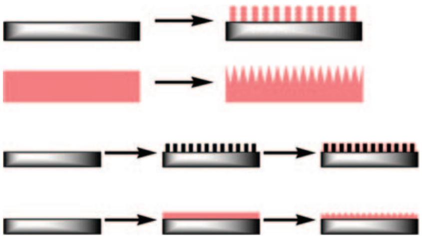
REVIEWS

Hydrophobic Effect

*C. R. Crick, I. P. Parkin** . . . 3568 – 3588

Preparation and Characterisation of Super-Hydrophobic Surfaces

Simply super! The interest in highly water-repellent surfaces has grown in recent years due to the desire for self-cleaning surfaces. This review identifies four methods for the construction of super-hydrophobic surfaces (see figure) along with a summation of the key properties of the surface that result in hydrophobicity. A summary of the different routes to super-hydrophobicity is also given.



COMMUNICATIONS

Alkylation

S. Bähn, S. Imm, K. Mevius, L. Neubert, A. Tillack, J. M. J. Williams, M. Beller** . . . . 3590 – 3593

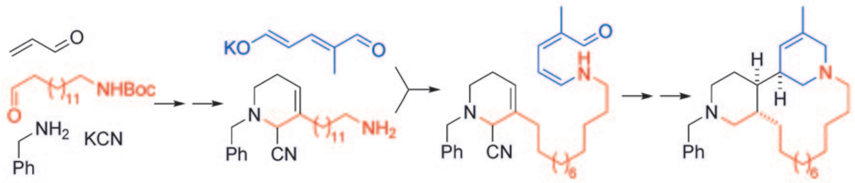
Selective Ruthenium-Catalyzed N-Alkylation of Indoles by Using Alcohols

Alcohols for alkylation! The first homogeneous-catalyzed N-alkylations of indoles with aliphatic alcohols proceed under transfer hydrogenation conditions. By the use of the Shvo catalyst and *p*-toluenesulfonic acid (PTSA) this atom-efficient reaction occurs highly selectively with water formed as the only byproduct (see scheme).

Biomimetic Synthesis

I. Sinigaglia, T. M. Nguyen, J.-C. Wypych, B. Delpech, C. Marazano* . . . . 3594 – 3597

Concise Access to a Model of the Marine Alkaloid Halicyclamine A through Macrocycle-Forming Addition of a 5-Aminopenta-2,4-dienal onto a 2,3-Dihydropyridinium Salt



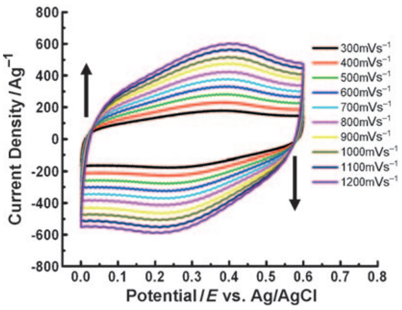
A biomimetic synthesis of a model compound for the marine alkaloid halicyclamine A is reported that involves a macrocyclization through the intramolecular addition of a 5-aminopenta-2,4-dienal onto a 2,3-dihydropyridinium salt generated in situ (see scheme). In this way, a monomacrocyclic model, with the same relative stereochemistry as that of the natural product, was obtained.

Template-Assisted Synthesis

Y. Wang, C. Y. Foo, T. K. Hoo, M. Ng, J. Lin** . . . . 3598 – 3603

Designed Smart System of the Sandwiched and Concentric Architecture of $RuO_2/C/RuO_2$ for High Performance in Electrochemical Energy Storage

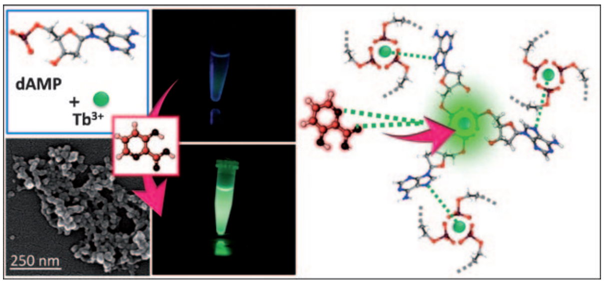
Energy storage: A sandwiched and concentric architecture of RuO_2/C/RuO_2 has been successfully synthesized through a template-assisted approach. This architecture exhibits novelty and innovation in the designed synthesis of hierarchical and functional systems and performed well in electrochemical testing, especially presenting excellent specific capacitance over very high scan rates (see figure).



Nanoparticles

*C. Aimé, R. Nishiyabu, R. Gondo, N. Kimizuka** 3604–3607

Switching On Luminescence in Nucleotide/Lanthanide Coordination Nanoparticles via Synergistic Interactions with a Cofactor Ligand

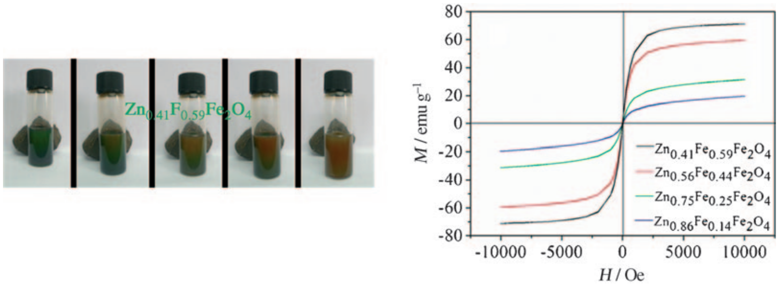


Coordination nanoparticles: Hydroxypicolinic acid (**1**) is easily incorporated into coordination nanoparticles (CNPs) self-assembled from nucleotides and terbium ions without impairing nanoparticle morphology. Compound **1** acts as a cofactor ligand that coordinates to Tb^{3+} ions that exist in the coordination networks, and this switches on the luminescence of CNPs (see graphic).

Superparamagnetism

W. Cheng, K. Tang, J. Sheng* 3608–3612

Highly Water-Soluble Superparamagnetic Ferrite Colloidal Spheres with Tunable Composition and Size

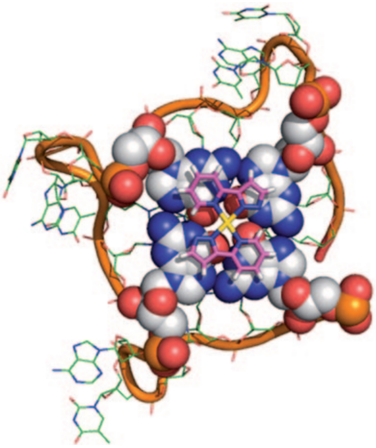


From green to red: Highly water-soluble superparamagnetic monodisperse ferrite colloidal spheres with tunable size and composition have been prepared by a simple one-step hydrothermal method. The zinc ferrite colloidal spheres show composition-dependent saturation magnetization. Surprisingly, the $Z_{0.41}Fe_{0.59}Fe_2O_4$ colloidal sphere aqueous suspension can be used for constructing photonic crystals (see figure).

Bioinorganic Chemistry

K. Suntharalingam, D. Gupta, P. J. Sanz Miguel, B. Lippert, R. Vilar** 3613–3616

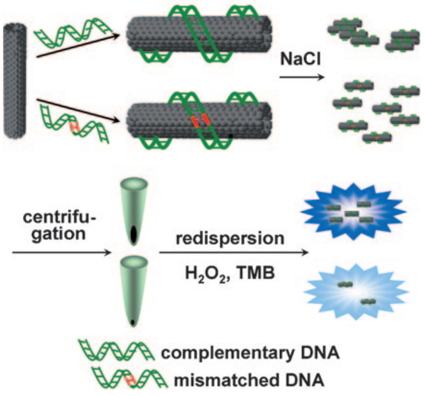
Synthesis, Structural Characterisation and Quadruplex DNA Binding Studies of a New Gold(III) Pyrazolylpyridine Complex



A golden quadruplex DNA: A new gold(III) pyrazolylpyridine complex has been synthesised and structurally characterised. The complex displays π–π interactions in the solid state. The DNA binding properties of the complex have been studied by fluorescent intercalator displacement assay, surface plasmon resonance and circular dichroism. These have shown that the complex interacts strongly with quadruplex DNA, in particular with *c-myc*. CD spectroscopy has also shown the ability of the complex to template the formation of a quadruplex structure from a singly stranded sequence of telomeric DNA (see picture for a qualitative docking of the complex on top of a quadruplex DNA structure).

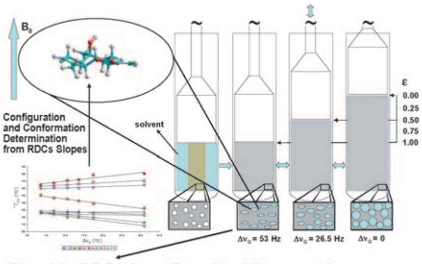
Single-Walled Nanotubes

SWNTs possess intrinsic peroxidase-like activity, catalyzing the reaction of peroxidase substrate 3,3,5,5-tetramethylbenzidene (TMB) in the presence of H_2O_2 to produce a color reaction. Here SWNTs have been used for label-free colorimetric detection of disease-associated single-nucleotide polymorphism with a direct detection limit of 1 nM.



NMR Spectroscopy

Tuneable RDCs: A fast and tunable method for measuring anisotropic NMR parameters using variable compression/relaxation of clean and reusable PMMA gels in $CDCl_3$ is introduced (see picture). No special devices are needed. The configuration and conformation of small molecules can be determined by using the RDC slopes without the need for performing a control experiment in isotropic conditions.

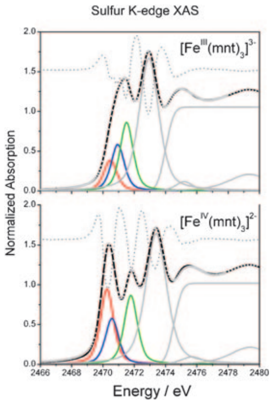


Tunable RDCs from Tunable Alignment by Variable Compression / Relaxation of a PMMA Gel

FULL PAPERS

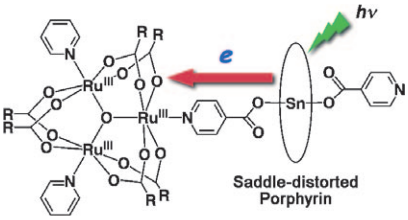
S Ligands

High-valent iron: The electronic structures of $[Fe^{III}(Et_2dtc)_{3-n}(mnt)_n]^{n-}$ (mnt = maleonitriledithiolate and Et_2dtc = diethyldithiocarbamato; $n = 3, 2, 1, 0$) and their one-electron oxidized analogues have been elucidated and correlated with the structural and spectroscopic parameters of the complexes (see figure). Despite the presence of noninnocent dithiolene ligands, the oxidized complexes are best described as genuine Fe^{IV} complexes.



Donor–Accepor Systems

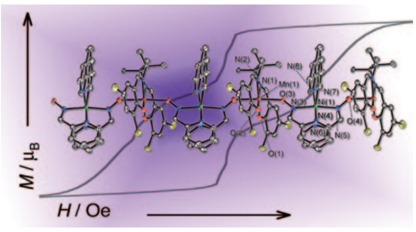
Saddle up! Saddle-distorted Sn^{IV} porphyrin complexes form stable conglomerates with trinuclear Ru clusters with use of pyridine carboxylates as linkers (see figure). These novel dyads exhibit efficient photoinduced electron transfer, in which Sn porphyrin moieties act as electron donors and Ru clusters act as electron acceptors.



Molecule-Based Magnets

H. Miyasaka, K. Takayama,*
A. Saitoh, S. Furukawa, M. Yamashita,
*R. Clérac** .... 3656 – 3662

Three-Dimensional Antiferromagnetic Order of Single-Chain Magnets: A New Approach to Design Molecule-Based Magnets

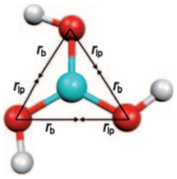


Chain gang: By controlling both intra- and interchain magnetic interactions in a new [$Mn^{III}Ni^{II}$] single-chain magnet (SCM) system, an antiferromagnetic (AF) ordered phase has been stabilized below 9.4 K. In this remarkable AF phase, a magnet-type behavior is observed experimentally in direct relation with the intrinsic SCM properties of the isolated chains composing the material.

Anomeric Effect

R. J. Gillespie, E. A. Robinson,*
J. Pilmé .... 3663 – 3675

Ligand Close Packing, Molecular Compactness, the Methyl Tilt, Molecular Conformations, and a New Model for the Anomeric Effect

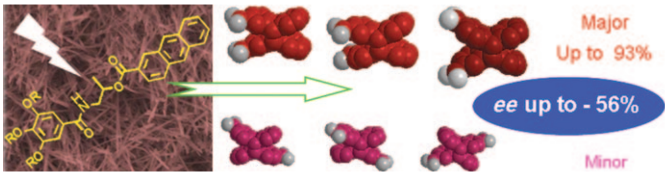


A new concept: We introduced the concept of compactness (see figure), which states that the equilibrium structure of a molecule is the most compact one. The concept was used to find the lowest energy conformation for molecules with two or more low-energy conformations, including molecules that exhibit the anomeric effect, thus providing a new explanation of this effect. We also used the concept to explain the "methyl tilt".

Supramolecular Chemistry

A. Dawn, T. Shiraki, S. Haraguchi,
H. Sato, K. Sada,
*S. Shinkai** .... 3676 – 3689

Transcription of Chirality in the Organogel Systems Dictates the Enantiodifferentiating Photodimerization of Substituted Anthracene

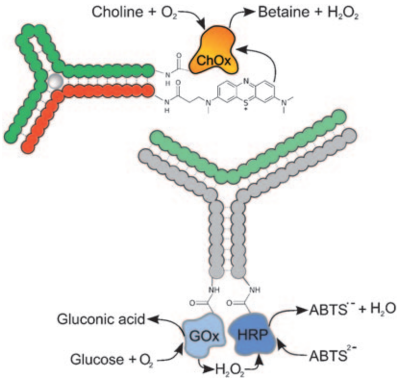


It takes a soft touch: Photodimerization of an anthracene that bears a chiral organogelator in the gel state produces photodimers with high regio- and enantioselectivities (see figure). The degrees of selectivities are different in strong, moderately strong, and weak gels, depending upon microenvironments that are controlled by the nature of the solvent and the gelation temperature.

Template Synthesis

R. Freeman, E. Sharon, C. Teller,
*I. Willner** .... 3690 – 3698

Control of Biocatalytic Transformations by Programmed DNA Assemblies



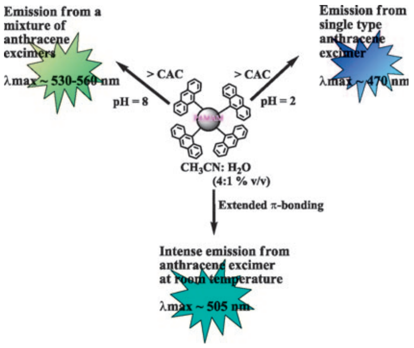
Controlled inhibition: Supramolecular complexes of aptamer subunits or Y-shaped nucleic acid structures act as templates for the programmed inhibition of enzymes or the activation of enzyme cascades (see picture). The modification of aptamer subunits causes the inhibition of the catalytic activity of choline oxidase (ChOx) by methylene blue. In another approach, the channeling of H_2O_2 from glucose oxidase (GOx) to horseradish peroxidase (HRP) was used to generate a reporter system. $ABTS^{2-}$ = azino[bis(3-ethylbenzthiazoline-6-sulfonic acid)].

Dendrimers

*P. K. Lekha, E. Prasad** .... 3699 – 3706

Aggregation-Controlled Excimer Emission from Anthracene-Containing Polyamidoamine Dendrimers

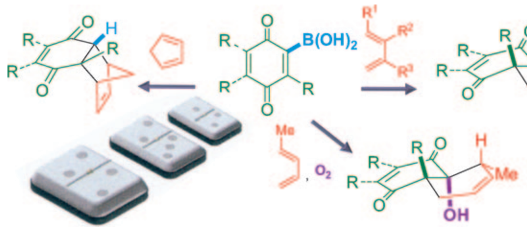
Tunable excimer emission from anthracene-modified polyamidoamine (PAMAM) dendrimers was achieved by controlling their aggregation propensity in an acetonitrile–water mixture. Since the aggregates are prearranged in the ground state, they readily form excimers on photoexcitation. Different types of anthracene excimers can be generated by altering the excitation wavelength and pH of the medium (see schematic; CAC = critical aggregation concentration).



Domino Reactions

*M. Veguillas, M. C. Redondo, I. García, M. Ribagorda,**
*M. Carmen Carreño** .... 3707 – 3719

Synthesis of Benzo- and Naphthoquinonyl Boronic Acids: Exploring the Diels–Alder Reactivity



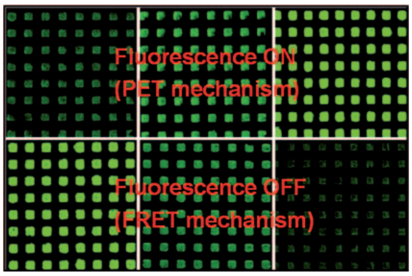
Highly reactive quinone dienophiles: The electron-withdrawing character of the boronic acid and its hydrogen bonding with the quinone carbonyl group are the key factors that induce high reactivity. The evolution of the Diels–Alder adducts through dehydroboration, protodeboronation or in situ oxidation provides a direct access to some otherwise elusive quinone adducts (see scheme).

Sensors

*J. L. Geng, P. Liu, B. H. Liu, G. J. Guan, Z. P. Zhang,**
*M.-Y. Han** .... 3720 – 3727

A Reversible Dual-Response Fluorescence Switch for the Detection of Multiple Analytes

On or off? It's a result both ways: A reversible dual fluorescence switch was fabricated, by the modification of the surface of silica nanoparticles with a nitrobenzoxadiazole fluorophore and an organic amine, for the detection of the herbicide 2,4-dichlorophenoxyacetic acid and 2,4,6-trinitrotoluene with opposite-response results (see images; PET: photoinduced electron transfer; FRET: fluorescence resonance energy transfer).

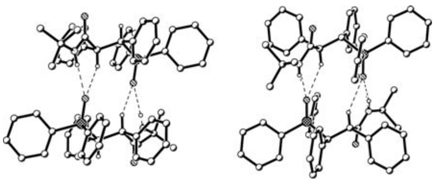


Solid-State Structures

M. Alajarín, C. López-Leonardo, Á. Álvarez-García, P. Llamas-Lorente, P. Sánchez-Andrada, J. Berná,* A. Pastor, D. Bautista,*
P. G. Jones .... 3728 – 3735

Synthesis and Molecular Structure of β-Phosphinoyl Carboxamides: An Unexpected Case of Chiral Discrimination of Hydrogen-Bonded Dimers in the Solid State

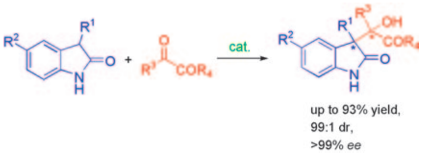
Only heterodimerisation! Diastereoisomeric β-phosphinoyl propionamides were obtained by the addition of aminophosphanes to diphenylcyclopropenone. An efficient method for the diastereoisomer interconversion has also been implemented. These compounds associate in the solid state, exclusively forming heterodimers of enantiomeric units linked by two bifurcated hydrogen bonds. The oxygen atom of the phosphoryl group of a molecule acts as a dual acceptor of the NH and CH of a neighbouring molecule (see figure).



Asymmetric Catalysis

*K. Shen, X. Liu, K. Zheng, W. Li, X. Hu, L. Lin, X. Feng** .... 3736 – 3742

Catalytic Asymmetric Synthesis of 3-(α-Hydroxy-β-carbonyl) Oxindoles by a Sc^{III}-Catalyzed Direct Aldol-Type Reaction

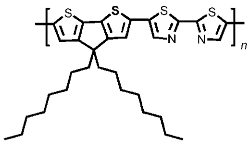


Easy access: The direct catalytic asymmetric aldol-type reaction of 3-substituted-2-oxindoles with glyoxal derivatives and ethyl trifluoropyruvate was successfully established through Sc^{III}-based enolate activation. 3-(α-Hydroxy-β-carbonyl) oxindoles with vicinal quaternary–tertiary or quaternary–quaternary stereocenters were delivered in up to 93 % yield, 99:1 diastereomeric ratio (dr), and >99 % enantiomeric excess (*ee*) under mild conditions (see scheme).

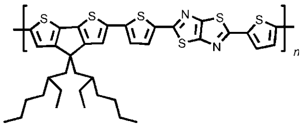
Polymers

I. H. Jung, J. Yu, E. Jeong, J. Kim, S. Kwon, H. Kong, K. Lee, H. Y. Woo, H.-K. Shim** .... 3743 – 3752

Synthesis and Photovoltaic Properties of Cyclopentadithiophene-Based Low-Bandgap Copolymers That Contain Electron-Withdrawing Thiazole Derivatives



PocCDT-BT



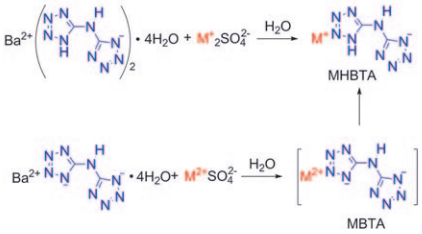
PehCDT-TZ

Mind the bandgap: Four types of cyclopentadithiophene (CDT)-based low-bandgap copolymers with two thiazole derivatives based on thiazolothiazole (TZ) and bithiazole (BT) structures have been synthesized (see picture for examples). The internal charge-transfer interaction between the electron-sufficient CDT unit and electron-deficient TZ or BT units in the polymeric backbone induces a low bandgap.

Energetic Materials

*Y. Guo, G.-H. Tao, Z. Zeng, H. Gao, D. A. Parrish, J. M. Shreeve** .... 3753 – 3762

Energetic Salts Based on Monoanions of *N,N*-Bis(1*H*-tetrazol-5-yl)amine and 5,5′-Bis(tetrazole)

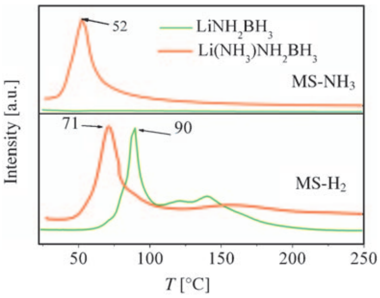


An explosive discovery: Salts based on the 5-(tetrazol-5-ylamino)tetrazolate (HBTA) anion were fully characterized (see scheme), including solid-state ^{13}C NMR spectroscopy. Predicted detonation pressures and detonation velocities are 19.4–33.6 GPa and 7677–9487 m s^{-1}.

Hydrogen Storage

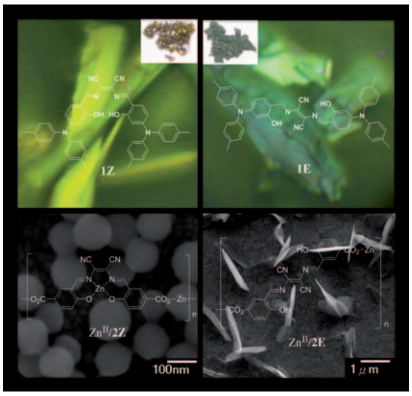
G. Xia, X. Yu, Y. Guo, Z. Wu, C. Yang, H. Liu, S. Dou* .... 3763 – 3769

Amminelithium Amidoborane Li(NH$_3$)NH$_2$BH$_3$: A New Coordination Compound with Favorable Dehydrogenation Characteristics



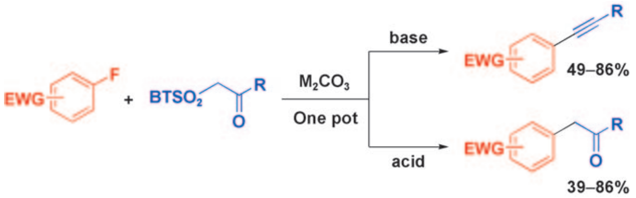
Hydrogen storage system: Lithium amidoborane, LiNH$_2$BH$_3$, has been shown to absorb/desorb ammonia at room temperature in a reversible manner. The product amminelithium amidoborane, Li(NH$_3$)NH$_2$BH$_3$, started to release hydrogen at about 40 °C and reached its peak at 71 °C, a much lower temperature than in the case of the pure LiNH$_2$BH$_3$.

Salen Ligands



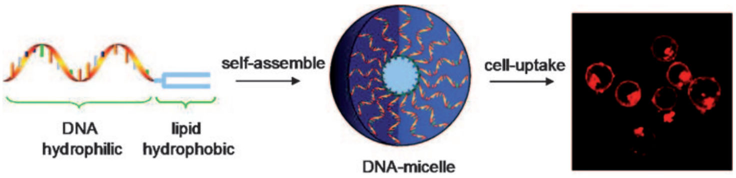
The absence or presence of light determines whether the synthesis of salen ligand **1** affords the *Z* or *E* isomer (**1Z** or **1E**, respectively; see upper images in the picture), which have distinctly different photophysical properties. Photoinduced **1Z**→**1E** isomerization takes place due to a charge-transfer reaction. Compound **2**, a strategically designed analogue of **1** bearing carboxyl groups, was also prepared, and its isomers **2Z** and **2E** exhibited remarkable differences in the morphology (nanostructure) of their infinite coordination polymers with Zn^{II} (lower images).

C–C Coupling



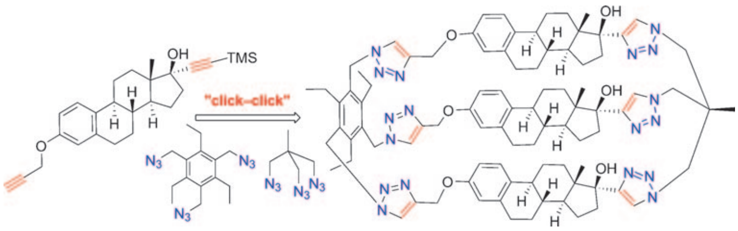
Metal-free coupling: Transition-metal-free formal Sonogashira coupling and α-carbonyl arylation reactions have been developed (see scheme; EWG = electron-withdrawing group, BT = benzothiazol-2-yl). Both transformations proceed through a key intermediate, which is generated by nucleophilic aromatic substitution (S_NAr) of β-carbonyl sulfones to electron-deficient aryl fluorides.

Micelles



Amphiphilic DNA spontaneously self-assembles into monodispersed micelle structures with a lipid core and a DNA corona in water. Experimental testing showed that these micelles have excellent thermal stability and cell membrane permeability (see scheme).

Natural Product Hybrids

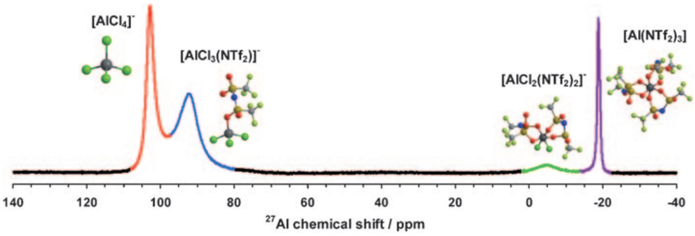


Natural product hybrid structures: Monoaddition of bis(alkynyl) dilithium reagents to various natural products bearing a carbonyl group has been used to obtain the scaffolds needed to access diverse natural product hybrids. Oligomeric steroid-, terpene-, and alkaloid-based derivatives incorporating diverse spacers to join these natural product scaffolds have been readily prepared from different alkynyl substrates in high-yielding Cu-mediated single-step reactions (see scheme).

Ionic Liquids

T. Rodopoulos, L. Smith,*
M. D. Horne, T. Rüther 3815–3826

Speciation of Aluminium in Mixtures of the Ionic Liquids [C_3mpip][NTf_2] and [C_4mpyr][NTf_2] with $AlCl_3$: An Electrochemical and NMR Spectroscopy Study

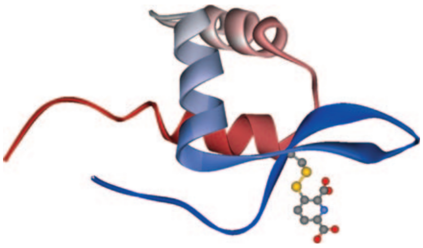


Who's responsible? Aluminium speciation in two bis(trifluoromethylsulfonyl)amide (NTf_2)-based ionic liquids (ILs) containing $AlCl_3$ was investigated by electrochemistry and NMR spectroscopy. Numerous Al-containing species were detected in solution (see figure), but [$AlCl_3(NTf_2)$]$^-$ is believed to be the one responsible for Al electrodeposition in both ILs.

NMR Spectroscopy

B. Man, X.-C. Su, H. Liang,
S. Simonsen, T. Huber, B. A. Messerle,
*G. Otting** 3827–3832

3-Mercapto-2,6-Pyridinedicarboxylic Acid: A Small Lanthanide-Binding Tag for Protein Studies by NMR Spectroscopy

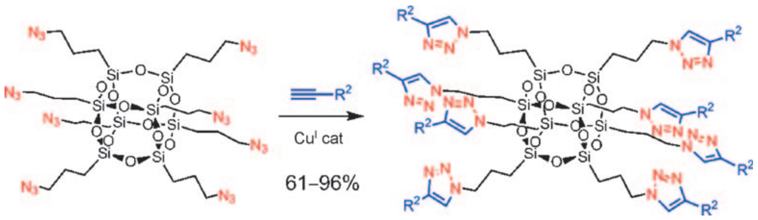


Small is beautiful: 3-Mercapto-2,6-pyridinedicarboxylic acid (3MDPA) is a novel tag for site-specific attachment of lanthanides and Co^{2+} to proteins, (see figure). It is the smallest lanthanide-binding tag yet reported and produces very different pseudocontact shifts than the previously published 4MMDPA tag. Its small size and rigidity make the 3MDPA tag a powerful tool for structural investigations of proteins by NMR spectroscopy.

Polyhedral Oligosilsesquioxanes

B. Trastoy, M. E. Pérez-Ojeda,
*R. Sastre, J. L. Chiara** 3833–3841

Octakis(3-azidopropyl)octasilsesquioxane: A Versatile Nanobuilding Block for the Efficient Preparation of Highly Functionalized Cube-Octameric Polyhedral Oligosilsesquioxane Frameworks Through Click Assembly

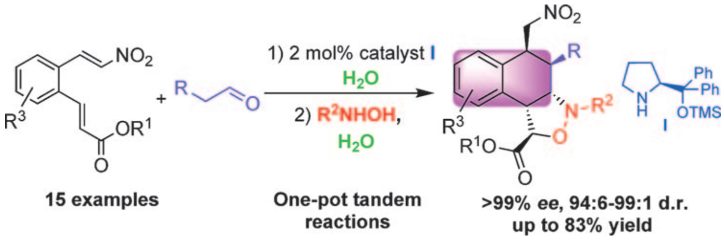


Clickety click! A one-step synthesis of an octaazidesilsesquioxane with perfect 3D cubic symmetry has been realized from a commercially available silsesquioxane by using an efficient diazotransfer reaction under very mild conditions (see scheme). This compound is an excellent nanobuilding block that can be readily octafunctionalized with a range of terminal alkynes by copper(I)-catalyzed 1,3-dipolar azide–alkyne cycloaddition to provide new functional nanocages, maintaining a perfect 3D cubic symmetry.

Asymmetric Synthesis

*B. Tan, D. Zhu, L. Zhang, P. J. Chua, X. Zeng, G. Zhong** .... 3842 – 3848

Water—More Than Just a Green Solvent: A Stereoselective One-Pot Access to All-Chiral Tetrahydronaphthalenes in Aqueous Media



A key role for water: A facile and highly stereoselective means of constructing heavily functionalized chiral tetrahydronaphthalene skeletons fused with an oxazolidine moiety has been developed. The strategy is based on an organocatalytic tandem Michael/nitrone formation/intramolecular [3+2] nitrone–olefin cycloaddition in aqueous media using rationally designed substrates. The water used as the reaction medium not only represents an environmentally benign solvent, but also helps to improve the reactivity and stereoselectivity.

Green Catalysis

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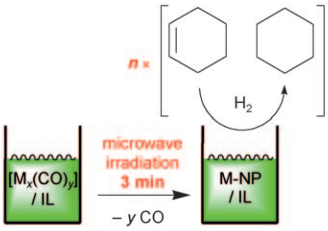
Microwave Irradiation for the Facile Synthesis of Transition-Metal Nanoparticles (NPs) in Ionic Liquids (ILs) from Metal–Carbonyl Precursors and Ru-, Rh-, and Ir-NP/IL Dispersions as Biphasic Liquid–Liquid Hydrogenation Nanocatalysts for Cyclohexene

Recycle and reuse: Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, and Ir metal nanoparticles (M-NPs) have been obtained by microwave, thermal, or photolytic decomposition from [$M_x(CO)_y$] in the ionic liquid (IL) 1-butyl-3-methylimidazolium tetrafluoroborate. Ru-, Rh-, and Ir-NP/IL dispersions function as highly active and easily recyclable hydrogenation catalysts (see graphic).



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