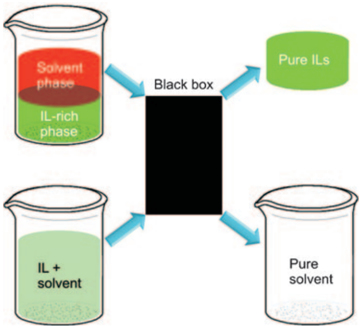
MINIREVIEWS

Ionic Liquids

*B. Wu, W. Liu, Y. Zhang,**
*H. Wang** .... 1804 – 1810

Do We Understand the Recyclability of Ionic Liquids?



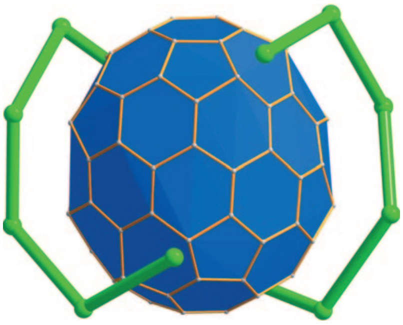
Recycling of "green" solvents: Recycling of ionic liquids with high efficiency is of key importance on going from the laboratory-scale to large-scale industrial application of these solvents.

COMMUNICATIONS

Fullerenes

K. S. Simeonov, K. Y. Amsharov,
*M. Jansen** .... 1812 – 1815

$C_{80}Cl_{12}$: A Chlorine Derivative of the Chiral D_2-C_{80} Isomer—Empirical Rationale of Halogen-Atom Addition Pattern

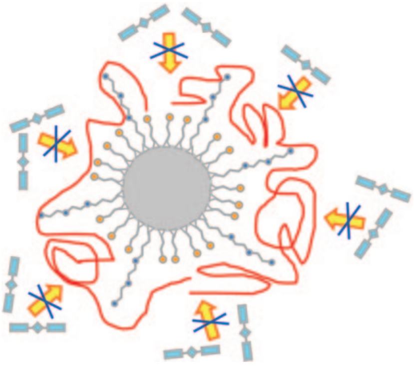


Welcome to the family! The constitution of the chiral D_2-C_{80} fullerene has been confirmed through single-crystal X-ray analysis of the chlorinated $C_{80}Cl_{12}$. The addition pattern of the chlorine atoms in the structure of $C_{80}Cl_{12}$ together with other structures of halogenated higher fullerenes is discussed. A stepwise principle of higher fullerene reactivity is proposed. Unusual short intermolecular chlorine–chlorine contacts are reported.

Heparin Chemosensor

*E. Climent, P. Calero, M. D. Marcos,**
R. Martínez-Máñez, F. Sancenón,*
J. Soto .... 1816 – 1820

Selective Chromofluorogenic Sensing of Heparin by using Functionalised Silica Nanoparticles Containing Binding Sites and a Signalling Reporter

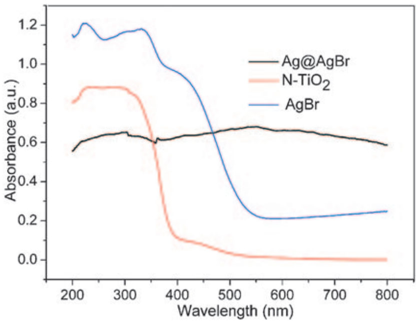


Heparin detective: Silica nanoparticles functionalised with ion-channel scaffolds were prepared and used for the chromofluorogenic sensing of heparin in aqueous environments (see figure). The surface of the nanoparticles was functionalised with polyamines (binding sites) and thiols. The reaction of a dye (squaraine) with the surface thiol groups was selectively inhibited by the coordination of heparin with the partly protonated polyamines.

Heterogeneous Catalysis

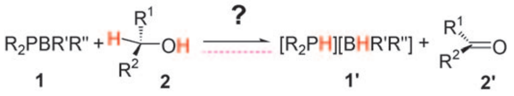
P. Wang, B. Huang, X. Zhang,*
X. Qin, H. Jin, Y. Dai, Z. Wang, J. Wei,
J. Zhan, S. Wang, J. Wang,
M.-H. Whangbo .... 1821 – 1824

Highly Efficient Visible-Light Plasmonic Photocatalyst Ag@AgBr



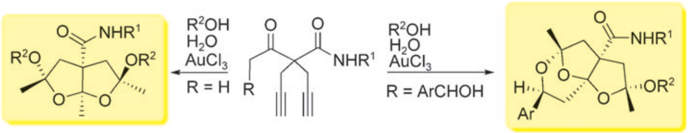
Visible improvements: Owing to the plasmon resonance of silver nanoparticles deposited on the surface of AgBr, the newly-prepared plasmonic photocatalyst Ag@AgBr has a strong absorption in the visible region (see picture) and shows high efficiency in the photodegradation of organic pollutants under visible light.

Reaction Mechanisms



Can phosphinoboranes promote hydrogenation of carbonyl moieties? By means of B3LYP and MPW1K density functional calculations the likelihood of the oxidation of alcohols by phosphinoboranes $R_2PBR'_2$ (**1**) was explored. As a proof-of-principle, a theoretical study that tests the reversibility of the alcohol oxidation is reported. The potential of **1** as a metal-free hydrogenation mediator is discussed for a series of hydrogen sources such as primary and secondary alcohols.

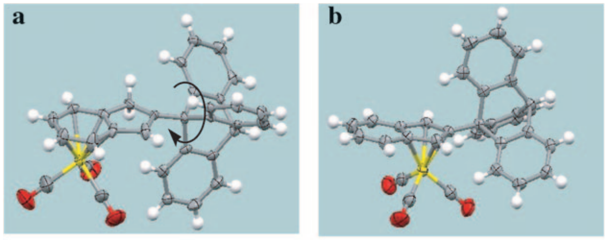
Domino Reactions



Single step: Fused bicyclic and bridged tricyclic ketals were synthesized in a single step from the reactions of easily available 4-acyl-1,6-diynes with H_2O and alkanols (see scheme). The highly efficient $AuCl_3$-catalyzed multicomponent domino reactions, involving five C−O bond formations, can proceed in a highly regio- and diastereoselective manner at room temperature under air and lead to structures of high molecular complexity from simple starting materials in an atom economic way.

FULL PAPERS

Organometallic Latch



free thermal rotation

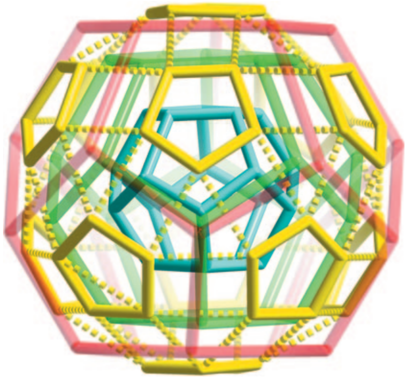
rotation is arrested

Metal clamping in operation! Deprotonation of $[\eta^6\text{-2-(9-triptycyl)indene}]$tricarbonylchromium induces a haptotropic shift of the organometallic fragment from the six-membered to the five-membered ring, as in **a**→**b**. In the anion, rotation of the molecular paddlewheel is blocked by the bulky tripod. X-ray crystal structures provide pictures of the system in both its “ON” and “OFF” states.

Polyoxometalates

T. Mitra, P. Miró, A.-R. Tomsa, A. Merca, H. Bögge, J. B. Ávalos, J. M. Poblet, C. Bo, A. Müller** .... 1844 – 1852

Gated and Differently Functionalized (New) Porous Capsules Direct Encapsulates' Structures: Higher and Lower Density Water

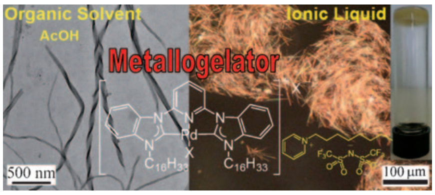


Either more or less neighbors favored? By deliberate choice of the internal ligands of the porous nanocapsules $[\{(Mo)Mo_5\}_{12}\{Mo_2(ligand)\}_{30}]^{n-}$, the respective cavities can be differently sized/functionalized. This allows one to trap, in two different corresponding capsules, 100 water molecules arranged in shells that exhibit more and less dense packing, respectively—the latter type in a capsule with smaller internal ligands; the picture shows the related 100 O atoms at the vertices of the four polyhedra, while two dodecahedra (shown in pale green and red) have only 10 H_2O molecules instead of 20.

Sol–Gel Chemistry

T. Tu, X. Bao, W. Assenmacher, H. Peterlik, J. Daniels, K. H. Dötz** .... 1853 – 1861

VIP Efficient Air-Stable Organometallic Low-Molecular-Mass Gelators for Ionic Liquids: Synthesis, Aggregation and Application of Pyridine-Bridged Bis(benzimidazolylidene)–Palladium Complexes

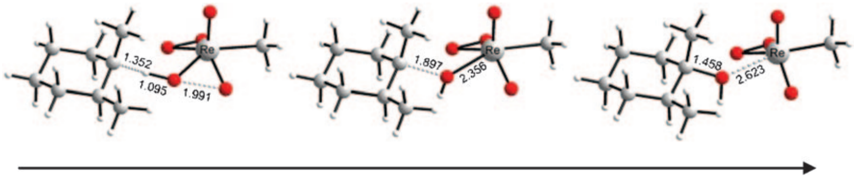


Beyond catalysis: Novel pincer-type pyridine-bridged bis(benzimidazolylidene)–palladium complexes have been synthesised and shown to efficiently gelate a variety of solvents and customary ionic liquids. π-Stacking, van der Waals interactions, hydrogen and metal–metal bonding are responsible for 3D gel networks formed by the metallogelators.

Reaction Mechanisms

*E. A. Karlsson, T. Privalov** .... 1862 – 1869

Oxidation of Ethers, Alcohols, and Unfunctionalized Hydrocarbons by the Methyltrioxorhenium/H_2O_2 System: A Computational Study on Catalytic C−H Bond Activation

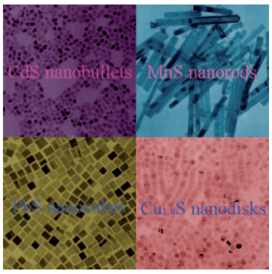


A concerted mechanism that does not involve an ionic intermediate was revealed by a DFT study on oxidation of ethers, alcohols, and unfunctionalized hydrocarbons by methyltrioxorhenium/H_2O_2. Instead, C−H insertion occurs through hydride transfer and then turns into a hydroxide transfer/rebound in a concerted fashion. The picture shows selected frames from an intrinsic reaction coordinate scan from the transition state to the product for the oxidation of *cis*-1,2-dimethylcyclohexane.

Nanostructures

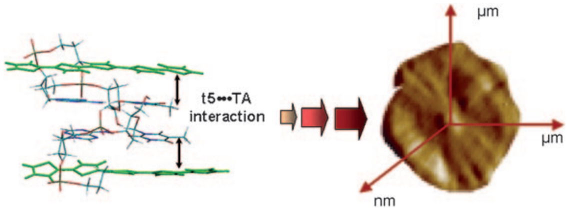
*D.-S. Wang, W. Zheng, C.-H. Hao, Q. Peng, Y.-D. Li** .... 1870 – 1875

A Synthetic Method for Transition-Metal Chalcogenide Nanocrystals



A facile wet route was applied to prepare a series of chalcogenide semiconductor nanocrystals (see figure) in controllable shapes and sizes, while a general bottom-up approach was adopted to transform these cyclohexane-soluble monodisperse nanocrystals into water-soluble colloidal spheres.

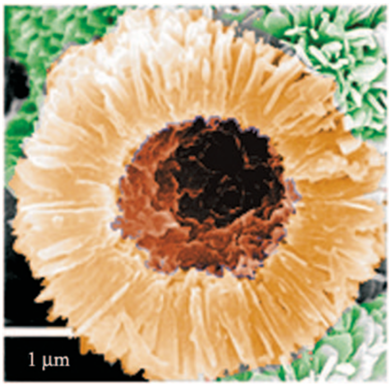
Oligonucleotides



Biodriven self-organization of α-quinquethiophene (t5): Cast films of $^{5'}$TA$^{3'}$-t5 are electroactive, photoluminescent, and chiral. Their growth is not directed by intermolecular Watson–Crick hydrogen bonding between the A···T moieties of interacting molecules, but is governed by intra- and intermolecular thiophene–nucleobase stacking interactions.

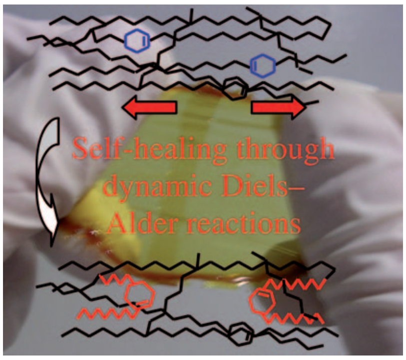
Nanostructures

$Co(OH)_2$ that blooms: Flowerlike hollow spherical architectures of cobalt hydroxide obtained through a facile solvothermal process are reported for the first time (see picture). Their growth process involves aggregation of cobalt hydroxide nanoparticles into solid spheres and a hollowing effect through subsequent dissolution-diffusion-redeposition of the smaller crystallites under the surface layer.

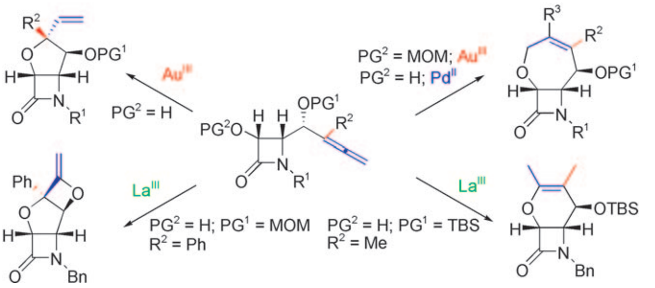


Dynamic Polymers

Polymer, heal thyself! Dynamic polymers formed by a reversible Diels–Alder reaction were formed and studied by using neutron scattering at room temperature. They were used to obtain thin films that displayed self-healing at room temperature (see figure).



Allenes

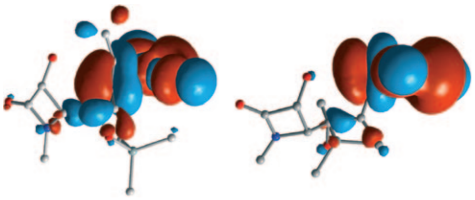


Guiding cyclization: The 5-*exo-trig* cyclization pathway of γ-allenols can be completely reversed either by changing the metal (Pd instead of Au) or by using a methoxymethyl protecting group, with 7-*endo-trig* alkoxycyclization then dominating instead (see scheme). In addition, the regioselectivity of the La-catalyzed cycloetherification can be modulated (5-*exo* versus 6-*endo* versus 7-*endo*) simply through subtle variation in the functionalization of the allene component.

Allenes

B. Alcaide, P. Almendros,**
*T. Martínez del Campo, E. Soriano,**
J. L. Marco-Contelles .... 1909 – 1928

Regioselectivity Control in the Metal-Catalyzed Functionalization of γ-Allenols, Part 2: Theoretical Study

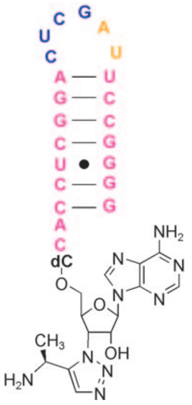


Calculating cyclization: Theoretical work directed towards the elucidation of the mechanisms of the gold-, palladium-, and lanthanum-catalyzed oxycyclizations (5-*exo* versus 6-*endo* versus 7-*endo*) of γ-allenols has been pursued in close relationship with the experimental study (Part 1, accompanying paper) and has corroborated the bench results to provide a complete study of the reactivity of γ-allenols under different metal-catalyzed conditions.

RNS Inhibitors

M. Chemama, M. Fonvielle,
M. Arthur, J.-M. Valéry,
*M. Etheve-Quelquejeu** ..... 1929 – 1938

Synthesis of Stable Aminoacyl-tRNA Analogues Containing Triazole as a Bioisoster of Esters

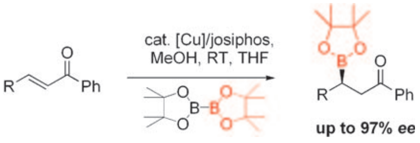


Stable analogues: An effective synthetic route involving cycloaddition between alkynes and azidonucleosides to afford a new class of stable aminoacyl-tRNA analogues such as depicted is presented. Biological evaluation showed that theses new compounds act as potent inhibitors of $FemX_{Wv}$ aminoacyl transferase, a novel drug target.

Conjugate Addition

*H.-S. Sim, X. Feng, J. Yun** 1939 – 1943

Copper-Catalyzed Enantioselective β-Boration of Acyclic Enones

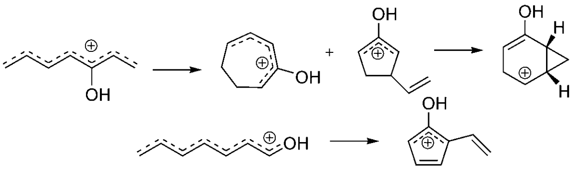


Josi or Mandy? Asymmetric conjugate addition of diboron to acyclic enones catalyzed by copper affords chiral organoboronates that possess a boronate group at the β stereocenter with excellent chemical yields and enantioselectivities (see scheme). This method accommodates the structural variation of acyclic enones and provides access to highly functionalized chiral organoboronates in one step.

Electrocyclizations

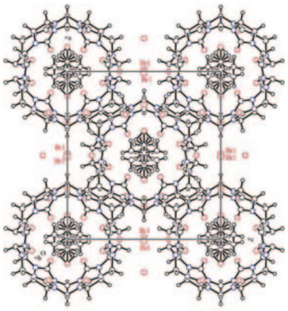
O. N. Faza, C. S. López, R. Álvarez,
*Á. R. de Lera** .... 1944 – 1956

Regio-, Peri-, and Torquoselectivity in Hydroxy Heptatrienyl Cation Electrocyclizations: The Iso/Homo-Nazarov Reaction



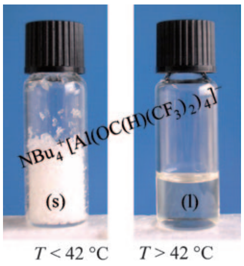
Competition: The electrocyclizations of 1- and 3-hydroxyheptatrienyl cations (see scheme) have been computationally studied at the B3LYP/6-311G(d) level. The 1-hydroxy system clearly favors a $4e^-$ over a $6e^-$ process, while for the 3-hydroxy isomer these mechanisms compete.

Water seeds: Complex stoichiometry/composition and degree of oligomerization (oligomeric supramolecular complex formation) of cucurbit[6]uril (CB[6]) with *N*-alkyl- and *N,N′*-dialkylpiperazine were investigated in aqueous solutions by means of isothermal titration calorimetry (ITC), ESI-MS, NMR and light scattering measurements.

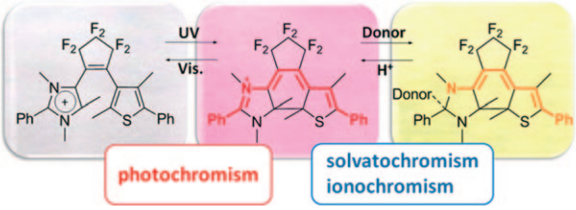

CB[6] –1-propylpiperazine

Supramolecular Chemistry

Weak and robust? Tetraalkylammonium salts of weakly coordinating fluorinated alkoxyaluminates are easily accessible, chemically robust materials that show interesting physico-chemical properties like low melting points, high electrochemical stability and electric conductivity in weakly polar solvents such as CH_2Cl_2, Ph-F and toluene.



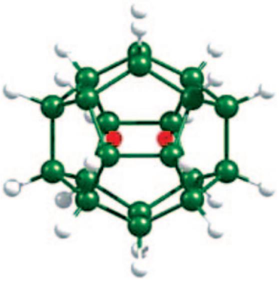
Ionic Liquids



Seeing red: Imidazolium-substituted diarylethenes show solvent- and ion-controlled chromisms in addition to reversible photochromic reactions. The shift of equilibrium between two closed-ring isomers with different π-conjugation length by interaction with nucleophilic species is responsible for the multichromic property (see scheme).

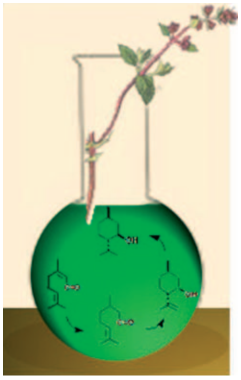
Solvatochromism

The shortest He–He distance! r(He–He) = 1.265 Å. The electronic interaction between confined pairs of He atoms in the $C_{20}H_{20}$ dodecahedrane cage is analyzed (see figure). A key observation about bonding that emerges uniquely from endohedral complexes is that a short internuclear separation does not necessarily imply the existence of a chemical bond.



Endohedral Complexes

Zeolites



Minty green: Zr–zeolite beta (Zr-beta) directs the one-pot catalytic cascade transformation of citral to menthols with high diastereoselectivity. The solid catalyst, a bifunctional Ni/Zr-beta or a composite Zr-beta–Ni/MCM-41 system, is easily recovered and reused in this green synthetic method (see figure).

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* Author to whom correspondence should be addressed

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SERVICE

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