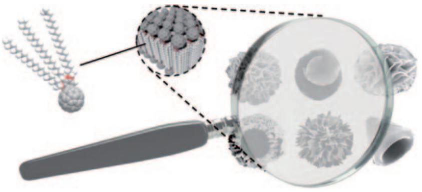
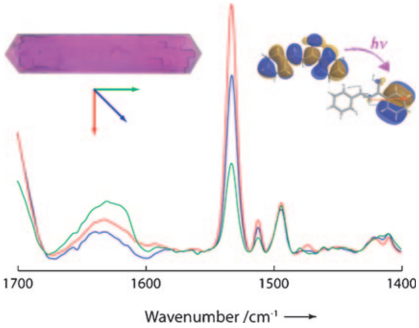
CONCEPTS

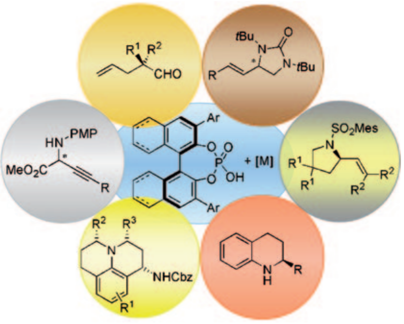
Uncommonly good: An unusual amphiphile composed strictly of hydrophobic units, fullerene (C_{60}), and long aliphatic chains behaves as an uncommon surfactant in organic media. Slight differences in the polarity and the chemical nature among these groups allow them to exhibit amphiphilicity. Their material aspects were also investigated (see graphic).

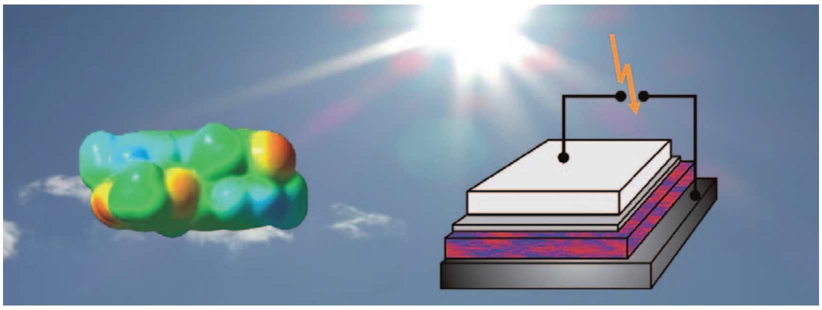


Molecules, line up! Synchrotron-based IR and UV/Vis microspectroscopic data and complementary theoretical calculations can be used to unambiguously identify transient carbocationic species generated in the acid-catalyzed oligomerization of styrene derivatives within ZSM-5. Polarization dependence of the IR and UV/Vis spectra is rationalized in terms of the vibrational and electronic transitions occurring in the confined molecules (see figure).



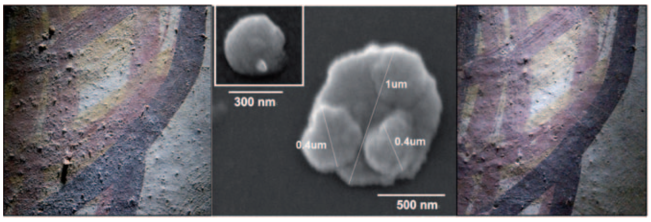
Combining acids and metals! The combination of chiral Brønsted acids and achiral or chiral transition-metal complexes emerged as a new strategy in asymmetric synthesis. The merged catalytic approach provides practical synthetic protocols that enable the synthesis of a broad range of compounds in a highly enantioselective fashion (see graphic).





Get organized! The recent successful utilization of highly dipolar merocyanine dyes in bulk heterojunction organic photovoltaic materials provides a convincing example for illustrating the importance of supramolecular organization principles in multifunctional organic materials.

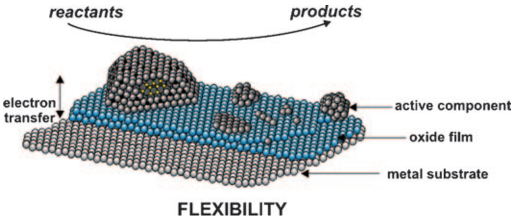
Nanotechnology



Paint the town red! Sulfation of wall paintings produces flaking and powdering of the paint layer. The combined action of calcium and barium hydroxide nanoparticles provides complete immobilisation of salts, and a durable re-cohesion effect on the paint layer (see graphic). The original carbonation process is re-generated to perfectly match the original physicochemical properties of the painting.

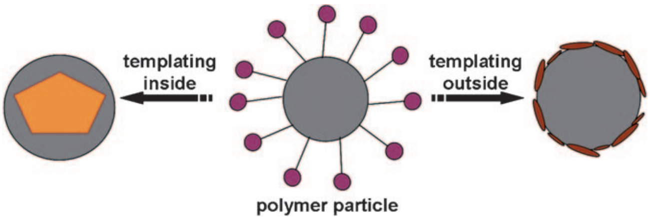
REVIEWS

Heterogeneous Catalysis



Scratching the surface: In this Review models for heterogeneous catalysis are discussed based on a surface-science approach (see figure). It is shown that models catching part of the complexity of the real system, which is connected with the finite size of active components and the flexibility of the arrangement of atoms in the active component, play an important part in determining the activity and selectivity of the system.

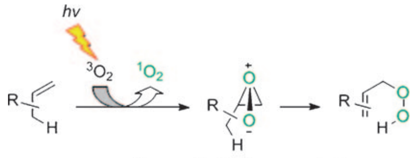
Biomimetic Mineralization



Close to the bone! Polymer nanoparticles can be used as versatile biomimetic templates to produce hybrid particles by employing either the volume or the surface of the polymer nanoparticle as templates (see picture). Such a concept is used to produce nanoparticles containing the bone mineral hydroxyapatite as the inorganic material. These particles could find application as regenerative fillers or as a scaffold for nucleation and growth of new bone material.

MINIREVIEWS

Concerted or stepwise? Recently, the mechanism of the singlet oxygen ene reaction has been a subject of renewed interest, particularly, whether the reaction is concerted or involves discrete intermediates. The majority of experimental and computational studies support a traditional stepwise mechanism involving a perepoxide-like intermediate (see scheme). This Minireview highlights some of the classical and most recent theoretical and experimental results relating to the mechanism of the $^1O_2$ ene oxyfunctionalization.



The most widely supported intermediate

Reaction Mechanisms

*M. N. Alberti, M. Orfanopoulos** 9414–9421

Unraveling the Mechanism of the Singlet Oxygen Ene Reaction: Recent Computational and Experimental Approaches

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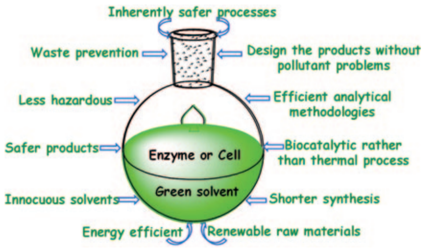
The future is bio, the future is green: Interest in implementing sustainable industrial technologies has propelled the use of biocatalysts (enzymes or cells), leading to high chemo-, regio- and stereoselectivity under mild conditions. We focus on different attempts to combine the valuable properties of green solvents with the advantages of using biocatalysts for developing cleaner synthetic processes (see figure).



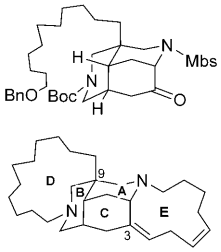
Green Chemistry

*M. J. Hernáiz, A. R. Alcántara, J. I. García, J. V. Sinisterra** 9422–9437

Applied Biotransformations in Green Solvents

COMMUNICATIONS

En route to madangamines: A unified strategy has been developed for the enantioselective assembly of functionalized diazatricyclic synthetic precursors of madangamines (see scheme; Bn = benzyl, Boc = *tert*-butoxycarbonyl, Mbs = *para*-methoxybenzenesulfonyl).



Madangamine D

Natural Products

M. Amat, M. Pérez, S. Proto, T. Gatti, J. Bosch** 9438–9441

First Enantioselective Synthesis of the Diazatricyclic Core of Madangamine Alkaloids

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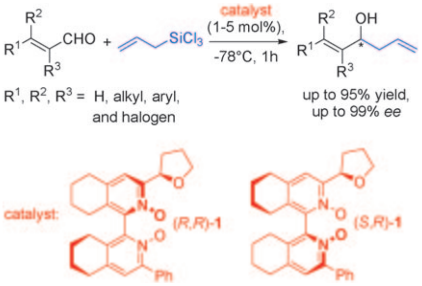
Being selective: The catalytic allylation of α,β-unsaturated aldehydes with allyltrichlorosilane in the presence of chiral 3,3′-unsymmetrically substituted bis(tetrahydroisoquinoline) *N*,*N*-dioxides was explored. The allylation of various aldehydes proceeded under mild reaction conditions (−78 °C) with high yields and enantioselectivity (see scheme). This allylation was applied in the synthesis of (*S*)-(−)-goniothalamin.



Asymmetric Synthesis

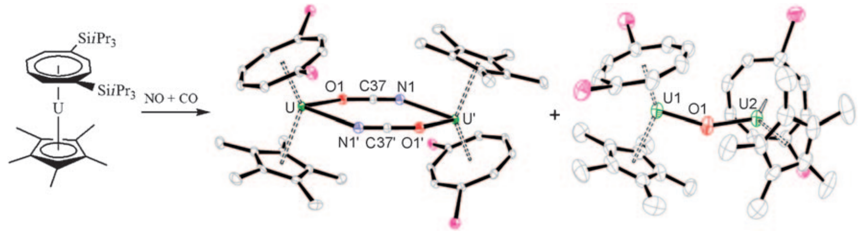
A. Kadlčíková, I. Valterová, L. Ducháčková, J. Roithová, M. Kotora** 9442–9445

Lewis Base Catalyzed Enantioselective Allylation of α,β-Unsaturated Aldehydes

Uranium Complexes

A. S. P. Frey, F. G. N. Cloke,
M. P. Coles,
P. B. Hitchcock* .... 9446 – 9448

VIP **U^{III}-Induced Reductive Co-Coupling of NO and CO to Form U^{IV} Cyanate and Oxo Derivates**

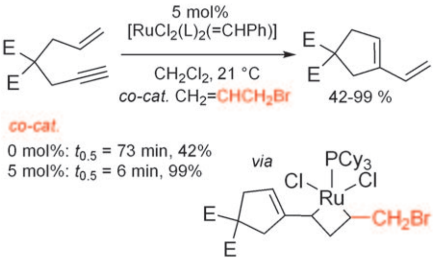


CO and NO give NCO and O! Sequential treatment of [U(η-C$_8$H$_6${Si*i*Pr$_3$-1,4}$_2$)(η-Cp*)] with CO followed by NO (or vice versa) affords a mixture of the bridging cyanate complex [{U(η-C$_8$H$_6${Si*i*Pr$_3$-1,4}$_2$)(η-Cp*)}$_2$-(μ-OCN)$_2$] and the bridging oxo complex [{U(η-C$_8$H$_6${Si*i*Pr$_3$-1,4}$_2$)(η-Cp*)}$_2$-(μ-O)], both of which have been structurally characterised (see scheme).

Ring-Closing Metathesis

G. C. Lloyd-Jones, A. J. Robinson,
L. Lefort, J. G. de Vries* .... 9449 – 9452

VIP **A Simple and Effective Co-Catalyst for Ring-Closing Enyne Metathesis Using Grubbs I type Catalysts: A Practical Alternative to "Mori's Conditions"**

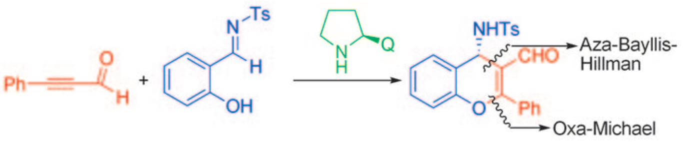


"Catch-and-release": Simple alk-1-enes are effective at liberating buta-1,3-dienes from vinyl alkylidene ruthenium complexes, as well as undergoing alkene–alkylidene exchange with enyne substrates to regenerate the alk-1-ene. This ability to "catch-and-release" ruthenium alkylidenes allows alk-1-enes higher than ethylene ("Mori's conditions") to be used as a co-catalysts in terminal enyne metathesis with the Grubbs generation I complex (L = PCy$_3$).

Asymmetric Synthesis

J. Alemán, A. Núñez, L. Marzo,
V. Marcos, C. Alvarado,
J. L. García Ruano* .... 9453 – 9456

Asymmetric Synthesis of 4-Amino-4*H*-Chromenes by Organocatalytic Oxa-Michael/Aza-Baylis–Hillman Tandem Reactions

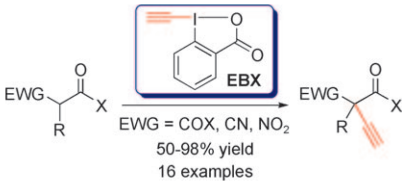


Quick off the mark! In this work we present the first highly enatioselective oxa-Michael/aza-Baylis–Hillman tandem reaction between 2-alkynals and salicyl *N*-tosylimine leading to optically active 4-amino-4*H*-chromenes (see scheme). This reaction takes place in less than 2 h with high yields and excellent enantioselectivities.

Hypervalent Iodine

*D. Fernández González, J. P. Brand,
J. Waser** .... 9457 – 9461

Ethynyl-1,2-benziodoxol-3(1*H*)-one (EBX): An Exceptional Reagent for the Ethynylation of Keto, Cyano, and Nitro Esters



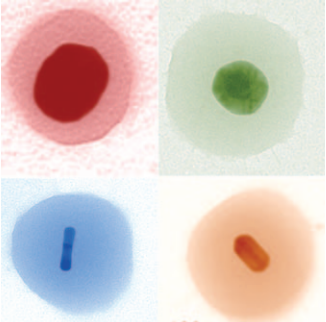
Hot alkyne! The in situ generation of ethynyl-1,2-benziodoxol-3(1*H*)-one (EBX) from a silyl-protected reagent by using TBAF is reported. EBX displayed exceptional acetylene transfer ability onto stabilized enolates (see scheme), even at −78 °C. The mild reaction conditions allowed the first ethynylation reactions of linear keto, cyano, and nitro esters in high yields to give all-carbon quaternary centers or non-natural amino acids after selective reduction of the nitro group.

CONTENTS

Nanoparticles

R. Contreras-Cáceres,
I. Pastoriza-Santos,
*R. A. Alvarez-Puebla, J. Pérez-Juste,**
A. Fernández-Barbero,
*L. M. Liz-Marzán** .... 9462 – 9467

Growing Au/Ag Nanoparticles within Microgel Colloids for Improved Surface-Enhanced Raman Scattering Detection



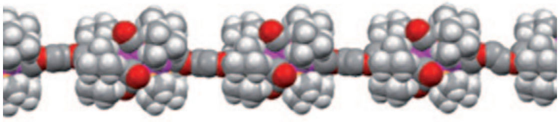
Microgel grow-bags: Surface-enhanced Raman scattering (SERS)-active bimetallic core–shell spheres can be grown inside poly(*N*-isopropylacrylamide) (pNIPAM) microgels (see figure).

FULL PAPERS

Platinum

P. Leoni, L. Marchetti, V. Bonuccelli,*
S. K. Mohapatra, A. Albinati,
S. Rizzato .... 9468 – 9477

Proton-Transfer Reactions on Hexanuclear Platinum Clusters: Reversible Heterolytic Cleavage of H_2 and C−H Activation Affording a Linear, Cluster-Containing Polymer

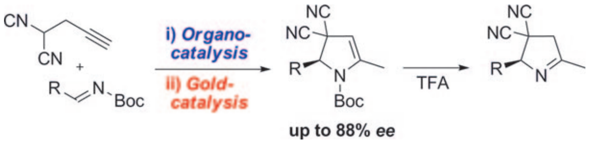


Chemical clusters: The reversible reaction of Brønsted acids, HA, with the hexanuclear dihydride $\{Pt_6\}H_2$ ($\{Pt_6\} = Pt_6(\mu\text{-}PtBu_2)(CO)_4$) affords anion-bonded $\{Pt_6\}A_2$, which reacts with dimethoxyethane to give the linear, cluster-containing polymer $[Pt_6(\mu\text{-}PtBu_2)_4(CO)_4(CH_2OCH_2CH_2OCH_2)]_x$ (see figure).

Organocatalysis

D. Monge, K. L. Jensen, P. T. Franke,
*L. Lykke, K. A. Jørgensen** 9478 – 9484

Asymmetric One-Pot Sequential Organo- and Gold Catalysis for the Enantioselective Synthesis of Dihydropyrrole Derivatives

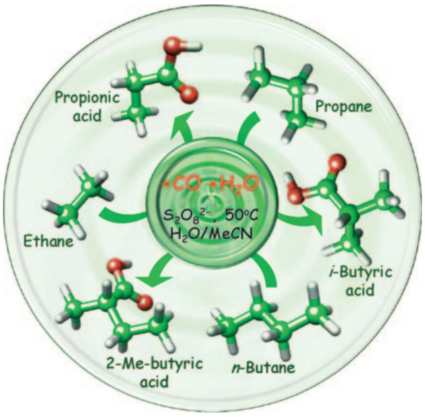


A golden combination: A direct asymmetric one-pot synthesis of optically active 2,3-dihydropyrroles from simple precursors is presented. The approach is based on a bifunctional organocatalytic Mannich-type reaction followed by Au^I-catalyzed alkyne hydroamination (see scheme; TFA = trifluoroacetic acid). To highlight the synthetic potential of the accessed heterocyclic compounds, their transformation into 1-pyrrolines is presented.

Alkane Functionalisation

M. V. Kirillova, A. M. Kirillov,
*A. J. L. Pombeiro** .... 9485 – 9493

Mild, Single-Pot Hydrocarboxylation of Gaseous Alkanes to Carboxylic Acids in Metal-Free and Copper-Promoted Aqueous Systems

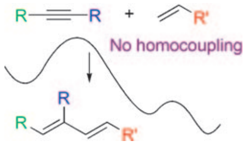


Active alkanes: Gaseous alkanes (ethane, propane and *n*-butane) efficiently react with carbon monoxide and water to give selectively, in a single-pot, the corresponding carboxylic acids in a metal-free and acid-solvent-free aqueous medium, under mild conditions (see figure).

Reaction Mechanisms

*S. T. Henriksen, D. Tanner, T. Skrydstrup, P.-O. Norrby** .... 9494 – 9501

DFT Investigation of the Palladium-Catalyzed Ene–Yne Coupling

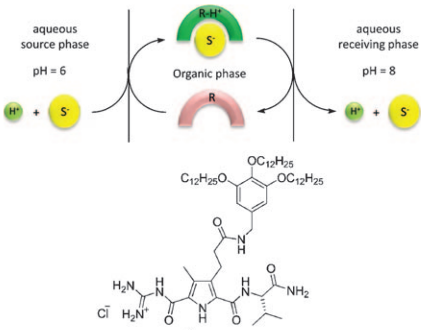


The perfect couple! The mechanism of the palladium-catalyzed intermolecular ene–yne coupling (see scheme) has been characterized by DFT. The absence of potential by-products from homocoupling could be fully rationalized.

Molecular Recognition

*C. Urban, C. Schmuck** ..... 9502 – 9510

Active Transport of Amino Acids by a Guanidiniocarbonyl–Pyrrole Receptor



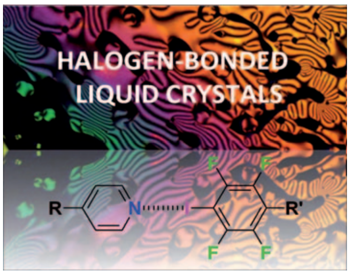
1

An amphiphilic receptor (1) transports N-acetylated amino acid carboxylates across a bulk liquid membrane (see graphic). In single experiments the release of the substrate determines the transport rate, whereas in competition experiments the affinity towards the receptor is decisive. Since **1** can only bind carboxylates in its protonated form, an overall symport of the amino acid carboxylate and a proton occurs. This allows for pH gradient driven active transport of the substrate.

Halogen Bonding

D. W. Bruce, P. Metrangolo,* F. Meyer, T. Pilati, C. Präsang, G. Resnati,* G. Terraneo, S. G. Wainwright, A. C. Whitwood* .... 9511 – 9524

Structure–Function Relationships in Liquid-Crystalline Halogen-Bonded Complexes

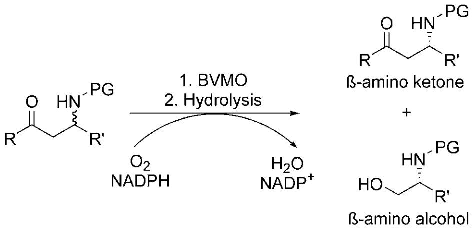


Clear as liquid crystals! New liquid-crystalline materials (see figure) were prepared by self-assembly driven by halogen bonding (XB) between a range of alkoxystilbazoles (XB acceptors) and derivatives of the 4-iodotetrafluorophenyl unit (XB donors). Despite the fact that the starting materials are not mesomorphic, the dimeric, halogen-bonded complexes obtained exhibited nematic and SmA phases, depending on the length of the alkyl chains present on the components.

Enzymatic Synthesis

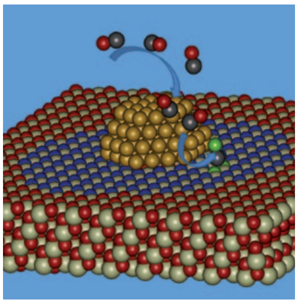
*J. Rehdorf, M. D. Mihovilovic, M. W. Fraaije, U. T. Bornscheuer** .... 9525 – 9535

Enzymatic Synthesis of Enantiomerically Pure β-Amino Ketones, β-Amino Esters, and β-Amino Alcohols with Baeyer–Villiger Monooxygenases



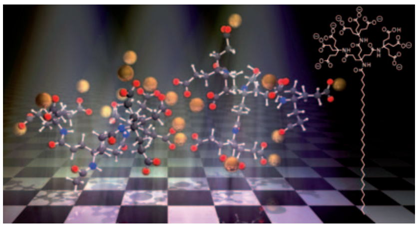
Nature's diversity: Kinetic resolution of structurally different aliphatic β-amino ketones was performed by using a collection of 16 different Baeyer–Villiger monooxygenases from various bacterial origins (see scheme). Excellent enantioselectivities for both normal and antipodal esters were observed and hydrolysis of Baeyer–Villiger esters yielded enantiopure β-amino alcohols.

Surface Chemistry



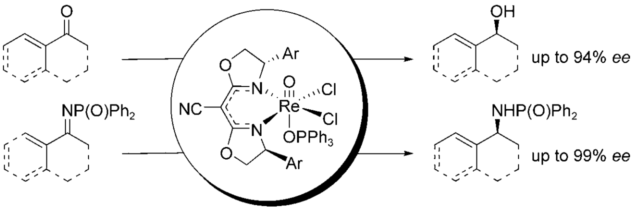
Model behaviour: A nanostructural model for the adsorption of CO on powder Au/ceria–zirconia catalysts, under conditions relevant to catalysis, is proposed by combining electron microscopy, computer modelling (see figure) and chemical analysis. This model highlights the key role of CO spillover in the adsorption on ceria–zirconia.

Specific-Ion Effects



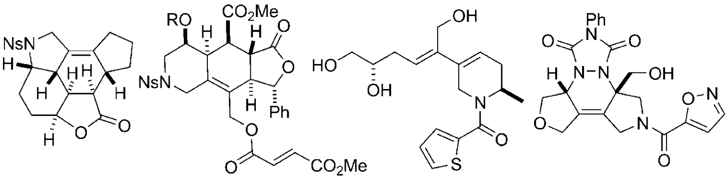
Stick together! The aggregation of amphiphilic polycarboxylates in water to structured micelles is strongly determined by the nature of the counterion. Sodium ions show the most pronounced counterion effect, favoring both intra- and intermicellar aggregation (see figure).

Enantioselective Catalysis



High-oxidation state bis-oxazoline rhenium(V)–oxo complexes (see scheme) catalyze the enantioselective reduction of ketones and imines under open-flask conditions. Additionally, the oxo complexes promote a tandem [3,3]-rearrangement–enantioselective reduction of propargyl and allenic alcohols.

Synthetic Methods

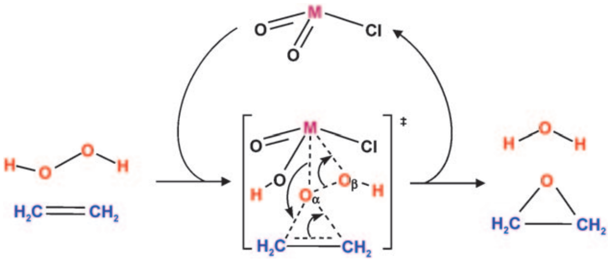


In search of scaffold diversity: The synthesis of a library of small molecules with high scaffold diversity is described. Initially, metathesis substrates were assembled from combinations of two or three building blocks. The range of scaffolds was extended through the subsequent exploitation of inter- and intramolecular Diels–Alder reactions. Fluorous tagging was used to facilitate the synthesis and functionalisation of the products (see scheme).

Hydrogen Peroxide Epoxidation

C. Dinoi, M. Ciclosi, E. Manoury, L. Maron, L. Perrin, R. Poli** .... 9572 – 9584

Olefin Epoxidation by H_2O_2/MeCN Catalysed by Cyclopentadienyloxidotungsten(VI) and Molybdenum(VI) Complexes: Experiments and Computations

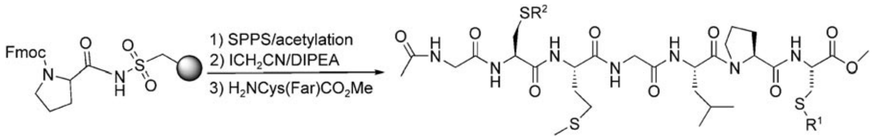


Tungsten is better: Compound $[Cp^*_2W_2O_5]$ is 50 times more active than $[Cp^*_2Mo_2O_5]$ for the quantitative and selective epoxidation of cyclooctene by H_2O_2 in acetonitrile (see scheme). A DFT study traces this difference to the greater oxophilicity of tungsten, which plays a determining role in the transition-state stabilisation.

Lipopeptides

*G. Triola, M. Gerauer, K. Görmer, L. Brunsveld, H. Waldmann** .... 9585 – 9591

Solid-Phase Synthesis of Lipidated Ras Peptides Employing the Ellman Sulfonamide Linker

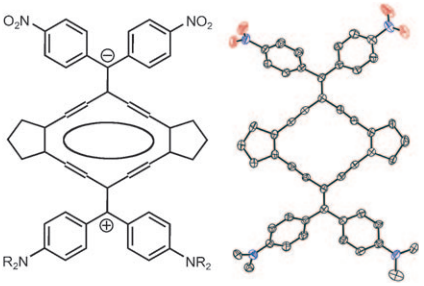


Safety catch: The solid-phase synthesis of differently lipidated peptides from the N-Ras family with the safety-catch sulfonamide linker has been established, including amino acid loading, peptide assembly and peptide release. The key step is the release of a prepeptide from the solid support with the C-terminal amino acid methyl ester under microwave irradiation (see scheme).

Push–Pull Chromophores

*Y.-L. Wu, F. Bureš, P. D. Jarowski, W. B. Schweizer, C. Boudon, J.-P. Gisselbrecht, F. Diederich** .... 9592 – 9605

Proaromaticity: Organic Charge-Transfer Chromophores with Small HOMO–LUMO Gaps

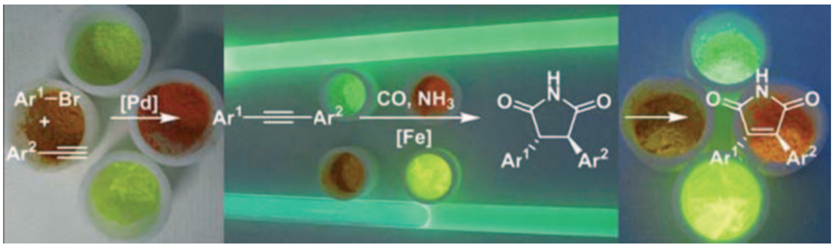


When charge transfer meets aromaticity: Charge transfer across quinoid and expanded quinoid π spacers was found to be highly efficient in conjunction with the aromatization of the spacer units based on experimental and theoretical evidence. A push–pull tetrakis(ethynediyl)-expanded quinoid compound (see figure) represents the first proaromatic radiaannulene, featuring a 14 π-electron perimeter in the charge-transfer geometry.

Iron Catalysis

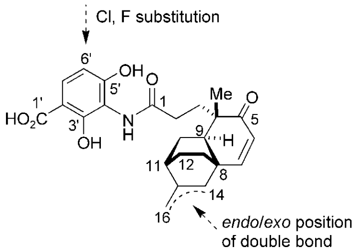
*S. Prateeptongkum, K. M. Driller, R. Jackstell, A. Spannenberg, M. Beller** .... 9606 – 9615

Efficient Synthesis of Biologically Interesting 3,4-Diaryl-Substituted Succinimides and Maleimides: Application of Iron-Catalyzed Carbonylations



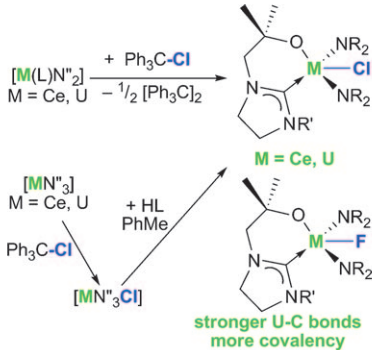
A novel synthetic strategy involving palladium-catalyzed Sonogashira reactions and iron-catalyzed double carbonylations allows for the synthesis of biologically interesting 3,4-diaryl-substituted succinimides and maleimides (see scheme).

The unnatural antibiotic *iso*-platencin, which is about as active as natural platencin (a novel antibiotic which is active against multiresistant pathogens), but much more selective, is presented as a new antibiotic lead structure (see figure). We describe efficient syntheses of three platencin analogues of varying activities, which allow further conclusions about the pharmacophoric part of the molecule.



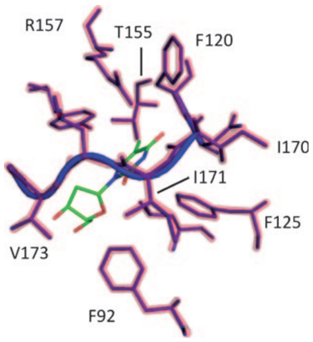
Total Synthesis

Accessing Ce^{IV}: The tetravalent oxidation state of cerium is unusual and often associated with multiconfigurational behaviour. Analysis of the bonding in tetravalent, rather than more conventional trivalent, f-block complexes shows the 5f metal bonds to softer ligands are stronger and more covalent than 4f analogues (see scheme). The use of trityl chloride as a simple oxidant to access Ce^{IV} is also shown.

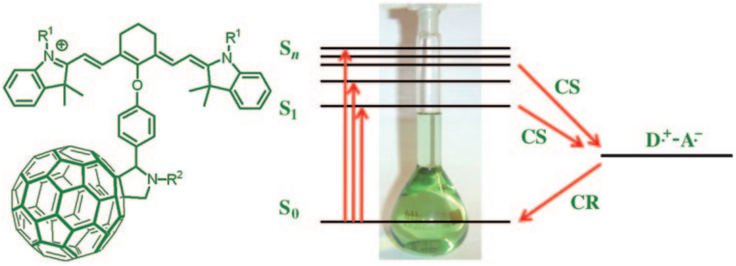


Actinide Chemistry

Resistance is futile! Computer-assisted protein modeling and parallel virtual screening led to the identification of antibiotic agents that combat clinically relevant drug-resistant *Staphylococcus aureus*. The non-nucleoside inhibitors target bacterial thymidine kinase (see figure).



Molecular Modeling



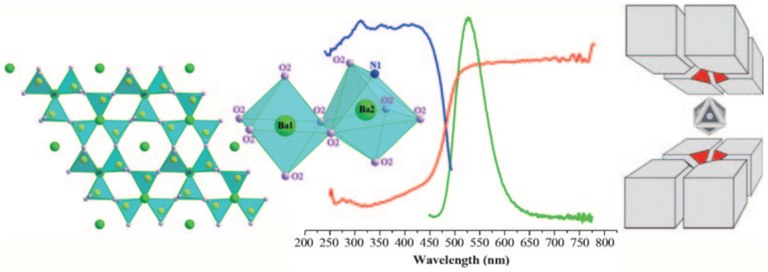
The higher the better: We have realized the rarely found scenario of a charge transfer that commences in a higher-energy excited state (see image), through the careful choice of electron donor and electron acceptor.

Heptamethine Cyanines

Green Phosphors

*C. Braun, M. Seibald, S. L. Börger, O. Oeckler, T. D. Boyko, A. Moewes, G. Miehe, A. Tücks, W. Schnick** .... 9646 – 9657

Material Properties and Structural Characterization of $M_3Si_6O_{12}N_2:Eu^{2+}$ ($M = Ba, Sr$)—A Comprehensive Study on a Promising Green Phosphor for pc-LEDs

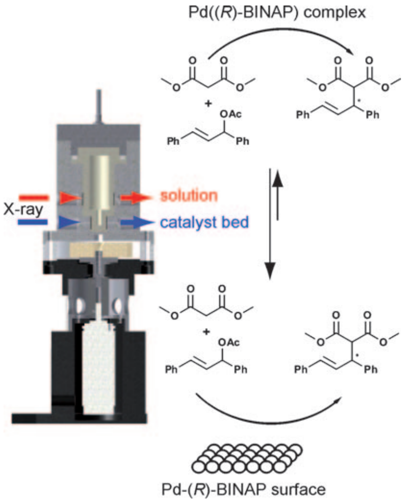


Give it the green light! The luminescence properties of $M_3Si_6O_{12}N_2:Eu^{2+}$ ($M = Ba,Sr$) render this layered Ba–oxonitridosilicate an interesting phosphor for pc-LEDs. Various improved syntheses lead to highly crystalline products as well as single crystals suitable for precise structure determination (see figure). In situ high-pressure and high-temperature investigations indicate the best sintering conditions. XES and XAS spectra were conducted for a better understanding of the electronic structure.

Catalysis

*S. Reimann, J.-D. Grunwaldt, T. Mallat, A. Baiker** .... 9658 – 9668

Asymmetric C−C Bond-Formation Reaction with Pd: How to Favor Heterogeneous or Homogeneous Catalysis?

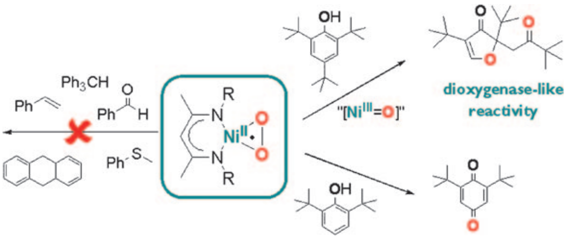


Homogeneous or heterogeneous? A combined approach by using catalytic experiments and in situ XANES spectroscopy was used to clarify the heterogeneous or homogeneous nature of the Pd/Al_2O_3–(*R*)-BINAP catalyst system (see graphic) applied in the enantioselective allylic alkylation of (*E*)-1,3-diphenylallyl acetate. Crucial factors that cause leaching were identified.

O−O Activation

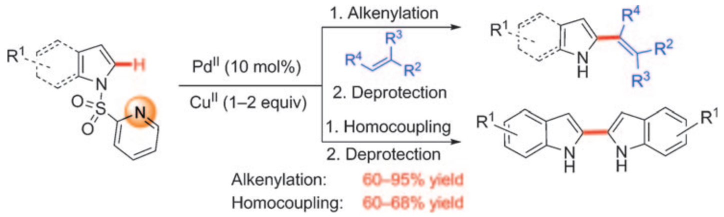
*A. Company, S. Yao, K. Ray, M. Driess** .... 9669 – 9675

Dioxygenase-Like Reactivity of an Isolable Superoxo–Nickel(II) Complex



Superoxo magic: The oxidizing ability of an isolable and thermally stable superoxo–nickel(II) towards exogenous organic substrates has been studied for the first time in detail (see scheme). The complex is suitable to oxidize O−H and N−H bonds and even shows a unique dioxygenase-like reactivity towards phenols to give unexpected oxidation products.

Direct C–H Functionalisation



Temporary control: The easily installed and removed *N*-(2-pyridyl)sulfonyl group directs the C–H functionalisation of indoles with complete regiocontrol for C2 and allows the final N deprotection by facile, reductive N–S cleavage (see scheme). This concept has been successfully applied to the C2–H alkenylation of indoles and pyrroles as well as to the dehydrogenative intermolecular homocoupling of indoles to afford 2,2′-biindoles.

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