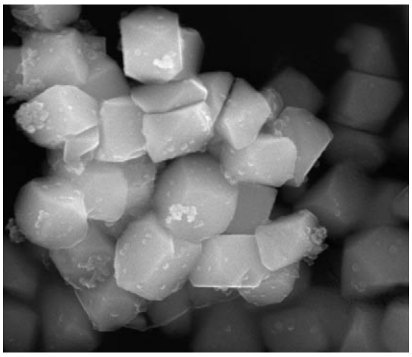
CONCEPTS

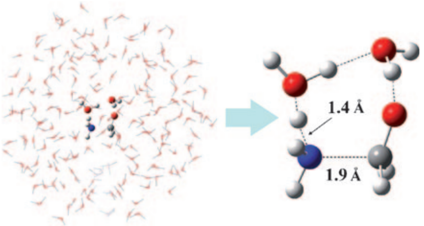
Far beyond lab curiosities: The synthesis of kinetically stabilized (sterically demanding substituents) and electronically stabilized (base stabilization) low-valent complexes of Groups 2, 12, 13, and 15 are summarized as well as their potential applications as selective reductants, unusual ligands in coordination chemistry, and as novel precursors in material sciences (see graphic).



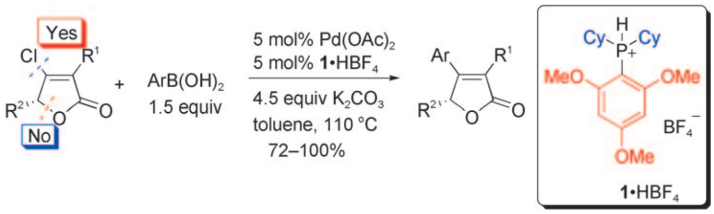
Organometallic Chemistry

COMMUNICATIONS

Zwitterionic intermediate? The results of fragment molecular orbital molecular dynamics simulations clearly revealed that amination of formaldehyde with ammonia at neutral pH proceeds by a stepwise mechanism through a zwitterionic intermediate in water (see figure).

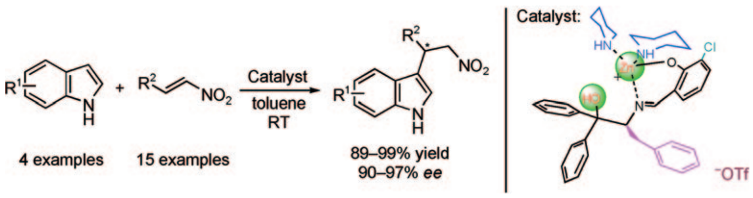


Reaction Mechanisms



Selective coupling: A readily available monophosphine HBF_4 salt, **1**·HBF_4, was applied to the highly selective coupling of the inert C–Cl bond in optically active β-chlorobutenolides in preference to the more reactive lactonic, allylic C–O bond in the presence of $Pd(OAc)_2$ as the catalyst.

Organochlorides



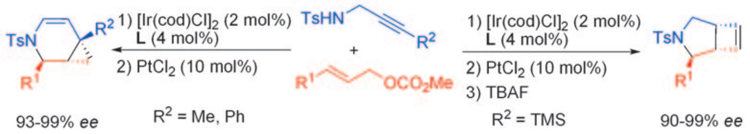
A role beyond base: A highly efficient, asymmetric Friedel–Crafts alkylation of indoles with nitroalkenes is presented that uses simple nitrogen compounds combined with Schiff base zinc(II) complexes as bifunctional catalysts (see scheme). The nitrogen compounds here play a crucial role as ligands as well as their traditional role as bases.

Asymmetric Combinatorial Catalysis

Asymmetric Synthesis

*J.-B. Xia, W.-B. Liu, T.-M. Wang, S.-L. You** .... 6442 – 6446

Enantioselective Synthesis of 3-Azabicyclo[4.1.0]heptenes and 3-Azabicyclo[3.2.0]heptenes by Ir-Catalyzed Asymmetric Allylic Amination of *N*-Tosyl Propynylamine and Pt-Catalyzed Cycloisomerization

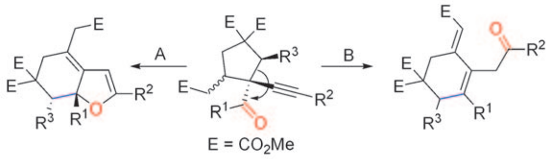


Irresistible! Highly regio- and enantioselective Ir-catalyzed allylic amination reactions of *N*-tosyl propynylamines have been realized. The resulting *N*-tosyl allylpropynylamines were transformed into highly enantioenriched 3-azabicyclo[4.1.0]heptenes and 3-azabicyclo[3.2.0]heptenes, respectively, in the presence of $PtCl_2$ (see scheme; Ts = tosyl, cod = 1,5-cyclooctadiene, TBAF = tetrabutylammonium fluoride, TMS = trimethylsilyl).

1,2-Alkyl Migration

*W. Li, Y. Li, J. Zhang** ..... 6447 – 6450

Gold-Catalyzed Domino Reactions Consisting of Regio- and Stereoselective 1,2-Alkyl Migration



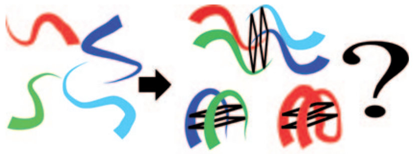
Conditions A: IPrAuCl/AgOMs (5 mol%), DCE, 80 °C
Conditions B: IPrAuCl/AgPF_6 (5 mol%), DCE, 80 °C

Good as gold: A cationic gold(I)-catalyzed domino reaction involving highly regio- and stereoselective 1,2-alkyl migration and heterocyclization or oxygen transfer was developed, in which the counteranion of the gold catalyst could control the product selectivity (see scheme; DCE = 1,2-dichloroethane, IPrAuCl = [1,3-bis(2,6-diisopropylphenyl)-1*H*-imidazol-2(3*H*)-ylidene]gold(I) chloride).

Analytical Methods

P. Groves, M. Webba da Silva** .... 6451 – 6453

Rapid Stoichiometric Analysis of G-Quadruplexes in Solution

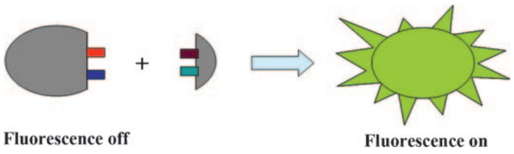


Spectroscopy on a G-string! Currently there is strong interest in the determination of the topology of nucleic acid G-quadruplexes due to their biotechnological potential and biological significance. This requires the evaluation of the strand oligomerization level. Here we demonstrate a method for routine assessment of the stoichiometry of nucleic acid quadruplexes in aqueous solutions.

Fluorescent Probes

W. Lin, X. Cao, L. Yuan, Y. Ding* .... 6454 – 6457

Double Functional Group Transformations for Fluorescent Probe Construction: A Fluorescence Turn-On Probe for Thioureas



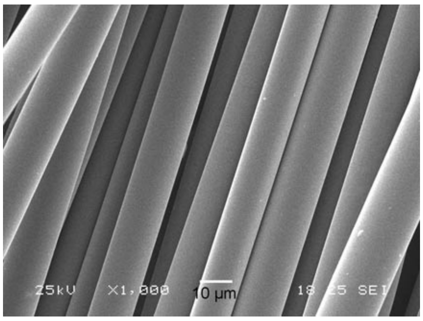
Double up: We have developed the first fluorescence turn-on probe for thioureas by the double functional group transformation strategy (see graphic). The probe is highly selective for thioureas over other structurally and chemically related species, which demonstrates the advantage of the double functional group transformation approach. Furthermore, we have shown that the probe could be employed to monitor thiourea in both water and soil samples.

Polymers

Y. Tang, J. Wang, X. Li, Z. Xie, H. Wang, W. Li, X. Wang* . . 6458 – 6462

Polymer-Derived SiBN Fiber for High-Temperature Structural/Functional Applications

Spun out to dry: Polymer-derived SiBN ceramic fiber, with excellent and thermally stable dielectric properties, resists crystallization up to 1700 and 1400 °C in nitrogen and in air, respectively, while retaining most of the room-temperature mechanical properties (see figure). The desirable combination of properties enables SiBN fiber to be a candidate for use as reinforcement in high-temperature, radar-wave-transparent ceramic composites.

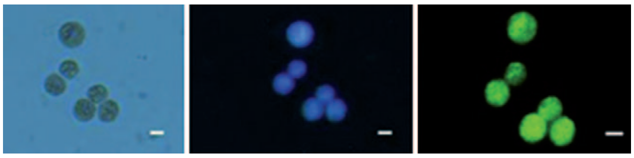


FULL PAPERS

Cell Imaging

C. Song, Z. Ye, G. Wang, J. Yuan, Y. Guan** . . . . 6464 – 6472

A Lanthanide-Complex-Based Ratiometric Luminescent Probe Specific for Peroxynitrite



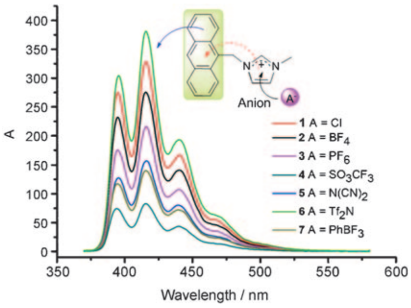
Shedding light on ONOO$^-$: A unique lanthanide-complex-based ratiometric luminescence probe, specific for peroxynitrite, has been synthesized and the performance of the probe for luminescent imaging of ONOO$^-$ in living cells was investigated (see figure). The new probe, with good ratiometric and time-gated capacities, provides a novel strategy for the luminescent imaging detection of ONOO$^-$ in living cells.

Functionalized Ionic Liquids

*Z. Fei, D.-R. Zhu, X. Yang, L. Meng, Q. Lu, W. H. Ang, R. Scopelliti, C. G. Hartinger, P. J. Dyson** . . . . 6473 – 6481

An Internal Fluorescent Probe Based on Anthracene to Evaluate Cation–Anion Interactions in Imidazolium Salts

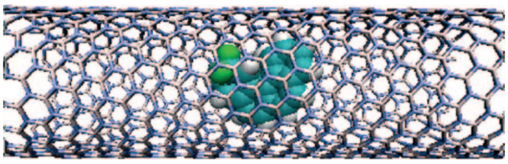
Cation–anion interactions: An anthracene moiety that has been incorporated into an imidazolium unit acts as an internal probe revealing insights into cation–anion interactions in the solid state and in solution (see graphic).



Molecular Dynamics

Z. G. Wang, C. L. Wang, P. Xiu, W. P. Qi, Y. S. Tu, Y. M. Shen, R. Zhou, R. Q. Zhang, H. P. Fang** 6482 – 6487

Size Dependence of Nanoscale Confinement on Chiral Transformation

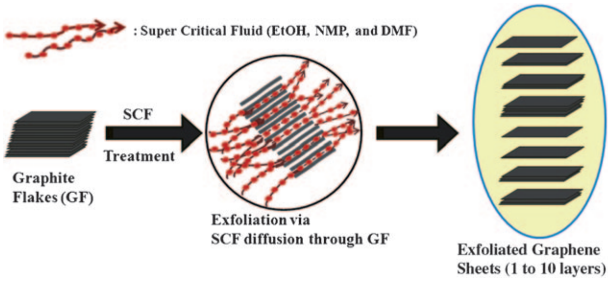


Size matters! The chiral transition of difluorobenzo[*c*]phenanthrene in a boron nitride nanotube occurs under orientation transformation of the molecules from a state parallel to the nanotube axis to a state almost perpendicular to the nanotube axis. Furthermore, the interactions between the chiral molecule and the nanochannel can characterize the chiral transition between these two conformational states.

Graphene Sheets

D. Rangappa, K. Sone, M. Wang, U. K. Gautam, D. Golberg, H. Itoh, M. Ichihara, I. Honma** . . . . 6488 – 6494

Rapid and Direct Conversion of Graphite Crystals into High-Yielding, Good-Quality Graphene by Supercritical Fluid Exfoliation

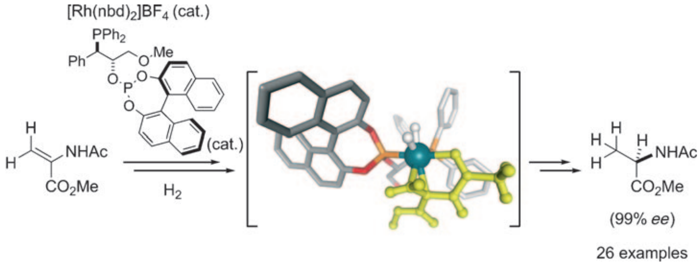


Smooth exfoliation: We have developed a novel supercritical fluid (SCF) exfoliation process for high-quality, gram-scale, processable graphene production. Our procedure is simple, fast, and involves direct one-pot exfoliation of graphite crystals down to a few (1–10) layered graphene sheets by SCF exfoliation (see figure). Direct conversion of graphite crystals to a high yield of graphene sheets is possible because of the high diffusivity and solvating power of SCFs.

Asymmetric Catalysis

H. Fernández-Pérez, S. M. A. Donald, I. J. Munslow, J. Benet-Buchholz, F. Maseras, A. Vidal-Ferran** . . . . 6495 – 6508

Highly Modular P–OP Ligands for Asymmetric Hydrogenation: Synthesis, Catalytic Activity, and Mechanism

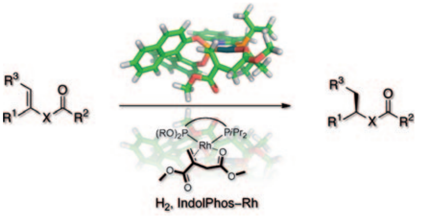


Hop on P–OP: Modular P–OP ligands (see figure), easily prepared in two synthetic steps, serve as highly efficient catalysts in the Rh-mediated asymmetric hydrogenation of functionalized alkenes.

Asymmetric Catalysis

*J. Wassenaar, M. Kuil, M. Lutz, A. L. Spek, J. N. H. Reek** 6509 – 6517

Asymmetric Hydrogenation with Highly Active IndolPhos–Rh Catalysts: Kinetics and Reaction Mechanism

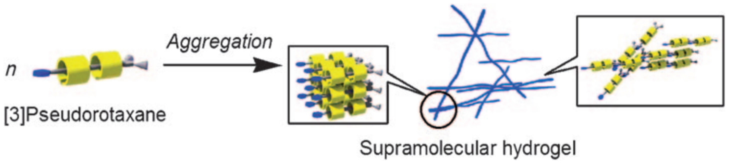


Just lock it! The reaction mechanism of the IndolPhos–Rh-catalyzed asymmetric hydrogenation of prochiral olefins has been investigated (see scheme). Unlike C_2-symmetric diphosphine ligands, the catalysts generated from this C_1-symmetric hybrid phosphine–phosphoramidite ligand seem to follow a lock-and-key mechanism in which the major diastereomeric substrate–catalyst complex leads to the product.

Supramolecular Chemistry

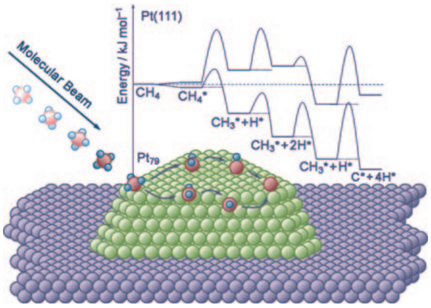
*T. Taira, Y. Suzaki, K. Osakada** . . . . 6518 – 6529

Hydrogels Composed of Organic Amphiphiles and α-Cyclodextrin: Supramolecular Networks of Their Pseudorotaxanes in Aqueous Media



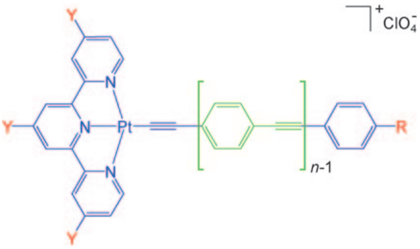
Supramolecular polymers are formed by aggregation of pseudorotaxanes formed from *N*-alkyl pyridinium compounds and α-cyclodextrin (α-CD), which occurs through interaction between α-CDs and π–π stacking of the alkyl pyridinium moieties (see schematic). The network structure of aggregated pseudorotaxanes forms a hydrogel below the sol–gel phase-transition temperature. Formation and degradation of the hydrogel are controlled by temperature and the presence of denaturing agents such as urea and phloroglucinol.

A fast run over the edge: Both the thermodynamics and the kinetics of CH_4 dehydrogenation to CH or C on Pt model catalysts are critically affected by the presence of low-coordination sites, such as edges and corners between facets, as shown by a combination of supersonic molecular beam and high-resolution photoelectron spectroscopy experiments with density functional calculations (see figure).



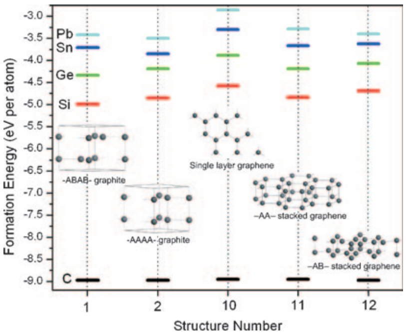
Methane Activation

Longer chain always leads to a redshift in energy? No! Platinum(II) complexes bearing terpyridine and acetylide ligands with alkyl and aryl groups have been synthesized and characterized both spectroscopically and theoretically. In particular, the chain length effect of $[Pt(tBu_3tpy)\{C{\equiv}C(C_6H_4C{\equiv}C)_{n-1}C_6H_4\text{-X-}4\}]^+$ (tBu_3tpy = 4,4′,4″-tri-*tert*-butyl-2,2′:6′,2″-terpyridine, X = H and NMe_2, Me = methyl) has been investigated (see graphic).



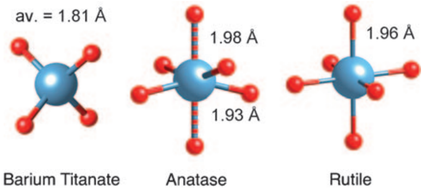
Platinum Chemistry

1D to 2D to 3D: What are the relative energies of various stable and metastable structures of the Group 14 elements in one, two, and three dimensions (see figure)? Why do they adopt the structures that they do? Why are Sn and Pb relatively low melting? These questions are made very much real for carbon by the synthesis and characterization of fullerenes, nanotubes, and graphene sheets. Will one find such structures for Si, Ge, Sn, and Pb? Will they be kinetically persistent? This paper provides some answers.



Group 14 Elements

The shape of things: Continuous shape measures (see picture) describe the pathways for ligand association/dissociation reactions and provide relevant structural information on secondary coordination and ill-defined coordination numbers.

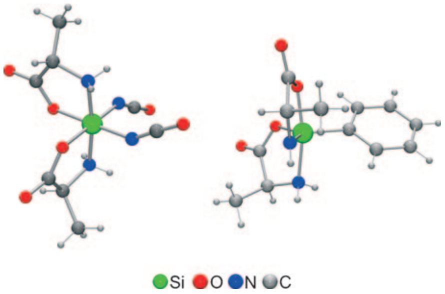


Continuous Shape Measures

Coordination Chemistry

*S. Cota, M. Beyer, R. Bertermann, C. Burschka, K. Götz, M. Kaupp, R. Tacke** .... 6582 – 6589

Neutral Penta- and Hexacoordinate Silicon(IV) Complexes Containing Two Bidentate Ligands Derived from the α-Amino Acids (*S*)-Alanine, (*S*)-Phenylalanine, and (*S*)-*tert*-Leucine

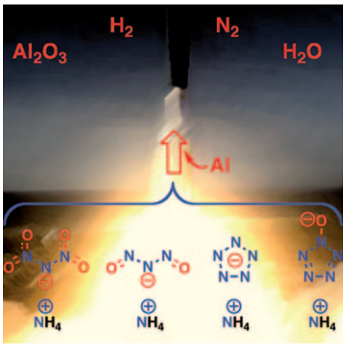


Silicon valley: Neutral penta- and hexacoordinate silicon(IV) complexes containing two bidentate ligands (see figure) derived from the α-amino acids (*S*)-alanine, (*S*)-phenylalanine, and (*S*)-*tert*-leucine have been synthesized and structurally characterized by single-crystal X-ray diffraction and NMR spectroscopy.

Rocket Propellants

*M. Rahm, T. Brinck** .... 6590 – 6600

Kinetic Stability and Propellant Performance of Green Energetic Materials

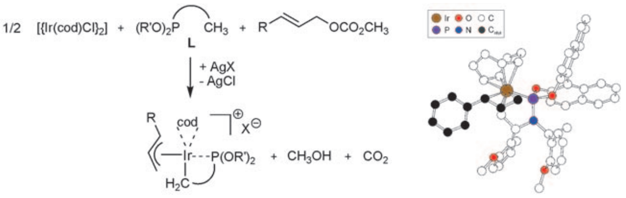


A green route to space: Performance characteristics, physical properties, and decomposition kinetics of dinitramide, trinitrogen dioxide, pentazole, and oxopentazole anions (see graphic) have been estimated by using modern quantum chemical calculations. These anions show promise as future high-energy-density materials.

Asymmetric Catalysis

*J. A. Raskatov, S. Spiess, C. Gnamm, K. Brödner, F. Rominger, G. Helmchen** .... 6601 – 6615

Ir-Catalysed Asymmetric Allylic Substitutions with Cyclometalated (Phosphoramidite)Ir Complexes—Resting States, Catalytically Active (π-Allyl)Ir Complexes and Computational Exploration

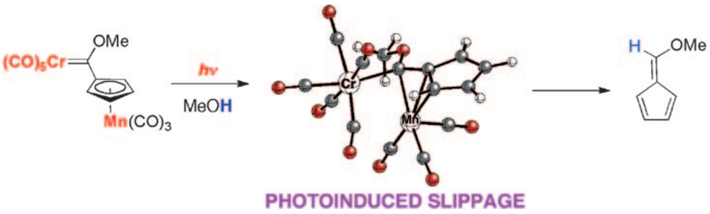


A knotty problem: The mechanism of the Ir-catalysed allylic substitution with phosphoramidites as ligands is complicated because of a reversible C–H activation step. In this context, a novel, one-pot procedure for the preparation of (π-allyl)Ir complexes was developed (see graphic). DFT calculations on the allyl complexes, transition states of the allylic substitution and product olefin complexes were carried out.

Carbene Complexes

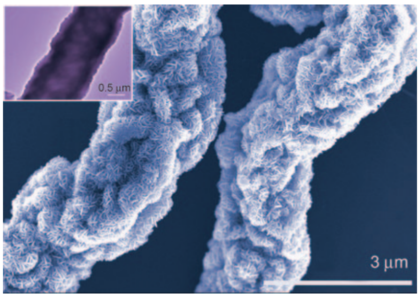
M. L. Lage, I. Fernández, M. J. Mancheño, M. Gómez-Gallego, M. A. Sierra** .... 6616 – 6624

The Electronic Structure and Photochemistry of Group 6 Bimetallic (Fischer) Carbene Complexes: Beyond the Photocarbonylation Reaction

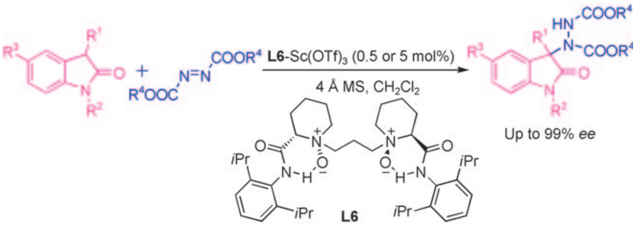


Given the slip: A new photochemical reaction is observed for cyclopentadienylmanganese-substituted Fischer carbenes. The reaction proceeds through a previously unreported photoslippage process (see scheme), and renders fulvenes as the only reaction products. Both computational and experimental results confirm the proposed mechanism.

The worm turns! The preparation of exquisite hierarchical worm-like $Co_{1-x}S$ ($x=0.75$) microtubes (see figure) by a one-pot complex–surfactant-assisted hydrothermal method is achieved for the first time. The hierarchical structures of the microtube wall are assembled from interleaving hexagonal nanoplates that have a side length of about 90 nm and a thickness of 22 nm.



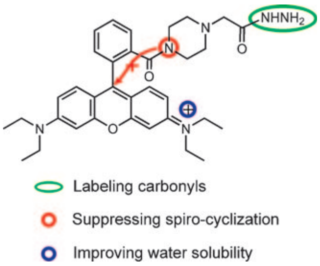
Cobalt Sulfide



Animated amination: An α-amination of 3-substituted oxindoles with azodicarboxylates catalyzed by a chiral Sc-$(OTf)_3$/*N*,*N*′-dioxide complex has been developed to afford the corresponding 3-amino-2-oxindole derivatives in high yields and with excellent enantioselectivities (see scheme; Tf: triflate; MS: molecular sieves). The procedure can tolerate a relatively wide range of substrates, and excellent results (92–96 % *ee*) can be obtained, even with a catalyst loading of 0.5 mol % under mild conditions.

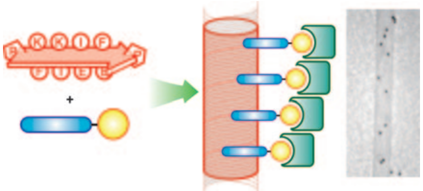
Asymmetric Catalysis

Making a splash! A new water-soluble reagent, rhodamine B piperazinoacetohydrazine, with improved spectroscopic and reaction properties (see scheme) has been designed, synthesized, and characterized for pyruvic acid labeling.



Biosensors

Anchors away! Small bifunctional anchors connecting sophisticated peptide nanofibers with proteins open up a field of nanomaterial engineering in peptide chemistry. The designed anchors, which have hydrophobic (alkyl and dipeptide) and binding (biotin and iminodiacetate) units, can arrange a protein along the striation of the peptide fibers (see figure).

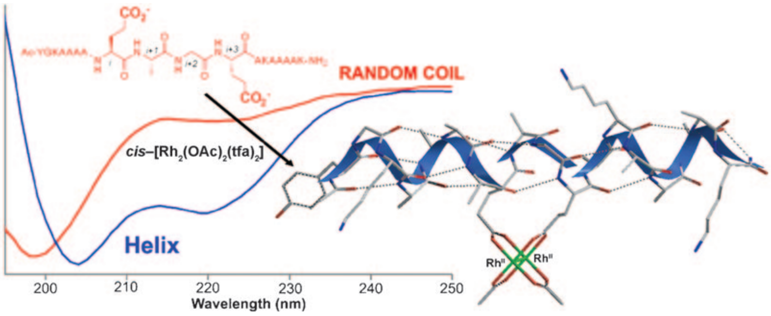


Nanomaterials

Dirohodium Metallopeptide Helices

A. N. Zaykov, B. V. Popp,
*Z. T. Ball** .... 6651 – 6659

Helix Induction by Dirhodium: Access to Biocompatible Metallopeptides with Defined Secondary Structure

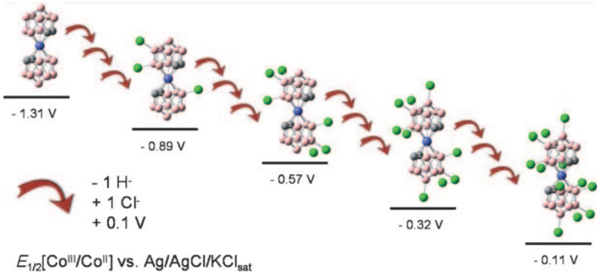


Helix or no helix: Dirhodium metallopeptides (see picture), formed from a reactive dirhodium metal complex and a natural polypeptide, have strong helix-inducing or helix-breaking properties, depending on the peptide sequence and the coordination geometry. One dirhodium metallopeptide exhibits stability in serum and low toxicity toward mammalian cells.

Redox Chemistry

P. González-Cardoso, A.-I. Stoica,
P. Farràs, A. Pepiol, C. Viñas,
*F. Teixidor** .... 6660 – 6665

Additive Tuning of Redox Potential in Metallacarboranes by Sequential Halogen Substitution

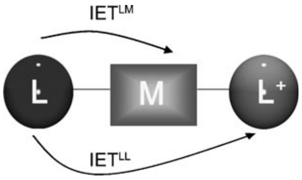


It all adds up! The first artificially made set of electron acceptors derived from a unique platform, Cs[3,3′-Co-$(C_2B_9H_{11})_2$], each differing from the predecessor by a fixed potential, is presented. The sequence of electron acceptors is made by substituting one, two or more hydrogen atoms with chlorine atoms. The effect is additive so that each substitution implies, on average, a 0.1 V anodic shift.

Electron Transfer

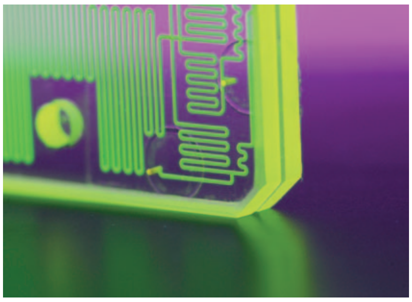
E. Evangelio, M.-L. Bonnet,
M. Cabañas, M. Nakano, J.-P. Sutter,
A. Dei, V. Robert,
*D. Ruiz-Molina** .... 6666 – 6677

Coexistence of Two Thermally Induced Intramolecular Electron Transfer Processes in a Series of Metal Complexes [M(Cat-N-BQ)(Cat-N-SQ)]/[M(Cat-N-BQ)$_2$] (M = Co, Fe, and Ni) bearing Non-Innocent Catechol-Based Ligands: A Combined Experimental and Theoretical Study



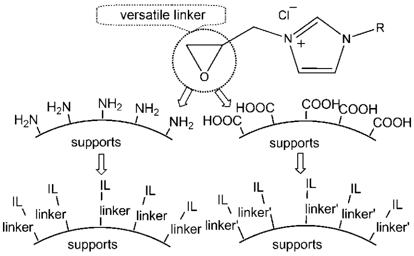
One complex, different processes: The different intermolecular electron transfer (IET) processes of a series of [M-(Cat-N-BQ)(Cat-N-SQ)]/[M(Cat-N-BQ)$_2$] complexes (in which M = Co, Fe, and Ni, and Cat-N-BQ and Cat-N-SQ denote the mono- or dinegative radical forms of the tridentate Schiff base ligand 3,5-di-*tert*-butyl-1,2-quinone-1-(2-hydroxy-3,5-di-*tert*-butylphenyl)-imine, respectively) have been studied by variable-temperature UV/Vis and NMR spectroscopies, and theoretical calculations. Depending on the metal ion, different behavior is observed.

Small streams: The sequential automated generation and further reactions of 3-hydroxymethylindoles in continuous-flow microreactors (see picture) are described. A diverse set of transformations, including magnesiations, electrophile trapping and acid-catalysed nucleophilic displacements, were readily achieved. The synthetic flow strategies could be coupled with a continuous liquid–liquid extraction workup protocol.



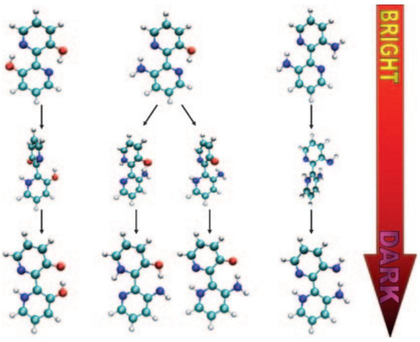
Continuous Flow Microreactors

Tied down but still active: By using the glycidyl group as a versatile and effective linker, glycidyl-containing ionic liquids (ILs) can be grafted onto both organic and inorganic supports (see scheme). 1-Glycidylbutylimidazolium chloride was successfully grafted onto polymer and silica supports functionalized with amino and carboxyl groups, respectively. All of the resultant polymer- and silica-based catalysts displayed high efficiency for CO_2 cycloaddition reactions with epoxides.



Heterogeneous Catalysis

Photomemory devices: The photochemical behavior of three isoelectronic compounds, [2,2′-bipyridyl]-3,3′-diamine, [2,2′-bipyridyl]-3,3′-diol, and the hybrid [2,2′-bipyridyl]-3-amine-3′-ol (see figure), has been theoretically analyzed to assess their potential applicability as photomemory devices. Other, more speculative, potential applications are also envisaged.



Photochemistry of Bipyridines

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