalization/Lewis acid mediated allylation reaction to provide highly substituted tetrahydropyrans with excellent enantioselectivity (see scheme; TMS = trimethylsilyl). All the carbon atoms in the tetrahydropyran ring are substituted with different groups, and the relative and absolute stereochemistry of the five contiguous carbon centers are completely controlled.

Organocatalysis

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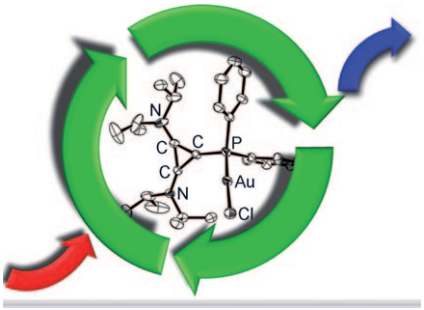
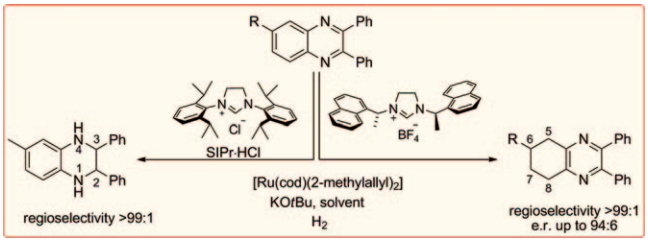


Cationic but electron-rich: Cyclopropenylylidene-stabilized phosphenium cations exhibit the electron richness of classical trialkyl and triaryl phosphines even though they carry a positive charge stemming from a cationic substituent directly bonded to the phosphorous atom. These two facts have been exploited to synthesize gold catalysts that can be easily recycled after use.

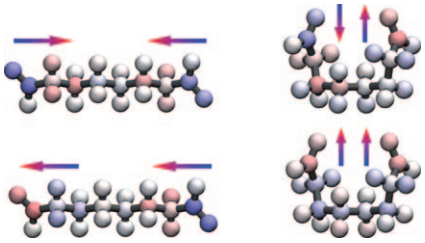
Ligand Design



Inflating flat bicycles: Proper choice of the N-heterocyclic carbene (NHC) ligand in Ru NHC complexes allows the completely regioselective ligand-controlled hydrogenation of either the heterocyclic or the carbocyclic ring of a substituted quinoxaline in quantitative yields. Chiral NHC ligands allow the challenging asymmetric hydrogenation of the carbocyclic ring of quinoxalines, yielding enantioenriched 5,6,7,8-tetrahydroquinoxalines with an enantiomeric ratio of up to 94:6.

Asymmetric Hydrogenation

The relationship between conformational changes of suberate dianions in water clusters and the corresponding spectroscopic characteristics were studied theoretically and by IR spectroscopy (see picture for the charge displacement associated with the excitation of the carboxylate symmetric stretching modes). Folded structures are stabilized by the formation of additional hydrogen bonds between the solvated dianion and H_2O molecules and should thus be retained in larger, microhydrated clusters.



Solvent-Mediated Folding

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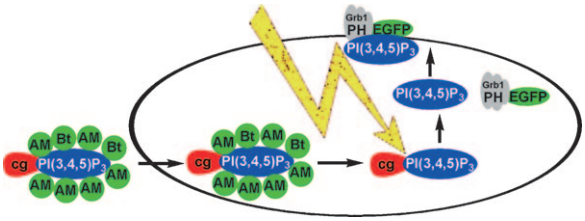
Signal Transduction



Unleashed inside cells: The signaling molecule $PI(3,4,5)P_3$ is prepared in a form that allows its cellular uptake and subsequent activation by light (see picture). The rapid eight-step synthetic sequence yields a stable derivative of the signaling molecule with high biological activity after deprotection ("uncaging") with a laser flash, in live cells.

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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Service