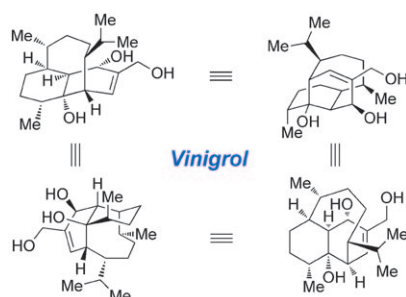


Vinigrol, a diterpene natural product, has been a fascinating target for total synthesis for over two decades. Recent synthetic studies that have ultimately allowed access to the coveted vinigrol scaffold, including the approaches reported by Barriault, Njardarson, and Hanna, as well as the first total synthesis of vinigrol, reported by Baran in 2009, are described.

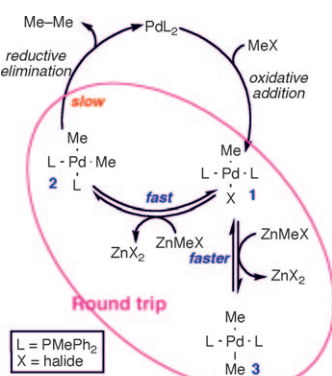


Total Synthesis

*A. D. Hutters, N. K. Garg** . . . 8586–8595
Synthetic Studies Inspired by Vinigrol

COMMUNICATIONS

Gets there in the end: The large rate difference of the slow reductive elimination and the fast transmetalation–retrotransmetalation steps allows Pd to visit complexes **3**, **2**, and **1** many times before coupling from **2** takes place. This fast recurrence of transformations offers many opportunities for the formation of undesired homocoupling products in Negishi reactions by statistically accessible “mistaken” retrotransmetalation events in the multitude of processes preceding the slower irreversible reductive elimination of the coupling product.

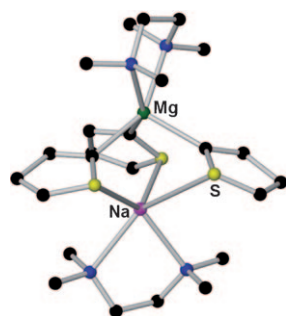


Reaction Mechanisms

B. Fuentes, M. García-Melchor, A. Lledós, F. Maseras, J. A. Casares, G. Ujaque,* P. Espinet** 8596–8599

Palladium Round Trip in the Negishi Coupling of *trans*-[PdMeCl(PMePh₂)₂] with ZnMeCl: An Experimental and DFT Study of the Transmetalation Step

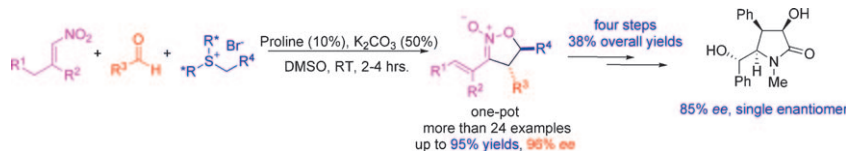
Metalation of sulfur heterocycles: Alkali-metal-mediated magnesiation has been employed to regioselectively metallate the S-heterocycles thiophene and tetrahydrothiophene at ambient temperature. The structural chemistry of the metallo-compounds is remarkably different from that previously observed for the corresponding O-heterocycles (see figure).



Heterocycles

*V. L. Blair, A. R. Kennedy, R. E. Mulvey, C. T. O'Hara** 8600–8604

Sodium-Mediated Magnesiation of Thiophene and Tetrahydrothiophene: Structural Contrasts with Furan and Tetrahydrofuran



Transforming isoxazoline-*N*-oxides: A concise asymmetric synthesis of isoxazoline-*N*-oxides is reported through secondary amine Lewis base catalyzed nitroalkene activation and sequential intermolecular condensation with aldehydes and ylides. Application of camphor-derived chiral sulfur ylides gave

the enantiomeric-enriched isoxazoline-*N*-oxides in excellent yields and stereoselectivity. Simple transformations of isoxazoline-*N*-oxide led to the gram-scale synthesis of a (–)-clausenamide analogue in four steps, with excellent stereochemistry control (see scheme).

Asymmetric Synthesis

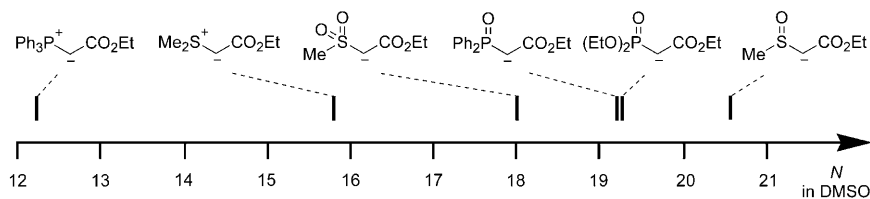
*C. Zhong, L. N. S. Gautam, J. L. Petersen, N. G. Akhmedov, X. Shi** 8605–8609

Concise Asymmetric Synthesis of Fully Substituted Isoxazoline-*N*-Oxide through Lewis Base Catalyzed Nitroalkene Activation

Ylides

R. Appel, H. Mayr* 8610–8614

Nucleophilic Reactivities of Sulfur Ylides and Related Carbanions: Comparison with Structurally Related Organophosphorus Compounds



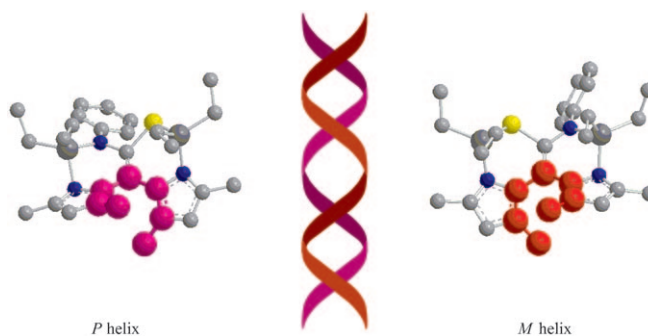
The nucleophilicity parameters of stabilized sulfur ylides, methylsulfonyl-, and methylsulfinyl stabilized carbanions have been determined from the rates of their reactions with benzhy-

drylium ions and quinone methides. Direct comparisons of the nucleophilic reactivities of sulfur and phosphorus ylides as well as their related carbanions have now become possible.

Coordination Complexes

A. Otero,* A. Lara-Sánchez,*
J. Fernández-Baeza,
C. Alonso-Moreno, J. Tejada,
J. A. Castro-Osma,
I. Márquez-Segovia,
L. F. Sánchez-Barba, A. M. Rodríguez,
M. V. Gómez 8615–8619

Straightforward Generation of Helical Chirality Driven by a Versatile Heteroscorpionate Ligand: Self-Assembly of a Metal Helicate by Using CH–π Interactions



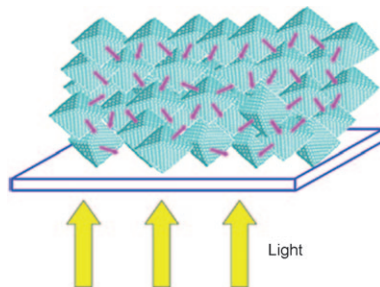
In a twist: The synthesis of novel architectures, through the use of versatile heteroscorpionate ligands, was

developed that allows helical chirality in aluminium complexes (see figure).

Solar Cells

Y.-F. Wang, J.-W. Li, Y.-F. Hou,
X.-Y. Yu, C.-Y. Su,
D.-B. Kuang* 8620–8625

Hierarchical Tin Oxide Octahedra for Highly Efficient Dye-Sensitized Solar Cells

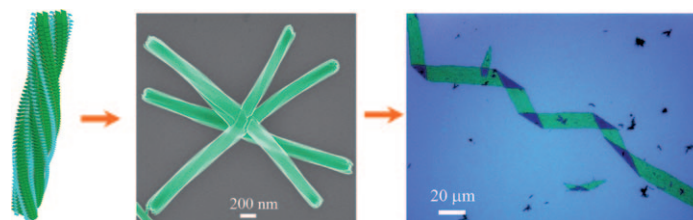


Hierarchical SnO₂ octahedra consisting of SnO₂ nanoparticles (≈ 30 nm in diameter) can be successfully fabricated by a fast sonochemical process followed by heat treatment (see figure). The dye-sensitized solar cell based on the photoelectrodes consisting of the bifunctional hierarchical octahedral SnO₂ shows a power conversion efficiency of 6.40%.

Helical Superstructures

Y. Yan, Y. Zhang, W. Hu,
Z. Wei* 8626–8630

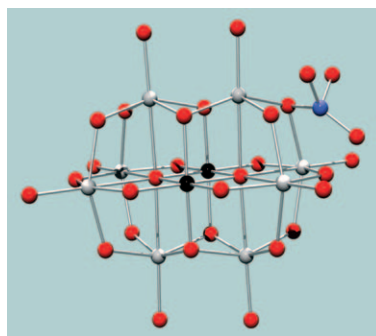
Hierarchical Crystalline Superstructures of Conducting Polymers with Homohelicity



Tuning hierarchical superstructures of helical nanofibers: Helical conducting polyaniline (PANI) nanofibers can self-assemble into linear nanofibers, branched nanofibers, and microribbons by controlling their aggregation pro-

cesses. Structural studies indicated that helical PANI molecules are arranged normal to the long axis of nanofibers, which is very similar to the arrangement of peptides in β sheets (see figure).

Borate: guilty and charged! The borate ion, and possibly carbonate, enhances rates of steady oxygen-isotope exchanges at some, but not all, structural sites in polyoxometalate ions. Addition of an oxygen atom to an incoming neutral boric acid molecule (blue = boron) from a bridging oxygen atom on a decametallate ion is shown here.



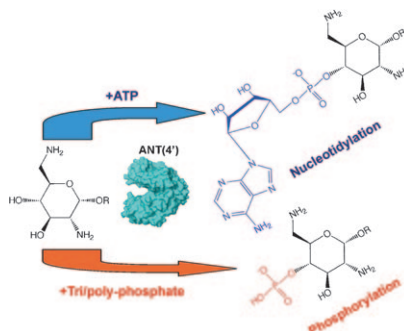
Polyoxometalates

*E. M. Villa, C. A. Ohlin, W. H. Casey** 8631–8634

Borate Accelerates Rates of Steady Oxygen-Isotope Exchange for Polyoxoniobate Ions in Water



A pocket of resistance: We have analysed the molecular determinants for nucleotide recognition by the resistance enzyme ANT(4'). Our results demonstrate that its binding epitope is restricted to the inorganic triphosphate fragment. Strikingly, this, together with longer polyphosphate oligomers, can be employed as cosubstrates in aminoglycoside inactivation (see figure), implying a change in the normal activity of the enzyme. These results have implications in the design of specific enzymatic inhibitors.



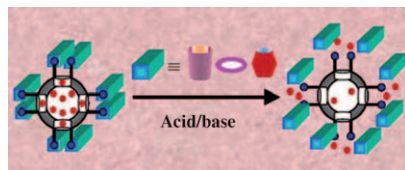
Nucleotide Binding

J. Revuelta, F. Corzana, A. Bastida, J. L. Asensio** 8635–8640

The Unusual Nucleotide Recognition Properties of the Resistance Enzyme ANT(4'): Inorganic Tri/Polyphosphate as a Substrate for Aminoglycoside Inactivation



Smart release on demand: A general pH-responsive supramolecular nanovalve operating in aqueous media has been designed by using mesoporous organosilica hollow nanospheres as nanocontainers (see picture). The nanovalve is capable of storing guest molecules within the hollow core and mesopore shell and releasing them on demand by acid/base triggering of the capping molecule, demonstrating a delicate vehicle for controlled release.



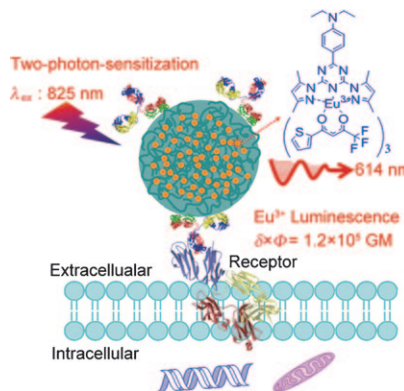
Supramolecular Chemistry

*W. Guo, J. Wang, S.-J. Lee, F. Dong, S. S. Park, C.-S. Ha** 8641–8646

A General pH-Responsive Supramolecular Nanovalve Based on Mesoporous Organosilica Hollow Nanospheres



Bionanoprobes with high dispersion stability in water, excellent photostability, and biocompatibility were prepared by encapsulating [Eu(tta)₃dpbt] (tta = thenoyltrifluoroacetate, dpbt = 2-(*N,N*-diethylanilin-4-yl)-4,6-bis-(3,5-dimethylpyrazol-1-yl)-1,3,5-triazine) in water-dispersible poly(methyl methacrylate-*co*-methacrylic acid) nanospheres and modifying the nanosphere surfaces with a monoclonal antibody (see scheme). The bionanoprobes exhibited excellent performance in the target-specific imaging of live cancer cells.



Imaging Agents

*G. Shao, R. Han, Y. Ma, M. Tang, F. Xue, Y. Sha, Y. Wang** ... 8647–8651

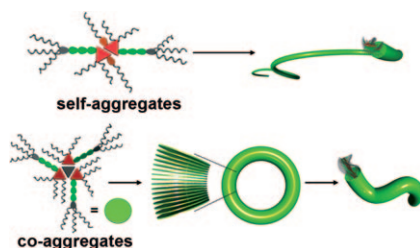
Bionanoprobes with Excellent Two-Photon-Sensitized Eu³⁺ Luminescence Properties for Live Cell Imaging



FULL PAPERS

Supramolecular Assembly

S. Yagai,* H. Aonuma, Y. Kikkawa,
S. Kubota, T. Karatsu, A. Kitamura,
S. Mahesh,
A. Ajayaghosh* 8652–8661



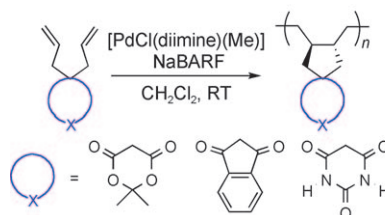
Line up! Oligo(*p*-phenylenevinylene)s capped on one end by a monotopic melamine hydrogen-bonding module can self- and co-aggregate with cyanuric acid to produce various self-assembled architectures (see figure).

Rational Design of Nanofibers and Nanorings through Complementary Hydrogen-Bonding Interactions of Functional π Systems

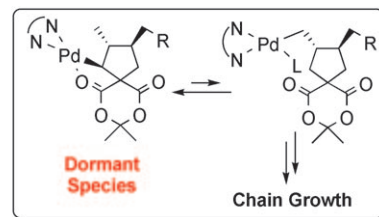
Polymerization

S. Park, T. Okada, D. Takeuchi,
K. Osakada* 8662–8678

Cyclopolymerization and Copolymerization of Functionalized 1,6-Heptadienes Catalyzed by Pd Complexes: Mechanism and Application to Physical-Gel Formation



Pd complexes with diimine ligands catalyze the cyclopolymerization of functionalized 1,6-heptadienes (see scheme), as well as their copolymeriza-

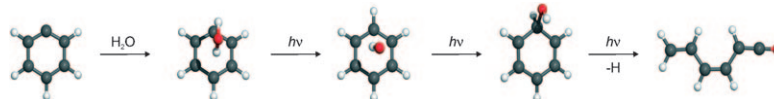


tion with ethylene and 1-hexene. The resultant polymers contain 1,2-*trans*-fused cyclopentane rings along the polymer chain.

Radical Reactions

A. Mardyukov, R. Crespo-Otero,
E. Sanchez-Garcia,
W. Sander* 8679–8689

Photochemistry and Reactivity of the Phenyl Radical–Water System: A Matrix Isolation and Computational Study



The phenyl radical forms a hydrogen-bonded complex with water that could be isolated in solid argon at 10 K. Visible-light irradiation results in the transfer of a hydrogen atom from water to the phenyl radical under for-

mation of a complex between OH and benzene. Prolonged irradiation results in the complete destruction of the benzene molecule and formation of a ring-opened ketene (see scheme).

Organogels

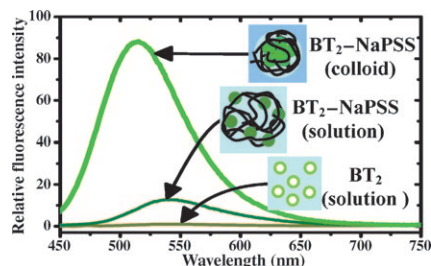
Y. Li, K. M.-C. Wong, A. Y.-Y. Tam,
L. Wu, V. W.-W. Yam* 8690–8698

Thermo- and Acid-Responsive Photochromic Spiroanthoxazine-Containing Organogelators



I like the way you move: A series of photochromic spiroanthoxazine derivatives has been designed, synthesized, and characterized by using ^1H NMR spectroscopy, FAB mass spectrometry, and elemental analysis. The photophysical and photochromic behavior has also been investigated. Two of the compounds have been shown to be capable of forming stable thermoreversible organogels in organic solvents (see figure).

In a new light: Polyelectrolyte (sodium poly(styrenesulfonate) (NaPSS)) complexation followed by polyelectrolyte-assisted nanoparticle formation induces fluorescence enhancement by nearly two orders of magnitude (see picture) in a quinodimethane-based molecule (7,7-bis(piperazinium)-8,8-dicyanoquinodimethane bis(*p*-toluenesulfonate) (BT₂)).



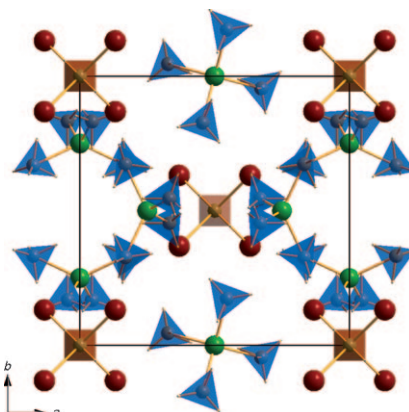
Nanoparticle Fluorescence

C. G. Chandaluri, A. Patra,
T. P. Radhakrishnan* 8699–8706

Polyelectrolyte-Assisted Formation of Molecular Nanoparticles Exhibiting Strongly Enhanced Fluorescence



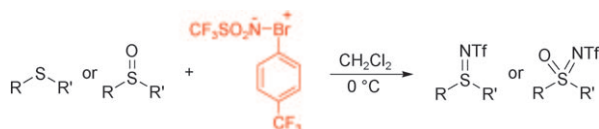
Mixed borohydrides: The synthesis, structure determination and decomposition pathway of a new complex double-cation borohydride with a very high hydrogen density are presented. The unique 3D-framework structure (see figure) contains complex anions [Al(BH₄)₄]⁻ and cations [Li₄(BH₄)₃]⁺, which rationalise the unexpected stoichiometry Al₃Li₄(BH₄)₁₃.



Powder Diffraction

I. Lindemann,* R. Domènech Ferrer,
L. Dunsch, Y. Filinchuk, R. Černý,*
H. Hagemann, V. D'Anna,
L. M. Lawson Daku, L. Schultz,
O. Gutfleisch 8707–8712

Al₃Li₄(BH₄)₁₃: A Complex Double-Cation Borohydride with a New Structure



Metal-free imination: Exposure of sulfides and sulfoxides to triflylimino-λ³-bromane in CH₂Cl₂ at 0°C results in a facile transfer of the sulfonylimino

group to sulfur atoms and affords *N*-triflylsulfilimines and -sulfoximines in high yields, under transition-metal-free conditions (see scheme).

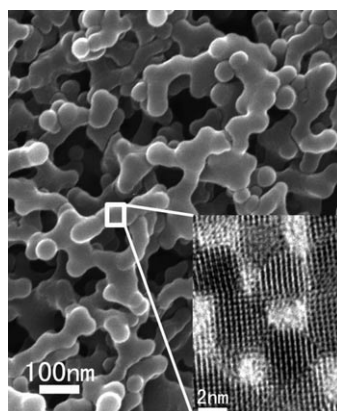
Synthetic Methods

M. Ochiai,* M. Naito, K. Miyamoto,
S. Hayashi, W. Nakanishi* . . 8713–8718

Imination of Sulfides and Sulfoxides with Sulfonylimino-λ³-Bromane under Mild, Metal-Free Conditions



Solid-solution photocatalyst: A hierarchical macro-/mesoporous (HMM) Ce_{0.49}Zr_{0.37}Bi_{0.14}O_{1.93} solid-solution network (see picture) has been fabricated by a polymerization–carbonization–oxidation route. The obtained material combines high specific surface area, HMM structure, and high crystallinity, and as a result shows a strong structure-induced enhancement of visible-light harvest and enhanced visible-light photocatalytic activity in the photo-degradation of methyl orange.



Photocatalysts

G. Xi, J. Ye* 8719–8725

Synthesis of Hierarchical Macro-/Mesoporous Solid-Solution Photocatalysts by a Polymerization–Carbonization–Oxidation Route: The Case of Ce_{0.49}Zr_{0.37}Bi_{0.14}O_{1.93}



Metathesis

E. Tzur, A. Szadkowska,
A. Ben-Asuly, A. Makal, I. Goldberg,
K. Woźniak, K. Grela,*
N. G. Lemcoff* 8726–8737



Studies on Electronic Effects in O-, N- and S-Chelated Ruthenium Olefin-Metathesis Catalysts

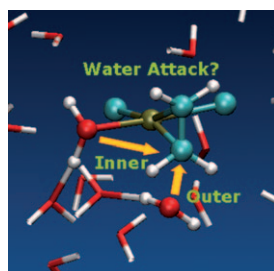
Latent catalysts: New ruthenium bidentate benzylidene catalysts based on sulfur and nitrogen chelation are presented (see figure). The catalysts were thoroughly characterised and

studied by spectroscopic and crystallographic techniques, and their reactivity in several metathesis reactions is described and analysed.

Nucleophilic Addition

A. Comas-Vives, A. Stirling,*
A. Lledós, G. Ujaque* 8738–8747

The Wacker Process: Inner- or Outer-Sphere Nucleophilic Addition? New Insights from Ab Initio Molecular Dynamics

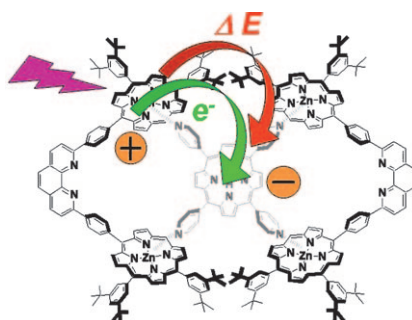


Wacker job: Does the nucleophilic addition step of the Wacker process proceed through an inner- or an outer-sphere mechanism (see image)? Ab initio molecular dynamics indicate that the outer-sphere mechanism is the less-energy-demanding pathway.

Supramolecular Chemistry

B. Ventura, L. Flamigni,* M. Beyer,
V. Heitz, J.-P. Sauvage 8748–8756

Unusual Photoinduced Electron Transfer from a Zinc Porphyrin to a Tetrapyrrolyl Free-Base Porphyrin in a Noncovalent Multiporphyrin Array

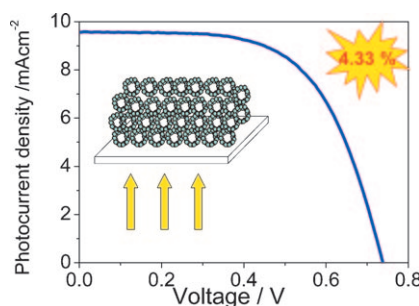


Something a little unusual: A surprising electron transfer from a zinc porphyrin to a free-base porphyrin is detected in a noncovalent pentaporphyrin array (see figure).

Zinc Oxide

C.-X. He, B.-X. Lei, Y.-F. Wang,
C.-Y. Su, Y.-P. Fang,
D.-B. Kuang* 8757–8761

Sonochemical Preparation of Hierarchical ZnO Hollow Spheres for Efficient Dye-Sensitized Solar Cells

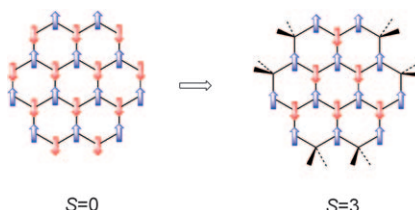


More efficient power conversion: Hierarchical ZnO hollow spheres (400–500 nm in diameter) consisting of ZnO nanoparticles with a diameter of approximately 15 nm have been successfully prepared by a facile and rapid sonochemical process. The power conversion efficiency of the dye-sensitized solar cells based on hierarchical ZnO hollow spheres is 4.33%, which represents a 38.8% increase compared to that of a ZnO nanoparticle photoelectrode (3.12%).

Molecular Magnetism

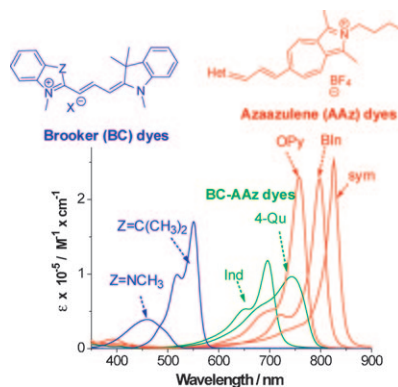
G. Trinquier, N. Suaud,
J.-P. Malrieu* 8762–8772

Theoretical Design of High-Spin Polycyclic Hydrocarbons



Smart saturation: Saturating properly chosen vertices of polycyclic conjugated hydrocarbons may lead to high-spin organic units (see figure).

Dye classification: Based on the results of quantum-chemical and spectral investigations of trimethine cyanine dye derivatives of 2-azaazulene, we propose a new classification of the terminal heterocycles (traditional Brooker's type and Azaazulene-like residues), and thus three types of cyanine dyes: Brooker's cyanines (BC), azaazulene-like (AAz) cyanines, and mixed AAz-BC dyes bearing the terminal groups of both types (see figure).

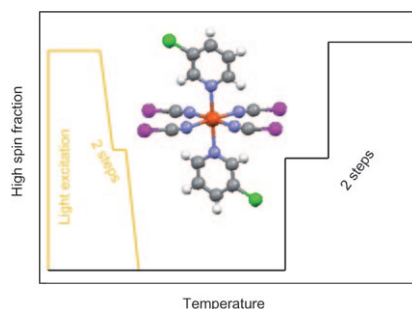


Electron Transitions

J. Bricks, A. Ryabitskii, A. Kachkovskii* 8773–8784

Studies of 2-Azaazulenium Derivatives: Unsymmetrical Trimethine Cyanine Dyes Bearing a 2-Azaazulenium Moiety as One of the Terminal Groups

Three out of five members of the $\text{Fe}(\text{X-py})_2[\text{Ag}(\text{CN})_2]_2$ ($\text{py} = \text{pyridine}$; $\text{X} = \text{H}, 3\text{-Cl}, 3\text{-Me}, 4\text{-Me}, 3,4\text{-Me}_2$) family of 2D polymeric spin-crossover (SCO) compounds (see picture) are among the rare examples of non-binuclear SCO compounds that show two-step behaviour not only in the thermal spin transition, but also in the relaxation of the photoinduced high-spin metastable state, as revealed by magnetic and calorimetric measurements.

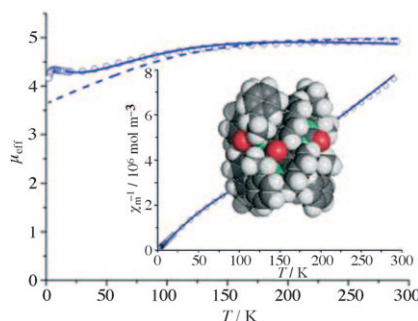


Spin-Crossover Compounds

J. A. Rodríguez-Velamazán, C. Carbonera, M. Castro, E. Palacios, T. Kitazawa, J.-F. Létard, R. Burriel* 8785–8796

Two-Step Thermal Spin Transition and LIESST Relaxation of the Polymeric Spin-Crossover Compounds $\text{Fe}(\text{X-py})_2[\text{Ag}(\text{CN})_2]_2$ ($\text{X} = \text{H}, 3\text{-methyl}, 4\text{-methyl}, 3,4\text{-dimethyl}, 3\text{-Cl}$)

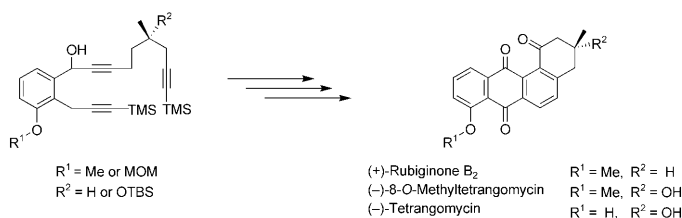
Magnetic helicates: Enantiomerically pure trinuclear helicate-type complexes are self-assembled in a hierarchical process. With paramagnetic metal ions they show some interesting magnetic behavior (see figure).



Self-Assembly

M. Albrecht, M. Fiege, P. Kögerler, M. Speldrich, R. Fröhlich, M. Engeser* 8797–8804

Magnetic Coupling in Enantiomerically Pure Trinuclear Helicate-Type Complexes Formed by Hierarchical Self-Assembly



Like, totally: A convergent and asymmetric total synthesis of naturally occurring angucyclinone antibiotics (+)-rubiginone B_2 , (-)-tetrangomycin,

and (-)-8-O-methyltetrangomycin by means of intramolecular cobalt-mediated [2+2+2] cycloaddition was established (see scheme).

Antibiotics

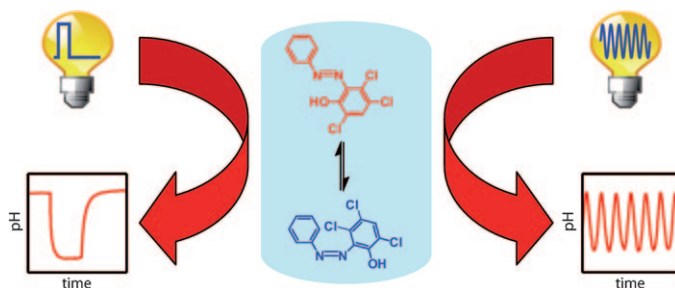
*C. Kesenheimer, A. Kalogerakis, A. Meißner, U. Groth** 8805–8821

The Cobalt Way to Angucyclinones: Asymmetric Total Synthesis of the Antibiotics (+)-Rubiginone B_2 , (-)-Tetrangomycin, and (-)-8-O-Methyltetrangomycin

Azo Compounds

M. Emond, T. Le Saux, S. Maurin,
J.-B. Baudin, R. Plasson,
L. Jullien* 8822–8831

**2-Hydroxyazobenzenes to Tailor pH
Pulses and Oscillations with Light**



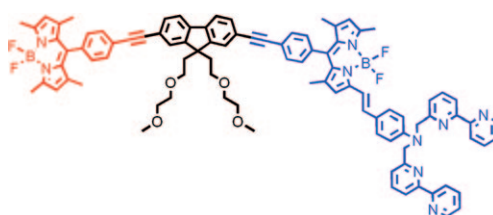
Sink or swing: The *trans*-to-*cis* isomerization of 2-hydroxyazobenzenes under UV light results in a tunable transient change of the protonation constant.

Up to 2 pH units of fast, reversible pH drops and pH oscillations have been generated by shaping single-wave-length illumination (see picture).

Energy Transfer

F. Puntoriero, F. Nastasi,
S. Campagna,* T. Bura,
R. Ziessel* 8832–8845

**Vectorial Photoinduced Energy
Transfer Between Boron–Dipyrro-
methene (Bodipy) Chromophores
Across a Fluorene Bridge**



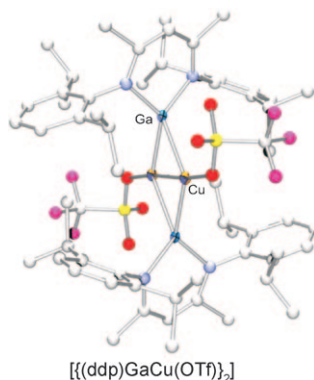
Energy exchange: Intercomponent photoinduced energy transfer takes place between different 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (Bodipy)

subunits separated by a fluorene spacer (see figure). The efficiency and rate of such a process can be tuned by the presence of protons.

Group 13 Elements

T. Bollermann, G. Prabusankar,
C. Gemel, R. W. Seidel, M. Winter,
R. A. Fischer* 8846–8853

**First Dinuclear Copper/Gallium
Complexes: Supporting Cu⁰ and Cu^I
Centres by Low-Valent Organogallium
Ligands**

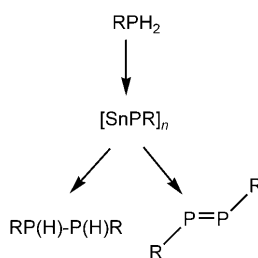


Right system? Reactions of suitable copper precursors with gallium(I) species lead to three dinuclear copper complexes with direct Cu–Ga donor–acceptor interactions. Depending on the ligand system and the oxidation state, complexes with very short Cu···Cu distances and also the first complex of Cu⁰ are formed (see picture).

Main Group Chemistry

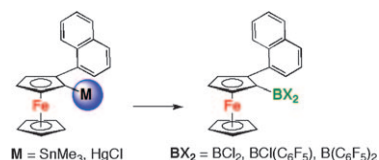
M. McPartlin, R. L. Melen, V. Naseri,
D. S. Wright* 8854–8860

**Formation and Rearrangement of Sn^{II}
Phosphanediide Cages**



Release me: Tin(II) phosphanediides are readily prepared by deprotonation of RPH₂ with Sn(NMe₂)₂ at room temperature. These species exhibit interesting thermolysis reactions, giving rise to diphosphanes, diphosphenes and tin metal on heating (see scheme).

Ferrocenylboranes go chiral: Enantiomerically pure naphthylferrocene derivatives NpFcM (NpFc=2-(1-naphthyl)ferrocene, M = SnMe₃, HgCl) have been prepared by directed *ortho*-metallation and subsequent selective transmetalation procedures. NpFcHgCl was successfully used as a precursor for the preparation of highly Lewis acidic planar chiral organoboranes (see scheme).



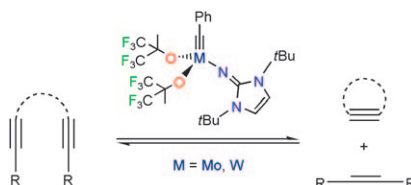
Ferrocenylboranes

J. Chen, K. Venkatasubbaiah, T. Pakkirisamy, A. Doshi, A. Yusupov, Y. Patel, R. A. Lalancette, F. Jäkle* 8861–8867

Planar Chiral Organoborane Lewis Acids Derived from Naphthylferrocene



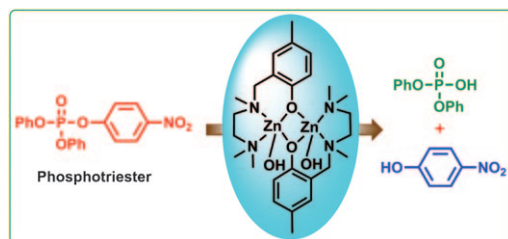
Alkyne metathesis: A new synthetic route to imidazolin-2-iminato molybdenum and tungsten benzyldiene complexes from [Mo(CO)₆] or [W(CO)₆] has been established that affords highly active catalysts for alkyne cross metathesis and ring-closing alkyne metathesis (see figure). The tungsten complex tends to show a superior catalytic performance, which is in line with DFT studies predicting a higher barrier for the molybdenum-based catalyst system.



Molybdenum and Tungsten Catalysts

B. Haberlag, X. Wu, K. Brandhorst, J. Grunenberg, C. G. Daniliuc, P. G. Jones, M. Tamm* 8868–8877

Preparation of Imidazolin-2-iminato Molybdenum and Tungsten Benzyldiene Complexes: A New Pathway to Highly Active Alkyne Metathesis Catalysts



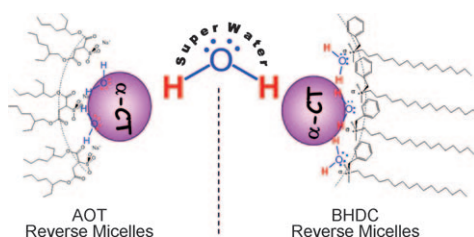
Functional mimics: Binuclear zinc(II) complexes that exhibit good metallo- β -lactamase (m β l) activity are poor mimics of phosphotriesterase (PTE) and vice versa, indicating that the binding of β -lactam substrates at the

binuclear zinc(II) center is different to that in phosphotriesters (see scheme). Furthermore, phosphodiester, the products from the hydrolysis of phosphotriesters, inhibit the PTE activity of m β l and its functional mimics.

Organophosphates

A. Tamilselvi, G. Mugesh* .. 8878–8886

Hydrolysis of Organophosphate Esters: Phosphotriesterase Activity of Metallo- β -lactamase and Its Functional Mimics



Superwater: The hydrogen-bond-donor ability of water for the hydrolysis of 2-naphthyl acetate catalyzed by α -chymotrypsin in reverse micelles (RMs) depends dramatically on the kind of surfactant used to create the micellar system. Thus, catalyst activity in RMs formed from the cationic surfactant

benzyl-*n*-hexadecyldimethylammonium chloride (BHDC) is much higher than in anionic sodium 1,4-bis-2-ethylhexylsulfosuccinate (AOT) RMs or pure water, because interaction with the cationic interface (see picture) increases the hydrogen-bond-donor capacity of water.

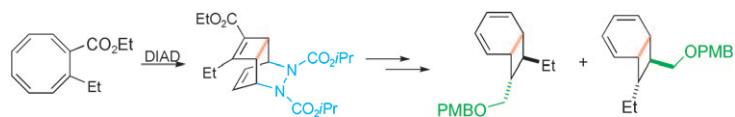
Enzyme Catalysis

F. Moyano, R. D. Falcone, J. C. Mejuto, J. J. Silber, N. M. Correa* .. 8887–8893

Cationic Reverse Micelles Create Water with Super Hydrogen-Bond-Donor Capacity for Enzymatic Catalysis: Hydrolysis of 2-Naphthyl Acetate by α -Chymotrypsin

Cycloaddition and Cycloreversion

R. L. Grange, M. J. Gallen, H. Schill,
J. P. Johns, L. Dong, P. G. Parsons,
P. W. Reddell, V. A. Gordon,
P. V. Bernhardt,
C. M. Williams* 8894–8903



Toss diazo into the ring! [4+2] Cycloaddition reactions between 1,8-disubstituted cyclooctatetraenes and diazo compounds provide either 2,3- or 3,4-disubstituted adducts. Product distribution can be controlled by modulating the dienophile or the electron density

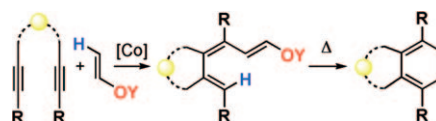
of the cyclooctatetraene. The adducts displayed selective action against various human tumour cell types, whilst also forming the basis of a new pathway to the synthetically challenging bicyclo[4.2.0]octa-2,4-diene family (see scheme).

[4+2] Cycloaddition Reactions Between 1,8-Disubstituted Cyclooctatetraenes and Diazo Dienophiles: Stereoelectronic Effects, Anticancer Properties and Application to the Synthesis of 7,8-Substituted Bicyclo[4.2.0]octa-2,4-dienes

Trienol Ethers

D. Lebaeuf, L. Iannazzo, A. Geny,
M. Malacria, K. P. C. Vollhardt,
C. Aubert,* V. Gandon* 8904–8913

Cobalt-Mediated Linear 2:1 Co-oligomerization of Alkynes with Enol Ethers to Give 1-Alkoxy-1,3,5-Trienes: A Missing Mode of Reactivity



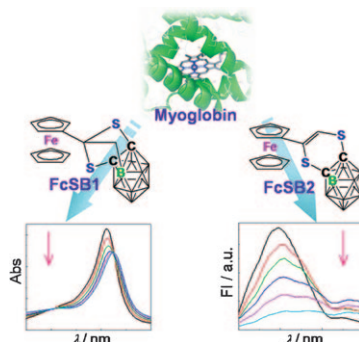
Competing pathways: Trienol ethers, including diborylated derivatives, are constructed by cobalt-mediated linear co-oligomerization of alkynes with enol ethers. This formal alkyne coupling/C–H activation sequence proceeds in a highly regio- and diastereo-

selective fashion. Thermal electrocyclic ring closure, coupled with dehydroalkoxylation, leads to arene derivatives (see figure), the sequence constituting a formal [2+2+2] cycloaddition of alkynes to acetylene.

Bioorganometallic Chemistry

C. Wu, B. Xu, J. Zhao, Q. Jiang,
F. Wei, H. Jiang, X. Wang,*
H. Yan* 8914–8922

Ferrocene-Substituted Dithio-carborane Isomers: Influence on the Native Conformation of Myoglobin Protein



Go bio! Two ferrocene-substituted dithio-*o*-carborane isomers (FcSB1 and FcSB2) show a different binding affinity to myoglobin and affect the spin state of the heme iron center and the conformation of aromatic fluorophores in the protein matrix. The exploration of such biointeractions provides insights into the promising bioapplications of the relevant multifunctional organometallic complexes.

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CORRIGENDUM

C. Ortiz Mellet,* J. M. Benito,
J. M. García Fernández* . . . 6728–6742

Preorganized, Macromolecular, Gene-Delivery Systems

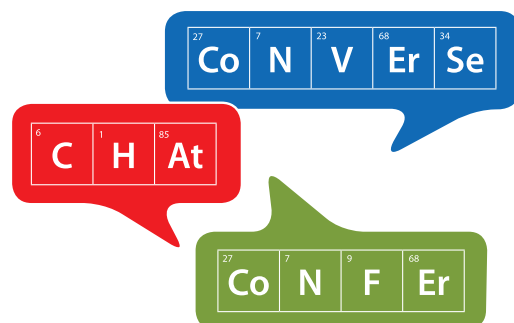
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In this article, reference [47] contains an incorrect author name and the wrong journal has been cited. The correct reference is given below. The authors apologize for this mistake.

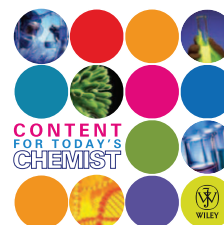
[47] R. Lalor, J. L. DiGesso, A. Mueller, S. E. Matthews, *Chem. Commun.* **2007**, 4907–4909.

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