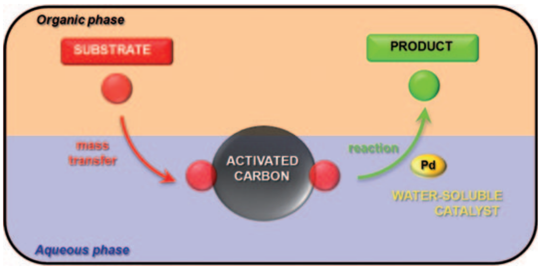
COMMUNICATIONS

Palladium Catalysis

*N. Kania, B. Léger, S. Fourmentin, E. Monflier, A. Ponchel** . . . 6138 – 6141

Activated Carbon as a Mass-Transfer Additive in Aqueous Organometallic Catalysis

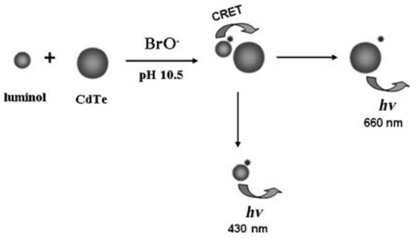


Carbon, on active duty: The addition of activated carbon into the reaction medium appears to be a simple and efficient method to solve mass-transfer limitations in aqueous organometallic catalysis (see figure).

Chemiluminescence

S. Zhao, Y. Huang, R. Liu, M. Shi, Y.-M. Liu** . . . . 6142 – 6145

A Nonenzymatic Chemiluminescent Reaction Enabling Chemiluminescence Resonance Energy Transfer to Quantum Dots

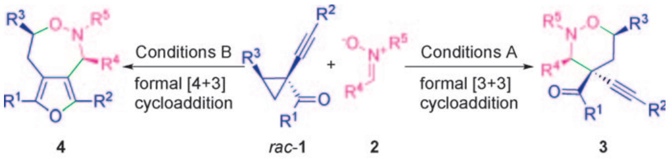


Glowing transfer: An efficient chemiluminescence resonance energy transfer (CRET) between a luminol donor and a quantum dot acceptor was observed for the first time from a nonenzymatic reaction involving luminol–NaBrO–CdTe quantum dots (see figure). This work represents significant progress from the previously reported observation of CRET between a luminol donor and a horseradish peroxidase conjugated quantum dot acceptor from an enzyme-catalyzed chemiluminescence reaction.

Tuning Regioselectivity

*Y. Zhang, F. Liu, J. Zhang** . . . . 6146 – 6150

Catalytic Regioselective Control in the Diastereoselective 1,3-Dipolar Cycloaddition Reactions of 1-(1-Alkynyl)cyclopropyl Ketones with Nitrones



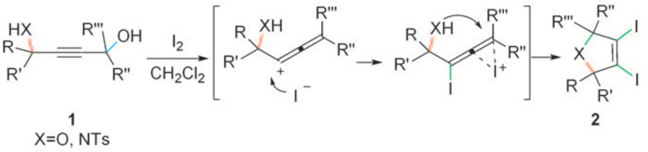
Conditions A: Sc(OTf)$_3$/1,10-phenanthroline (10 mol%), MS 4Å, DCE, 28- 32 °C.
Conditions B: Ph$_3$PAuOTf (2 mol%), DCM, room temperature.

The power of the catalyst: The cycloaddition pattern of 1-(1-alkynyl)cyclopropyl ketones **1** with nitrones **2** can be controlled by subtle alterations in the choice of catalyst. From the same two starting materials, two useful heterocyclic compounds can be selectively prepared.

Domino Reactions

*K.-G. Ji, H.-T. Zhu, F. Yang, X.-Z. Shu, S.-C. Zhao, X.-Y. Liu, A. Shaukat, Y.-M. Liang** . . 6151 – 6154

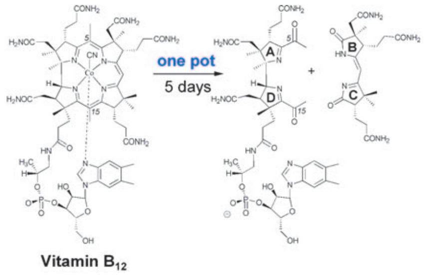
A Novel Iodine-Promoted Tandem Cyclization: An Efficient Synthesis of Substituted 3,4-Diiodoheterocyclic Compounds



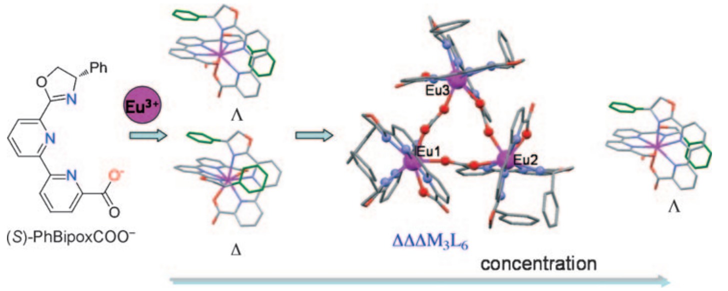
Iodine sets allenes ringing: A novel iodine-promoted tandem cyclization reaction of but-2-yne-1,4-diol and 4-aminobut-2-yn-1-ol derivatives leading to substituted 3,4-diiodoheterocyclic compounds has been developed (see scheme). In this reaction, a trace amount of water is needed. Both the iodine anion and cation generated from I$_2$ are used in the reaction. The resulting iodides can then be used in palladium-catalyzed coupling reactions. The reaction conditions are metal-free, mild, and environmentally friendly.

Natural Products

Demetallation of B_{12}: A one-pot synthesis of the metal-free AD and BC fragments of vitamin B_{12} that combines photo-oxidative scission with subsequent unprecedented demetallation of the natural product is described (see scheme).



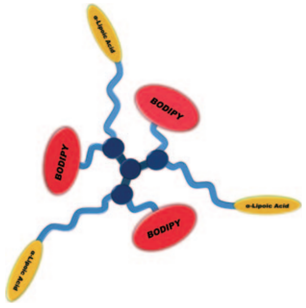
Cluster Compounds



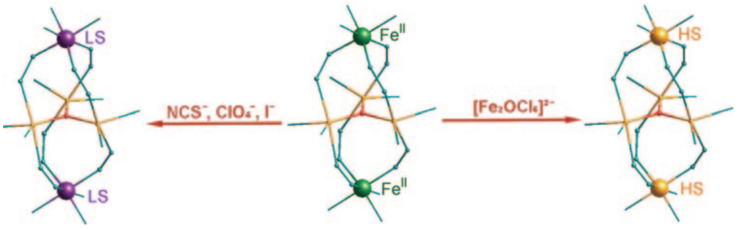
A homochiral triangle: An enantiopure europium triangle selectively self-assembles from a new bipyoxazoline−carboxylate ligand in a concentration-dependent process (see scheme).

Biological Activity

Double trouble! Orthogonally functionalised dendrimers have been constructed by using a versatile approach that is widely applicable for therapeutics and diagnostics by combining imaging agents and therapeutics for synergistic effects. Dendrimers containing a covalently linked dipyrromethene boron difluoride (BODIPY) dye and α-lipoic acid perform complementary biological functions and target intracellular lipid droplets (see figure).



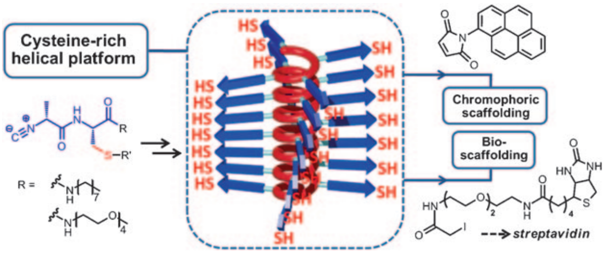
Spin Transitions



Polynuclear Fe^{II} Clusters: A new family of $\{Fe_5\}$ cluster compounds formulated with $[\{Fe^{II}(\mu\text{-bpt})_3\}_2Fe^{II}_3(\mu_3\text{-}O)]X_2$ have been synthesised from the solvothermal reactions of 4-amino-3,5-bis(pyridine-2-yl)-1,2,4-triazole with ferrous salts. The spin states of the two apical iron(II) ions in the cationic pentanuclear $\{Fe_5\}$ clusters can be tuned to give the high-spin states by the $[Fe_2OCl_6]^{2-}$ anion and the low-spin states by $SCN^-/ClO_4^-/I^-$ (see scheme).

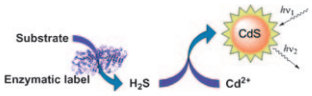
FULL PAPERS

Click Chemistry



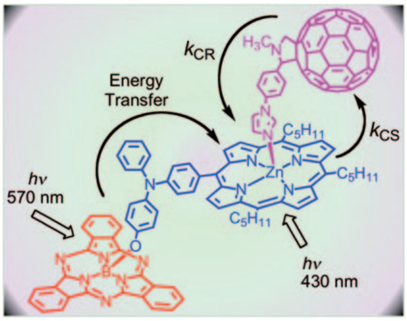
A thio-millipede invasion! Helical polyisocyanides containing the alanine–cysteine motif in their side chains have been prepared. The cysteine sulfur atoms are regularly aligned along the polymer axis (see scheme), which provides a unique platform for the scaffolding of various entities by using, for example, the versatile thio-click-chemistry postmodification approach.

Quantum Dots



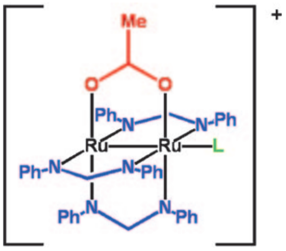
Dot products: We have developed two analytical assays for enzymatic activity based on the generation of quantum dots from enzymatic products. These assays were applied to the detection of acetylcholine esterase and alkaline phosphatase. These enzymes induce the formation of H_2S, which in the presence of cadmium cations yields CdS quantum dots.

Electron Transfer



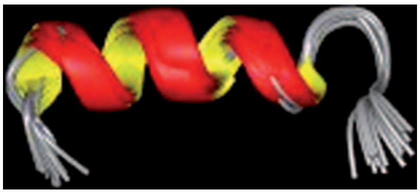
Long live the tetrad! Efficient charge separation and a long-lived charge-separated state, in nonpolar toluene, of a self-assembled tetrad formed by axial coordination of a fulleropyrrolidine appended with an imidazole ligand coordinating to the zinc center of subphthalocyanine–triphenylamine–zinc porphyrin was achieved (see picture).

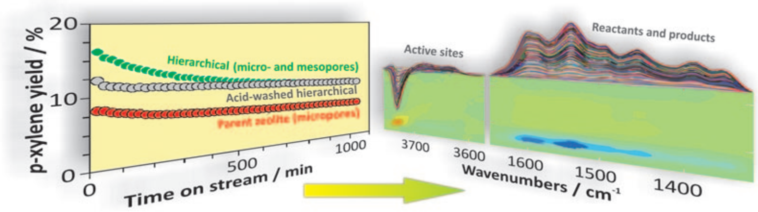
Diruthenium Complexes



Feel the influence! The influence of the axial ligand on the energy of the orbitals that constitute the HOMO level of the unit $[Ru_2(DPhF)_3(O_2CMe)(L)]^+$ was analysed using DFT calculations. The calculations demonstrate that an increase in the π-acceptor character of the ligand L leads to the stabilisation of the low-spin state. Intermediate spin systems are also explained.

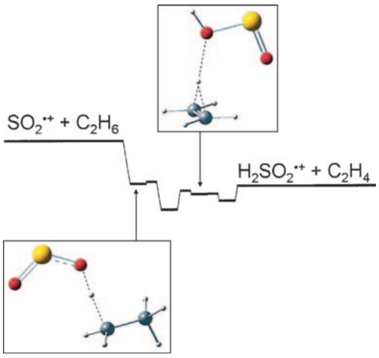
The sum of its parts: The copper(II)-binding features of doppel (hDpl) are driven by an aspartic residue. Analyses show that the hDpl(122–139) peptide fragment (see figure) effectively maintains its helical nature even when excised from full-length hDpl. The EPR spectra of each Cu^{II} complex has features that overlap the data for the Cu^{II}–hDpl interaction and can thus be used to model these interactions in the hDpl α-3 helix.

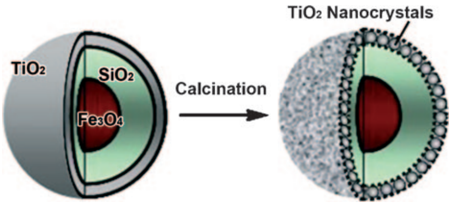




Shaping up: The benefits of hierarchical porous zeolites in shape-selective reactions were demonstrated for the isomerization of *o*-xylene over mesoporous ZSM-5. The introduction of intracrystalline mesopores and modification of the acid site distribution were tuned to optimize the catalytic performance (see graphs).

Two at once: The $SO_2^{\bullet+}$ radical cation assists an exothermic and effective conversion of ethane to ethylene by double C–H activation at room temperature. Charge and spin effects are strictly related to geometrical constraints of short-lived intermediates, like the ion–molecule complexes containing the ethyl radical and the ethyl cation, respectively (see figure).



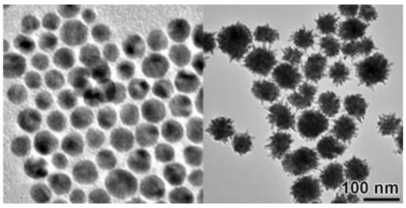


Sol–gel and calcination: Core–shell structured $Fe_3O_4/SiO_2/TiO_2$ nanocomposites with enhanced photocatalytic activity that are capable of fast magnetic separation have been successfully synthesized by combining two steps of a sol–gel process with calcination (see figure).

Nanocrystal Catalysis

*S. Song, R. Liu, Y. Zhang, J. Feng, D. Liu, Y. Xing, F. Zhao, H. Zhang** .... 6251 – 6256

Colloidal Noble-Metal and Bimetallic Alloy Nanocrystals: A General Synthetic Method and Their Catalytic Hydrogenation Properties

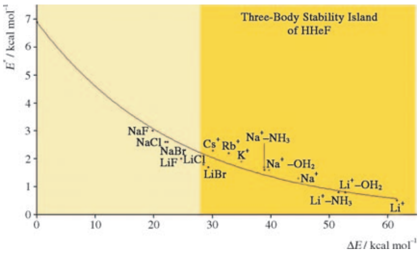


Noble-metal nanocatalyst: A general single-step strategy has been developed for the direct thermal decomposition of noble-metal salts in octadecylamine to synthesize octahedron- and rod-shaped noble-metal aggregate nanocrystals and their alloys without introducing any additive into the system (see figure). The catalytic ability of the nanocrystals has been investigated.

Helium Chemistry

*M. Giordani, P. Antoniotti, F. Grandinetti** .... 6257 – 6264

Stabilization of HHeF by Complexation: Is it a Really Viable Strategy?

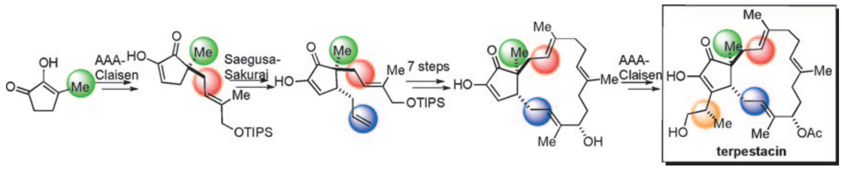


HHeF: Can it be stabilized? The intrinsically unstable HHeF is probably observable only in solid helium at the highest pressures. Alternatively, it could be trapped in cold matrices, but this requires stabilization by complexation effects. The ligands shown in the dark zone of the graphic definitely stabilize HHeF with respect to H + He + F, but drastically reduce the H–He–F bending barrier. Overall, the results cast doubts on the conceivable stabilization of HHeF by complexation.

Total Synthesis

B. M. Trost, G. Dong, J. A. Vance* .... 6265 – 6277

Cyclic 1,2-Diketones as Core Building Blocks: A Strategy for the Total Synthesis of (−)-Terpestacin

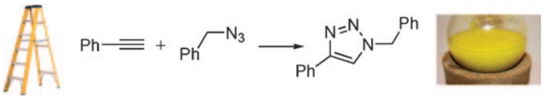


A diosphenol strategy: A unique strategy has been developed for the enantioselective total synthesis of (−)-terpestacin based on the unusual reactivity of diosphenols. By multiple usage of the diosphenol α-diketone functionality, twice in the "Pd AAA-Claisen" protocol (AAA = asymmetric allylic alkylation) and once by the employment of its oxidized form, the ene-1,2-dione, stereoselective alkylation of cyclopentane-1,2-diketones could be achieved in a programmatically controlled fashion.

Alkyne–Azide Chemistry

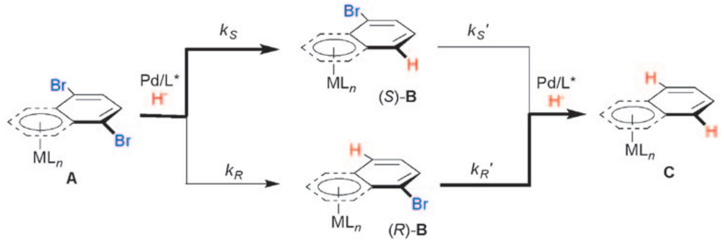
*B. R. Buckley, S. E. Dann, H. Heaney** .... 6278 – 6284

Experimental Evidence for the Involvement of Dinuclear Alkynylcopper(I) Complexes in Alkyne–Azide Chemistry



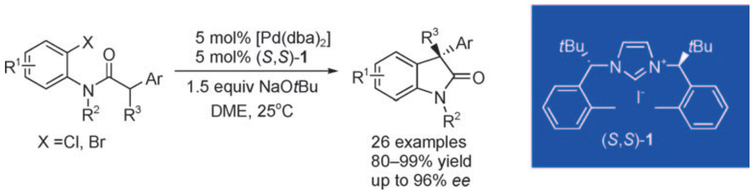
Synthesis and ladders! Dinuclear alkynylcopper(I) complexes are prepared by a robust and simple protocol and function as efficient catalysts in copper-catalysed alkyne–azide cycloaddition reactions (see scheme), as predicted by the Ahlquist–Fokin calculations. We also show that the same copper(I) derivatives are formed during reactions by using the Sharpless–Fokin protocol.

Asymmetric Catalysis



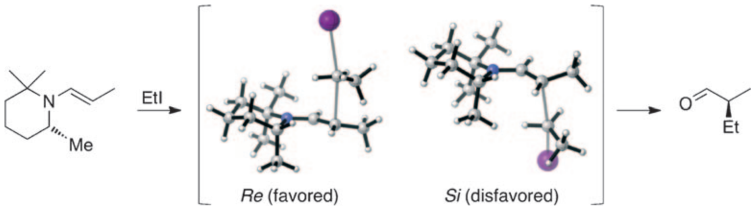
Planar chirality—catalytic desymmetrization: A Pd-catalyzed asymmetric hydrogenolysis reaction gives access to highly enantioenriched planar chiral fused arene chromium and ruthenium complexes. Key elements for the efficiency of the process are the use of a very bulky chiral phosphoramidite ligand, DABCO as a borane trapping reagent, as well as substantial kinetic resolution, which helps to enhance the stereochemical outcome of the reaction.

Asymmetric Catalysis



$A^{1,3}$-strain to the rescue: New Enders/Herrmann-type chiral N-heterocyclic carbene ligands were developed and applied in asymmetric palladium-catalyzed α-arylations of amides, producing 3-alkyl-3-aryloxindoles with high enantioselectivities (up to 96 %). The ligand aryl location and orientation is fixed by conformational locking that minimizes $A^{1,3}$-strain and enables optimal transfer of chiral information.

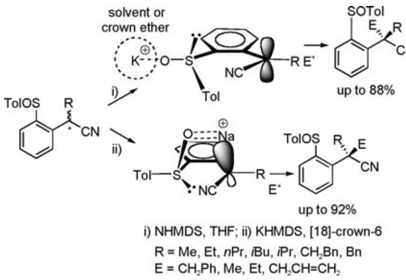
Asymmetric Induction



The origins of asymmetric induction in the intermolecular alkylation reaction of piperidine-based enamines (see scheme) were investigated and described by using density functional theory.

Quaternization

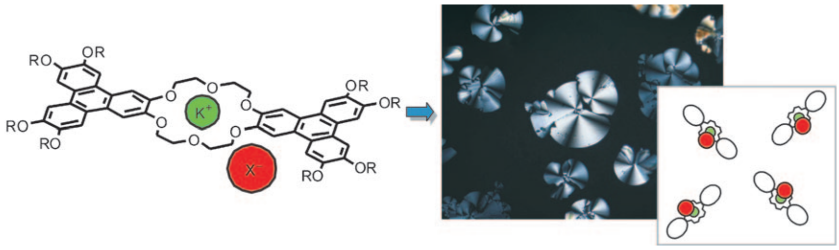
Remote stereocontrol: Enantiomerically enriched α,α-disubstituted phenylacetonitriles were prepared by stereoselective quaternization of 2-alkyl-2-[2-(*p*-tolylsulfinyl)phenyl]acetonitriles with different alkyl halides in the presence of bases (see scheme). The stereochemical course of the reactions has been rationalized and supported by NMR spectroscopic studies.



Columnar Mesophases

*M. Kaller, C. Deck, A. Meister, G. Hause, A. Baro, S. Laschat** .... 6326 – 6337

Counterion Effects on the Columnar Mesophases of Triphenylene-Substituted [18]Crown-6 Ethers: Is Flatter Better?

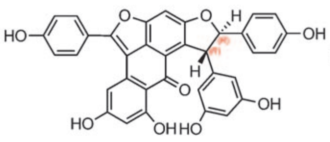


Is flatter better? Triphenylene-substituted dibenzo[18]crown-6 ethers and their complexes form Col_r mesophases with *c*2*mm*, *p*2*mg* or, in the case of X = SCN, *p*2*gg* symmetry in the unit cell (see graphic). With respect to mesophase stabilities, the counterion plays a decisive role rather than the flat and extended aromatic core.

Natural Products

*H. M. Ge, W. H. Yang, Y. Shen, N. Jiang, Z. K. Guo, Q. Luo, Q. Xu, J. Ma, R. X. Tan** .... 6338 – 6345

Immunosuppressive Resveratrol Aneuploids from *Hopea chinensis*



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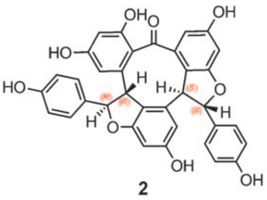

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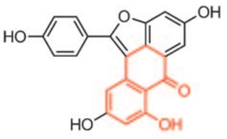


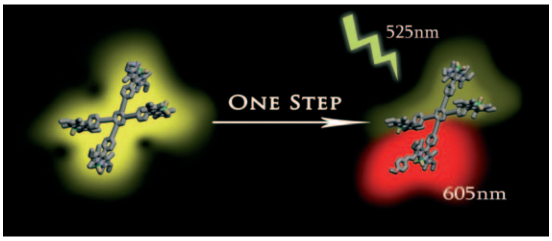
3

Two resveratrol aneuploids, hopeachinols A (**1**) and B (**2**), and a potent immunosuppressive polyphenol diptoindonesin G (**3**) were characterized from *Hopea chinensis*. The structures were elucidated by comprehensive spectroscopic analysis and computational quantum-chemical methods. The distinct structure and immunosuppressive profile of **3** recommended it as a good starting molecule for relevant drug discovery.

Dyes/Pigments

*O. A. Bozdemir, Y. Cakmak, F. Sozmen, T. Ozdemir, A. Siemiarczuk, E. U. Akkaya** .... 6346 – 6351

Synthesis of Symmetrical Multichromophoric Bodipy Dyes and Their Facile Transformation into Energy Transfer Cassettes

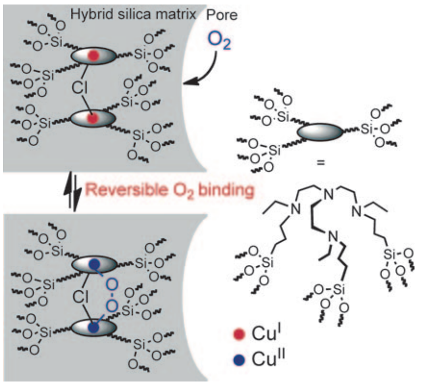


One step to energy-transfer cassettes: Symmetrical multichromophoric boron–dipyrromethene (Bodipy) dyes were converted into efficient energy-transfer cassettes in one step. The resulting cassettes have large extinction coefficient antenna modules and Stokes shifts.

Porous Materials

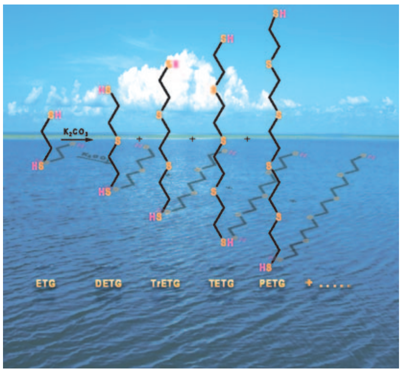
*C. Suspène, S. Brandès, R. Guilard** .... 6352 – 6364

Reversible Coordination of Dioxygen by Tripodal Tetraamine Copper Complexes Incorporated in a Porous Silica Framework



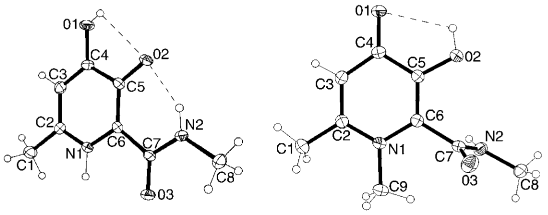
O_2 or not to O_2: A silylated tetraethoxysilated tripodal tetraamine (TREN)-based copper(II) complex has been incorporated in a microporous silica matrix under micellar conditions and by using a double templating method. After surfactant removal by acidic washings and re-metalation with copper(II), the material was shown to reversibly bind O_2 with high selectivity (see picture) versus N_2 and CO, thanks to the confinement of the copper complexes within the short-range lamellar framework.

Oligomerization



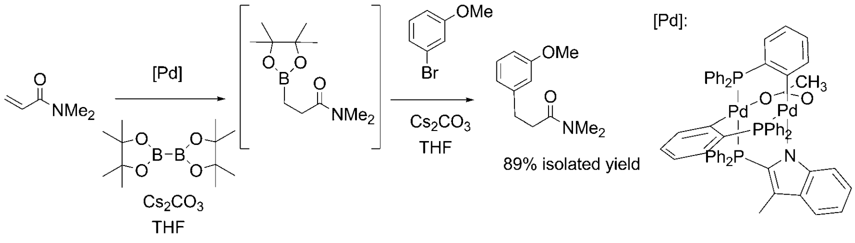
Any H(SCH$_2$CH$_2$)$_n$SH, anytime: A remarkable alkali carbonate induced self-condensation of ethylenedithioglycol (ETG) provides the oligomers: di- (DETG), tri- (TrETG), tetra- (TETG), pentathiaethylenethioglycol (PETG), and so on (see image) without hazardous byproducts. The most efficient carbonate was K$_2$CO$_3$, both in organic and in aqueous media.

Hydrogen-Bond Effects



Hydrogen-bond effects: Crystal structures of 1-unsubstituted and 1-methyl-substituted pyridinone (see figure) demonstrate that the amido group is almost perpendicular to the pyridine plane in the latter structure and planar for the former structure in which a strong hydrogen bond exists between the 2 and 3 positions. The presence of this hydrogen bond was found to dramatically influence the physicochemical properties of the molecule.

Tandem β-Boration/Arylation



Dual-action catalysts: Stable dimeric palladium complexes with diphenyl(3-methyl-2-indolyl)phosphine in a P,N-bridging coordination mode have been synthesised in high yield. These compounds showed high activity and selectivity in the catalytic β-boration of α,β-unsaturated esters, ketones, aldehydes and amides (see scheme).

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* Author to whom correspondence should be addressed

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