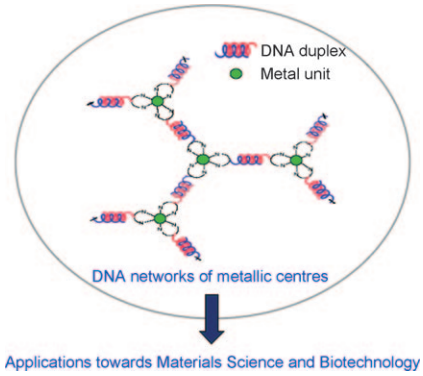
CONTENTS

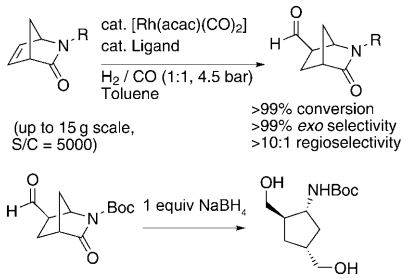
CONCEPTS

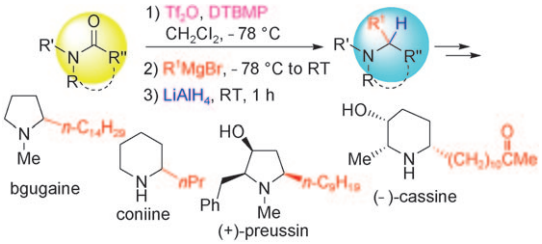
DNA goes nano! Ordered networks of metallic units based on DNA self-assembly (see figure) exhibit interesting functions and properties and are currently being developed for the fabrication of nanometer-scale devices.



COMMUNICATIONS

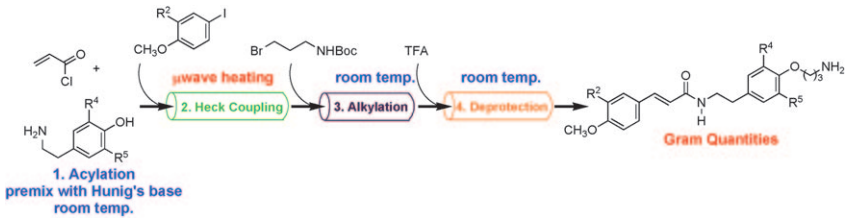
Customising a bicycle: Rh-catalysed asymmetric hydroformylation of a bicyclic lactam, 2-azabicyclo-[2.2.1]hept-5-en-3-one, was investigated. The use of a chiral diphosphite ligand, (*R*,*R*)-Kelliphite, enables excellent selectivity towards one regioisomer combined with excellent productivity and perfect *exo* selectivity. The products are versatile precursors to highly desired functionationalised cyclopentylamines (see scheme).





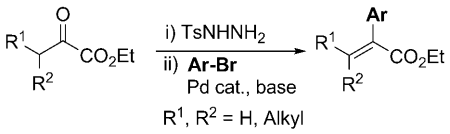
Direct entry: One-pot reductive alkylation of lactams/amides with Grignard reagents has been realized via lactam/amide activation with Tf_2O. This method opens a direct entry to α-alkylated amines. The versatility of the method is illustrated by the concise syntheses of bioactive alkaloids (±)-bgugaine, (±)-coniine, (+)-preussin, and (−)-cassine.

Synthetic Methods



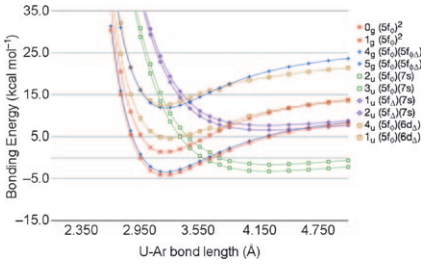
A flowing future! A multistep, general flow chemistry protocol has been developed for the preparation of tyramine-based natural products. The process integrates room-temperature reactions with high-temperature Heck coupling reactions, where the heat has been supplied by microwave irradiation. As a proof of concept for 'scaling out' to attain larger quantities of the desired products, the four primary tyramine-based natural products were prepared on a gram scale using this synthetic protocol.

Cross-Coupling Reactions



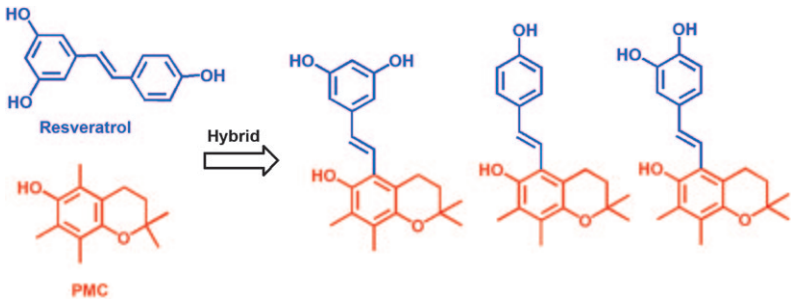
Important synthetic intermediates and direct precursors of the prophen class of anti-inflammatory agents, 2-arylacrylates are prepared in one step from ethyl pyruvate by employing the recently developed Pd-catalyzed cross-coupling between tosylhydrazones and aryl halides. Moreover, substituted 2-oxoesters afford tri- and tetrasubstituted functionalized alkenes.

Noble Gas Matrices



Ground state reversal from a neon to an argon matrix is confirmed by CASSCF/CASPT2 calculations (see picture) and new stepwise laser-ablated experiments.

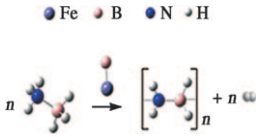
Radical Scavengers



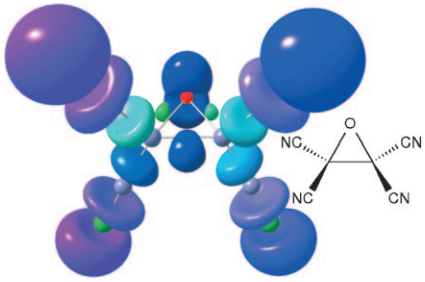
A winning combination: Resveratrol derivatives incorporating a chroman moiety of vitamin E were constructed, resulting in the remarkable enhancement in tris(2,4,6-trichloro-3,5-dinitrophenyl)methyl radical (HNTTM•)-scavenging activity as compared with the parent molecules (see scheme). Reaction kinetic analysis, oxidative product identification, and redox potential determination demonstrate that the reaction is governed by a sequential proton-loss electron-transfer (SPLET) mechanism.

CONTENTS

Nano-alloy: Crystalline polyaminoborane is formed upon releasing 1.0 equivalent H_2 from ammonia borane at 60 °C catalyzed by a nano-FeB alloy. Our experimental results show that about 1.0 and 1.5 equiv H_2 can be released at 60 and 100 °C, respectively.

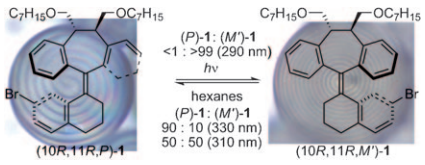


No longer hidden! An extension of the capabilities of the X-ray diffraction experiment is introduced. Locations of electron pairs within a molecule can be measured and made visible (see figure). This is demonstrated on a series of epoxides, for which ring strain, crystal, and substituent effects can be quantified. Comparison with experimental and theoretical electron-density analyses shows the advantages of the new method.

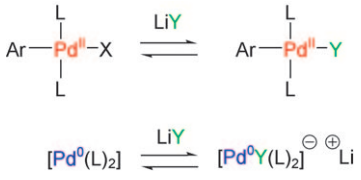


FULL PAPERS

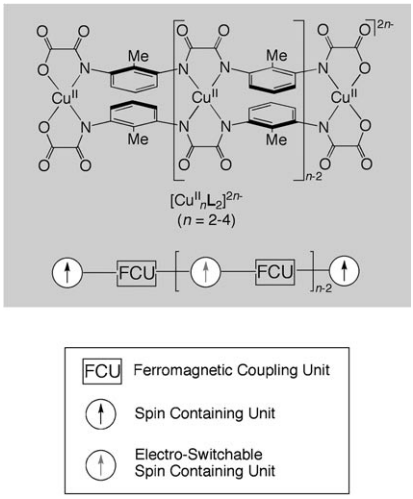
Doped for chirality: (10*R*,11*R*)-Dialkoxymethyldibenzosuberane-based helicenes **1** with 7-bromo-α-tetralin-type fragments were synthesized. Complete switching selectivity (*P*/*M*′, <1:>99) was observed in hexane upon irradiation at 290 nm. The reversed photoisomerization was also achieved with high selectivity (*P*/*M*′, 90:10) at 330 nm.



Halides—one stone, two birds! An unprecedented dual role of halide anions in the Stille reaction has been discovered. First halides can increase or decrease the turnover-limiting transmetallation rate through in situ halide metathesis (top equation). Second, halides stabilize the Pd^0 catalyst, preventing its decomposition, keeping the catalyst loading in the catalytic cycle high throughout the whole reaction (bottom equation).

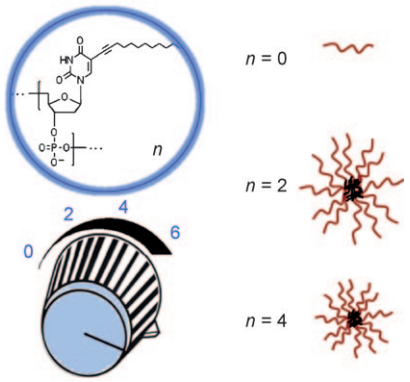


Molecular Wires



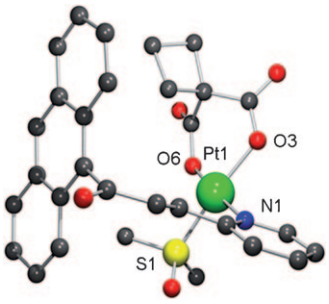
Down to the wire: The side-by-side self-assembly of a novel series of linear homo- and heterotopic oligo(2-methyl-1,3-phenyleneoxalamide) ligands by Cu^{II} ions leads to double-stranded di-, tri-, and tetranuclear copper(II) string complexes of *meso*-helicate type, which behave as effective electro-switchable metal–organic wires (see graphic).

Micellar Aggregates



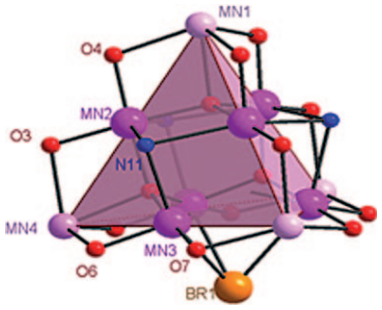
Tuning up the base: A strategy is proposed for tuning the size and stability of DNA-based micelle systems through precise incorporation of hydrophobic nucleobases. The effects of the positions and number of the modified nucleobases are investigated for a small family of such micelles (see picture).

Platinum Chemistry



Test the water! The cytostatic compounds *cis*-[Pt(A9pyp)(dmso)Cl_2] (**1**) and [Pt(A9pyp)(dmso)(cbdca)] (**2**) (A9pyp = (*E*)-[1-(9-anthryl)-3-(2-pyridyl)-2-propenone) as carrier ligand; cbdca = cyclobutane dicarboxylate) have been found to add water across the enone C=C bond of the ligand A9pyp. The water addition occurs in the presence of carbonate buffer, and has been followed in detail using NMR spectroscopy and ESI-MS.

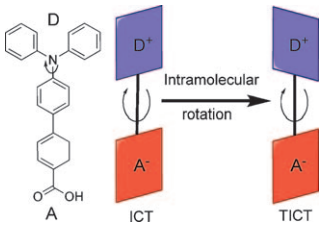
Cluster Compounds



Really cool clusters: Three structurally related mixed-valent polynuclear manganese complexes with supertetrahedral Mn_{10} building blocks (an example is shown here) were prepared and magnetothermal analyses were performed. All the complexes possess very high ground-spin states and very small anisotropy. The magnetically isotropic nature of the complexes prompted the study of their magnetothermal properties.

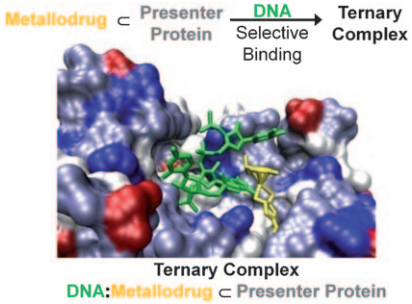
CONTENTS

To dye for: A series of organic dyes that feature a 1,3-cyclohexadiene conjugated moiety integrated into the π-conjugated framework has been synthesized and studied. Dye-sensitized solar cells based on these have shown appreciable conversion efficiency. Studies suggest the accessibility of the twisted internal charge-transfer state (TICT) in polar solvents (see figure).



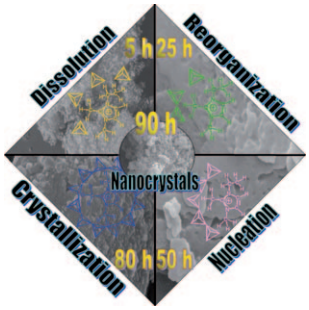
Energy Conversion

Match of the DNA: Chemo-genetic modifications of a ruthenium metallodrug-presenter protein assembly (varying the complex or mutating the presenter protein) modulates the binding to different DNA targets (see figure).

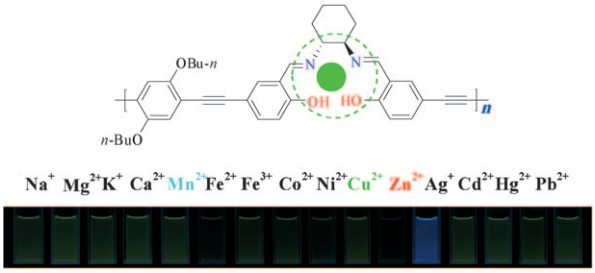


DNA Recognition

Growth control: Nucleation and growth processes of MnAlPO-5 nanosized crystals under ionothermal synthesis conditions are reported herein. Samples were examined at various stages of crystal growth of nanosized MnAlPO-5 under ionothermal conditions (see figure).



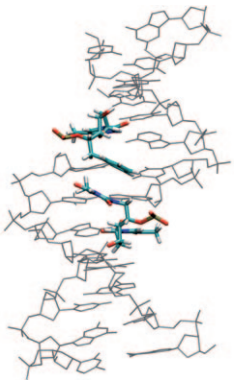
Ionic Liquids



Sensing sensibility: A chiral polymer incorporating an (*R,R*)-salen moiety was synthesized and exhibits an excellent fluorescence response toward Zn^{2+}. The fluorescent color of the polymer changed to bright blue instead of weak yellow after addition of Zn^{2+}, which could be easily detected by the naked eye (see picture).

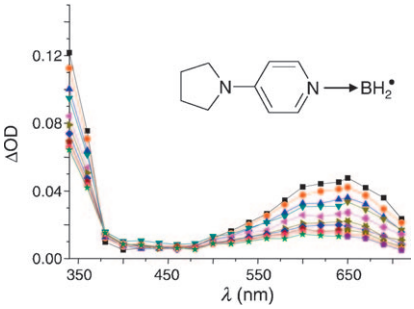
Sensors

Nucleic Acids



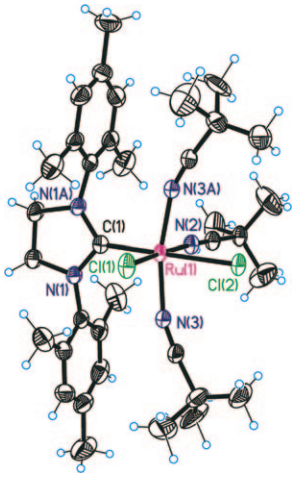
Communication in the minor groove: A series of aromatic moieties were inserted in the minor groove of DNA through 5′-(*S*)-*C*-substituted nucleosides. A strong and specific interaction was found between a thymine and a phenyl group in a crossed (−3)-zipper motif. Modelling revealed that the interaction is due to aromatic stacking across the minor groove (see figure).

Boranes



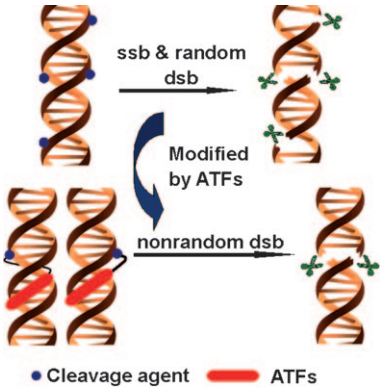
Radical thoughts: New N-heteroaryl boranes that exhibit low B–H bond-dissociation energy (BDE) are presented; excellent hydrogen-transfer properties have been found. Both the generation and the reactivity of the associated boryl radicals have been investigated through the direct detection of the different boryl radicals by laser flash photolysis (see graph).

Ring-Opening Polymerization



ROMPing around: A series of cationic and neutral Ru^{II} complexes based on N-heterocyclic carbenes have been synthesized and investigated for use as latent initiators for the photoinitiated ROMP by using different norborn-2-ene- and *cis*-cyclooctene-based monomers.

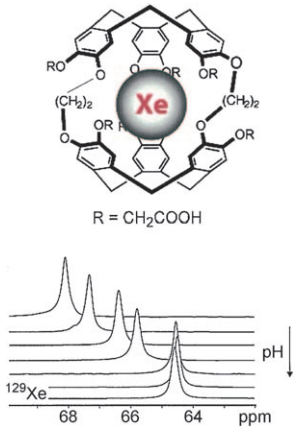
DNA Cleavage



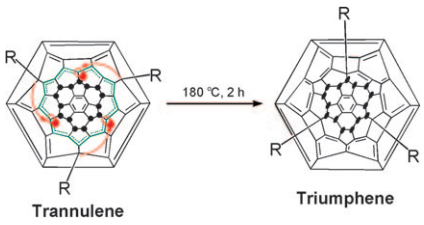
A new family of artificial transcription factor-based conjugates is designed and evaluated as effective double-strand DNA cleavage agents. When modified by polyamide, some non-selective and random cleavage agents were restricted within narrow limits when they interacted with double-strand DNA. These results are not only applicable to hydrolytic cleavage, but also to oxidative cleavage.

CONTENTS

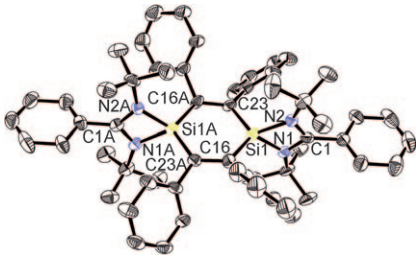
(Xe)eing is believing! The interaction of hyperpolarized xenon with two water-soluble cryptophanes reveals interesting sensing properties. The presence of ionic substituents on the aromatic rings of the cage molecules renders the chemical shift of encapsulated xenon dependent on pH (see figure). When the ionic groups are, however, closer to the cavity portals, the nature of the counterion influences both the thermodynamics and the kinetics of the xenon binding.



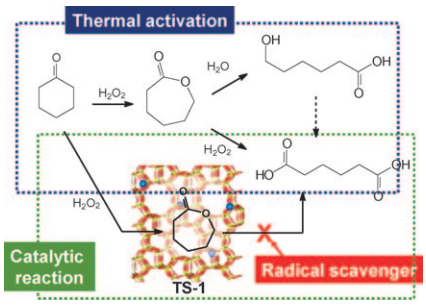
Colorful dance: A new class of compounds named "triumphenes" has been generated from trannulenes through an unprecedented migration of three organic addends (see figure).



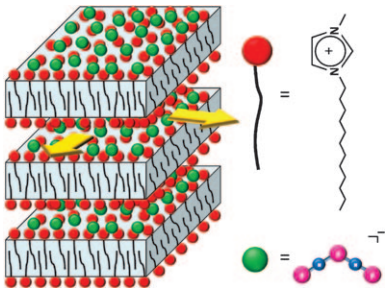
The new radicals: A novel amidinate-stabilized singlet delocalized biradicaloid [LSi(μ_2-C_2Ph_2)$_2$SiL] (L = PhC(N*t*Bu)$_2$) has been synthesized successfully by the reaction of [{PhC(N*t*Bu)$_2$}Si]$_2$ with diphenylacetylene. X-ray crystallography and DFT calculations show that the diradicals are stabilized by the amidinate ligand and the delocalization within the Si(μ_2-C_2Ph_2)$_2$Si six-membered ring (see figure).



Oxidation control: In the oxidation of cyclohexanone with hydrogen peroxide under conditions aimed at obtaining ε-caprolactone, a thermally activated radical reaction leads to the concurrent formation of adipic acid (see figure). The relevant reaction rates are modified when Ti-silicalite is used as catalyst. The proper choice of solvent, which may also act as a radical scavenger, also allows control over the reaction rates.

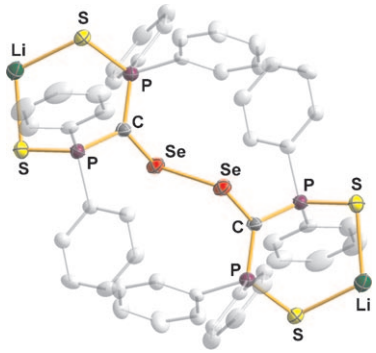


Ionic Liquid Crystals



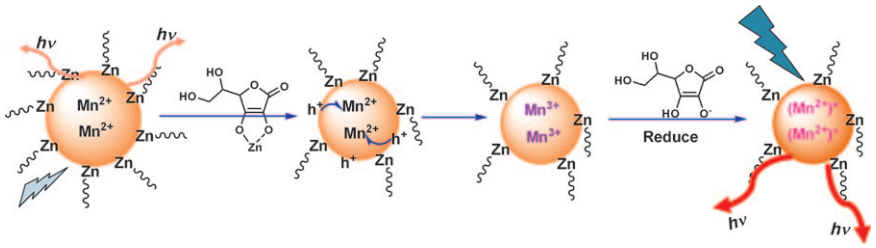
Ion-conductive layer: The $(FH)_2F^-$ salts combined with 1-alkyl-3-methylimidazolium cations with long alkyl chains show smectic A_2 liquid crystalline mesophases. Highly anisotropic conductivity was observed in the smectic layer structure (see graphic).

Chalcogen Dimers



Versatility in chalcogenides: Tetradentate dimeric dianions $[(SPh_2P)_2CEEC(PPh_2S)_2]^{2-}$ (E = S, Se) with long, central chalcogen–chalcogen bonds (see figure) are formed by one-electron oxidation of the tridentate monomers $[(E)C(PPh_2S)_2]^{2-}$. Two-electron oxidation of $[SeC(PPh_2S)_2]^{2-}$ produces the neutral selone $[(Se)C(PPh_2S)_2]$ as a LiI adduct.

Sensors



Vitamin see: The chelating ability of ascorbic acid (AA) enables the extraction of Mn and Zn from the surface of tripolyphosphate-capped Mn-doped ZnS quantum dots (QDs) generating more holes that are subsequently trapped by Mn^{2+}. The reducing property of AA results in the reduction of Mn^{3+} to Mn^{2+} in an excited state, thus enhancing the excitation and orange emission of the QDs (see scheme). Such AA-induced phosphorescence enhancement enables selective detection of AA with a detection limit of 9 nM.

* Author to whom correspondence should be addressed

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