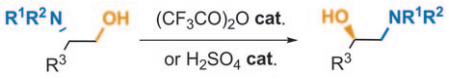
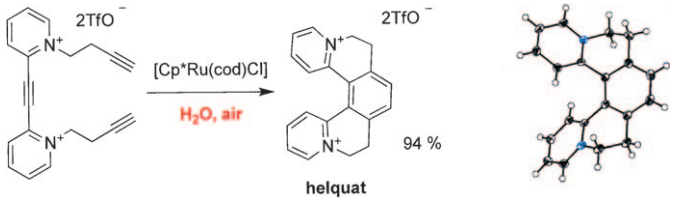
CONCEPTS

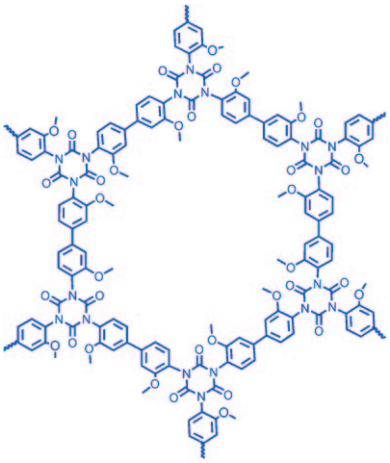


Rearranging amino alcohols: Treatment of β-amino alcohols derived from α-amino acids with a catalytic amount of $(CF_3CO)_2O$ or H_2SO_4 leads to the formation of rearranged β-amino alcohols with good yield and high enantioselectivity (see scheme).

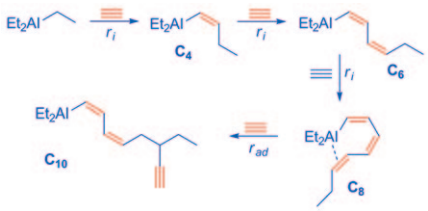
COMMUNICATIONS



As easy as one, two, three: Relying on a facile [2+2+2]-cycloisomerization strategy, we have developed a robust three-step synthetic entry into a novel family of helical extended diquats (helquats). The key metal-catalyzed step proceeds in water under aerobic conditions to produce a water-soluble, blue fluorophore (picture; TfO = triflate). The electrochemical manifold of the parent helquat features two reversible one-electron reduction steps.

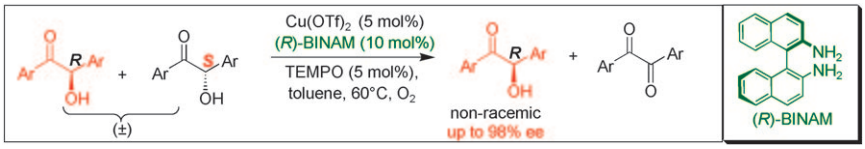


Support your catalyst: A new method has been developed to synthesize microporous polyisocyanurate (see figure). This polymer possesses urea-type rigid functional framework, high surface area, and permanent microporous structure. It is successfully applied as a support for iron oxide, and demonstrates excellent activity, selectivity and recyclability in the oxidation of benzyl alcohol to benzaldehyde with hydrogen peroxide in water.



Growth at both ends: The reaction of acetylene with triethylaluminium has been revisited (see scheme), and unlike the Aufbau reaction with ethylene, growth at aluminium produces branched acetylene oligomers. This hitherto unseen process seems to occur via both conventional migratory insertion and a second mode of acetylene addition across unsaturation in the growing chain, thus giving rise to a peculiar oligomer distribution.

CONTENTS

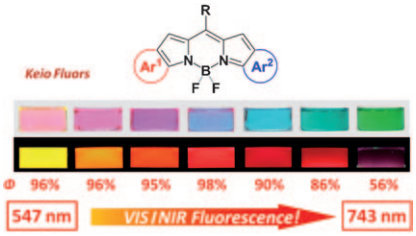


GO for it! An enantiopure galactose oxidase (GO) enzyme model has been synthesized from readily available (*R*)-binam and $Cu(OTf)_2$ (see scheme; TEMPO = 2,2,6,6-tetramethyl-piperidin-1-oxyl), and has been effectively used as an efficient chiral catalyst for the oxidative kinetic resolution of secondary alcohols. This is the first chiral copper-catalyzed oxidative kinetic resolution of racemic benzoins and the simplest method for the synthesis of highly important enantiomerically enriched benzoins.

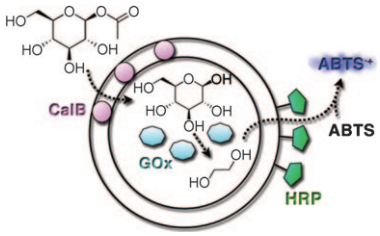
A concise synthesis of phosphatidylinositol dimannoside (PIM_2) from commercially available *myo*-inositol 1,3,5-orthoformate via a highly regioselective and stereoselective 6-*O*-mannosylation of the *myo*-inositol-derived *meso*-4,6-diol as a key step was carried out in 9 steps (see scheme) and in 13% overall yield.

FULL PAPERS

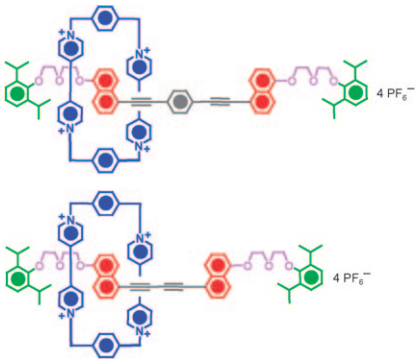
New fluorescent dyes—any color you want: A new series of bright and long-wavelength fluorescent dyes (Keio Fluors), with sophisticated optical performance, have been created. Our "tailor-made" strategy allowed easy and fine tuning of emission peaks over a wide spectral range from the visible to the near-infrared region.



An enzyme triad: A porous polymersome was equipped with three different enzymes at three spatially separate locations: *Candida antarctica* lipase B (CalB) in its lumen, glucose oxidase (GOx) in its bilayer membrane and horseradish peroxidase (HRP) conjugated to its surface (see figure; ABTS = 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonic acid)). The encapsulation efficiency of the enzymes was determined, and their activity as part of a three-enzyme cascade reaction was investigated.

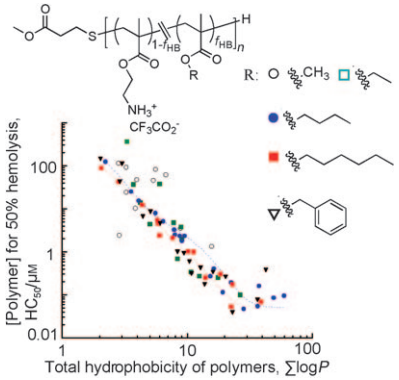


Rotaxanes



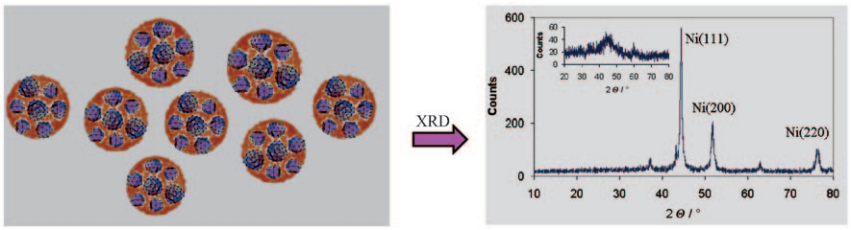
Rigidity makes for faster molecular shuttles: In the rigid donor–acceptor degenerate [2]rotaxanes, the tetracationic cyclophane shuttles back and forth between the two monosubstituted naphthalene stations via the rigid linker in the dumbbell-shaped components. Introducing rigidity has led to faster shuttling processes, corresponding to lower energy barriers than those formed in more flexible donor–acceptor rotaxanes.

Polymers



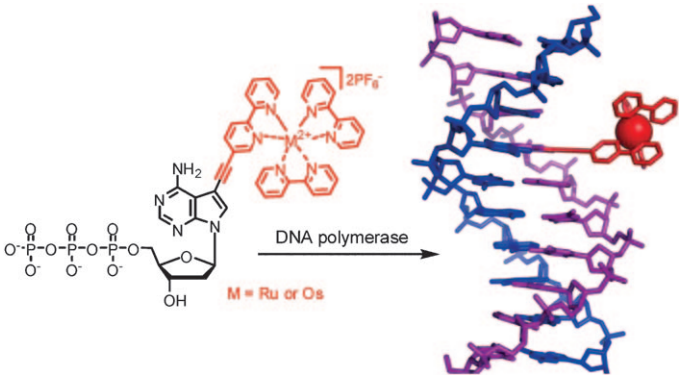
The antimicrobial and hemolytic activities of cationic polymethacrylate derivatives are driven by the total hydrophobicity of polymers (see picture). Polymer hydrophobicity results in collapse of the polymer chain in solution, causing a turnover of hemolytic activity. This effect also limits the efficacy and selectivity of synthetic polymers towards bacteria relative to erythrocytes.

Nanomaterials



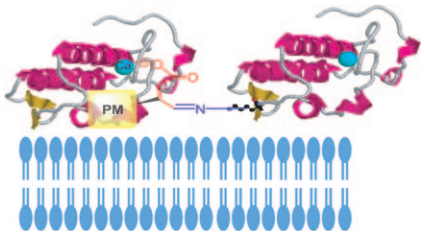
Complex nanostructure! A systematic investigation on the catalytic Ni-B nanoparticles (see figure) reveals that the material has a highly unusual ultrafine nanostructure that offers an explanation as to why the catalyst is highly active in hydrogenation and dehydrogenation reactions.

CONTENTS

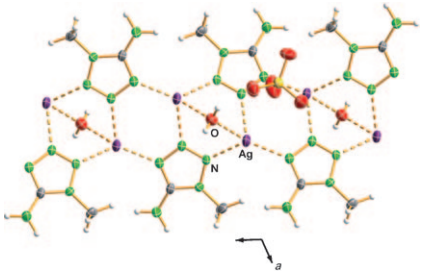


Metal-labeled DNA: DNA-bearing $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ complexes have been constructed by polymerase incorporation of the corresponding base-modified nucleoside triphosphates (see figure). The Ru-modified DNA was luminescent, while the Os complexes could be detected by electrochemistry. A complete four-color redox labeling of DNA has been developed and used for mini-sequencing.

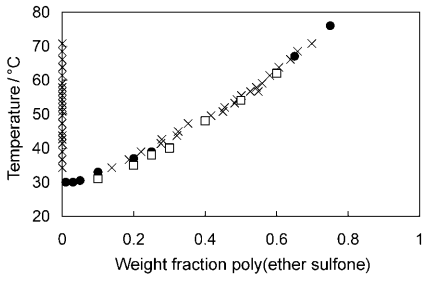
Two is better than one? The amphiphilic petrosaspongiolide M (PM), a γ-hydroxybutenolide marine terpenoid, specifically inhibits human group IIA secretory phospholipase A_2 (sPLA$_2$-IIA). PM selectively reacts with the Lys67 residue located near the enzyme–membrane interfacial binding surface. Covalent modification of PM generates a PLA$_2$-bound phospholipid-like molecule that can target the active site of another sPLA$_2$-IIA unit (see picture). This unusual binding mode would lead to a potent dual inhibition.



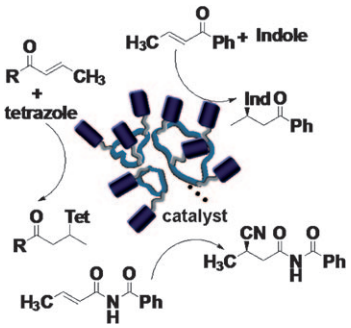
Full of energy! A new family of silver complexes with heterocyclic ligands and perchlorate or nitrate anions with interesting structural details, such as a heteronorborane skeleton (see picture), are presented. The energetic properties of these materials are compared with those of the proton analogues, revealing increased sensitivities and good thermal stabilities.



And relax! A new and elegant method for studying the phase behavior of liquid (polymer) blend systems by using T_2 NMR relaxometry is reported (see figure for the coexistence curve of P(EO-*ran*-PO)/PES as constructed by a stepwise isothermal T_2 NMR relaxometry experiment (×), starting from four blends with well-chosen compositions).

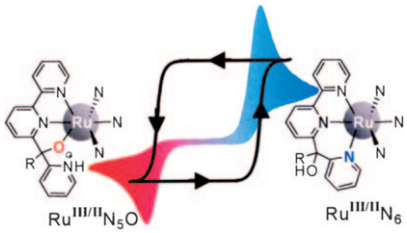


Asymmetric Catalysis



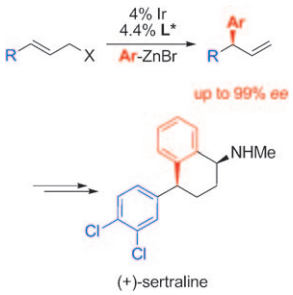
Lending support! AlCl–salen (salen = *N*,*N*′-bis(salicylidene)ethylenediamine dianion) catalysts attached to macrocyclic oligomeric cyclooctene supports through linkers of varying length and flexibility demonstrate the importance of support architecture on catalytic activity for bimetallic as well as monometallic reactions (see scheme).

Molecular Switches



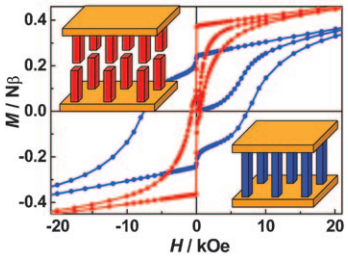
Reversible switching of a ligand-bound ambidentate motif between N and O coordination in the Ru^{II} and Ru^{III} state, respectively, is shown by Ru complexes with an ambidentate ligand and a substituted terpyridine ligand (Y-tpy). The potential difference of the $Ru^{III/II}$ couple of about 0.5 V between the isomers results in a bistable electrochemical response of these molecular switches (see scheme; only N donors of tpy ligand shown).

Asymmetric Synthesis



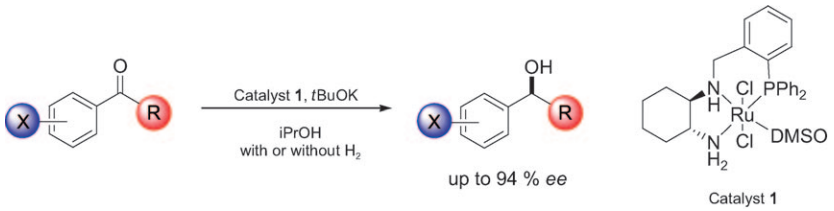
Instant transfer: This full paper describes the development of a catalytic system that allows for high enantioselectivities in the allylic arylation of nonsymmetrical electrophiles and was applied towards the formal synthesis of (+)-sertraline (see scheme). The emphasis of this research was placed on the scope, the limitations, the synthetic applications, and the mechanistic aspects of this system.

Molecular Magnets



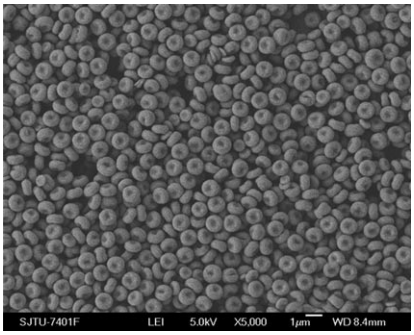
Ordered about: Cobalt(II)–azide layers are isolated or cross-linked by organic ligands to give 2D or 3D molecular magnets that exhibit unusual long-range-ordering properties that combine spin canting, metamagnetism, and exotic hysteresis (see figure). The two materials contain almost identical layers, which allow us to determine the influence of the interlayer separation on the magnetic properties.

CONTENTS



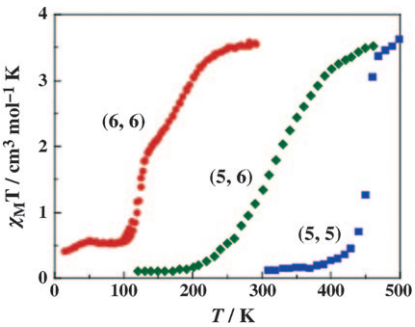
Making some room: A new class of ruthenium catalyst derived from a tridentate P^N^N ligand (see picture) has been shown to be active in the enantioselective hydrogenation and transfer hydrogenation of bulky, deactivated ketones—substrates that are problematic using most Noyori-type catalysts.

Lanthanide orthovanadate: Nearly monodisperse YVO_4 architectures with persimmon-like (shown here), cube-like and nanoparticle shapes have been synthesised on a large scale by a complexing-agent-assisted solution route. The shape and size of these as-prepared architectures can be tuned effectively by controlling the reaction conditions.

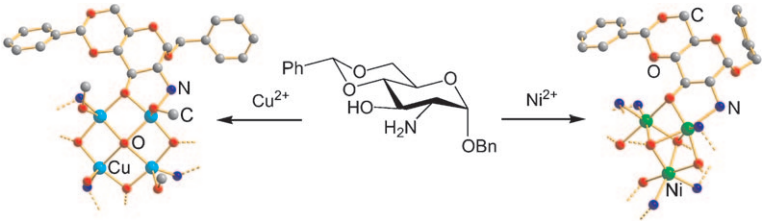


Rearrange your chemistry! Herein we report the one-pot synthesis of several N-heterocyclic compounds by rearrangement reactions of *N*-aryl-2-vinylaziridines (see scheme). To rationalize the experimental results reported in this paper, a theoretical study was also performed.

Strain effects on spin-transition temperature: Structural and magnetic studies (see figure) of a family of iron(II) complexes show that the spin-crossover temperature depends on the strain effects from the size of chelate rings. The effect of the successive reduction in size from a six- to five-membered chelate ring independently on the counterion nature leads to a rise in transition temperature.

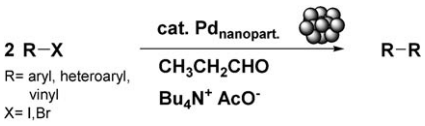


Carbohydrate Ligands



Sweet control: Depending on their functionalization aminoglucose ligands were found to support different structural motifs. This leads to an unexpected μ_4-OH-bridged tetranuclear copper as well as a trinuclear nickel complex with a ferromagnetic ground state (see figure).

Biaryl Synthesis



An unusual reduction: A new method for synthesising symmetrical biaryls has been developed by making use of Pd colloids as the catalyst, an aldehyde as the reducing agent and an ionic liquid as the reaction medium (see scheme). Aryl bromides and iodides are activated without the use of special additives or ligands, under relatively mild conditions (reaction temperatures ranging from 40 to 90 °C).

* Author to whom correspondence should be addressed

Supporting information on the WWW (see article for access details).

VIP Full Papers labeled with this symbol have been judged by two referees as being "very important papers".

A video clip is available as Supporting Information on the WWW (see article for access details).

SERVICE

Issue 4/2009 was published online on January 7, 2009

