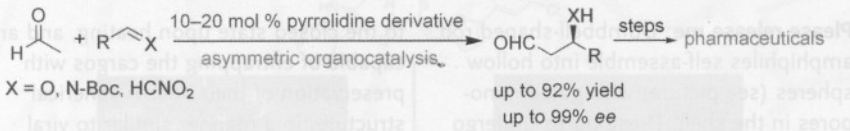
VIP ***The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:***

News

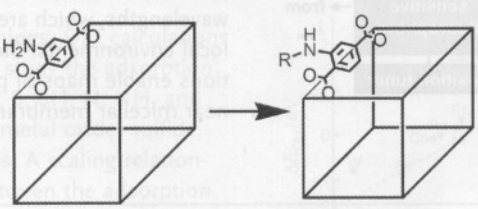
Books

Highlights



Big step, small molecule: Although acetaldehyde is the simplest of enolizable carbonyl compounds, and low-molecular-weight enamine/iminium-ion organocatalysis is the more elegant and most economical way to introduce chirality into a molecule, the first reports of the direct catalytic asymmetric reactions of acetaldehyde with electrophiles have just recently appeared (see scheme; Boc = *tert*-butyloxycarbonyl). Elaboration of the obtained adducts provides precursors for the synthesis of pharmaceuticals.

Organocatalysis



MOF Tuning: Recent progress on post-synthetic covalent modification of MOF (metal–organic framework) materials has led to the discovery of exciting new porous inorganic materials. These results involve transformation of the organic groups of MOFs without altering the three-dimensional structure.

Metal–Organic Frameworks

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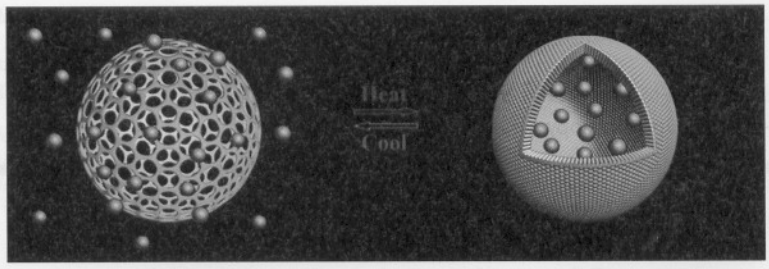
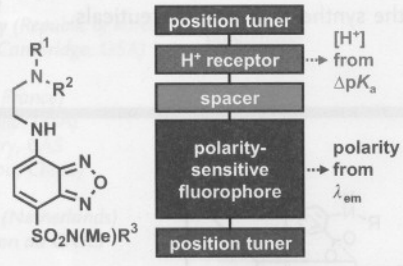
Reviews

As Bernini's David, in the prime of adolescence, fought Goliath armed only with a sling and a stone, organocatalysis uses simple organic molecules to address some fundamental issues of organic synthesis. Important questions concern the chemical efficiency of such processes and the development of viable and simple routes to natural products and drug candidates.

Communications



Please release me: Dumbbell-shaped rod amphiphiles self-assemble into hollow spheres (see picture) with gated nanopores in the shell. These pores undergo reversible transitions from the open state to the closed state upon heating, and are capable of entrapping the cargos with preservation of their hollow spherical structure, in a manner similar to viral capsids.



Hi-fi mapping: Multiplexing fluorescent sensors that simultaneously target proton concentration and polarity move to micellar nanospaces, self-regulate their positions, and report their pK_a values and wavelengths, which are controlled by their local environments. Such sensory functions enable maps of proton gradients near micellar membranes to be drawn.

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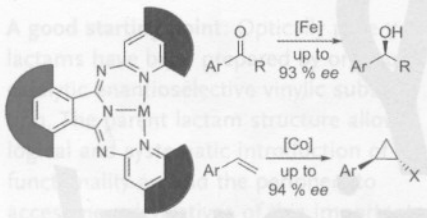
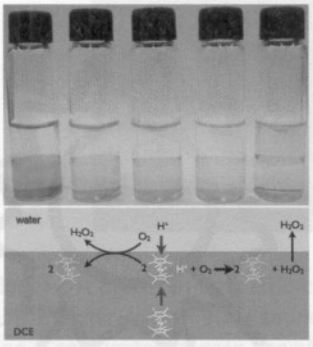


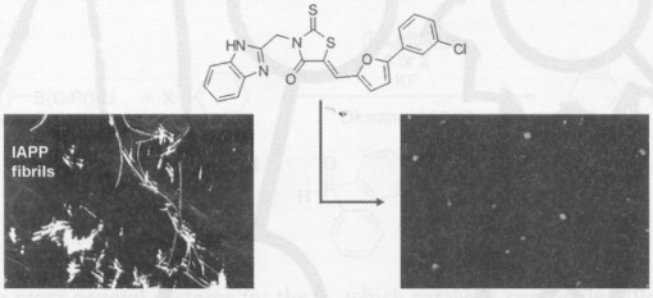
Protect your back: Chiral wedges (red, see scheme) at the wingtips of bis(2-pyridylimino)isoindole (bpi) pincer ligands with an appropriate protective hedge (green), to block the metal center from backside attack, in the backbone represent a new class of efficient 3d-metal catalysts. These catalysts gave excellent enantioselectivities in the iron-catalyzed hydrosilylation of arylketones and in the cobalt-catalyzed cyclopropanation of alkenes.

Asymmetric Catalysis



Hydrogen peroxide generation at a liquid | liquid interface occurs with a yield of 20% with respect to the concentration of reducing agent (decamethylferrocene). The liquid | liquid interface supplies electrons from the reducing agent and protons from the aqueous phase to drive the reduction of O_2 into H_2O_2, which is extracted into the aqueous phase during the course of reaction (see picture; DCE = 1,2-dichloroethane).

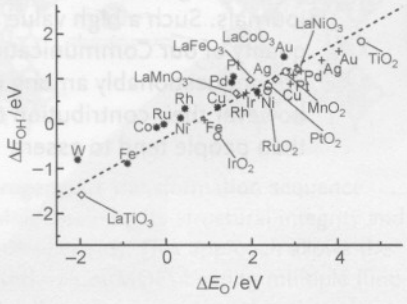
Hydrogen Peroxide Production



Small and effective: The pathological aggregation of amylin (IAPP), which leads to type II diabetes mellitus, is effectively inhibited by small-molecule rhodanine-based inhibitors at nanomolar concentrations. The prevention of aggregation by treatment with the inhibitor is demonstrated by AFM (see image).

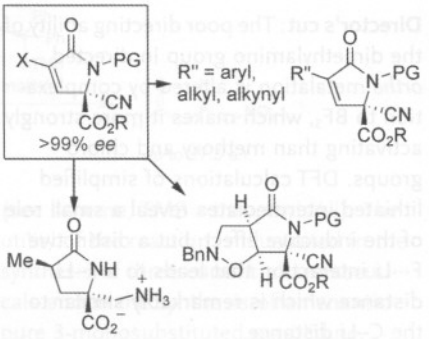
Small-Molecule Inhibitors

Getting on top of things: DFT calculations have been used to study the adsorption energies of O, OH, S, SH, N, NH, and NH_2 on transition metal oxide, sulfide, and nitride surfaces. A scaling relationship was found between the adsorption energies of the intermediates and the adsorption energies of the atoms which is independent of the metal and depends only on the number of H atoms in the molecule (see graph).

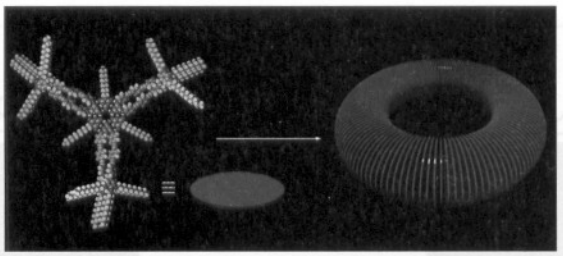


Surface Adsorption

A good starting point: Optically pure γ-lactams have been prepared by organocatalytic enantioselective vinylic substitution. The parent lactam structure allows logical and systematic introduction of functionality around the periphery to access new derivatives of this important class of molecules. Bn = benzyl, PG = protecting group.

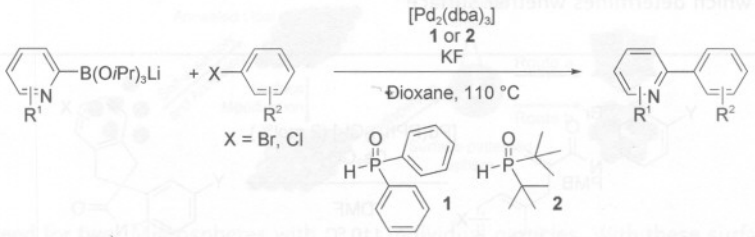


Asymmetric Synthesis



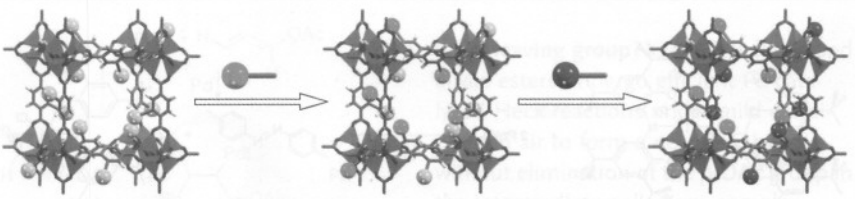
Nanodonuts! A hydrogen-bonded cyclic assembly (rosette, left) of a melamine featuring π-conjugated oligo(*p*-phenyleneethynylene) hierarchically self-organizes with a cyanurate in decane under dilute conditions to form toroidal nanostructures (right) with a diameter of 40 nm.

Self-Assembly



One of the most general systems for the cross-coupling of aryl and heteroaryl bromides and chlorides with 2-pyridyl-derived nucleophiles has been developed, for which catalysts comprising $[Pd_2(dba)_3]$ and either diaryl (**1**) or dialkyl phosphine oxide (**2**) supporting ligands were found to be ideal (see scheme).

Cross-Coupling Reactions



More than a one-trick pony: Postsynthetic modification of metal–organic frameworks (MOFs) permits stepwise, "tandem" modification of the lattice. An MOF bearing reactive functional groups can be subjected to a controllable, heterogeneous transformation sequence while retaining its structural integrity and microporosity. This approach allows the synthesis of MOFs bearing multiple functional groups (represented in the scheme by green and pink spheres).

Metal–Organic Frameworks

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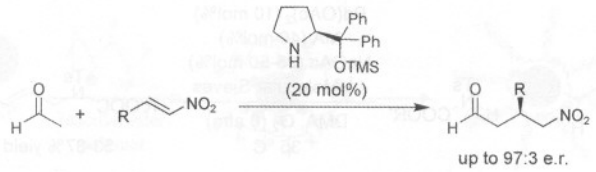
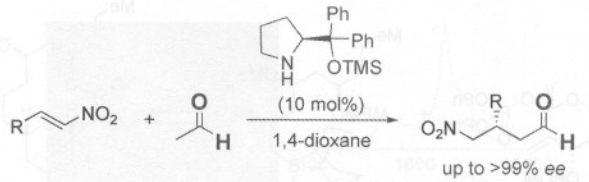


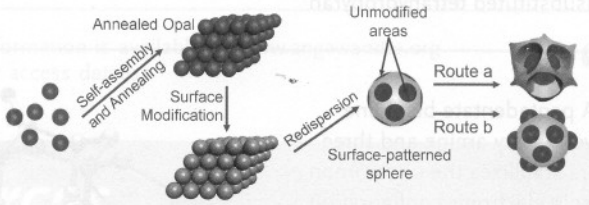
Acetaldehyde, now a big contender: A silyl prolinol derivative was found to catalyze the first Michael addition of acetaldehyde with both aromatic and aliphatic nitroolefins in excellent enantioselectivities (see scheme, TMS = trimethylsilyl). The utility of the reaction is illustrated in the synthesis of three current pharmaceuticals and in the synthesis of an enantiopure 3-monosubstituted pyrrolidine.

Organocatalysis



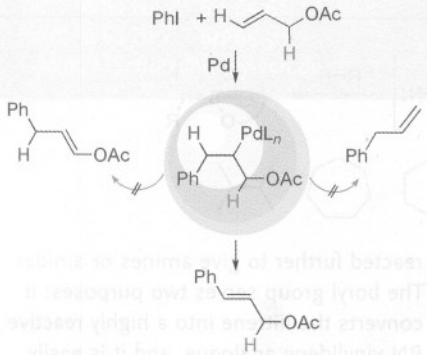
An acetaldehyde breakthrough: The catalytic asymmetric Michael addition reaction of acetaldehyde and various nitroalkenes in the presence of a chiral diphenylprolinol silyl ether organocatalyst is described (see scheme; TMS = trimethylsilyl). The desired 1,4-addition products, α-unsubstituted γ-nitro aldehydes, were obtained in good yields with excellent enantioselectivities.

Organocatalysis



One seed for two: Microspheres with patterned surfaces were obtained by modifying the surface of microspheres of a self-assembled colloidal crystal and redispersion of the colloidal crystal into individual particles. With these surface-patterned spheres as seeds, two types of nonspherical particles were fabricated by the seeded particle growth method.

Surface Patterning



What leaving group? Organic halides and allylic esters undergo efficient Pd-catalyzed Heck reactions under mild conditions in air to form a new C–C bond without elimination of the β-OAc group in the intermediate palladium complex. Instead a highly regioselective β-H elimination takes place to provide substituted derivatives of allylic alcohols (see scheme).

Heck Reaction

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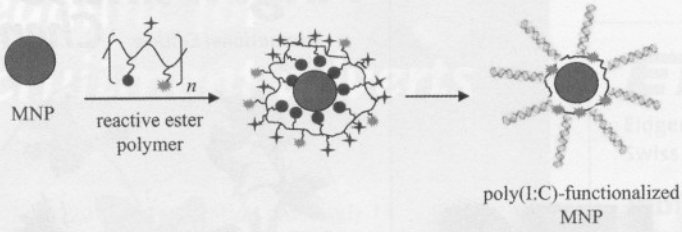
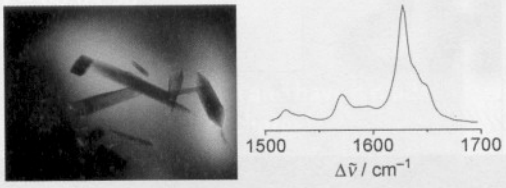


Magnetic Nanoparticles

Specific cell recognition: Magnetic γ-Fe_2O_3 nanoparticles (MNPs) functionalized with a fluorescently labeled polymer and polyinosinic-polycytidylic acid [poly-(I:C)] allow the specific visualizion of the TLR3 receptors on the the surface of Caki-1 cells. The expression of TLR3 on the Caki-1 cells was demonstrated independently by RT-PCR and immunostaining techniques.



Photoreceptors

Crystals of the photoreceptor phytochrome were studied nondestructively by resonance Raman spectroscopy. The spectra of the chromophore-binding domains (CBD) of phytochrome from *Deinococcus radiodurans*, from which three-dimensional structures have been determined, demonstrate the same chromophore structure in the parent Pr state as in solution. Unlike CBD, crystals of phytochrome from *Agrobacterium tumefaciens* including the CBD and the PHY domain can be photoconverted to a Meta-Rc-like state.

Supporting information is available on www.angewandte.org (see article for access details).

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