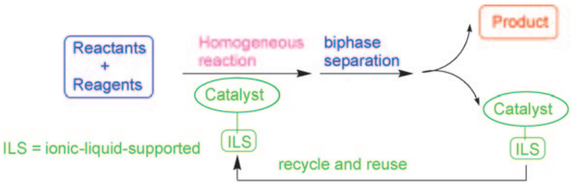
CONTENTS

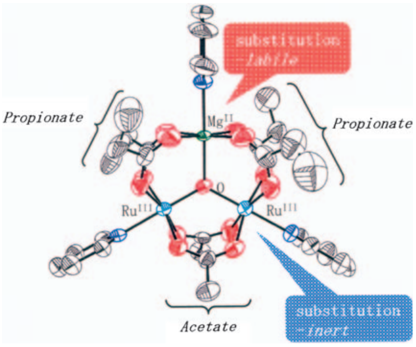
CONCEPTS



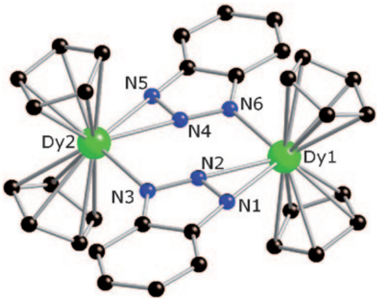
Lending support! ILS catalysts represent a new and very effective class of catalysts that are used to facilitate the asymmetric synthesis of compounds that contain new C–C and C–O bonds (see scheme). There are many advantages to using ILS catalysts: they are nontoxic, environmentally benign, and, most important, recyclable. An overview of the design, synthesis, mode of action, and effectiveness of this class of catalysts is reported.

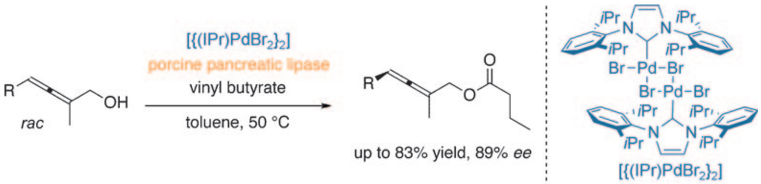
COMMUNICATIONS

At the right places: Owing to substitution-lability difference in disparate metal centers, an oxo-centered heterometallic trinuclear acetato complex [$Ru_2MgO(CH_3COO)_6(py)_3$] (py = pyridine; see picture) undergoes site-selective substitution of propionates and ferrocenycarboxylates in a stepwise manner. The new substituted families have been successfully separated by chromatography and fully characterized.



Organometallic single-molecule magnet: Studies of two dimeric organometallic dysprosium compounds reveal one to be the first organometallic single-molecule magnet (see picture). A comparison of the magnetic properties and electronic structures of the two compounds shows that Dy···Dy interactions have a profound influence on the dynamic magnetic behaviour, while having little effect on the static magnetic measurements.



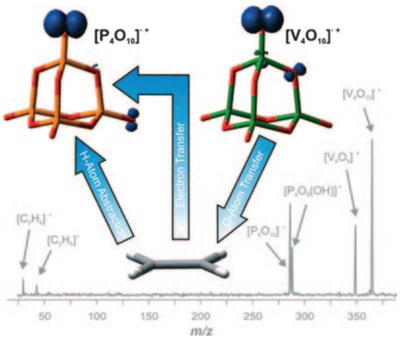


At the palladium: Dimeric palladium bromide complexes bearing monodentate *N*-heterocyclic carbene ligands have been identified as efficient catalysts for the chemoselective racemization of axially chiral allenyl alcohols. In combination with porcine pancreatic lipase as biocatalyst, a dynamic kinetic resolution has been developed, giving access to optically active allenes in good yield and high enantiomeric purity (see scheme).

C–H Activation

*N. Dietl, M. Engeser, H. Schwarz** .... 4452 – 4456

Competitive Hydrogen-Atom Abstraction versus Oxygen-Atom and Electron Transfers in Gas-Phase Reactions of $[X_4O_{10}]^{\cdot+}$ (X = P, V) with C_2H_4

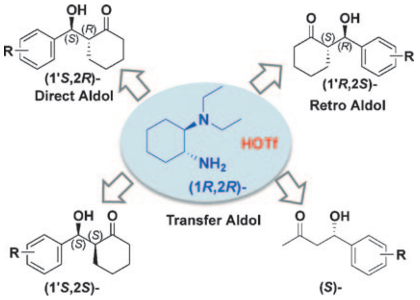


Why so different? The comparison of the reaction of “bare” $[P_4O_{10}]^{\cdot+}$ and $[V_4O_{10}]^{\cdot+}$ with ethene by mass-spectrometric and computational studies permits insight into mechanistic aspects of the competition between C–H bond activation and oxygen-atom and electron transfers. Whereas $[P_4O_{10}]^{\cdot+}$ reacts by homolytic C–H bond cleavage and electron transfer, the isostructural $[V_4O_{10}]^{\cdot+}$ shows only oxygen-atom transfer (see picture).

Aldol Reactions

S. Luo, P. Zhou, J. Li, J.-P. Cheng** .... 4457 – 4461

Asymmetric Retro- and Transfer-Aldol Reactions Catalyzed by a Simple Chiral Primary Amine

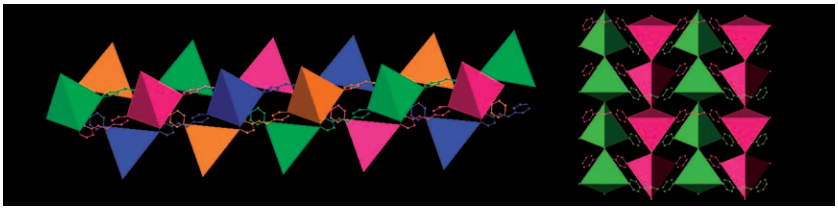


One stone four birds: A single chiral primary amine was found to catalyze unprecedented asymmetric retro-aldol and transfer-aldol reactions, leading to four different chiral aldol adducts from one common chiral source with up to 99:1 d.r. and 99 % *ee* (see scheme).

Metal–Organic Frameworks

P. Vaqueiro, M. L. Romero, B. C. Rowan, B. S. Richards* .... 4462 – 4465

Arrays of Chiral Nanotubes and a Layered Coordination Polymer Containing Gallium–Sulfide Supertetrahedral Clusters



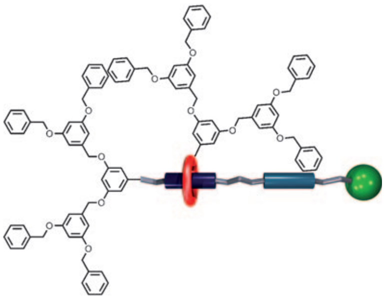
Organically functionalised supertetrahedral clusters: Two novel coordination polymers, consisting of chiral helical nanotubes and of composite layers, have been obtained by linkage of gallium–sulfide supertetrahedral clusters and dipyridyl ligands (see picture).

FULL PAPERS

Molecular Machines

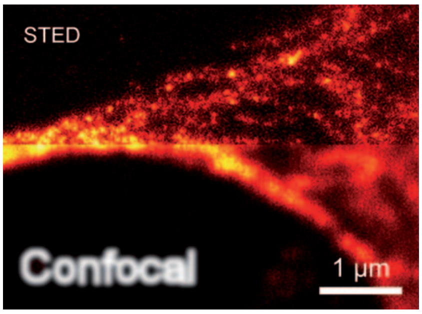
*D. A. Tramontozzi, N. D. Suhan, S. H. Eichhorn, S. J. Loeb** 4466 – 4476

The Effect of Incorporating Fréchet Dendrons into Rotaxanes and Molecular Shuttles Containing the 1,2-Bis(pyridinium)ethane⊂[24]Crown-8 Templating Motif



A not so “shuttle” variation: Attaching dendritic units to both the axle and wheel components of a molecular shuttle increases the barrier to shuttling and skews the distribution of co-conformations in favor of a single recognition site (see scheme for one possible conformation). Since shuttling causes a dramatic change in the shape of the molecule (>1 nm in length), this demonstrates the potential of using interlocked components to manipulate the size and shape of macromolecules.

Marker molecules: The newly synthesized fluorinated rhodamines are cell-permeable and perform excellently in optical microscopy applications, such as single-molecule detection and stimulated emission depletion (STED) nanoscopy (see picture).



Nanoscopy

G. Y. Mitronova, V. N. Belov, M. L. Bossi, C. A. Wurm, L. Meyer, R. Medda, G. Moneron, S. Bretschneider, C. Eggeling,* S. Jakobs, S. W. Hell** .... 4477 – 4488

New Fluorinated Rhodamines for Optical Microscopy and Nanoscopy

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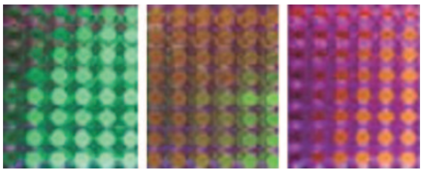
Tongues and drugs: γ-Hydroxybutyric acid (GHB), a colourless, odourless and tasteless chemical, has become one of the most dangerous illicit drugs of abuse today. There is an urgent need for simple, easy-to-use sensors for GHB in solution. We present a colorimetric sensor array based on supramolecular host–guest complexes of fluorescent dyes with organic capsules (cucurbiturils) for the detection of GHB (see graphic).



Sensors

*L. A. Baumes, M. Buaki Sogo, P. Montes-Navajas, A. Corma, H. Garcia** .... 4489 – 4495

A Colorimetric Sensor Array for the Detection of the Date-Rape Drug γ-Hydroxybutyric Acid (GHB): A Supramolecular Approach

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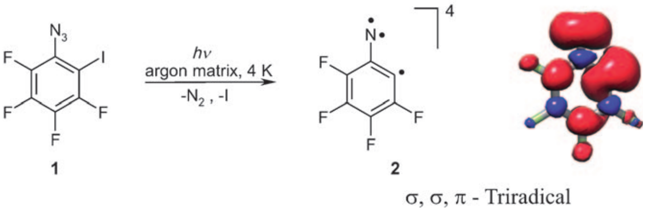

Quartet nitreno triradical 2 was obtained by irradiation of 2-iodo-3,4,5,6-tetrafluorophenyl azide (**1**) in an argon matrix at 4 K and characterized by EPR spectroscopy. Electronic structure calculations in combination with the experimental results allow a detailed understanding of the properties of this unusual new type of high-spin organic molecule.

Radicals

*D. Grote, C. Finke, S. Kossmann, F. Neese, W. Sander** .... 4496 – 4506

3,4,5,6-Tetrafluorophenylnitren-2-yl: A Ground-State Quartet Triradical

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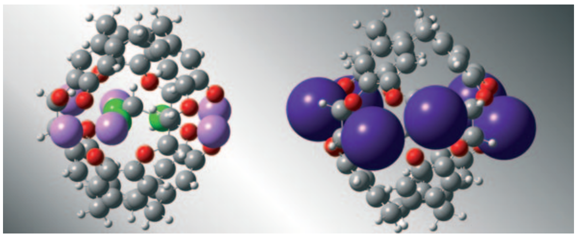

Guest encapsulation: Enantiopure water-soluble cryptophanol exhibits unusual chiroptical properties in water under basic conditions. The chiroptical properties are strongly dependent on the type of alkali metal ion (Li^+, Na^+, K^+, Cs^+) surrounding the cryptophane and whether or not a guest molecule is present inside the cavity of the host (see figure). This compound may be a good sensor for small, neutral molecules in aqueous solvent.

Chiroptical Properties

A. Bouchet, T. Brotin, D. Cavagnat, T. Buffeteau** .... 4507 – 4518

Induced Chiroptical Changes of a Water-Soluble Cryptophane by Encapsulation of Guest Molecules and Counterion Effects

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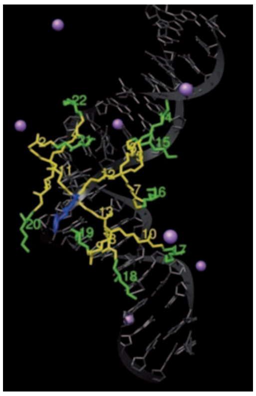
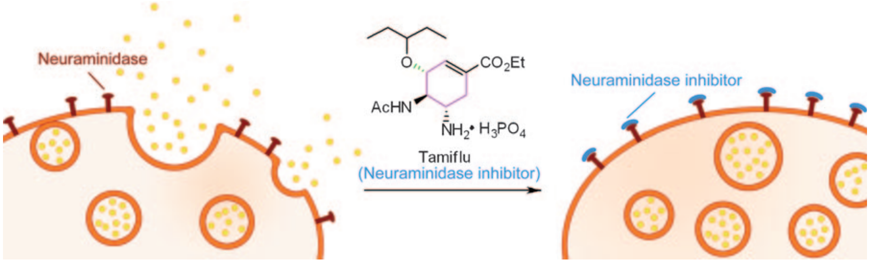
DNA

Bending over backwards: We have combined theory and experiment to obtain deep insights into the interaction between dendrons and DNA (such as depicted). By modifying the surface amines, the thermodynamics of binding were tuned, enabling the development of more effective systems for gene delivery, with lower toxicity. Modelling indicated that these modified dendrons gave rise to deformations of the DNA double helix.

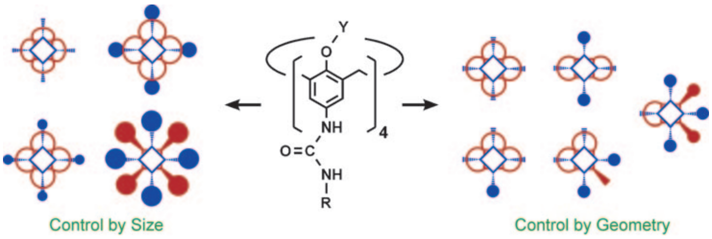


Antiviral Agents



Tamiflu: A novel and practical synthesis of Tamiflu by using cheap reagents and abundantly available starting materials (D-glucal) has been developed, and allows late-stage functionalization for the flexible synthesis of Tamiflu analogues. The active metabolite of Tamiflu, oseltamivir carboxylate, significantly inhibits the vesicular exocytosis (regulated secretion) of PC12 cells (see figure).

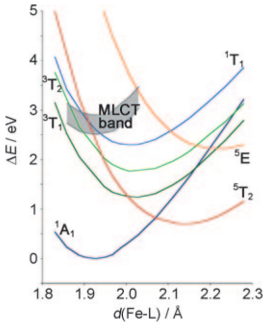
Supramolecular Chemistry



Self-sorting: The combination of four urea residues of different size with four (aliphatic) loops of different lengths connecting adjacent urea residues (see figure) can be used for the selective dimerization of tetraureacalix[4]arenes. Additional selectivities can be created by the geometrical match or mismatch of loops and bulky substituents in tetraurea derivatives with less than four loops or bulky residues.

Magnetic Properties

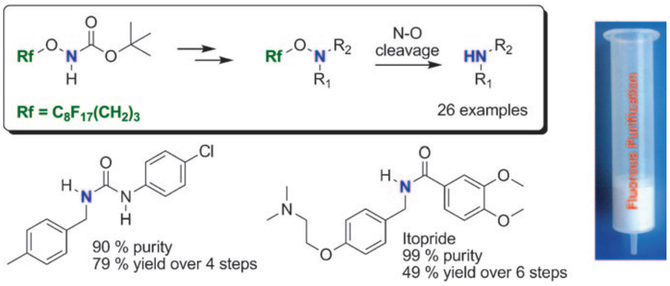
Light induces SCO: The fast low-spin to high-spin conversion in $[Fe^{II}(bpy)_3]^{2+}$ (bpy = bipyridine) was studied by ab initio calculations. The energy dependence of the metal-to-ligand charge transfer (MLCT) band was determined and it was found that both the singlet and the triplet MLCT states have their equilibrium distance in the Franck–Condon region (see figure).



Fluorous Chemistry

*S. D. Nielsen, G. Smith, M. Begtrup, J. L. Kristensen** 4557–4566

Synthesis and Application of a New Fluorous-Tagged Ammonia Equivalent

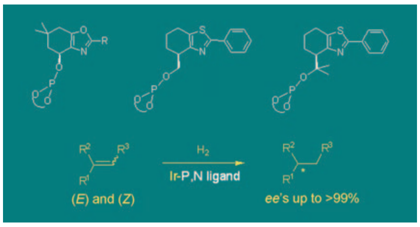


Fluorous purification to the rescue! A novel fluorous-tagged ammonia equivalent has been developed. The scope of the fluorous N–O linker is exemplified by the synthesis of itopride, a drug used for the treatment of functional dyspepsia (see scheme).

Asymmetric Catalysis

J. Mazuela, A. Paptchikhine, O. Pàmies, P. G. Andersson, M. Diéguez** 4567–4576

Adaptative Biaryl Phosphite–Oxazole and Phosphite–Thiazole Ligands for Asymmetric Ir-Catalyzed Hydrogenation of Alkenes

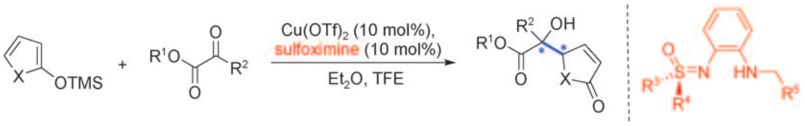


Adaptive chemistry: A library of phosphite–oxazole/thiazole ligands has been applied to the Ir-catalyzed asymmetric hydrogenation of several largely unfunctionalized *E*- and *Z*-trisubstituted and 1,1-disubstituted terminal alkenes (*ee* values up to >99 %; see scheme).

Asymmetric Catalysis

*M. Frings, I. Atodiresei, Y. Wang, J. Runsink, G. Raabe, C. Bolm** 4577–4587

C_1-Symmetric Aminosulfoximines in Copper-Catalyzed Asymmetric Vinylogous Mukaiyama Aldol Reactions

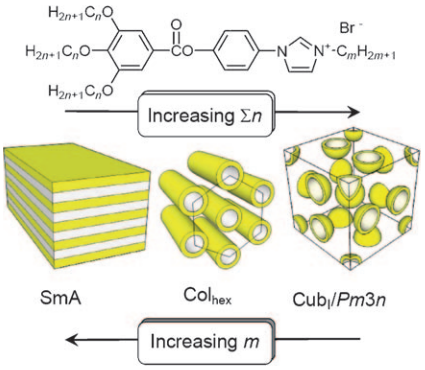


Tuning for high *ee*: Combinations of $Cu(OTf)_2$ and readily available C_1-symmetric aminosulfoximines afford catalysts for vinylogous Mukaiyama-type aldol reactions (see scheme). After fine-tuning of the ligand backbone, excellent stereoselectivities and very high yields can be achieved.

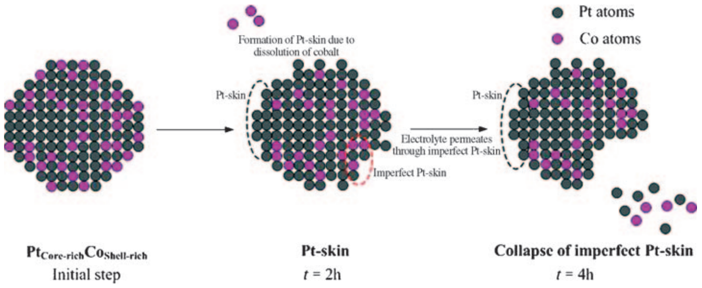
Ionic Liquid Crystals

X. Cheng, X. Bai, S. Jing, H. Ebert, M. Prehm, C. Tschierske** .. 4588–4601

Self-Assembly of Imidazolium-Based Rodlike Ionic Liquid Crystals: Transition from Lamellar to Micellar Organization



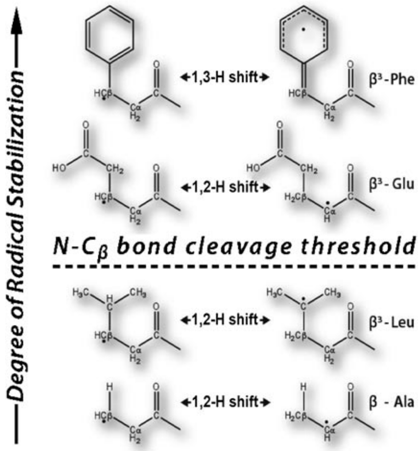
The long and short of it! Imidazolium-based ionic liquid crystals with extended rodlike cores have been synthesized. By changing the molecular structure the mode of self-assembly can be tuned from nematic to 1D (SmA) to 2D (Col_{hex}) and 3D (Cub_I/*Pm*3*n*). Short N-terminal alkyl chains prefer to be separated from the long C-terminal chains to give rise to bilayer phases and core-shell aggregates (see image).



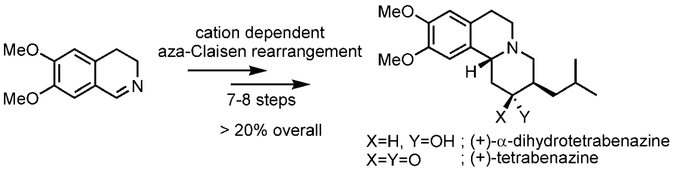
Only skin-deep: Pt-rich core/Co-rich shell bimetallic nanoparticles (NPs) subjected to chemical dealloying produce a Pt skin on the surface (see picture). These NPs show significant enhancement of the oxygen reduction reaction (ORR) relative to pure Pt. When the dealloying process lasts too long, the Pt-skin feature collapses resulting in loss of ORR activity.

Bimetallic Catalysts

Cleavage priority in peptides: Dissociation of diverse β-amino acids incorporated into α-peptides, driven by radical-ion chemistry, is probed by electron-capture and -transfer dissociation (ECD/ETD) tandem mass spectrometry. The radical stability of amino acid side chains dominates the N–$C_β$ bond rupture of β-amino acids in ECD/ETD to a substantially larger extent than it does with α-amino acids (see figure).



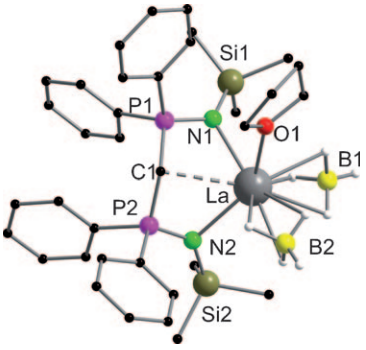
Peptide Cleavage



Drug synthesis: A highly concise asymmetric total synthesis of (+)-tetrabenazine (see graphic), a drug for treatment of chorea associated with Huntington's disease, and of its active metabolite (+)-α-dihydrotetrabenazine has been accomplished. Our route features an unprecedented cation-dependent aza-Claisen rearrangement to establish the carbon framework and two stereogenic centers of tetrabenazine.

Total Synthesis

Caprolactone polymerization: The borohydrides $[\{(Me_3SiNPPh_2)_2CH\}La(BH_4)_2(thf)]$ (see picture) and $[\{(Me_3SiNPPh_2)_2CH\}Ln(BH_4)_2]$ (Ln = Y, Lu) have been synthesized by two different synthetic routes and used as initiators in the ring-opening polymerization (ROP) of ε-caprolactone (CL). At 0 °C, the molar mass distribution values reached the narrowest values ever obtained for the ROP of CL initiated by such a species.

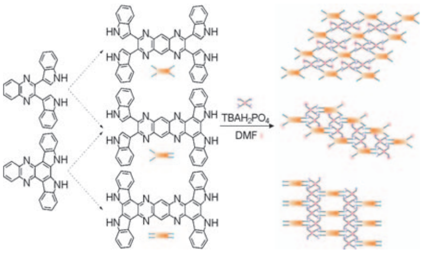


Ring-Opening Polymerization

Supramolecular Chemistry

*T. Wang, X.-P. Yan** .... 4639 – 4649

Pyrazino[2.3-*g*]quinoxaline-Bridged Indole-Based Building Blocks: Design, Synthesis, Anion-Binding Properties, and Phosphate-Directed Assembly in the Solid State

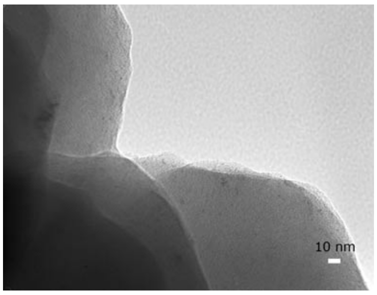


Network design: Building blocks with two indole-based binding sites strongly bind two anions with specific topology and dimensionality (see picture). These receptors interact with tetrabutylammonium dihydrogen phosphate (TBAH$_2$PO$_4$), which leads to the formation of a series of multidimensional, metal-free, coordination polymers with designed architecture in the solid state.

Monolithic Supported Catalysts

*R. Bandari, T. Höche, A. Prager, K. Dirnberger, M. R. Buchmeiser** .... 4650 – 4658

Ring-Opening Metathesis Polymerization Based Pore-Size-Selective Functionalization of Glycidyl Methacrylate Based Monolithic Media: Access to Size-Stable Nanoparticles for Ligand-Free Metal Catalysis

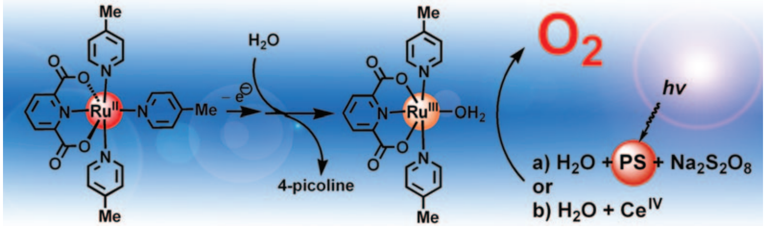


Metal nanoparticle catalysts: A novel ring-opening metathesis polymerization based approach to the pore-size-selective functionalization of electron-beam-triggered free-radical polymerization derived monoliths has been developed. This concept allows the creation and immobilization of metal nanoparticles within small pores (see figure), which can be used as effective catalysts. High turnover numbers of 167 000 and 63 000 were achieved in Heck- and Suzuki-type couplings.

Homogeneous Catalysis

*L. Duan, Y. Xu, M. Gorlov, L. Tong, S. Andersson, L. Sun** ...... 4659 – 4668

Chemical and Photochemical Water Oxidation Catalyzed by Mononuclear Ruthenium Complexes with a Negatively Charged Tridentate Ligand

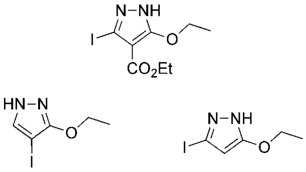


Efficient water oxidation: A mononuclear Ru^{II} complex (see scheme) undergoes ligand exchange to give the related aqua complex, which catalyzes water oxidation with a high turnover frequency (initially 0.23 turnovers^{-1}) by using Ce^{IV} as the oxidant in solution at pH 1.0. Photochemical water oxidation was achieved by using a three-component system containing this catalyst, a Ru-based sensitizer, and a sacrificial electron acceptor.

Organic Synthesis

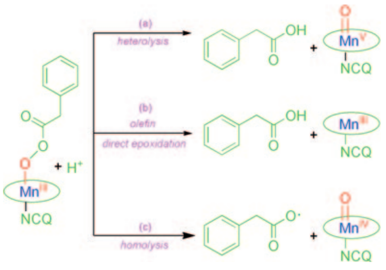
*S. Guillou, Y. L. Janin** ..... 4669 – 4677

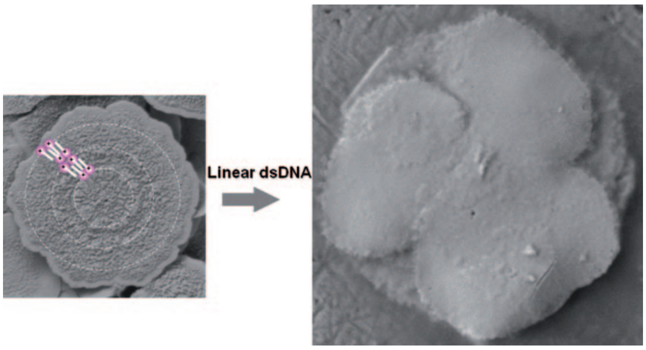
5-Iodo-3-Ethoxypyrazoles: An Entry Point to New Chemical Entities



Open up your chemical mind! After achieving a simple preparation of various iodinated 3-alkoxypyrazoles, their potential use as building blocks to gain access to new chemical entities was illustrated by the use of Lam and Cham N-arylation, Suzuki–Miyaura C4- and C5-arylation, and Negishi C5-benzylation (see scheme).

Multiple Mn−O oxidants: The multiple active oxidants Mn^{V}=O, Mn^{IV}=O, and Mn^{III}–OOC(O)R, based on the depicted intermediate, operate simultaneously in olefin epoxidation (see scheme), and their participation can be controlled by changing the substrate concentration. These results provide important clues for a resolution of the long-standing dichotomy of views pertaining to the nature of the active oxidants derived from Mn-containing complexes.





All together now! *N,N′*-Dialkylmethylenediimidazolium salts were synthesized and showed self-organization into multilayer vesicles. These vesicles exhibit hydrodynamic diameters that vary according to the alkyl chain length or the nature of the anion. In addition, linear double-stranded (ds) DNA can be entrapped within the vesicles bilayer and can be protected towards enzymatic cleavage (see figure).

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* Author to whom correspondence should be addressed

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