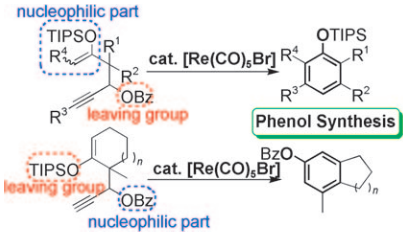
COMMUNICATIONS

Cycloaddition

*K. Saito, Y. Onizawa, H. Kusama, N. Iwasawa** .... 4716 – 4720

Rhenium(I)-Catalyzed Cyclization of Silyl Enol Ethers Containing a Propargyl Carboxylate Moiety: Versatile Access to Highly Substituted Phenols

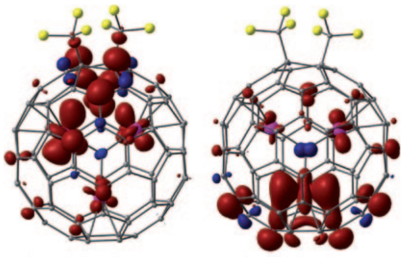


Selective migration: The rhenium-catalyzed reaction of 2-siloxy-1-en-5-ynes containing an acyloxy substituent at the propargylic position gave highly substituted phenols in good yields (see scheme). Depending on the structure of the silyl enol ether, either nucleophilic addition of this moiety or 1,2-acyloxy migration occurs to give two kinds of synthetically useful, substituted phenols.

Spectroelectrochemistry

A. A. Popov, N. B. Shustova, A. L. Svitova, M. A. Mackey, C. E. Coumbe, J. P. Phillips,* S. Stevenson,* S. H. Strauss,* O. V. Boltalina,* L. Dunsch** .... 4721 – 4724

Redox-Tuning Endohedral Fullerene Spin States: From the Dication to the Trianion Radical of $Sc_3N@C_{80}(CF_3)_2$ in Five Reversible Single-Electron Steps



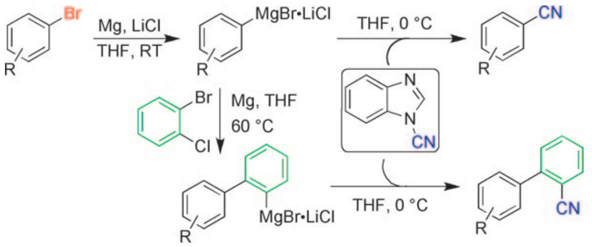
$Sc_3N@C_{80}(CF_3)_2^{-\bullet}$ $Sc_3N@C_{80}(CF_3)_2^{3-\bullet}$

The first endohedral trianion captured: $Sc_3N@C_{80}(CF_3)_2$ (see figure) exhibits three reversible reductions and two reversible oxidations and affords the facile generation of the monocation, monoanion, and trianion in solution, which can be characterized by ESR and absorption spectroscopies. This is the first time that such a broad range of charged states of any endohedral fullerene has been spectroscopically characterized.

Heterogeneous Catalysis

*P. Anbarasan, H. Neumann, M. Beller** .... 4725 – 4728

A Convenient Synthesis of Benzonitriles via Electrophilic Cyanation with *N*-Cyanobenzimidazole

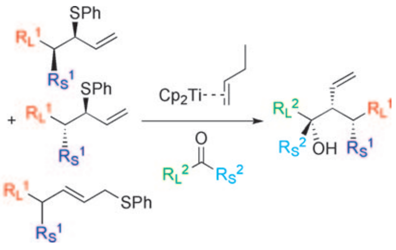


Couplings: *N*-Cyanobenzimidazole has been used in the synthesis of aryl- and heteroarylnitriles from the corresponding Grignard reagents (see scheme). This electrophilic cyanation is further extended to the synthesis of 2-cyano-1,1′-biaryls through a domino Grignard-coupling/cyanation strategy.

Diastereoselective Synthesis

T. Takeda, T. Nishimura, Y. Yatsumonji, K. Noguchi, A. Tsubouchi* .... 4729 – 4732

Highly Stereoselective Preparation of Tertiary Homoallylic Alcohols with Multiple Stereogenic Centers

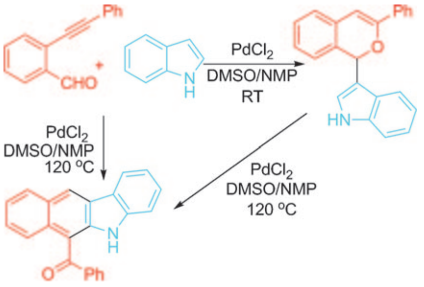


Taking on the stereoselective challenge: A variety of *tert*-homoallylic alcohols containing three or four adjacent stereocenters were prepared, in one step with high diastereoselectivity, by the reaction of chiral allyltitanocenes, generated by the desulfurizative titanation of isomeric mixtures of allylic sulfides, with achiral or chiral ketones.

Indoles

*R.-Y. Tang, J.-H. Li** .... 4733 – 4738

PdCl$_2$-Catalyzed Domino Reactions of 2-Alkynylbenzaldehydes with Indoles: Synthesis of Fluorescent 5*H*-Benzo[*b*]-carbazol-6-yl Ketones

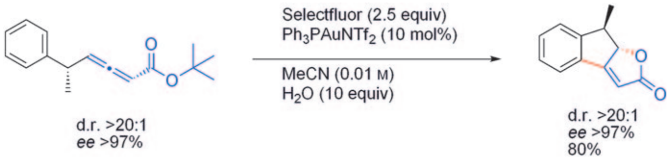


Synthetic methods: A new, selective Pd-catalyzed domino reaction of 2-alkynylbenzaldehydes with indoles has been developed for the synthesis of 5*H*-benzo[*b*]carbazol-6-yl ketones. The isobenzopyrylium complex is trapped by indole at room temperature to give 3-(1*H*-isochromen-1-yl)-1*H*-indoles, which can be transformed into 5*H*-benzo[*b*]carbazol-6-yl ketones by raising the temperature (see scheme). These ketones exhibit intense fluorescence and interact with metal ions to enhance the fluorescence intensity.

Gold Catalysis

M. N. Hopkinson, A. Tessier,
A. Salisbury, G. T. Giuffredi,
L. E. Combettes, A. D. Gee,
*V. Gouverneur** .... 4739 – 4743

Gold-Catalyzed Intramolecular Oxidative Cross-Coupling of Nonactivated Arenes

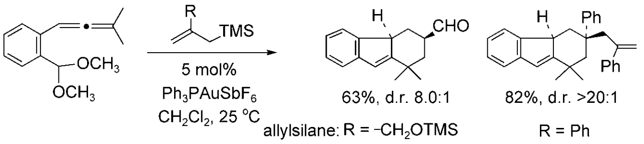


An (Au)some coupling! Gold-catalyzed cascade C–O cyclizations of benzyl-substituted allenoate esters followed by intramolecular oxidative C–C cross-coupling involving aryl C–H functionalization were performed with Selectfluor as the oxidant (see scheme). This operationally simple and mild procedure benefits from complete axis-to-center chirality transfer and allows for the preparation of surprisingly uncommon tricyclic motifs.

Gold Catalysis

T.-M. Teng, M.-S. Lin, D. Vasu,
S. Bhunia, T.-A. Liu,
*R.-S. Liu** .... 4744 – 4748

Gold-Catalyzed Dealkoxylative Carbocyclization/[3+3] Annulation Cascade of Acetal–Allene or Ketal–Allene Substrates



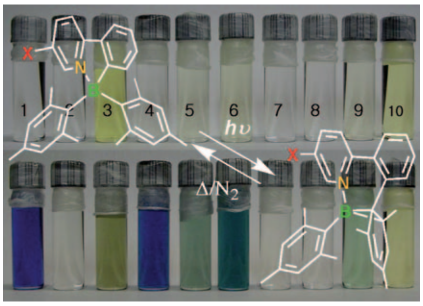
Rapid construction: We report the first successful implementation of a catalytic tandem carbocyclization/annulation cascade reaction (e.g., see scheme) using acetal–allene or ketal–allene substrates through a dealkoxylative mode. This gold catalysis enables a rapid stereocontrolled construction of oxacyclic or carbocyclic frameworks.

FULL PAPERS

Organoboron Chemistry

H. Amarne, C. Baik, S. K. Murphy,
*S. Wang** .... 4750 – 4761

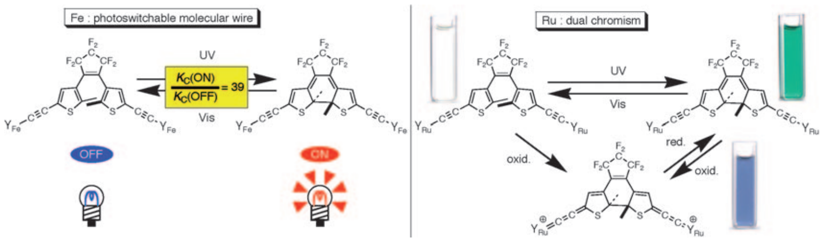
Steric and Electronic Influence on Photochromic Switching of N,C-Chelate Four-Coordinate Organoboron Compounds



A boron chameleon! A series of four-coordinate organoboron compounds B(N,C-L)Mes$_2$ (Mes = mesityl), in which N,C-L is a chelate ligand, have been found to undergo photoisomerization. Steric congestion has been found to be a key driving force in the photoisomerization process. The nature of the substituent X (see scheme) and the chelate ligand have also been found to have a distinct impact on the color change and the rate of the photoisomerization process.

Molecular Electronics

Photochromic Organometallics with a Dithienylethene (DTE) Bridge, [Y−C≡C−DTE−C≡C−Y] (Y = {MCp*(dppe)}): Photoswitchable Molecular Wire (M = Fe) versus Dual Photo- and Electrochromism (M = Ru)

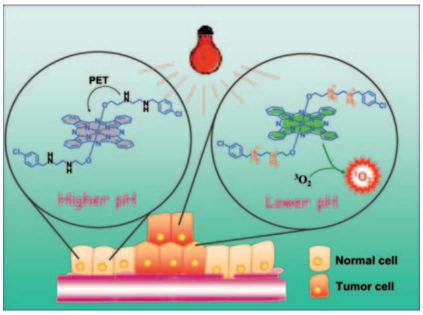


Dual photo- and electrochromism: Dinuclear acetylide-type complexes bridged by a photochromic dithienylethene unit (DTE) have been prepared, and their wirelike and switching behavior (see graphic; Y = {MCp*(dppe)}; M = Fe, Ru), as well as their oxidation chemistry, has been investigated. Communication between the two metal centers of the iron complex can be switched by the photochemical, ring-opening/closing cycle of the DTE moiety, and the ruthenium complex exhibits dual photo- and electrochromism.

Fluorescence

Phthalocyanine–Polyamine Conjugates as pH-Controlled Photosensitizers for Photodynamic Therapy

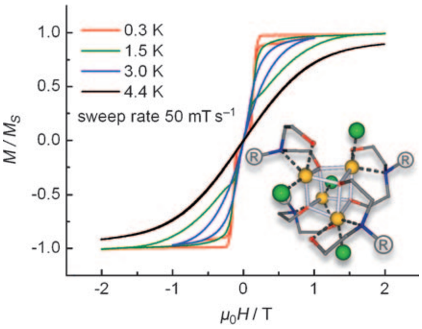
Smart response: Under acidic conditions, the fluorescence emission and efficiency at generating singlet oxygen and superoxide radicals of this series of phthalocyanine–polyamine conjugates is greatly enhanced (see figure). The phthalocyanine shown in the figure shows the most desirable pH-responsive properties, which makes it a promising tumor-selective fluorescence probe and photosensitizer for photodynamic therapy.



Magnetochemistry

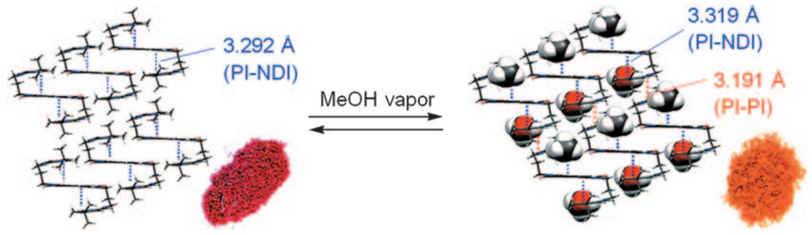
Synthesis, Magnetic Properties, and STM Spectroscopy of Cobalt(II) Cubanes $[Co^{II}_4(Cl)_4(HL)_4]$

Inversion of magnetoanisotropy: The novel tetranuclear Co^{II} cubane $[Co^{II}_4(Cl)_4(HL^2)_4]$ shown in the figure ($R = n$Bu) was synthesized from N-substituted diethanolamine H_2L^2, LiH, and Co^{II} ions ($D > 0$ K). It exhibits an easy-axis type of single-molecule magnet behavior with an energy barrier of $\Delta \approx 55.8$ K ($D = -1.55$ K), which is comparable to that of $\{Mn_{12}\}$, and a blocking temperature of 4.4 K, but the hysteresis loops are collapsed owing to fast zero-field relaxation.



Vapochromic Crystals

Dynamic Vapochromic Behaviors of Organic Crystals Based on the Open–Close Motions of S-Shaped Donor–Acceptor Folding Units

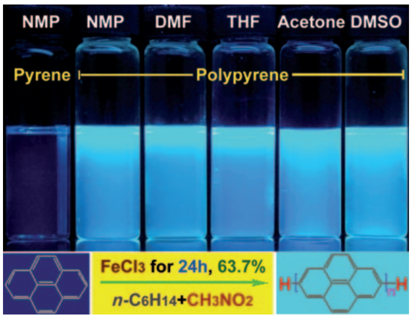


Chameleon chemistry: The first vapochromic organic crystals are described with respect to their preparation, color change, adsorption/desorption properties, crystal structures, and color-change mechanism (see picture).

Conducting Materials

X.-G. Li, Y.-W. Liu, M.-R. Huang,**
S. Peng, L.-Z. Gong,
*M. G. Moloney** .... 4803 – 4813

Simple Efficient Synthesis of Strongly Luminescent Polypyrene with Intrinsic Conductivity and High Carbon Yield by Chemical Oxidative Polymerization of Pyrene

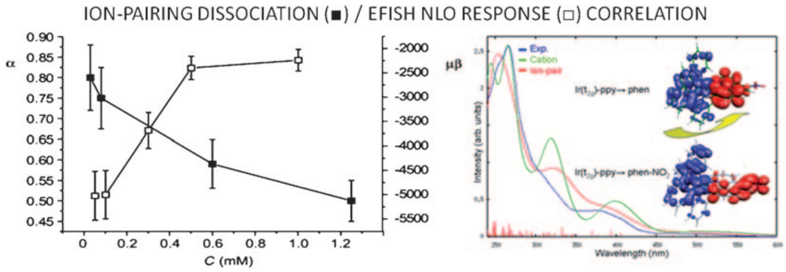


Strong turquoise luminescence in various solvents (see picture), selective quenching by Fe^{3+}, controllable conductivity between 3.4×10^{-8} and $81.2\ S\,cm^{-1}$, and a high carbon yield of 70.6 % at 1300 °C are exhibited by polypyrene synthesized by direct chemical oxidative polymerization of pyrene with $FeCl_3$ in n-C_6H_{14}/CH_3NO_2. It has potential applications as a luminescent material, an Fe^{3+} detector, and intrinsically electrical conducting functional and ablative materials.

Nonlinear Optics

A. Valore, E. Cariati, C. Dragonetti,
S. Righetto, D. Roberto, R. Ugo,*
F. De Angelis, S. Fantacci,*
*A. Sgamellotti, A. Macchioni,**
D. Zuccaccia .... 4814 – 4825

Cyclometalated Ir^{III} Complexes with Substituted 1,10-Phenanthrolines: A New Class of Efficient Cationic Organometallic Second-Order NLO Chromophores

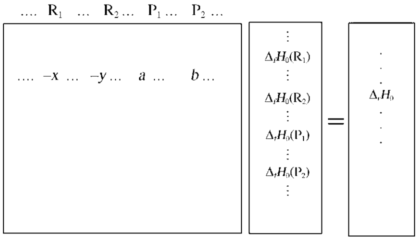


E-fishing for light: The electrical-field-induced second-harmonic generation (EFISH) NLO response of a class of cyclometalated Ir^{III} cationic complexes is found to increase upon dilution in apolar solvents, correlating with the fraction of dissociated ion pairs measured by using ^{1}H and ^{19}F PGSE NMR spectroscopy.

Atom-Based Thermochemistry

*A. G. Császár,**
T. Furtenbacher .... 4826 – 4835

From a Network of Computed Reaction Enthalpies to Atom-Based Thermochemistry (NEAT)

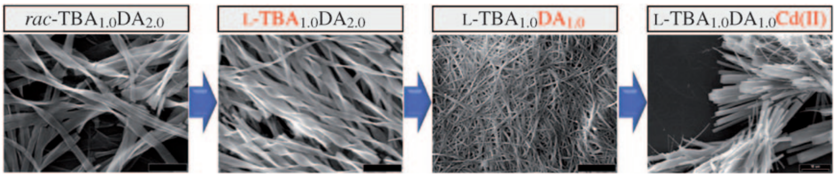


A NEAT idea: A simple, fast, weighted, linear least-squares refinement protocol and code for inverting the information contained in a network of quantum chemically computed 0 K reaction enthalpies is presented. This protocol, dubbed NEAT, leads, after an inversion, to 0 K enthalpies of formation (Δ_fH_0) from computed reaction enthalpies (Δ_rH_0; see graphic).

Nanostructure Fabrication

D. Jang, H. Y. Lee, M. Park, S. R. Nam,
*J.-I. Hong** .... 4836 – 4842

Nano- and Microstructure Fabrication by Using a Three-Component System



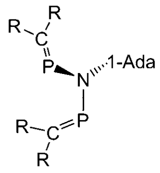
Three's company! We have suggested a simple method to make various nano- and microstructures from simple organic building blocks and metal ions in water through noncovalent interactions (see picture). This method can be applied to the fabrication of various conducting nanomaterials or to organic templates for inorganic nanostructures.

Density Functional Calculations

R. M. Bîrzoi, D. Bugnariu, R. G. Gimeno, D. Lungu, V. Zota, C. Daniliuc, P. G. Jones, Z. Benkõ, L. Könczöl, L. Nyulási, R. Bartsch, W.-W. du Mont, E. Niecke* 4843–4851

Imino-Bridged Bisphosphaalkenes (2,4-Diphospha-3-azapentadienes)

Strained PNPs: Bisphosphaalkenes $(R_2C{=}P)_2NR'$ ($R = SiMe_2Me$, $SiMe_2$*i*Pr; $R' =$ *t*Bu, 1-adamantyl (1-Ada), 2,4,6-*t*$Bu_3C_6H_2$ (Mes*)) have been examined (see scheme). DFT calculations on less-strained iminobisphosphaalkenes provide a likely mechanistic explanation for rearrangements by silyl-group migration.

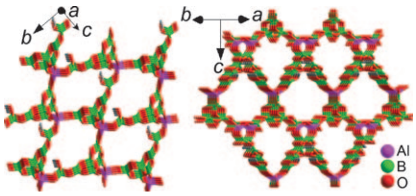


Template Synthesis

*J. Zhou, W.-H. Fang, C. Rong, G.-Y. Yang** 4852–4863

A Series of Open-Framework Aluminoborates Templated by Transition-Metal Complexes

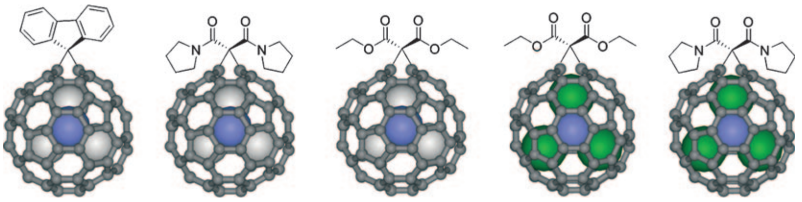
A new frame of reference: A series of new open-framework aluminoborates (ABOs) have been made by transition-metal complex (TMC) templates under hydrothermal conditions. The structures not only exhibit two distinct types of 3D acentric frameworks (see picture), but also represent the only examples of 3D ABOs templated by TMCs.



Metallofullerenes

*J. R. Pinzón, T. Zuo, L. Echegoyen** 4864–4869

Synthesis and Electrochemical Studies of Bingel–Hirsch Derivatives of $M_3N@I_h$-C_{80} (M = Sc, Lu)



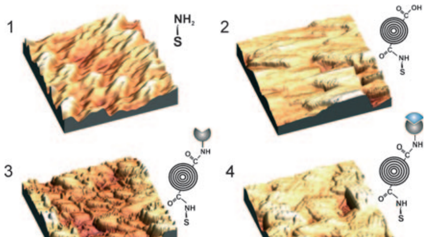
TNT: New experimental conditions for the preparation of Bingel–Hirsch derivatives of trimetallic nitride template endohedral metallofullerenes (TNT-EMFs) $M_3N@I_h$-C_{80} (M = Sc, Lu; see graphic) were found. Electrochemical studies conducted with the prepared derivatives showed the influence of the addends on the reduction potentials relative to the pristine fullerene species.

Nanostructures

J. Luszczyn, M. E. Plonska-Brzezinska, A. Palkar, A. T. Dubis, A. Simionescu, D. T. Simionescu,* B. Kalska-Szostko, K. Winkler, L. Echegoyen** 4870–4880

Small Noncytotoxic Carbon Nano-Onions: First Covalent Functionalization with Biomolecules

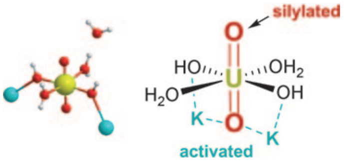
Know your onions: The first covalent functionalization of noncytotoxic oxidized carbon nano-onions (CNOs) with biomolecules has been reported. Multilayers were prepared on gold surfaces and the process was monitored by using surface plasmon resonance (SPR) spectroscopy and atomic force microscopy (AFM). The picture shows 1: Au/thiol; 2: Au/thiol/CNOs; 3: Au/thiol/CNOs/biotin, and 4: Au/thiol/CNOs/biotin/avidin layers.



Density Functional Calculations

*A. Yahia, P. L. Arnold, J. B. Love, L. Maron** 4881–4888

The Effect of the Equatorial Environment on Oxo-Group Silylation of the Uranyl Dication: A Computational Study

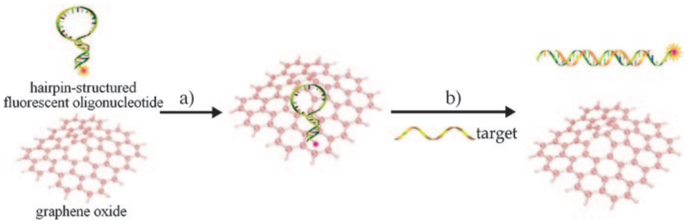


Any equatorial ligand will do: A DFT study of the silylation of the U–O bond in a macrocyclic uranyl complex demonstrates the importance of the presence, but not the identity, of the equatorial ligands upon the silylation of the uranyl U–O bond, and the influence of the oxo-potassium interaction at the opposing oxo group (see figure).

Molecular Beacons

C.-H. Lu, J. Li, J.-J. Liu, H.-H. Yang, X. Chen,* G.-N. Chen* 4889–4894

Increasing the Sensitivity and Single-Base Mismatch Selectivity of the Molecular Beacon Using Graphene Oxide as the "Nanoquencher"

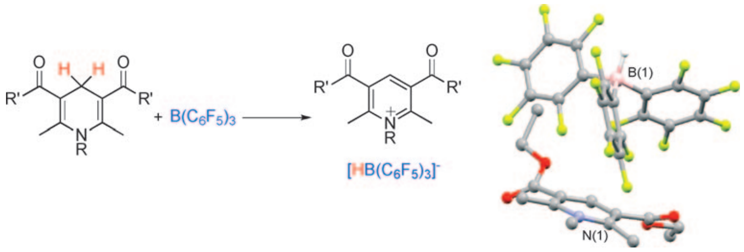


Honing beacons: We present a novel, highly sensitive, selective, and economical molecular beacon using graphene oxide as the "nanoquencher". The key components of the novel graphene oxide quenched molecular beacon are the hairpin-structured fluorophore-labeled oligonucleotide and graphene oxide sheet, which functions as both "nanoscaffold" for the oligonucleotide and "nanoquencher" for the fluorophore (see figure).

Organic Hydrides

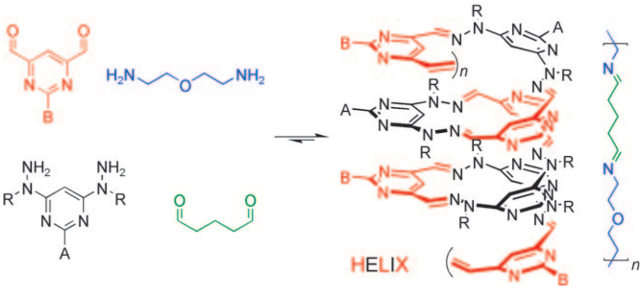
J. D. Webb, V. S. Laberge, S. J. Geier, D. W. Stephan, C. M. Crudden** 4895–4902

Borohydrides from Organic Hydrides: Reactions of Hantzsch's Esters with $B(C_6F_5)_3$



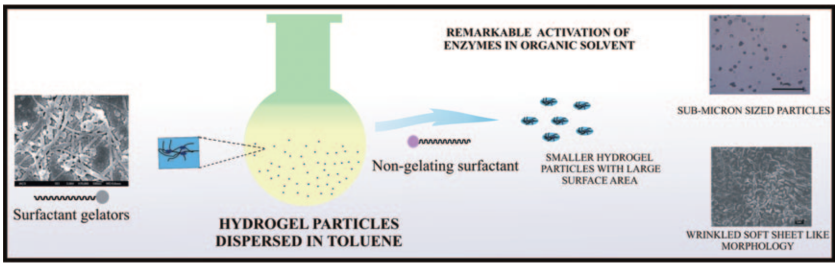
Borohydrides from organic hydrides: Hantzsch's esters have been shown to act as hydride donors for $B(C_6F_5)_3$, generating a pyridinium borohydride salt (see scheme, R′ = OEt, R = Me). Hydride transfer occurred quantitatively at temperatures as low as −50 °C. Substituents on the carbonyl group and the nitrogen atom proved to be important in terms of the stability of the resulting salt, which decomposed upon standing at room temperature by re-addition of the borohydride to the pyridinium.

Helical Folding



In the mix: A mixture of four components first led preferentially to the formation of two groups of macrocycles as the kinetic products. Thereafter, the dynamic library evolved towards the expression of a helically folded strand (see scheme; R = Me, A = 3,4,5-$(MeO)_3C_6H_2$, B = Ph). Its formation provides the driving force for the adaptation/evolution of the constitutional dynamic library network towards the selection and amplification of the most stable library member and its agonist.

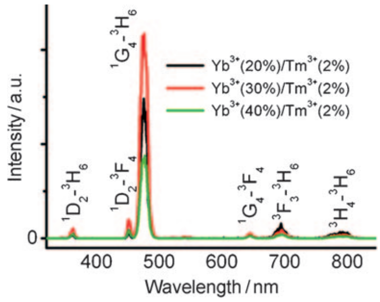
Enzyme Activation



Hydrogel supports based on surfactant gelators lead to remarkable activation of heme proteins and enzymes immobilized in their amphiphilic networks (see left SEM image) in organic solvents. Doping of these hydrogels with nongelating anionic surfactants resulted in formation of smaller hydrogel particles (see schematic and top-right SEM image) with even higher enzyme activity and modified gel morphology (bottom-right SEM image).

Energy Transfer

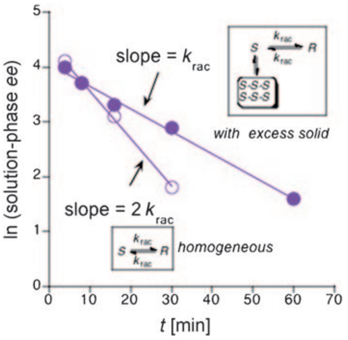
Upconversion luminescence tuning of β-$NaYF_4$ nanorods under 980 nm excitation has successfully been achieved by tridoping with Ln^{3+} ions with different electronic structures. The effects of Ce^{3+} ions on $NaYF_4$:Yb^{3+}/Ho^{3+} as well as Gd^{3+} ions on $NaYF_4$:Yb^{3+}/Tm^{3+}(Er^{3+}) have been studied in detail (see figure for an example).



Homochirality

C. Viedma, B. J. V. Verkuijl, J. E. Ortiz, T. de Torres, R. M. Kellogg,* D. G. Blackmond** 4932–4937

Solution-Phase Racemization in the Presence of an Enantiopure Solid Phase

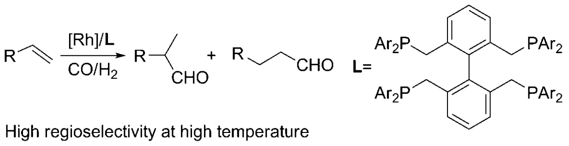


Single-handed: Results from monitoring concentration profiles during the interconversion of enantiomers in solution both in the presence and absence of solid-phase crystals, together with an analytical treatment (see figure) of the racemization process, helps to decouple solution- and solid-phase processes, and unequivocally reconfirms the validity of the Meyerhoffer double solubility rule for systems under solution racemization conditions.

Asymmetric Synthesis

S. Yu, X. Zhang, Y. Yan, C. Cai, L. Dai, X. Zhang** 4938–4943

Synthesis and Application of Tetraphosphane Ligands in Rhodium-Catalyzed Hydroformylation of Terminal Olefins: High Regioselectivity at High Temperature



High regioselectivity at high temperature

Hot spot: A new class of substituted tetraphosphane ligands has been developed and applied in the rhodium-catalyzed regioselective hydroformylation of terminal olefins (see scheme). The high regioselectivity at high temperature shown by these tetraphosphane ligands is remarkable when considering the low regioselectivity commonly observed under similar reaction conditions using other bisphosphite analogues.

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* Author to whom correspondence should be addressed

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