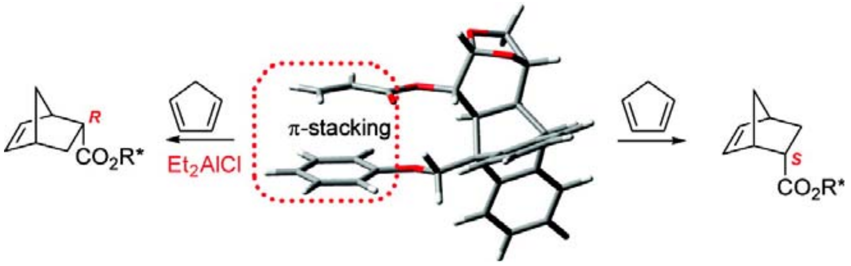
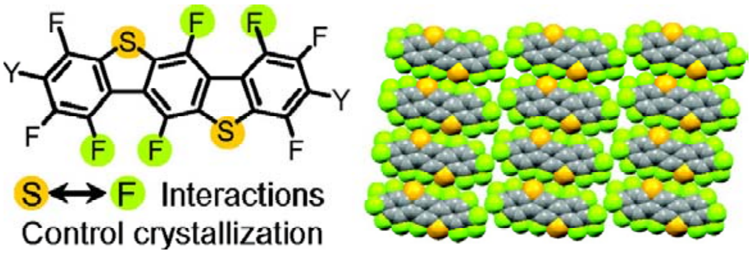
- π-Stacking Effect on Levoglucosenone Derived Internal Chiral Auxiliaries. A Case of Complete Enantioselectivity Inversion on the Diels-Alder Reaction
  Salotti A. M.; Fernández I.; Spanevello R. A.; Miguel Á.; Sierra M.; G. Suárez A. G. *Org. Lett*. **2008**, *10*, 3389-3392.
  Abstract :



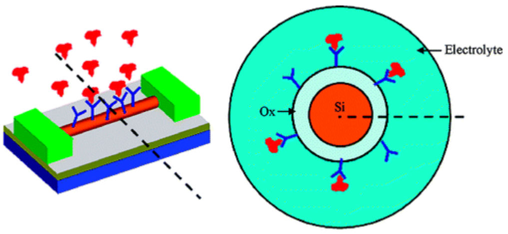
Detailed quantum chemical calculations, experimental evidence, and NMR data rationalize the participation of π-stacking interaction in the highly asymmetric Diels-Alder reaction using levoglucosenone derived internal chiral auxiliaries, including the appealing effect of inversion of the enantioselectivity by coordination of the substrate with Et2AlCl.

- Highly Fluorinated Benzobisbenzothiophenes
  Wang Y.; Parkin S. R.; Gierschner J.; Watson M. D. *Org. Lett*. **2008**, *10*, 3307-3310.
  Abstract :



Expedient, facile syntheses of highly fluorinated benzobisbenzothiophenes (BBBT) are reported. Defined peripheral arrangements of sulphur and fluorine atoms lead to extensive crystalline networks of edge-to-edge S-F close contacts. The effects of various substitution patterns on self-assembly and electronic properties are described.

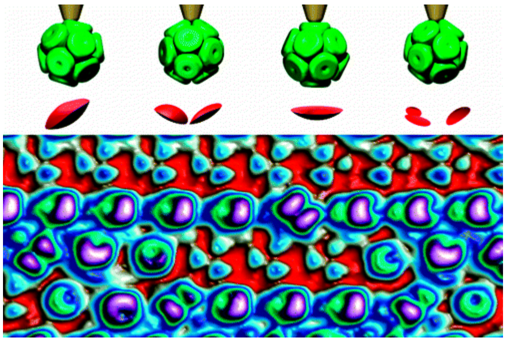
- Screening-Limited Response of NanoBiosensors
  Nair, P. R.; Alam, M. A. *Nano Lett.* **2008**, *8*, 1281–1285.
  Abstract:



Despite tremendous potential of highly sensitive electronic detection of biomolecules by nanoscale biosensors for genomics and proteomic applications, many aspects of experimentally observed sensor response (S) are difficult to understand within isolated theoretical frameworks of kinetic response or electrolyte screening. In this paper, we combine analytic solutions of Poisson–Boltzmann and diffusion-capture equations to show that the electrostatic screening within an ionic environment limits the response of nanobiosensor such that $S(t) \sim c_1(\ln(\rho_0) - \ln(I_0)/2 + \ln(t)/D_F + c_2[\mathrm{pH}]) + c_3$ where

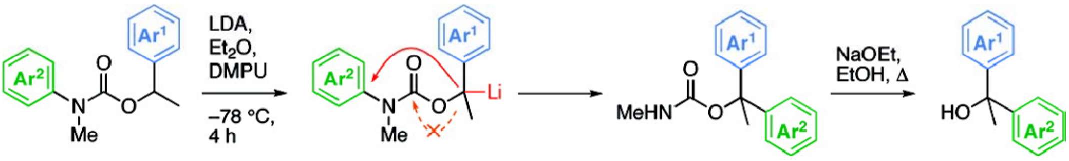
c_i are geometry-dependent constants, ρ_0 is the concentration of target molecules, I_0 the salt concentration, and D_F the fractal dimension of sensor surface. Our analysis provides a coherent theoretical interpretation of a wide variety of puzzling experimental data that have so far defied intuitive explanation.

- Conductance of Oriented C_{60} Molecules
  Néel, N.; Kröger, J.; Limot, L.; Berndt, R. *Nano Lett.* **2008**, *8*, 1291–1295.
  Abstract:



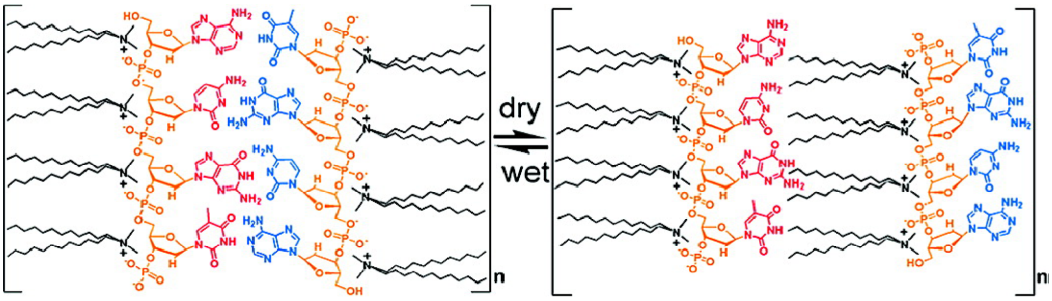
C_{60} molecules adsorbed to Cu(100) are contacted with the tip of a cryogenic scanning tunneling microscope. Images with submolecular resolution reveal distinct orientations of the molecules. We find that the orientation significantly affects the conductance of the contact despite the high symmetry of C_{60}.

- N to C Aryl Migration in Lithiated Carbamates: α-Arylation of Benzylic Alcohols
  Clayden, J.; Farnaby, W.; Grainger, D. M.; Hennecke, U.;Mancinelli, M.; Tetlow, D. J. ; Hillier, I. H.; Vincent , M. A. *J. Am. Chem. Soc.* **2009**, *131*, 3410–3411.
  Abstract:



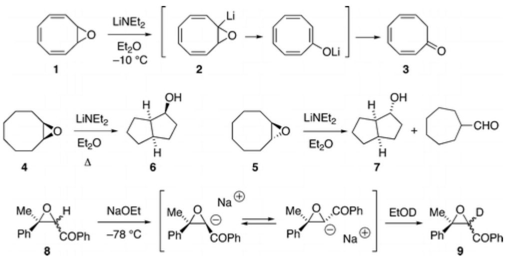
We report a new mode of reactivity displayed by lithiated O-benzyl carbamates carrying an N-aryl substituent: upon lithiation, the N-aryl group is transferred cleanly from N to C. An arylation of the carbamate results, providing a route to α,α-arylated secondary or tertiary alcohols. We also report density functional theory calculations supporting the proposal that arylation proceeds through a dearomatizing attack on the aromatic ring, a significantly lower energy pathway than the 1,2-acyl transfer observed with related N-alkyl carbamates.

- Reversible Structural Switching of a DNA−DDAB Film
  Neumann, T.; Gajria, S.; Tirrell, M.; Jaeger, L. *J. Am. Chem. Soc.*, **2009**, *131*, 3440–3441.
  Abstract:



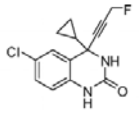
We describe the novel structure and behavior of a DNA–DDAB complex film cast from an organic solvent and exhibiting a structural switching transition as it is dried or wetted with water. The film was easily prepared by formation of a complex between the negatively charged phosphate groups of DNA and the positively charged headgroup of the surfactant DDAB. This complex was then purified, dried, dissolved in 2-propanol, and cast onto a glass slide to form a self-standing film by means of slow evaporation. While the structure of the dried film was found to be composed of single-stranded DNA and a monolayer of DDAB, upon hydration of the film, the structure switched to double-stranded DNA complexed to a bilayer of DDAB. We expect this phenomenon to serve as a useful model for the design of new responsive materials and programmable self-assembly.

- α-Substituted α-Lithiated Oxiranes: Useful Reactive Intermediates
  Capriati, V.; Florio, S.; Luisi, R. *Chem. Rev.* **2008**, *108,* 1918-1942.
  Abstract:

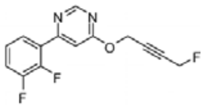


Epoxides, strained three-membered ring heterocycles, are among the most versatile intermediates in organic chemistry. The paramount interest for this type of heterocyclic system is amply justified by the great number of biologically significant molecules that contain this motif within their structures and its large use as synthetic building block. This review will focus on generation, reactivity, and synthetic applications of α-metallated oxiranes with special attention addressed to α-lithiated oxiranes.
Most of the work on this topic has been done over the past 15−20 years. The field has been comprehensively reviewed by Satoh in 1996, by Mori, and, more recently, by Hodgson, Chemla, and Florio. However, efforts are still carried out in order to elucidate aspects concerned with generation, structural features, reactivity [carbanions or carbenoids (as a noun), meant, according to Closs and Moss definition, as “intermediates capable to exhibit reactions qualitatively similar to those of carbenes without necessarily being free divalent carbon species”, thermal as well as configurational stability and stereochemistry of their reactions.

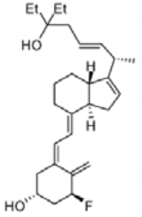
- The Chemistry of Propargylic and Allylic Fluorides
  Pacheco, M. C. ; Purser, S. ; Gouverneur, V. *Chem. Rev.* **2008**, *108,* 1943-1981.
  Abstract:



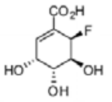
Reverse transcripatse inhibitor **1**



Insecticide **2**



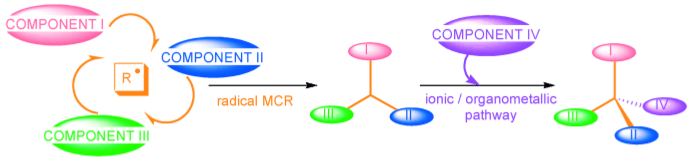
Ro 26-9228 **3**



6*R*-F-Shikimic acid **4**

The presence of fluorine is very often highly advantageous in pharmaceutical and agrochemical compounds as well as in performance materials. In response to a growing demand for complex fluorinated molecules, chemists are continuously seeking ingenious methods for their preparation. Molecular fluorine and inorganic fluoride sources are reagents available for fluorination and are used for the synthesis of large quantities of “primary” fluorinated building blocks. The development of various nucleophilic and electrophilic fluorinating reagents of tuned reactivity has allowed for the production of a larger portfolio of fluorinated building blocks used for further functional group manipulation and for the fluorination to be programmed as a key step in the synthetic sequence of complex fluorinated targets. Chiral, nonracemic fine chemicals featuring a fluorinated stereogenic center are more often prepared, relying on a key C−F bond-forming process, as very few chiral fluorinated building blocks are commercially available to date. Two building blocks that may feature a fluorinated stereogenic center are propargylic and allylic monofluorides. The importance of these compounds in racemic or enantioenriched form as key functional groups cannot be underestimated and is possibly best compared with the long-established value of the corresponding propargylic and allylic alcohols in natural and non-natural product synthesis. Propargylic and allylic fluorides are structural motifs found in important life science compounds such as insecticides, herbicides, and fungicides or fluorinated Vitamin D and prostanoid analogues. In addition, they are potentially amenable to countless functional manipulations.

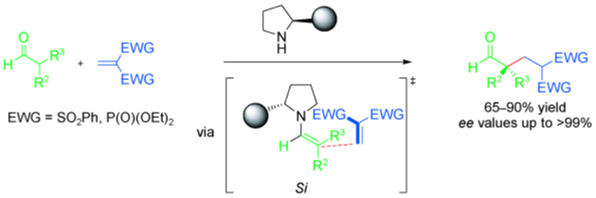
- Radical and Radical-Ionic Multicomponent Processes
  Godineau, E.; Landais, Y. *Chem. Eur. J.* **2009**, *15*, 3044-3055.
  Abstract:



All in one pot! Radical, radical-ionic, and radical-organometallic MCR are highly convergent processes, representing a useful pathway to molecular and structural diversity (see scheme). This concept article highlights recent developments in the field and shows the potential of the strategy for the economical elaboration of various kinds of organic substrates.

Progress in multicomponent reactions (MCRs) based on ionic and organometallic processes has recently allowed the synthesis, with high efficiency, of large collections of drug-like molecules. In contrast, MCRs based on cascade radical reactions appear to have attracted, so far, much less interest. This concept article highlights the latest progress in the field and underlines the potential of such an approach. The collected examples demonstrate that radical and radical-ionic MCRs are highly convergent processes leading to useful structural diversity.

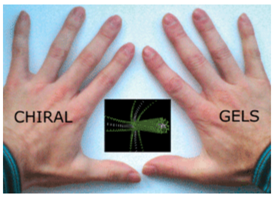
- Enantioselective Organocatalytic Conjugate Addition of Aldehydes to Vinyl Sulfones and Vinyl Phosphonates as Challenging Michael Acceptors
  Sulzer-Mossé, S.; Alexakis, A.; Mareda, J.; Bollot, G.; Bernardinelli, G.; Filinchuk Y. *Chem. Eur. J.* **2009**, *15*, 3204-3220.
  Abstract:



Chiral framework: Chiral amines with pyrrolidine frameworks catalyze the enantioselective conjugate addition of a wide range of aldehydes to various vinyl sulfones and vinyl phosphonates in high yields and with enantioselectivities up to >99 % *ee* (see scheme). The high versatility of the Michael adducts is exemplified by various functionalizations with conservation of the optical purity.

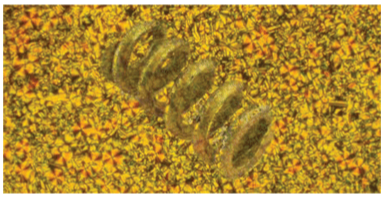
Chiral amines with a pyrrolidine framework catalyze the enantioselective conjugate addition of a broad range of aldehydes to various vinyl sulfones and vinyl phosphonates in high yields and with enantioselectivities up to >99 % *ee*. This novel process provides synthetically useful chiral γ-*gem*-sulfonyl or phosphonyl aldehydes which can be widely functionalized with retention of the enantiomeric excess. Mechanistic insights including DFT calculations are explored in detail.

- Lost in translation? Chirality effects in the self-assembly of nanostructured gel-phase materials
  Smith, D. K. *Chem. Soc. Rev.* **2009**, *38*, 684 – 694.
  Abstract:



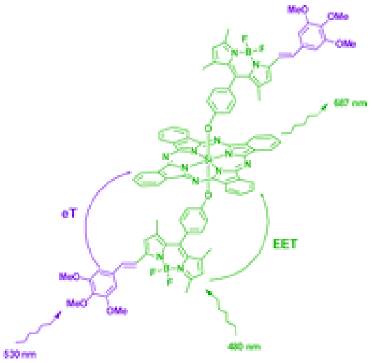
Gel-phase materials are generated when molecular building blocks assemble into nanoscale architectures, usually ˋone-dimensional´ fibrils, which hierarchically assemble into bundles and subsequently form an entangled sample spanning network, capable of preventing the flow of bulk solvent. This *tutorial review* explores the vital role of chirality in gel formation. In particular, we focus on how fundamental self-assembly processes can translate molecular scale chiral information into nanoscale architectures, and then into the macroscopic behaviour of the gel. Chiral molecular gels have potential applications in nanofabrication and as addressable functional nanomaterials.

- Twists in mesomorphic columnar supramolecular assemblies
  Vera, F.; Serrano, J. L.; Sierra, T. *Chem. Soc. Rev.* **2009**, *38*, 781 – 796.
  Abstract:



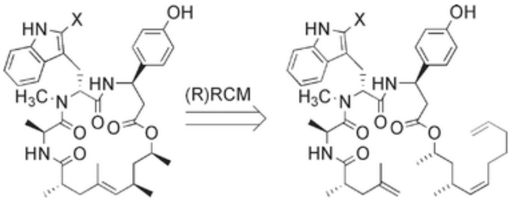
This *tutorial review* provides insight into helical columnar assemblies based on thermotropic as well as lyotropic liquid crystals on the basis of the structural characteristics that promote hierarchical self-organization. The structural features of molecular materials that can present helical organizations imply the action of different driving forces that include π-interactions, hydrogen bonding or metal-coordination. In addition, columnar liquid crystals offer the possibility of combining these interactions towards the control of the geometry and orientation of the supramolecular organization leading to well-defined helical columnar assemblies.

- Switching the photo-induced energy and electron-transfer processes in BODIPY–phthalocyanine conjugates.
  Liu, J. Y.; Ermilov, E. A.; Röder, B.; Ng, D. K. P. *Chem. Commun*. **2009**, 1517 – 1519.
  Abstract :



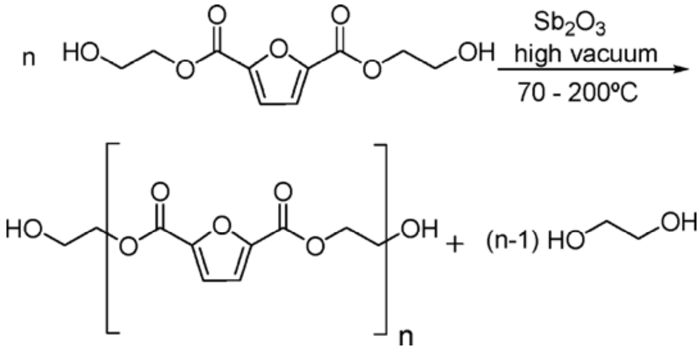
Two novel silicon(IV) phthalocyanines substituted axially with two BODIPY or mono-styryl BODIPY moieties have been synthesised, which exhibit predominantly a photo-induced energy or electron-transfer process in toluene depending on the axial substituents.

- Solid-phase based total synthesis of Jasplakinolide by ring-closing metathesis.
  Tannert, R.; Hu, T. S.; Arndt, H. D.; Waldmann, H. *Chem. Commun.* **2009**, 1493 – 1495.
  Abstract :



The study of classical ring-closing metathesis and relay ring-closing metathesis in a total synthesis of Jasplakinolide and its desbromo analog is described.

- Polymers from Renewable Resources: A Challenge for the Future of Macromolecular Materials.
  Gandini, A. *Macromolecules*, **2008**, *41*, 9491-9504.
  Abstract:

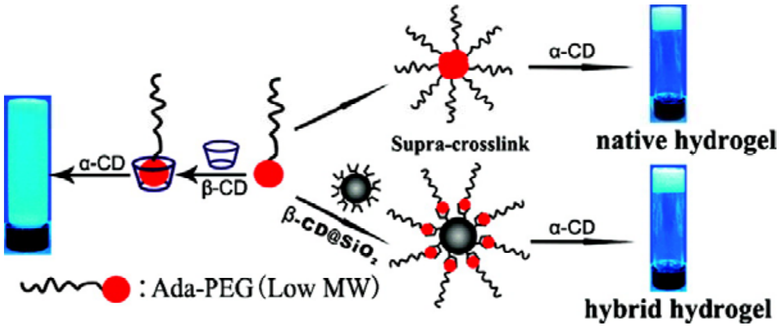


This perspective article examines the state of the art regarding the field of polymers from renewable resources and attempts to give a critical appraisal of the situation related to a representative number of specific materials, in terms of their interest, present degree of advancement, and prospective development within short and medium-term projections. The selected examples include polysaccharides and their derivatives, lignin, suberin, vegetable oils, tannins, natural monomers like terpenes, and monomers derived from sugars, with particular emphasis on furan derivatives and lactic acid, bacterial cellulose, and poly(hydroxyalkanoates), ending with a brief assessment of the potential role of glycerol and ethanol as future precursors to monomers.

- Supramolecular Hydrogels Made of End-Functionalized Low-Molecular-Weight PEG and α-Cyclodextrin and Their Hybridization with SiO_2 Nanoparticles through Host−Guest Interaction.

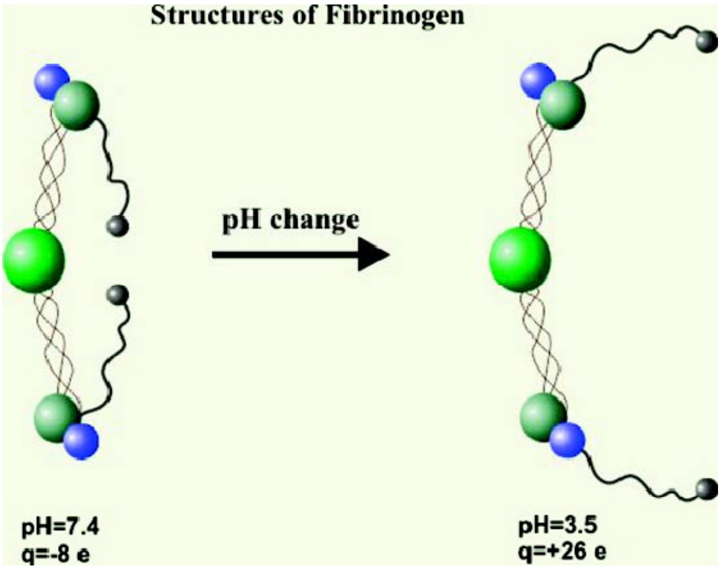
  Guo, M.; Jiang, M.; Pispas, S.; Yu, W.; Zhou, C. *Macromolecules* **2008**, *41*, 9744-9749.

  Abstract:



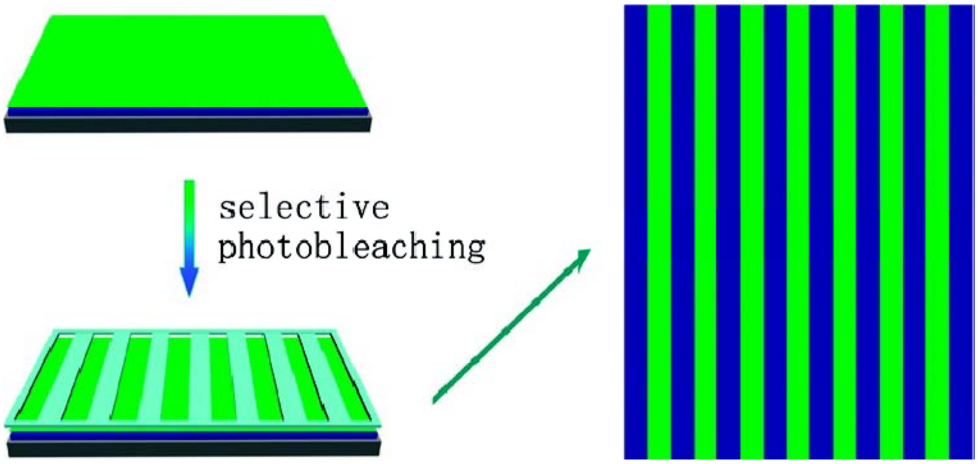
As quite generally stated in the literature, low-molecular-weight (MW) poly(ethylene glycol) (PEG) (M_n less than 2K) and α-cyclodextrin (α-CD) can lead to only crystalline precipitates (not hydrogels). However, in this study we found that: (1) adamantane monoend-functionalized low-MW PEG (Ada-PEG, M_n= 1.1 or 2K) and α-CD lead to hydrogels but not to crystalline precipitates and (2) β-cyclodextrin (β-CD) surface-functionalized silica nanoparticles (β-CD−SiO_2) can be well dispersed in low-MW Ada-PEG and α-CD aqueous mixtures, resulting in hybrid hydrogels. The hydrophobic aggregation of Ada-PEG in case 1 and the further functionalization of β-CD−SiO_2 with PEG chains due to the inclusion complexation between β-CD and the Ada group attached to PEG in case 2 were found to play a key role as a supra-crosslink that promoted the gelation of the inclusion complexes of α-CD and the low-MW Ada-PEG. The resultant native and hybrid hydrogels retained the basic characteristics of the supramolecular physical hydrogels, especially the shear-thinning property. The mechanical strength and the viscosity of the hybrid hydrogel were greatly improved in comparison with those of the corresponding native hydrogels.

- Structure of Fibrinogen in Electrolyte Solutions Derived from Dynamic Light Scattering (DLS) and Viscosity Measurements
  Wasilewska, M.; Adamczyk, Z.; Jachimska, B. *Langmuir* **2009**, *25*, 3698-3704.
  Abstract:



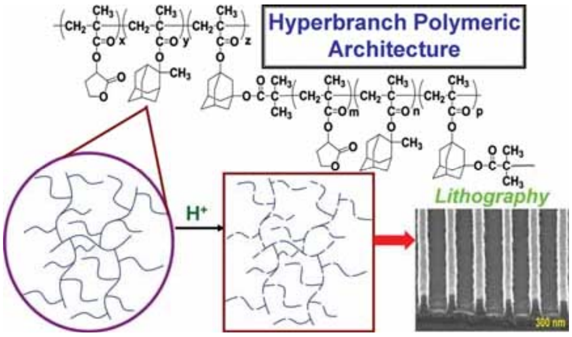
Bulk physicochemical properties of bovine plasma fibrinogen (Fb) in electrolyte solutions were characterized. These comprised determination of the diffusion coefficient (hydrodynamic radius), electrophoretic mobility, and isoelectric point (iep). The hydrodynamic radius of Fb for the ionic strength of 0.15 M was 12.7 nm for pH 7.4 (physiological conditions) and 12 nm for pH 9.5. Using these values, the number of uncompensated (electrokinetic) charges on the protein N_c was calculated from the electrophoretic mobility data. It was found that for physiological condition (pH 7.4, $I = 0.15$), $N_c = -7.6$. For pH 9.5 and $I = 10^{-2}$, $N_c = -26$. On the other hand, N_c became zero independent of the ionic strength at pH 5.8, which was identified as the iep. Consequently, for pH <5.8, N_c attained positive values, approaching 26 for lower ionic strength and pH 3.5. It was also found from the hydrodynamic diameter measurements that for a pH range close to the iep, that is, 4−7, the stability of Fb suspension was very low. These physicochemical characteristics were supplemented by dynamic viscosity measurements, carried out as a function of Fb bulk volume concentration, for various pH values. Using these experimental data the contour length of 80 nm was predicted for Fb molecules in electrolyte solutions. On the other hand, the effective length of the molecule was 53−55 nm for physiological conditions, which suggested a collapsed state of the terminal chains. However, for the range of pH outside the iep, its effective length increased to 65−68 nm. This was interpreted in terms of a significant unfolding of the terminal chains of Fb caused by electrostatic repulsion. The effective charge, contour length, and effective length data derived in this work seem to be the first of this type reported in the literature.

- Creating Bicolor Patterns via Selective Photobleaching with A Single Dye Species
  Gao, L.; Lu, N.; Hao, J.; Hu, W.; Shi, G.; Wang, Y.; Chi, L. *Langmuir* **2009**, *25*, 3894-3897.
  Abstract:



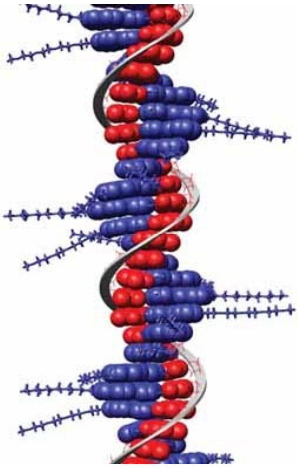
Bicolor fluorescent pattern in thin polymer film is fabricated via a photobleaching process. Dye molecules exhibit monomer emission when they are dispersed inside the polymer and aggregate emission when they are on the surface of the polymer. Thus, a mixed emission of monomer and aggregate can be obtained by evaporating a single dye species on the polymer film. Bicolor pattern in thin polymer film is readily formed by selective photobleaching. This process is particularly attractive for the fabrication of bicolor patterns on flat substrates using a single dye species, which is of potential applications in photonic/electronic devices.

- Hyperbranched Polymers for Photolithographic Applications - Towards Understanding the Relationship between Chemical Structure of Polymer Resin and Lithographic Performances.
  Chochos, C. L.; Ismailova, E.; Brochon, C.; Leclerc, N.; Tiron, R.; Sourd, C.; Bandelier, P.; Foucher, J.; Ridaoui, H.; Dirani, A.; Soppera, O.; Perret, D.; Brault, C.; Serra, C. A.; Hadziioannou, G. *Adv. Mater*. **2009**, *21*, 1121-1125.
  Abstract:



A chemically amplified resist based on a hyperbranched polymer resin is demonstrated for the first time. The hyperbranched polymer is synthesized using the atom-transfer radical polymerization (ATRP) technique, and resists prepared from this hyperbranched polymer present good pattern profiles and line-edge roughness (3) values comparable to those of the reference (commercial) resist.

- Supramolecular Organization of ssDNA-Templated pi-b;-Conjugated Oligomers via Hydrogen Bonding.
  Surin, M.; Janssen, P. G. A.; Lazzaroni, R.; Leclère, P.; Meijer, E. W.; Schenning, A. P. H. J. A*dv. Mater*. **2009**, *21*, 1126-1130.
  Abstract:

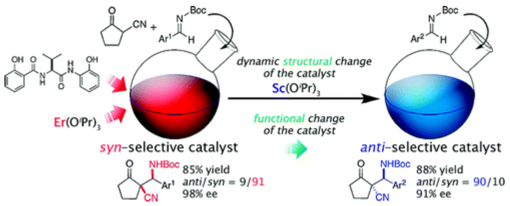


The templated self-assembly of water-soluble -conjugated molecules bearing a diaminotriazine moiety H-bonding to a single-strand oligothymine template leads to defined structures. We study these assemblies with molecular modeling, circular dichroism spectroscopy, and scanning probe microscopy, to get a better understanding of the factors governing the supramolecular organization and structural order.

- Observation of Direct Sulfenium and Selenenium Group Transfer from Thiiranium and Seleniranium Ions to Alkenes
  Denmark, S. E.; Collins, W. R.; Cullen, M. D. *J. Am. Chem. Soc.* **2009**, *131*, 3490–3492.
  Abstract:

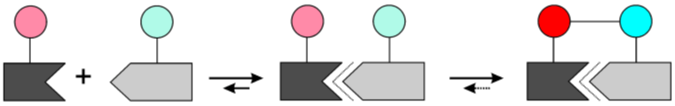
Sulfenium and selenenium ions undergo a stereospecific transfer from the corresponding three-membered ring species (“-iranium ions”) to unactivated alkenes with varying facility. The thiiranium and seleniranium hexafluoroantimonates could be generated by treatment of the corresponding chloro sulfides or selenides with silver hexafluoroantimonate, followed by removal of the silver chloride by filtration. Clean ^{1}H, ^{13}C, and ^{77}Se NMR spectra could be recorded for these species. Treatment of the *S*-phenylthiiranium ion with an alkene leads to a slow transfer of the sulfenium group at 0 °C. However, the *S*-methylthiiranium ion did not transfer the sulfenium group, even at room temperature. On the other hand, both the *Se*-phenyl- and *Se*-butylseleniranium ions transferred the selenenium moiety instantaneously at −70 °C. By measuring the equilibrium position for these transfers from both directions, the relative stability of the 1-phenylseleniranium ions could be established: *cis*-tetramethylene < *trans*-2,3-dipropyl ∼ *trans*-2,3-diisopropyl < *cis*-hexamethylene.

- Linking Structural Dynamics and Functional Diversity in Asymmetric Catalysis
  Nojiri, A.; Kumagai, N.; Shibasaki, M. *J. Am. Chem. Soc.* **2009**, *131*, 3779–3784.
  Abstract:



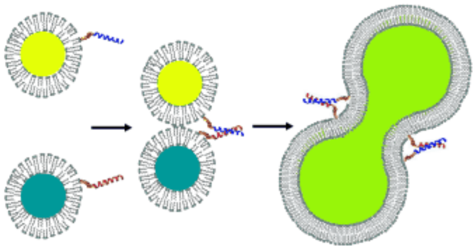
Proteins, the functional molecules in biological systems, are sophisticated chemical devices that have evolved over billions of years. Their function is intimately related to their three-dimensional structure and elegantly regulated by conformational changes through allosteric regulators and a number of reversible or unidirectional post-translational modifications. This functional diversification in response to external stimuli allows for an orderly and timely progression of intra- and extracellular events. In contrast, enantioselective catalysts generally exhibit limited conformational flexibility and thereby exert a single specific function. Exploiting the features of conformationally flexible asymmetric ligands and the variable coordination patterns of rare earth metals, we demonstrate dynamic structural and functional changes of a catalyst in asymmetric catalysis, leading to two distinct reaction outcomes in a single flask.

- Covalent Capture: Merging Covalent and Noncovalent Synthesis
  Prins, L. J.; Scrimin, P. *Angew. Chem. Int. Ed.* **2009**, *48*, 2288 – 2306.
  Abstract:



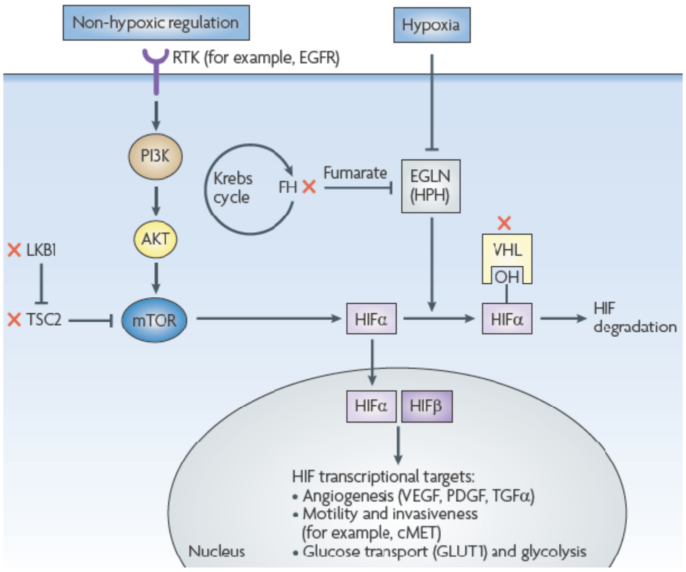
Coming together: The act of bringing the right molecules together is enough to induce irreversible or reversible formation of a covalent bond. The covalent capture strategy, in which a supramolecular interaction leads to the formation of a covalent bond (see scheme), can be utilized in very different biological and synthetic systems and can be used for numerous applications.

- A Reduced SNARE Model for Membrane Fusion
  Marsden, H. R.; Elbers, N. A.; Bomans, P. H. H.; Sommerdijk, N. A. J. M.; Kros, A. *Angew. Chem. Int. Ed*. **2009**, *48*, 2330 –2333.
  Abstract:



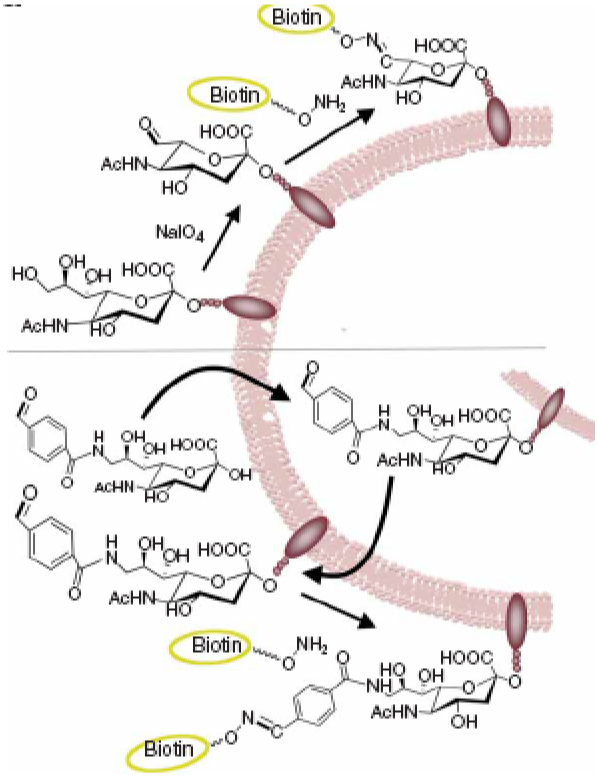
Let's get together: A minimal model system was developed to mimic the SNARE-protein-mediated fusion of biological membranes (see picture). Fusion between two populations of liposomes is controlled by a pair of complementary lipidated oligopeptides that form noncovalent coiled-coil complexes and thereby force the membranes into close proximity to promote fusion. The model system displays the key characteristics of in vivo fusion events.

- Molecular targets for cancer chemoprevention
  William Jr, W. N.; Heymach, J. V.; Kim, E. S.; Lippman, S. M. *Nature Review Drug Discovery* **2009**, *8*, 213-225.
  Abstract:



Vaccines targeting infections with hepatitis B virus, a risk factor for hepatocellular cancer, and human papillomavirus, a risk factor for cervical cancer, are considered major clinical cancer chemoprevention successes. Molecularly targeted agents can prevent breast cancer (raloxifene and tamoxifen), colorectal adenomas (celecoxib), and prostate cancer (finasteride). Nevertheless, the broad translation of chemoprevention to the clinic is not yet a reality. Continuing research of molecular targets promises to expand the reach of chemoprevention and to personalize it as well.

- High-efficiency labeling of sialylated glycoproteins on living cells
  Zeng, Y.; Ramya, T. N. C.; Dirksen, A.; Dawson, P. E.; Paulson, J. C. *Nature Methods* **2009**, *6*, 207-209.
  Abstract:



We describe a simple method for efficiently labeling cell-surface sialic acid–containing glycans on living animal cells. The method uses mild periodate oxidation to generate an aldehyde on sialic acids, followed by aniline-catalyzed oxime ligation with a suitable tag. Aniline catalysis dramatically accelerates oxime ligation, allowing use of low concentrations of aminooxy-biotin at neutral pH to label the majority of cell-surface sialylated glycoproteins while maintaining high cell viability.