EDITORIAL

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Frontiers of Chemistry in Paris

On May 21, a Friday before a long weekend in most European countries, a symposium will take place at which 10 illustrious speakers including four Nobel Laureates will discuss some of the current frontiers of chemical research (see Table 1). As the symposium celebrates the 10th anniversary of *ChemBioChem* and *ChemPhysChem*, the lectures naturally focus on the interfaces of chemistry with physics, biology, and medicine. This focus should, however, be inspiring for every chemist regardless of whether his or her own research deals with synthetic organic or theoretical inorganic chemistry or any other specialised field. The symposium should be particularly attractive to PhD students and postdocs who can also present posters. While the symposium itself is only a one-day event, the posters will be available online for a three-month period.

Table 1. Lectures.

Gerhard Ertl	Reactions at Surfaces: From Atoms to Complexity
Michel Orrit	Nano-optics: A Window on Structure and Dynamics at Molecular Scales
Marc Fontecave	From Enzymes to Nanocatalysts: The Case of Hydrogenases
Alan R. Fersht	Tumour Suppressor p53: From Structure to Drug Discovery
Michael Grätzel	Molecular Photovoltaics and Mesoscopic Solar Cells
Roger Y. Tsien	Breeding and Building Molecules for Imaging
Nicolas Winssinger	Translating Instructions into Function by Self Assembly
Luisa De Cola	Nanomaterials: Properties, Assemblies and Biomedical Applications
Ada Yonath	The Ribosome: The Remnant of an Ancient Translation Apparatus
Jean-Marie Lehn	From Supramolecular Chemistry towards Adaptive Chemistry

Figure 1. Maison de la Chimie.

As *ChemBioChem* and *ChemPhysChem* are published by Wiley-VCH on behalf of ChemPubSoc Europe (which comprises 14 European chemical societies including the Société Chimique de France, SFC), the symposium has been organized by all three associations (with the help of LDO, a professional organizer of scientific conferences). The venue is most fittingly the Maison de la Chimie in the heart of Paris (Figure 1). The moderate registration fee covers coffee breaks and a buffet lunch. Are you interested? Then please go to http://www.chembiophyschem.org for more information.

I look forward to seeing you in Paris!

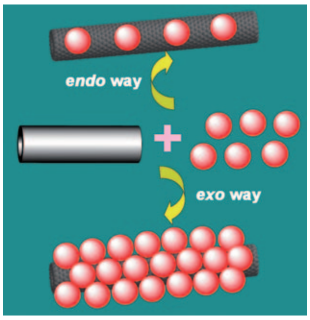
Peter Goelitz

REVIEWS

Nanomaterials

*R. Singh, T. Premkumar, J.-Y. Shin, K. E. Geckeler** 1728–1743

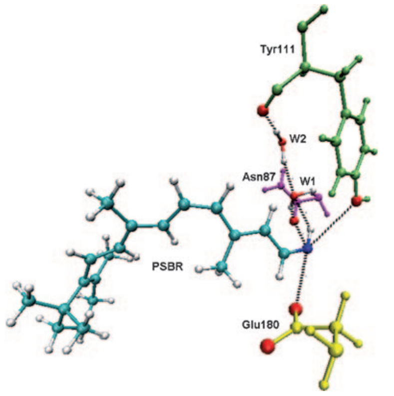
Carbon Nanotube and Gold-Based Materials: A Symbiosis



The interaction between carbon materials and gold provides access to new hybrid materials with useful properties for various potential applications. Here we provide an overview of the recent progress in this area by exploring the various synthesis approaches and types of assemblies, and study the diverse applications of the resulting composites (see graphic).

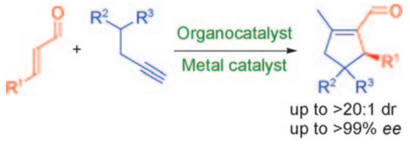
COMMUNICATIONS

Chemistry of vision in an invertebrate: A comprehensive QM/MM evaluation of the structure and spectral tuning mechanism of squid rhodopsin is reported for the first time. A negatively charged Glu180 residue is found to be the principal counterion and the strong electrostatic interaction between the 11-*cis*-retinal chromophore and counterion is responsible for the origin of spectral tuning from gas phase (604 nm) to the protein environment (490 nm).

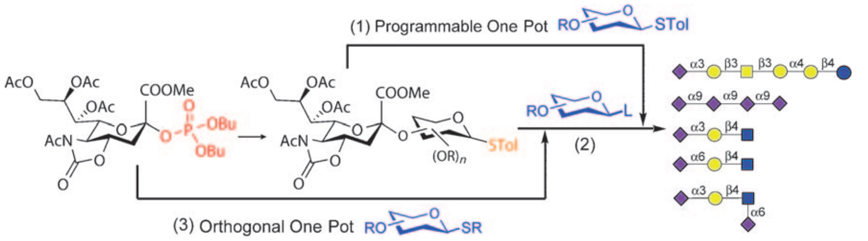


Protein Structures

A multicatalytic, asymmetric cascade reaction sequence of α,β-unsaturated aldehydes with alkyne-tethered nucleophiles has been developed. Organocatalytic iminium–enamine catalysis combined with Lewis acid alkyne activation gave cyclopentene carbaldehyde products in good yields and excellent stereoselectivities (see scheme). To highlight the potential of the sequence, a key structure for the preparation of a fusicoccane diterpenoid analogue was synthesized.



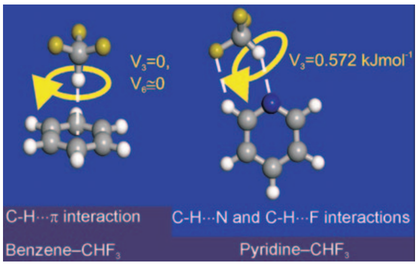
Organocatalysis



Hubble, bubble, toil, and trouble: The use of a new sialyl phosphate donor allows the stereoselective, one-pot multicomponent synthesis of α-sialooligosaccharides (see scheme).

Glycosylation

All change: The dynamics, location, and hydrogen-bond features of CHF_3 change drastically on going from the benzene–CHF_3 to the pyridine–CHF_3 molecular adduct. The barrier to internal rotation increases from almost nothing to $\approx 0.6\,kJ\,mol^{-1}$; the CHF_3 moiety moves into the ring plane from above, and a C–H···N linkage replaces the C–H···π contact (see figure).

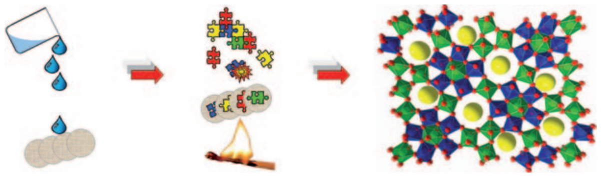


Molecular Complexes

Synthetic Methods

A. Simon,
*E. V. Kondratenko** 1765–1767

The “Flash” Method: A Shortcut for Producing the $Cs_x(W,Nb)_5O_{14}$ Structure

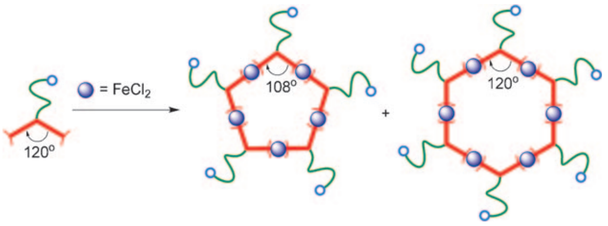


In a flash! A novel synthetic method for the formation of materials with $Cs_x(W,Nb)_5O_{14}$ structure is introduced. This flash method is based on a cellulose-templated technique and convinces with a short preparation time, a high yield of the crystalline product, and a minor elemental leakage compared to the standard slurry and hydrothermal methods.

Self-Assembly

Y.-T. Chan, C. N. Moorefield, M. Soler,
*G. R. Newkome** 1768–1771

Unexpected Isolation of a Pentameric Metallomacrocycle from the Fe^{II}-Mediated Complexation of 120° Juxtaposed 2,2′:6′,2′′-Terpyridine Ligands



Pentamer—the black sheep in the family! Fe^{II}-mediated complexation of acetyl-protected, carbohydrate-functionalized 3,5-di(2,2′:6′,2′′-terpyridinyl)arenes possessing a 120° angle between two terpyridines afforded the predesigned hexamer and the unexpected pentamer (see scheme); both formed self-assembled nanofibers.

C−H Activation

M. Kitahara, K. Hirano, H. Tsurugi,
*T. Satoh, M. Miura** 1772–1775

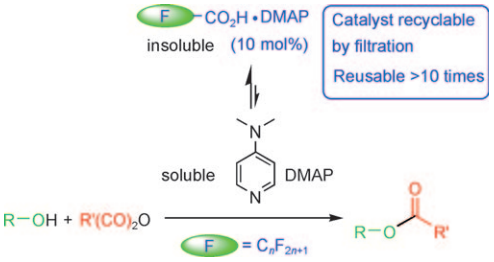
Copper-Mediated Direct Cross-Coupling of 1,3,4-Oxadiazoles and Oxazoles with Terminal Alkynes

The simplest coupling: Copper-mediated direct oxidative cross-coupling of 1,3,4-oxadiazoles and oxazoles with terminal alkynes proceeds through cleavage of sp^2 C−H and sp C−H bonds to furnish the corresponding alkynylazoles in good yields. The reaction is tolerant toward various substitution patterns of substrates and allows the facile construction of azole-core π-conjugated systems.

Green Chemistry

D. Vuluga, J. Legros, B. Crousse,*
D. Bonnet-Delpon 1776–1779

Fluorous 4-*N*,*N*-Dimethylaminopyridine (DMAP) Salts as Simple Recyclable Acylation Catalysts



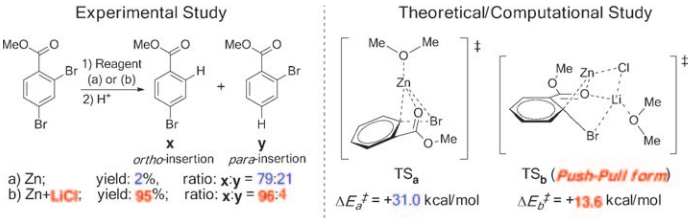
Pass the salt please! A simple fluorous salt of 4-*N*,*N*-dimethylaminopyridine ($C_7F_{15}CO_2H{\cdot}DMAP$) that acts as an effective recyclable organocatalyst for esterification under solvent- and base-free conditions is reported. This catalyst is readily accessible, easy to handle and to recover, and constitutes an attractive alternative for cleaner and safer acylation reactions (see scheme).

CONTENTS

Reaction Mechanisms

C.-Y. Liu, X. Wang, T. Furuyama, S. Yasuike, A. Muranaka, K. Morokuma,* M. Uchiyama** 1780–1784

Reaction Mechanism for the LiCl-Mediated Directed Zinc Insertion: A Computational and Experimental Study



Tired of wondering about the role of LiCl in the DoI reaction of zinc? Kinetic/thermodynamic competitive experiments and DFT calculations were performed to clarify the regioselectivity and reaction mechanism/pathways of lithium chloride-promoted directed zinc insertion into bromobenzenes. The results strongly suggest that the LiCl-containing "push–pull form" transition state (**TS**$_\mathbf{b}$) is formed at an early stage, thus accelerating the reaction rate of zinc insertion. (DoI = directed *ortho* insertion.)

FULL PAPERS

Redox Chemistry

*A. Ambrosi, M. Pumera** . . 1786–1792

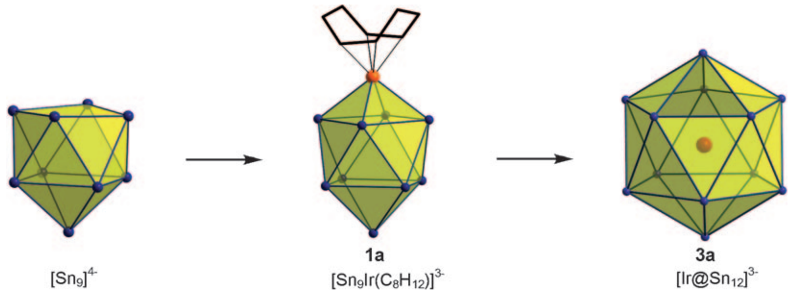
Regulatory Peptides Are Susceptible to Oxidation by Metallic Impurities within Carbon Nanotubes

The not-so-pretty face of carbon nanotubes: The redox properties of the regulatory peptide L-glutathione are affected by the presence of nickel oxide impurities within single-walled carbon nanotubes. Glutathione is a very important peptide, present in all living cells. The level of glutathione regulates higher-order cell systems including redox regulator proteins. Glutathione is also present in skin whiteners, which are often used in Asian countries (see photo).

Intermetalloid Clusters

*J.-Q. Wang, S. Stegmaier, B. Wahl, T. F. Fässler** 1793–1798

Step-by-Step Synthesis of the Endohedral Stannaspherene $[Ir@Sn_{12}]^{3-}$ via the Capped Cluster Anion $[Sn_9Ir(cod)]^{3-}$

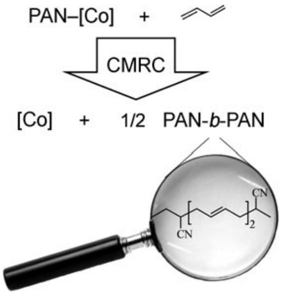


Open to nonmembers: $[Ir@Sn_{12}]^{3-}$ is a unique example of an icosahedral tetrel cluster encapsulating a metal atom that is not a member of Group 10. Single-crystal structure determination shows that the novel Zintl ion cluster has nearly perfect I_h point symmetry. The endohedral $[Ir@Sn_{12}]^{3-}$ cluster was synthesized in two steps (see scheme: blue spheres, Sn atoms; orange spheres, Ir atoms; black line: 1,5-cyclooctadienyl).

Polymerization

A. Debuigne, R. Poli, J. De Winter, P. Laurent, P. Gerbaux, P. Dubois, J.-P. Wathelet, C. Jérôme, C. Detrembleur* .... 1799 – 1811

Cobalt-Mediated Radical Coupling (CMRC): An Unusual Route to Midchain-Functionalized Symmetrical Macromolecules

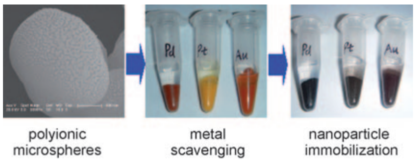


Chemistry under control: A controlled cobalt-mediated radical polymerization and radical coupling reaction (CMRP and CMRC) led to well-defined midchain-functionalized symmetrical polymers. New synthetic possibilities, structure of the coupling products, and the CMRC mechanism were examined through a magnifying glass (see figure; PAN = poly(acrylonitrile)).

Heterogeneous Catalysis

*S. Li, J. Wang, Y. Kou, S. Zhang** .... 1812 – 1818

Ionic-Liquid-Grafted Rigid Poly(*p*-Phenylene) Microspheres: Efficient Heterogeneous Media for Metal Scavenging and Catalysis

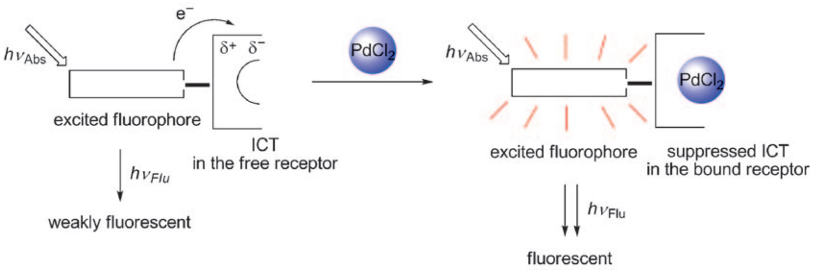


Support your local catalyst! Guanidinium ionic-liquid-grafted rigid poly(*p*-phenylene) microspheres are a suitable scaffold for efficient metal scavenging and nanoparticle immobilization (see figure). The combination of nanoparticles and fragments of ionic liquids on the microsphere surfaces enhance the activity and durability of the catalyst.

Molecular Sensors

*T. Schwarze, W. Mickler, C. Dosche, R. Flehr, T. Klamroth, H.-G. Löhmannsröben, P. Saalfrank, H.-J. Holdt** .... 1819 – 1825

Systematic Investigation of Photoinduced Electron Transfer Controlled by Internal Charge Transfer and Its Consequences for Selective $PdCl_2$ Coordination

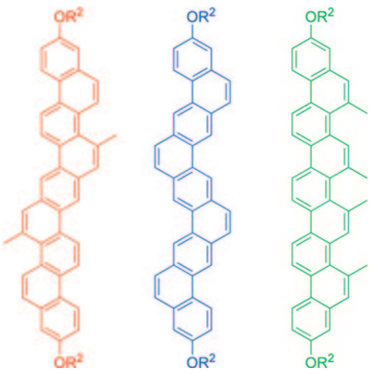


Fluoroionophores consisting of a fluorophore, an alkylene spacer, and a push–pull dithiomaleonitrile receptor were systematically investigated with a view to regulating photoinduced electron transfer by means of intramolecular charge transfer (ICT). The fluorescence properties can be manipulated by varying the fluorophore groups and the spacer length, and fluorescence enhancement on selective complexation of $PdCl_2$ (see scheme) was used to develop a highly sensitive molecular sensor for detecting small quantities of Pd^{II} (ca. 100–1000 ng).

Polyaromatic Oligomers

*T.-A. Chen, T.-J. Lee, M.-Y. Lin, S. M. A. Sohel, E. W.-G. Diau, S.-F. Lush, R.-S. Liu** .... 1826 – 1833

Regiocontrolled Synthesis of Ethene-Bridged *para*-Phenylene Oligomers Based on Pt^{II}- and Ru^{II}-Catalyzed Aromatization



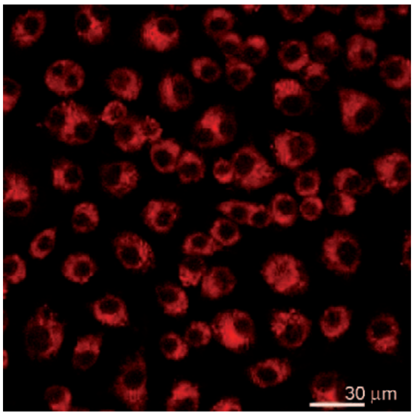
New BPAHs: The regiocontrolled syntheses of ethene-bridged *para*-phenylenes is reported in three distinct classes by using Pt^{II}- and Ru^{II}-catalyzed aromatization (see scheme). The spectra of these regularly growing arrays show a pattern of extensive π conjugation with increasing array sizes, as well as showing that large arrays of these oligomers are prone to twist from planarity.

Fluorescent Probes

*P. Li, T. Xie, X. Duan, F. Yu, X. Wang, B. Tang** .... 1834 – 1840

A New Highly Selective and Sensitive Assay for Fluorescence Imaging of $^{\bullet}$OH in Living Cells: Effectively Avoiding the Interference of Peroxynitrite

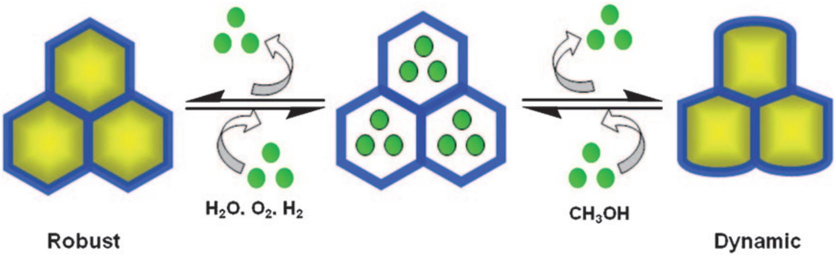
Lighting up radicals: A new nonredox fluorescent probe to realize the imaging of $^{\bullet}$OH in living cells (see image) was designed and synthesized. This probe rapidly responded to $^{\bullet}$OH with a detection limit of 18 pM. It was quite photostable and not very sensitive to the pH value. Other reactive oxygen species and relevant intracellular components did not interfere.



Coordination Networks

*J.-J. Jiang, L. Li, M.-H. Lan, M. Pan, A. Eichhöfer, D. Fenske, C.-Y. Su** .... 1841 – 1848

Thermally Stable Porous Hydrogen-Bonded Coordination Networks Displaying Dual Properties of Robustness and Dynamics upon Guest Uptake

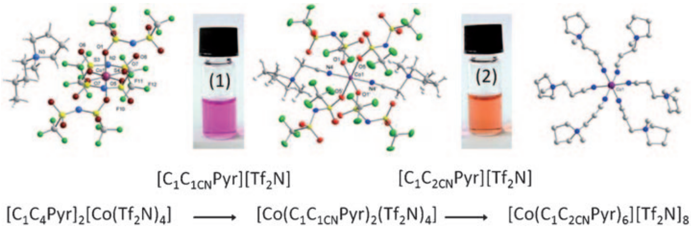


Dual-functional networks: Assembly of monomeric [Ln(ntb)Cl_3] (ntb = tris(benzimidazol-2-ylmethyl)amine) coordination units containing both hydrogen-bond donors and acceptors results in the formation of hydrogen-bonded networks sustained by N−H···Cl or C−H···Cl hydrogen bonds. The polymorphism in the hydrogen-bonded networks gives rise to different channels that show differentiating adsorption of guests.

Ionic Liquids

P. Nockemann, M. Pellens, K. Van Hecke, L. Van Meervelt, J. Wouters, B. Thijs, E. Vanecht, T. N. Parac-Vogt, H. Mehdi, S. Schaltin, J. Fransaer, S. Zahn, B. Kirchner, K. Binnemans* .... 1849 – 1858

Cobalt(II) Complexes of Nitrile-Functionalized Ionic Liquids



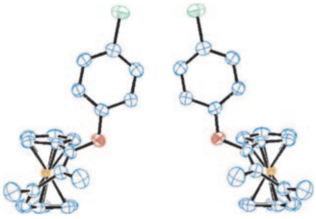
Watch this space! The coordinating abilities of nitrile-functionalized pyrrolidinium ionic liquids toward cobalt(II) ions depend on the alkyl spacer length between the nitrogen atom of the pyrrolidinium core and the nitrile functional group (see figure). The crystal structures of the cobalt(II) solvates shown give an insight into the coordination chemistry of these ionic liquids.

Metallocenes

*J. Ma, B. Kühn, T. Hackl, H. Butenschön** .... 1859 – 1870

Transannular Addition of Phenols to 1,1′-Dialkynylferrocenes: Unanticipated Formation of Phenoxy[4]ferrocenophanedienes

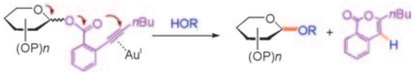
No alkyne metathesis was observed with 1,1′-dialkynylferrocenes using the Mortreux catalyst system. Instead, phenols react in the presence or absence of [$Mo(CO)_6$] with formation of phenoxy[4]ferrocenophanedienes (see figure), presumably via a vinyl cation intermediate.



Glycosylation

*Y. Li, X. Yang, Y. Liu, C. Zhu, Y. Yang, B. Yu** 1871–1882

Gold(I)-Catalyzed Glycosylation with Glycosyl *ortho*-Alkynylbenzoates as Donors: General Scope and Application in the Synthesis of a Cyclic Triterpene Saponin

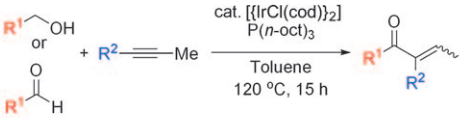


A rich, powerful donor: With an activation mechanism and reaction conditions totally different to previous glycosylation reactions, shelf-stable glycosyl *ortho*-alkynylbenzoates are versatile, efficacious, and generally applicable when used as donors in the present gold(I)-catalyzed protocol (see scheme).

Intermolecular Hydroacylation

S. Hatanaka, Y. Obora, Y. Ishii** 1883–1888

Iridium-Catalyzed Coupling Reaction of Primary Alcohols with 2-Alkynes Leading to Hydroacylation Products

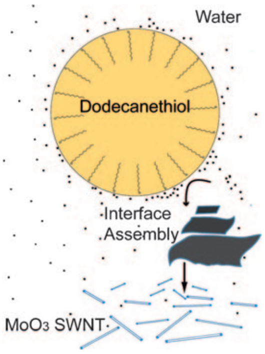


It's intermolecular! A novel iridium-catalyzed transformation of primary alcohols with 2-alkynes afforded hydroacylation products (see scheme). The experimental mechanistic investigation revealed that the reaction proceeded through the initial formation of homoallylic alcohols followed by dehydrogenation and isomerization, which leads to the hydroacylation products.

Nanotubes

*S. Hu, X. Ling, T. Lan, X. Wang** 1889–1896

Cluster-Based Self-Assembly Route toward MoO_3 Single-Walled Nanotubes

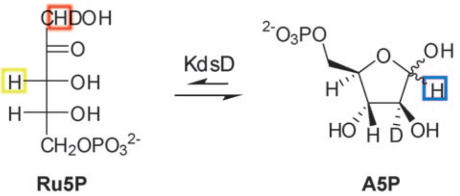


Construction site: Single-walled MoO_3 nanotubes have been synthesized in a water–thiol two-phase system (see figure) and the conditions and mechanism for their production carefully discussed. Based on these results, a new mechanistic viewpoint is presented, combining the traditional synthetic chemistry of nanomaterials with that of polyoxometalates.

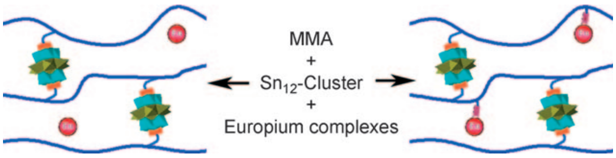
Enzyme Inhibitors

*C. Airoldi, S. Sommaruga, S. Merlo, P. Sperandeo, L. Cipolla, A. Polissi, F. Nicotra** 1897–1902

Targeting Bacterial Membranes: NMR Spectroscopy Characterization of Substrate Recognition and Binding Requirements of D-Arabinose-5-Phosphate Isomerase



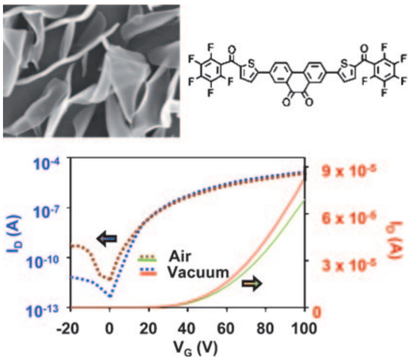
API substrate binding studies: Arabinose-5-phosphate isomerase (API) is an aldo–keto isomerase catalyzing the reversible isomerization of D-ribulose-5-phosphate (Ru5P) to D-arabinose-5-phosphate (A5P), and has an essential role in the survival of Gram-negative bacteria. By exploiting saturation transfer difference (STD) NMR spectroscopy, the structural requirements necessary for KdsD (an API enzyme) substrate recognition and binding were identified with the aim of designing new API inhibitors (see scheme).



Will Eu enter the matrix? Novel hybrid materials doped with europium complexes, using polymer-based oxo–hydroxo butyltin clusters as nano building blocks, have been constructed (see figure), and their structures and optical properties have been investigated.

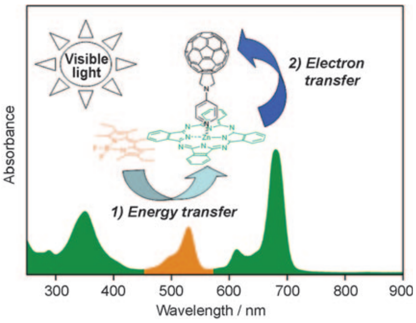
Luminescence

Get those electrons moving! In this contribution we report a family of phenacyl–thiophene-based oligomer (see figure) and polymer semiconductors exhibiting solution-processed electron mobility (μ_e) up to $\approx 0.3\ \mathrm{cm^2V^{-1}s^{-1}}$ and an air-stable μ_e of $0.015\ \mathrm{cm^2V^{-1}s^{-1}}$.

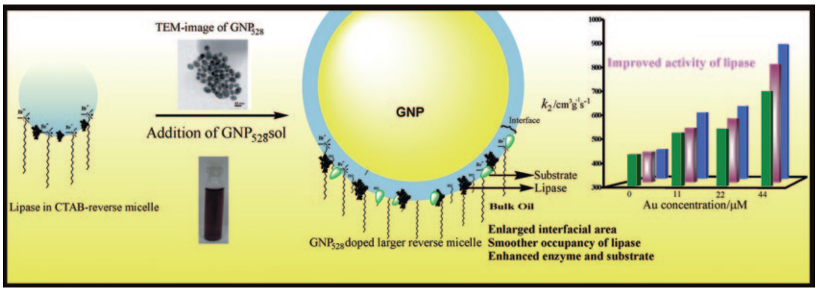


Semiconductors

Long live the hybrid! The synthesis and photophysical properties of a peripherally substituted Bodipy–zinc phthalocyanine dyad that absorbs over much of the visible spectral region are described. Axial coordination of a C_{60} derivative at phthalocyanine affords an electron donor–acceptor hybrid that, upon photoexcitation, undergoes a sequence of energy- and electron-transfer reactions (see figure).



Photochemistry



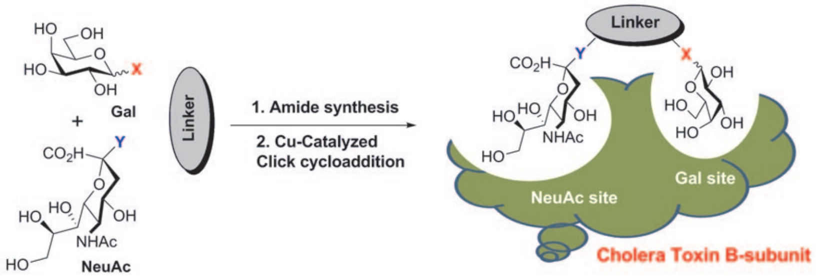
Enhanced performance: The activity of lipase is enhanced in cationic reverse micelles doped with gold nanoparticles (GNPs; see picture). The size and concentration of the GNPs were varied to understand their effect on lipase activity. In the presence of larger-sized GNPs (ca. 15–20 nm), the activity of lipase increases up to 2.5-fold higher than in cetyltrimethylammonium bromide (CTAB) reverse micelles without GNPs. This result becomes more significant because GNPs activate lipase selectively in the reverse micelles but deactivate the enzyme in water.

Microemulsions

Carbohydrate Mimics

*P. Cheshev, L. Morelli, M. Marchesi, Č. Podlipnik, M. Bergström, A. Bernardi** .... 1951 – 1967

Synthesis and Affinity Evaluation of a Small Library of Bidentate Cholera Toxin Ligands: Towards Nonhydrolyzable Ganglioside Mimics

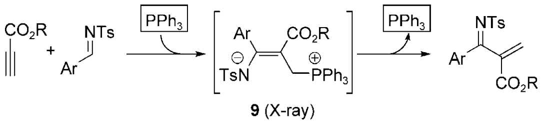


Toxic clean up: Novel cholera toxin ligands were identified by synthesizing and screening a library of bidentate molecules containing both a galactose and a sialic acid fragment (see figure).

Phosphane Catalysis

*H. Liu, Q. Zhang, L. Wang, X. Tong** .... 1968 – 1972

PPh_3-Catalyzed Reactions of Alkyl Propiolates with *N*-Tosylimines: A Facile Synthesis of Alkyl 2-[aryl-(tosylimino)methyl]acrylate and an Insight into the Reaction Mechanism

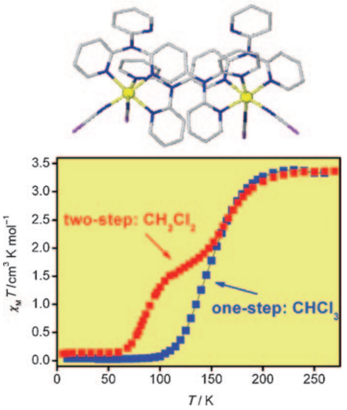


Phosphanomenal! A new PPh_3-catalyzed synthesis of alkyl 2-[aryl(tosylimino)methyl]acrylate from propiolates and *N*-tosylimines has been developed (see scheme). Deuterium-labelling experiments show that the reaction mechanism involves several hydrogen-transfer processes, which strongly rely on the nature of the reaction media. The stable phosphonium–enamine zwitterion, which has an important role in the catalytic cycle, was isolated and characterised by X-ray analysis.

Dinuclear Spin Crossover

*J. J. M. Amoore, S. M. Neville, B. Moubaraki, S. S. Iremonger, K. S. Murray, J.-F. Létard, C. J. Kepert** .... 1973 – 1982

Thermal- and Light-Induced Spin Crossover in a Guest-Dependent Dinuclear Iron(II) System

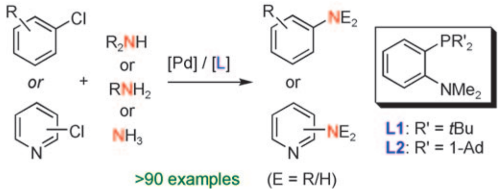


A question of solvent: The thermal- and light-induced spin-crossover properties of the dinuclear iron(II) complex shown can be controlled by variation of the amount and type of solvent molecules present in the crystal lattice. Either a one- or two-step spin transition can be observed based on solvent type. Furthermore, the photomagnetic properties can be turned 'on' or 'off' by solvent manipulation.

Amination Catalysts

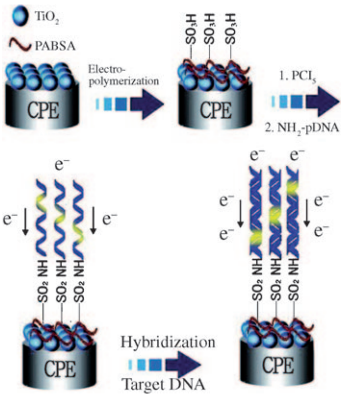
*R. J. Lundgren, A. Sappong-Kumankumah, M. Stradiotto** .... 1983 – 1991

A Highly Versatile Catalyst System for the Cross-Coupling of Aryl Chlorides and Amines



New amination catalysts: A highly active and widely applicable catalyst system for the cross-coupling of aryl chlorides to amines has been developed by employing the structurally simple and robust ligands **L1** and **L2** (see graphic). Suitable amine partners include primary and secondary aryl and alkyl amines, imines, hydrazones, lithium amide, and ammonia, with typical catalyst loadings of 1–0.02 mol % Pd.

Look, no indicator! The electrochemical signal changes of conductive PABSA/TiO_2 nanosheet membranes can be used to detect DNA hybridization directly. DNA immobilization and hybridization causes the DNA/PABSA/TiO_2 hybrid to undergo changes to its conformational, electroconductive, and interfacial properties, which were monitored by impedance measurements and adopted as signals for indicator-free DNA detection (see figure).



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