The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:

A. Scarso, L. Pellizzaro, O. De Lucchi, A. Linden, F. Fabris**
Gas Hosting in Enantiopure Self-Assembled Oximes

*S. Wittrock, T. Becker, H. Kunz**
Synthetic Vaccines from Tumor-Associated Glycopeptide Antigens by Immunocompatible Linking to Bovine Serum Albumin through Thioether Formation

M. Manoli, R. D. L. Johnstone, S. Parsons, M. Murrie, M. Affronte, M. Evangelisti, E. K. Brechin**
A Ferromagnetic Mixed-Valent Mn Supertetrahedron: Towards Low-Temperature Magnetic Refrigeration with Molecular Clusters

X. Lou, G. Zhang, I. Herrera, R. Kinach, O. Ornatsky, V. Baranov, M. Nitz,* M. A. Winnik**
Polymer-Based Elemental Tags for Sensitive Bioassays

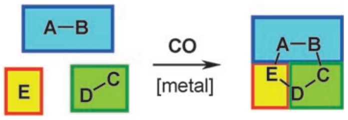
*Y. Sawada, K. Matsumoto, T. Katsuki**
Titanium-Catalyzed Asymmetric Epoxidation of Nonactivated Olefins with Hydrogen Peroxide

Obituary

Books

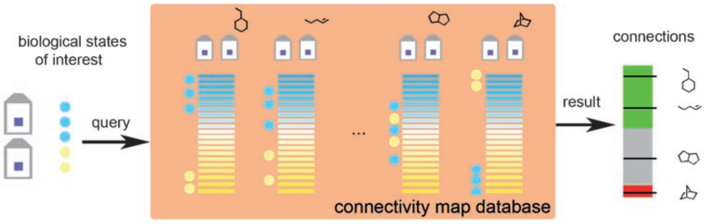
Highlights

Heterocyclic Chemistry



An assembly line for heterocycles: Multicomponent reactions have become a highly valuable tool for the generation of compound libraries particularly of heterocyclic drug candidates. In particular, metal-assisted transformations have enabled the further extension of established methods and development of new strategies. This Highlight presents some innovative examples in which carbon monoxide is used to generate diverse heterocycles.

Small-Molecule Profiles



Let's look at a map: Significant improvements in the analysis of gene-expression data and of large data sets have led to the development of the so-called "connectivity map", an open database of profiles of small molecules (gene-expression patterns) used to clarify the connections between genes, diseases, and drugs.

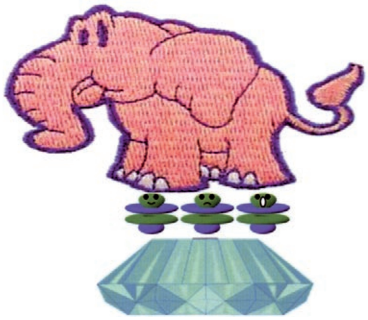
Reviews

High-Pressure Chemistry

W. Grochala,* R. Hoffmann,* J. Feng,*
N. W. Ashcroft* ______ **3620–3642**

The Chemical Imagination at Work in *Very* Tight Places

Extreme chemistry: There is a place for chemical intuition and bonding ideas in the structure and electronics of matter under high pressure. When increased density is the only imperative, van der Waals space is first squeezed out. This step is followed by an increase in coordination (often involving multicenter electron-deficient or electron-rich bonding), a differential compression of anions, metallization, Peierls distortions, and a regime of unusual packing and correlation effects.

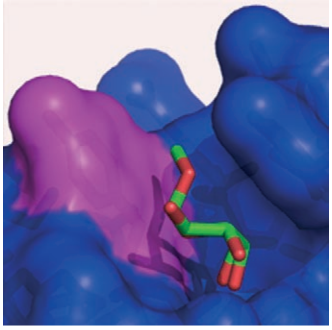


Communications

Sugar–Aromatic Complexes

J. Screen, E. C. Stanca-Kaposta,
D. P. Gamblin, B. Liu, N. A. Macleod,
L. C. Snoek,* B. G. Davis,*
J. P. Simons* ______ **3644–3648**

IR-Spectral Signatures of Aromatic–Sugar Complexes: Probing Carbohydrate–Protein Interactions

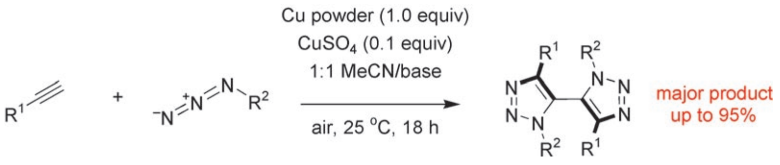


Key interactions: Sugar–arene complexes have been created in molecular-beam experiments and observed by IR ion-dip spectroscopy in the gas phase. These complexes are powerful models of the selective recognition seen in protein–sugar complexes, for example between the galactose-specific lectin from *Artocarpus hirsute* and MeGal (see picture).

Click Chemistry

Y. Angell, K. Burgess* ______ **3649–3651**

Base Dependence in Copper-Catalyzed Huisgen Reactions: Efficient Formation of Bistriazoles



Click, click: Using a carbonate base as an additive in the copper-accelerated click reaction of alkynes and azides led to an oxidative coupling to form predominately 5,5′-bistriazoles (see scheme). The reaction proved more facile for propargylic ethers and less hindered substrates. Use of an optically active azide gave separable atropisomeric products and provides a convenient access to optically pure derivatives.

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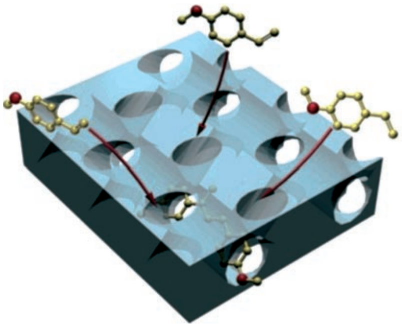
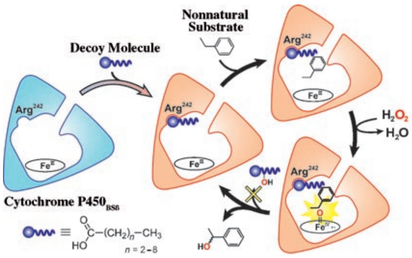


Pore geometry matters: Microspectroscopy with polarized light reveals that in the oligomerization of styrene on large ZSM-5 crystals, different pore geometries may lead to distinct reaction products aligned within straight pores of the zeolite. In the body of the crystal, zigzag pore openings provide access for monomer molecules to diffuse inside and react with the dimer, whereas oligomerization at the edges leads toward mainly dimeric products.

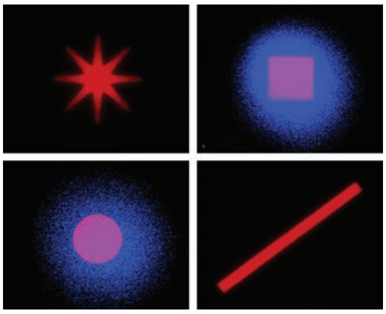
Zeolite Catalysts



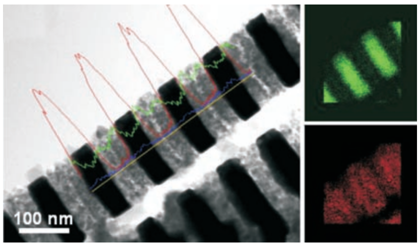
Trick or treat: Cytochrome P450$_{BS\beta}$ was transformed into a monooxygenase suitable for practical use by employing a simple substrate trick. The substrate specificity of P450$_{BS\beta}$ was altered drastically by a decoy molecule, while its intrinsic advantage, the use of hydrogen peroxide, was retained. The catalytic activities and the enantioselectivity of the H_2O_2–P450$_{BS\beta}$ system are highly dependent on the structure of the decoy molecule.

Enzyme Catalysis

Ship shape: At what level of simplicity is emergent behavior possible? An emergent property can arise at the level of a biochemical reaction network. Hemostasis, which regulates blood clotting, can respond to the shape of a patch of surface stimulus. This response can be understood from chemical principles, as demonstrated with numerical simulations and a simplified nonbiological, chemical system.

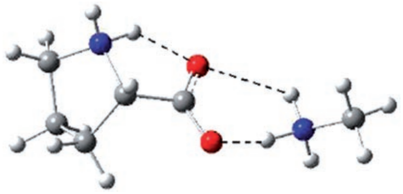


Enzyme Models



Stripped wires: Multifunctional (magnetic and optical) iron–gold barcode nanowires were electrochemically fabricated using nanoporous templates. Structural analysis by TEM elemental line scan and mapping (see images) clearly revealed the well-separated, bamboo-like nanostructures composed of Fe and Au strips.

Nanostructures



Separate charges: Zwitterionic proline can be effectively stabilized by protonated methylamine in the gas phase (see calculated structure; C gray, H white, N blue, O red), as shown by accurate binding-energy measurements and IR fingerprint spectra. These results imply that organic ions may provide an effective means of stabilizing the zwitterionic structures of amino acids, which are of fundamental importance in biological systems.

Zwitterionic Structures

R. Wu, T. B. McMahon* **3668–3671**

Stabilization of the Zwitterionic Structure of Proline by an Alkylammonium Ion in the Gas Phase

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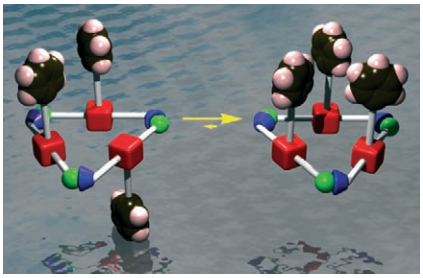
Ring a ring of benzenes: An unsubstituted N-confused metalloporphyrin forms both C_3- and C_1-symmetric trimers in solution, whereas its monophenyl-substituted analogue forms exclusively C_3-symmetric trimers (see picture) owing to significant stabilizing noncovalent interactions between the three phenyl groups, as evaluated both experimentally and theoretically.



Benzene Trimers

T. Morimoto, H. Uno,
H. Furuta* **3672–3675**

Benzene Ring Trimer Interactions Modulate Supramolecular Structures

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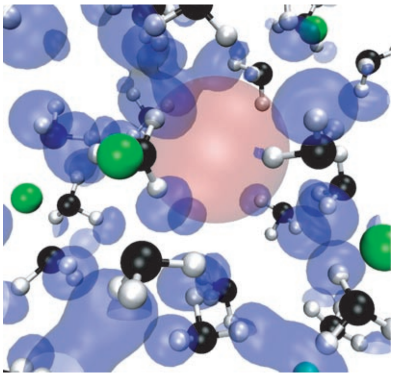
Where are the solvated electrons in strongly metallic lithium/ammonia solutions? Ab initio simulations show that they are not preferentially localized close to the void centers (red sphere) but accumulate at the void/solvent interface (blue isosurfaces). Furthermore, void formation itself can be reproduced by simply "stretching" pure ammonia, without any unbound electrons.



Lithium in Ammonia

A. Chandra,* D. Marx* **3676–3679**

Creating Interfaces by Stretching the Solvent Is Key to Metallic Ammonia Solutions

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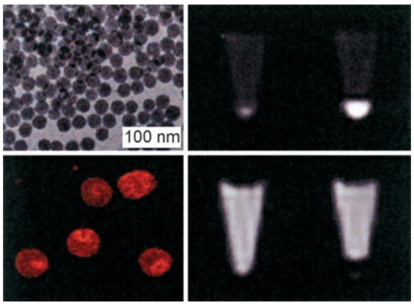


Lighting things up: Multifunctional silica nanoparticles containing a luminescent core and a paramagnetic coat are prepared, and their utility as multimodal imaging probes is demonstrated in vitro. Monocyte cells can be labeled with the hybrid nanoparticles with greater than 98% efficiency and do not experience measurable toxicity even at a high loading of 0.123 mg per 5000 cells.

Imaging Agents

W. J. Rieter, J. S. Kim, K. M. L. Taylor, H. An,
W. Lin, T. Tarrant, W. Lin* **3680–3682**

Hybrid Silica Nanoparticles for Multimodal Imaging

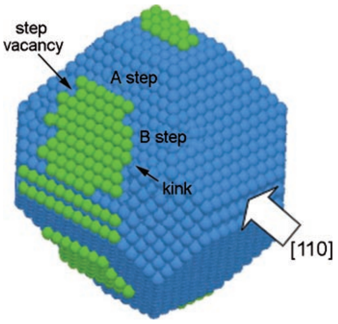
Contents

Electron Microscopy

L. C. Gontard, L.-Y. Chang,
C. J. D. Hetherington, A. I. Kirkland,
D. Ozkaya,
R. E. Dunin-Borkowski* ____ **3683 – 3685**

Aberration-Corrected Imaging of Active Sites on Industrial Catalyst Nanoparticles

Picture perfect: Information about the local topologies of active sites on commercial nanoparticles can be gained with atomic resolution through spherical-aberration-corrected transmission electron microscopy (TEM). A powder of Pt nanoparticles on carbon black was examined with two advanced TEM techniques based on recent developments in hardware (aberration correction) and computation (exit wavefunction restoration).

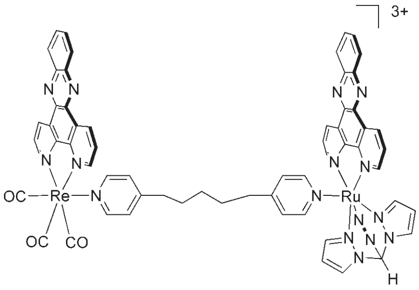


DNA Intercalators

S. P. Foxon, T. Phillips, M. R. Gill,
M. Towrie, A. W. Parker, M. Webb,
J. A. Thomas* ____________ **3686 – 3688**

A Multifunctional Light Switch: DNA Binding and Cleavage Properties of a Heterobimetallic Ruthenium–Rhenium Dipyridophenazine Complex

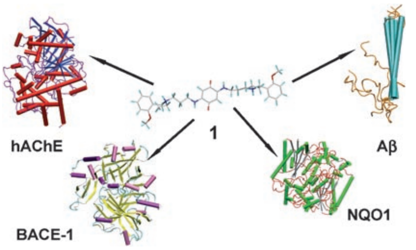
A DNA Swiss-army knife: Photo- and biophysical studies on the hetero-dinuclear complex [{Ru(tpm)(dppz)}(μ-dpp[5]){*fac*-(CO)$_3$Re(dppz)}]$^{3+}$ (see structure; tpm = tris(1-pyrazolyl)methane; dppz = dipyrido[3,2-*a*:2′,3′-*c*]phenazine; dpp[5] = 4,4′-dipyridylpentane) reveal that it is both a DNA light switch and a direct cleaving agent.



Neurochemistry

A. Cavalli, M. L. Bolognesi, S. Capsoni,
V. Andrisano, M. Bartolini, E. Margotti,
A. Cattaneo, M. Recanatini,
C. Melchiorre* ____________ **3689 – 3692**

A Small Molecule Targeting the Multifactorial Nature of Alzheimer's Disease



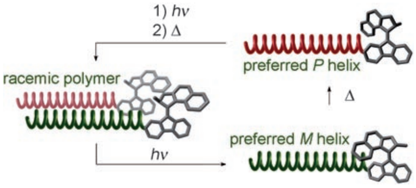
Sights set on a cure: Memoquin (**1**) affects several mechanisms relevant to Alzheimer's disease (AD): the formation of reactive oxygen species, the processing and aggregation of amyloid β (Aβ) peptides, and acetylcholinesterase activity. In animal models, **1** causes a remarkable decrease in the formation of AD neurodegenerative hallmarks and a significant reversal of behavioral deficits. hAChE, BACE-1, and NQO1 are enzymes targeted by **1**.

Macromolecular Helicity

D. Pijper, B. L. Feringa* ____ **3693 – 3696**

Molecular Transmission: Controlling the Twist Sense of a Helical Polymer with a Single Light-Driven Molecular Motor

Twisted sisters: Transmission of chirality from a light-driven rotary molecular motor to the macromolecular level of a polyisocyanate allows fully reversible control of the preferred helical sense of the polymer backbone (see picture).

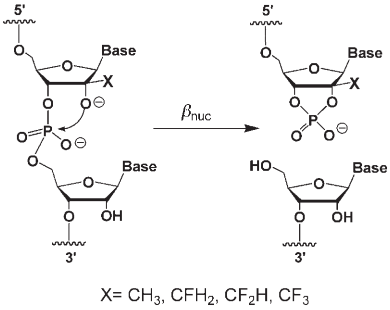


Contents

RNA Cleavage

J.-D. Ye, N.-S. Li, Q. Dai,
J. A. Piccirilli* ______________ **3714–3717**

The Mechanism of RNA Strand Scission: An Experimental Measure of the Brønsted Coefficient, β_{nuc}

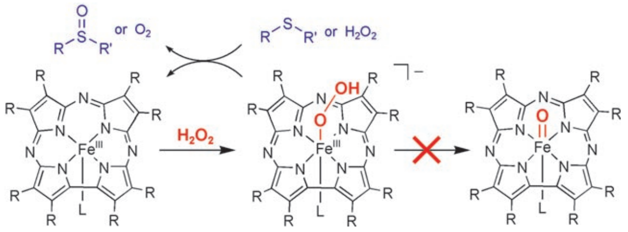


A closer look at RNA cleavage: A series of fluorine-bearing nucleotide analogues (X) were incorporated into RNA to perturb the pK_a value of the 2′-OH group systematically. These analogues enable the use of physical organic approaches to investigate bonding to the nucleophile during the RNA scission reaction. Measurement of the Brønsted coefficient, β_{nuc}, provides new insights into the transition-state structure for this classic reaction.

Ferric Hydroperoxides

W. D. Kerber, B. Ramdhanie,
D. P. Goldberg* ______________ **3718–3721**

H_2O_2 Oxidations Catalyzed by an Iron(III) Corrolazine: Avoiding High-Valent Iron–Oxido Species?

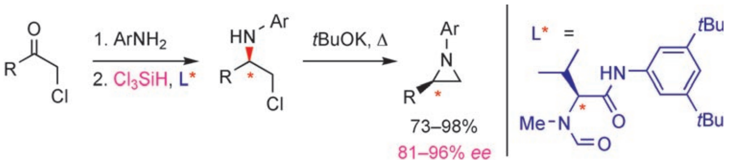


Things aren't always what they seem: The first iron corrolazine complex is shown to activate H_2O_2 towards sulfide oxidation and peroxide dismutation. Although these reactions are typical of a high-valent iron–oxido species, the data point to a ferric hydroperoxide species as the active oxidant (see scheme).

Chiral Aziridines

A. V. Malkov,* S. Stončius,
P. Kočovský* ______________ **3722–3724**

Enantioselective Synthesis of 1,2-Diarylaziridines by the Organocatalytic Reductive Amination of α-Chloroketones



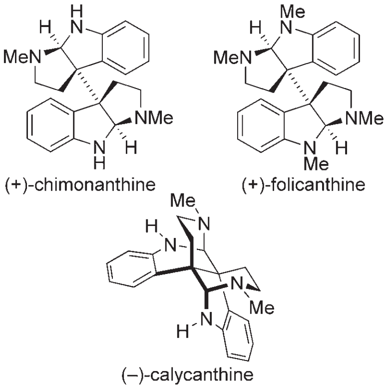
One-sided triangles: A simple protocol has been developed for the synthesis of highly useful single enantiomers of 1,2-diarylaziridines. The method involves conversion of the readily available α-chloroacetophenones into the corresponding imines, followed by an enantioselective reduction with Cl_3SiH catalyzed by the L-valine-derived formamide L* and ring closure to give the desired aziridines (see scheme).

Natural Products

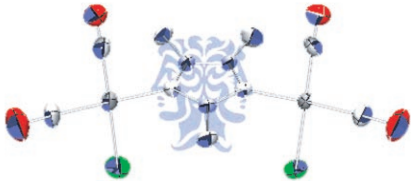
M. Movassaghi,*
M. A. Schmidt ______________ **3725–3728**

Concise Total Synthesis of (−)-Calycanthine, (+)-Chimonanthine, and (+)-Folicanthine

Conjoined twins: An efficient and convergent strategy for the synthesis of the dimeric hexahydropyrroloindole alkaloids, (+)-chimonanthine, (+)-folicanthine, and (−)-calycanthine, is described. The simultaneous formation of the vicinal quaternary stereocenters by using a reductive dimerization reaction provides an access to the optically active key intermediate on a gram scale.

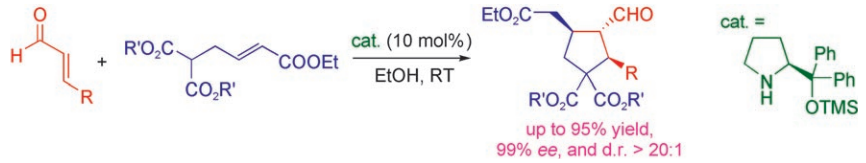


N-Heterocyclic Carbenes



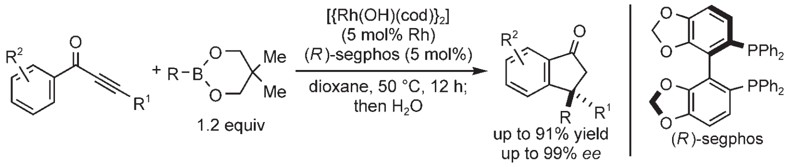
Double trouble: A series of complexes of rhodium and iridium has been obtained with a triazolediylidene ligand, which behaves as an extraordinarily versatile Janus-type ligand to form dinuclear complexes. The dinuclear complexes showed improved catalytic properties over their mononuclear counterparts. The picture shows a diiridium complex of 1,2,4-trimethyltriazole-3,5-diylidene (Ir gray, C white, N blue, O red, Cl green).

Organocatalysis



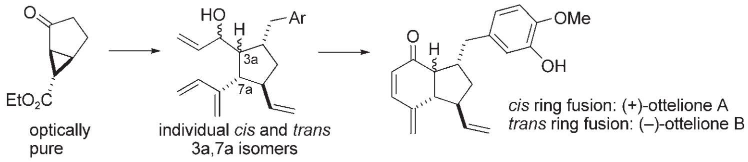
Do a double take: A novel highly enantio- and diastereoselective cascade double Michael reaction, in which two C–C bonds and three contiguous stereogenic centers are formed, has been developed. The one-pot process, which was efficiently catalyzed by the chiral diphenylprolinyl trimethylsilyl (TMS) ether, is a facile approach to synthetically useful chiral cyclopentanes (see scheme).

Asymmetric Catalysis



Rapid access to enantioenriched indanones that are difficult to obtain by other methods is gained through the highly enantioselective addition of aryl boronates to aryl alkynyl ketones under rhodium catalysis (see scheme). The resulting 3,3-disubstituted 1-indanones can be converted into a range of potentially useful indan derivatives with high stereoselectivity. R^1 = Si(alkyl)$_3$, GeEt$_3$; R^2 = F, Me, OMe; cod = 1,5-cyclooctadiene.

Natural Products



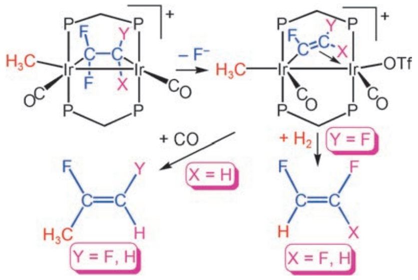
To A and B: The extremely powerful antitumor agents ottelione A and B have been synthesized from D-ribose. Key steps in the synthesis involve the use of a cyclopropane unit fused onto a five-membered ring to control the stereochemistry and later to serve as a precursor to a vinyl group, and a highly regioselective ring-closing metathesis (see scheme).

Contents

C–F Activation

D. J. Anderson, R. McDonald,
M. Cowie* ______ **3741 – 3744**

Carbon–Fluorine Bond Activation in Fluoroolefins: Clear Documentation of Cooperative C–F Bond Activation by Adjacent Metal Centers

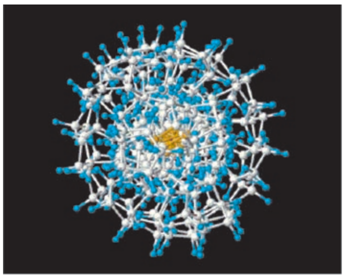


F^- off: Fluoroolefins bridging a pair of iridium centers are susceptible to abstraction of a fluoride ion while those bound to a single metal center are not. The resulting bridging fluorovinyl groups also undergo fluoride abstraction to yield the corresponding vinylidenes, whereas terminal fluorovinyl groups are unreactive. Selective replacement of one fluorine substituent by either hydrogen or a methyl group can be effected (see scheme, Tf = trifluoromethanesulfonyl).

Polymer Structures

C. Karafilidis, K. Angermund, B. Gabor,
A. Rufińska, R. J. Mynott,*
G. Breitenbruch, W. Thiel,
G. Fink* ______ **3745 – 3749**

Helical Microstructure of Polynorbornene



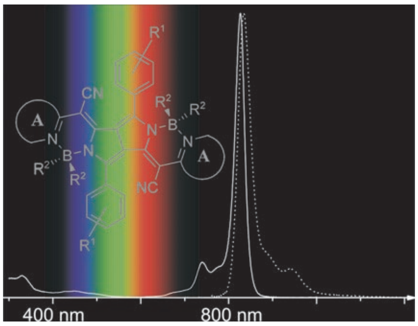
Why don't you melt? The zirconocene-catalyzed polymerization of norbornene proceeds by σ-bond metathesis to give 2-*exo*,7′-*syn* linkages in the main chain and 2-*exo*,2′-*exo*-linked mononorbornyl branches. The resulting helical structure is very compact (see picture, view along helical axis), which hinders conformational changes and explains the insolubility of the polynorbornene and why it cannot be melted.

NIR dyes

G. M. Fischer, A. P. Ehlers, A. Zumbusch,
E. Daltrozzo* ______ **3750 – 3753**

Near-Infrared Dyes and Fluorophores Based on Diketopyrrolopyrroles

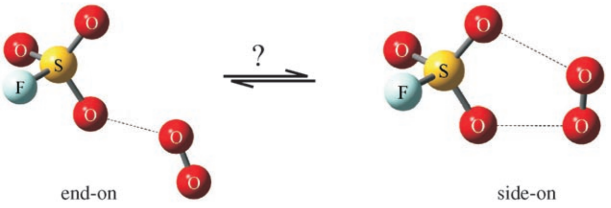
NIRly there: The chromophore of compounds with intramolecular H bonds have been rigidified by substitution of the protons of the N–H⋯N bridges by BR_2 groups (R = F, Ph). This stiffening and the polymethine character of the chromophores affords dyes with intense fluorescence at room temperature and high NIR absorption, but virtually no absorption in the visible range (see the picture for an example, ——: absorption, •••••: fluorescence).



Fluorooxy Radicals

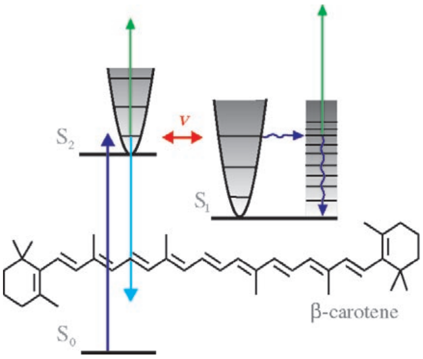
H. Beckers, P. Garcia, H. Willner,*
G. A. Argüello, C. J. Cobos,
J. S. Francisco* ______ **3754 – 3757**

Side-On versus End-On Bonding of O_2 to the FSO_3 Radical: Matrix Isolation and Ab Initio Study of FSO_5



end-on side-on

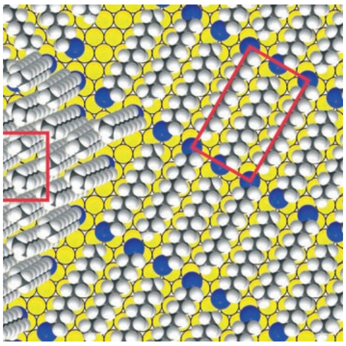
Quantum-chemical calculations predict the existence of two almost equal-energy isomers of the FSO_5 radical with either side-on or end-on bonding of O_2 to FSO_3 (see picture). The structure of this polyoxy radical isolated in solid noble-gas matrices and formed by the reaction of FSO_3 with molecular oxygen has now been revealed by IR and UV spectroscopic investigations.



What happens next? Oscillatory dynamics during internal conversion of β-carotene from the "bright" S_2 to the "dark" S_1 electronic state is observed by femtosecond broadband transient absorption and fluorescence. The spectral evolution was described quantitatively by modeling the quantum dynamics in a three-level system, and the vibronic coupling element was determined ($V \approx 95\ \mathrm{cm}^{-1}$).

Femtochemistry

Lying low: Alkanethioacetates do not form the same dense thiolate monolayers on gold that are obtained from alkanethiols. A multitechnique study shows instead the formation of a kinetically stable monolayer with mostly flat-lying thiolate molecules (see model; blue S). This extraordinary structure results from the diminished reactivity of the thioacetate group towards the gold surface.



Self-Assembled Monolayers

Supporting information is available on the WWW (see article for access details).

A video clip is available as Supporting Information on the WWW (see article for access details).

Service