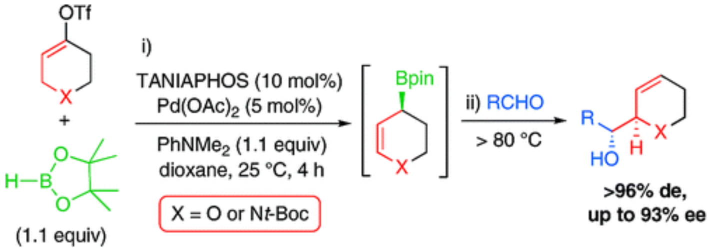
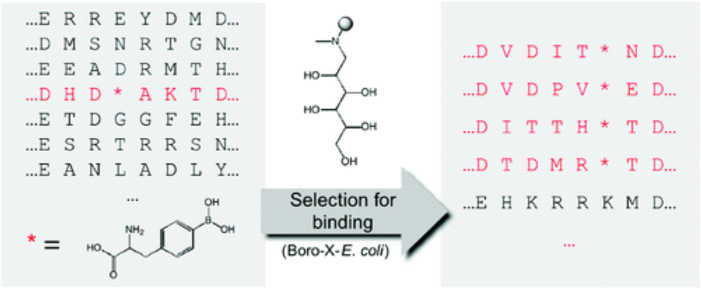
- α-Hydroxyalkyl Heterocycles via Chiral Allylic Boronates: Pd-Catalyzed Borylation Leading to a Formal Enantioselective Isomerization of Allylic Ether and Amine
  Lessard, S.; Peng, F.; Hall, D. G. *J. Am. Chem. Soc.* **2009**, *131*, 9612–9613.
  Abstract:



An efficient catalytic enantioselective preparation of synthetically useful pyranyl and piperidinyl allylic boronates was achieved via a palladium-catalyzed borylation/isomerization reaction on the corresponding alkenyl triflates. The influence of the base and solvent was found to be crucial on the regio- and enantioselectivity of this reaction. The overall borylation process constitutes a successful example of formal asymmetric isomerization of allylic ether/amine. The resulting allylic boronate reagents add to various aldehydes in a one-pot process to give synthetically useful alpha-hydroxyalkyl derivatives in high stereoselectivity.

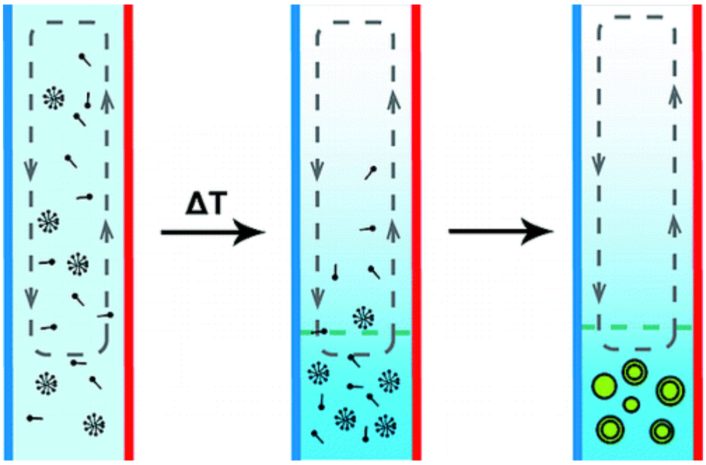
- Evolution of Proteins with Genetically Encoded "Chemical Warheads"
  Liu, C. C.; Mack, A. V.; Brustad, E. M.; Mills, J. H.; Groff, D.; Smider, V. V.; Schultz, P. G. *J. Am. Chem. Soc.* **2009**, *131*, 9616–9617.
  Abstract:


...E R R E Y D M D...
...D M S N R T G N...
...E E A D R M T H...
...D H D * A K T D...
...E T D G G F E H...
...E S R T R R S N...
...E A N L A D L Y...
...
* =

...D V D I T * N D...
...D V D P V * E D...
...D I T T H * T D...
...D T D M R * T D...
...E H K R R K M D...
...

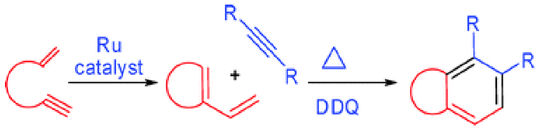
We recently developed a phage-based system for the evolution of proteins in bacteria with expanded amino acid genetic codes. Here we demonstrate that the unnatural amino acid p-boronophenylalanine (BF) confers a selective advantage in the evolution of glycan-binding proteins. We show that an unbiased library of naïve antibodies with NNK-randomized VH CDR3 loops converges upon mutants containing BF when placed under selection for binding to a model acyclic amino sugar. This work represents a first step in the evolution of carbohydrate-binding proteins that use a reactive unnatural amino acid "warhead" and demonstrates that a "synthetic" genetic code can confer a selective advantage by increasing the number of functional groups available to evolution.

- Formation of Protocell-like Vesicles in a Thermal Diffusion Column
  Budin, I.; Bruckner, R. J.; Szostak, J. W. *J. Am. Chem. Soc.* **2009**, *131*, 9628–9629.
  Abstract:



Many of the properties of bilayer membranes composed of simple single-chain amphiphiles seem to be well-suited for a potential role as primitive cell membranes. However, the spontaneous formation of membranes from such amphiphiles is a concentration-dependent process in which a significant critical aggregate concentration (cac) must be reached. Since most scenarios for the prebiotic synthesis of fatty acids and related amphiphiles would result in dilute solutions well below the cac, the identification of mechanisms that would lead to increased local amphiphile concentrations is an important aspect of defining reasonable conditions for the origin of cellular life. Narrow, vertically oriented channels within the mineral precipitates of hydrothermal vent towers have previously been proposed to act as natural Clusius–Dickel thermal diffusion columns, in which a strong transverse thermal gradient concentrates dilute molecules through the coupling of thermophoresis and convection. Here we experimentally demonstrate that a microcapillary acting as a thermal diffusion column can concentrate a solution of oleic acid. Upon concentration, self-assembly of large vesicles occurs in regions where the cac is exceeded. We detected vesicle formation by fluorescence microscopy of encapsulated dye cargoes, which simultaneously concentrated in our channels. Our findings suggest a novel means by which simple physical processes could have led to the spontaneous formation of cell-like structures from a dilute prebiotic reservoir.

- Advanced approach to polycyclics by a synergistic combination of enyne metathesis and Diels–Alder reaction
  Kotha, S.; Meshram, M.; Tiwari, A. *Chem. Soc. Rev.* **2009**, *38*, 2065 – 2092.
  Abstract:

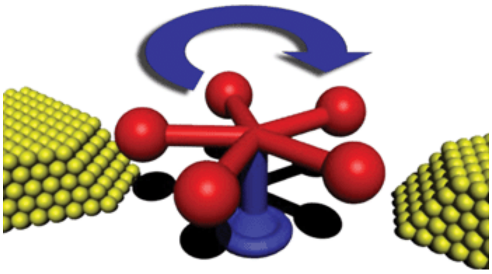


Enyne metathesis (EM) has widely been used to prepare various synthetic and natural products. Further, a sequential use of EM and Diels–Alder (DA) reactions generates highly functionalized and intricate polycarbocycles and heterocyclic frameworks. In this *critical review* we describe the application of a unique combination of EM and DA reactions to prepare various amino acid derivatives, natural products and heterocycles. Some of the heterocyclic targets include cyclic peroxides, siloxanes and various nitrogen (or oxygen) containing compounds. Use of ethylene and cyclooctadiene (COD) for improving the yield of EM products are also discussed (69 references).

- Prototypes of molecular motors based on star-shaped organometallic ruthenium complexes

Vives, G.; Jacquot de Rouville, H.-P.; Carella, A.; Launay, J.-P.; Rapenne, G. *Chem. Soc. Rev.* **2009**, *38*, 1551 – 1561.

Abstract:

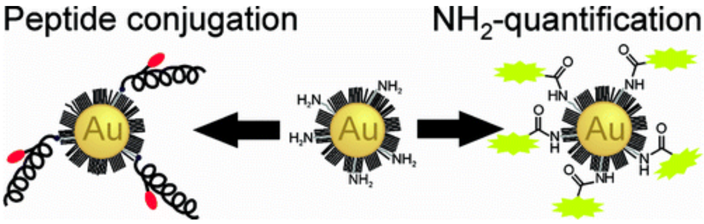


This *tutorial review* presents our strategy to control the rotation in a molecular rotary motor, and the family of star-shaped ruthenium complexes designed to perform such a task. The molecules have a piano-stool structure with a "stator" meant to be grafted on a surface, and a "rotor" bearing redox-active groups, so that addressing the molecule with nano-electrodes would trigger rotation.

- Quantification and Reactivity of Functional Groups in the Ligand Shell of PEGylated Gold Nanoparticles via a Fluorescence-Based Assay

  Maus, L.; Spatz, J. P.; Fiammengo, R. *Langmuir* **2009**, *25*, 7910–7917.

  Abstract:

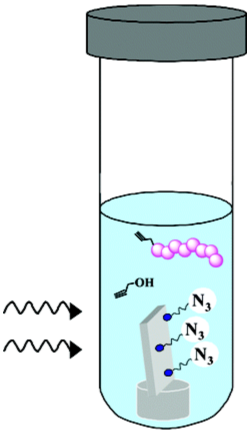


We present a fluorescence-based assay for the characterization of functionalized gold nanoparticles (AuNPs) capped with a self-assembled monolayer of mixed thiols derived from poly(ethylene glycol) (PEG). These water-soluble AuNPs carry primary amino groups at the solvent-exposed interface, which can be used for further conjugation of biologically active molecules. The reported assay allows quantification of the average number of functionalizable amino groups per particle (NNH2) with a relative uncertainty below or equal to (14% (95% confidence interval), thus providing essential information for the successive derivatization of the AuNPs. Here, a fluorescently labeled derivative of peptide-neurotoxin conantokin-G was coupled to the amino groups of the particle ligand shell via a flexible linker. We quantitatively determined the average number of peptides per particle (Npept) and the yield of the two-step conjugation strategy. AuNPs carrying 50-70 copies of the peptide were obtained. In addition, we have gained insights into the deterioration of the selfassembled monolayer due to thiol desorption with time. Under ordinary storage conditions in solution and at room temperature, a decrease inNNH2 between 48%and 75%could be observed at the end of the period of investigation (42-56 days). Slow desorption of the conjugated peptides upon storage was also observed and quantified (∼25% in 14 days).

- Fast Surface Modification by Microwave Assisted Click Reactions on Silicon Substrates

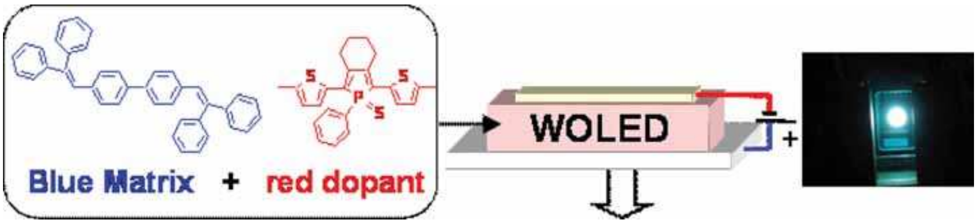
  Haensch, C.; Erdmenger, T.; Fijten, M. W. M.; Hoeppener, S.; Schubert, U. S. *Langmuir* **2009**, *25*, 8019–8024.

  Abstract:



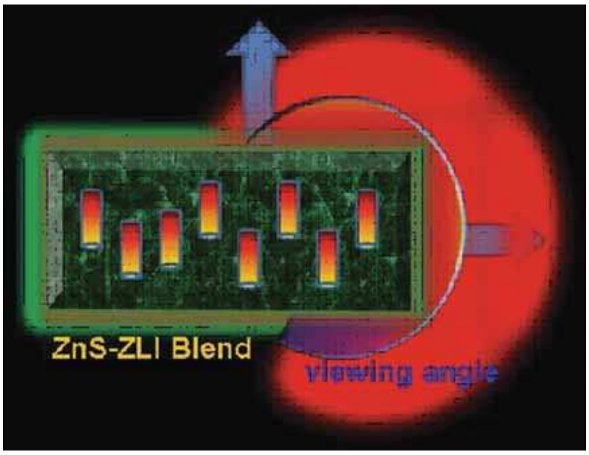
Microwave irradiation has been used for the chemical modification of functional monolayers on silicon surfaces. The thermal and chemical stability of these layers was tested under microwave irradiation to investigate the possibility to use this alternative heating process for the surface functionalization of self-assembled monolayers. The quality and morphology of the monolayers before and after microwave irradiation was analyzed by surface-sensitive techniques, such as Fourier transform infrared (FTIR) spectroscopy, atomic force microscopy (AFM), and contact angle measurements. As a model reaction, the 1,3-dipolar cycloaddition of organic azides and terminal acetylenes was tested for the chemical modification of functional azide monolayers. Low and high molar mass compounds modified with an acetylene group were successfully clicked onto the surfaces as confirmed by FTIR spectroscopy andAFMinvestigations. It could be verified that the reaction can be performed in reaction times of 5 min, and a comparison to conventional heating mechanisms allowed us to conclude that the elevated reaction temperatures result in the fast reaction process.

- Tunable Organophosphorus Dopants for Bright White Organic Light-Emitting Diodes with Simple Structures
  Fadhel,O.; Gras, M.; Lemaitre, N.; Deborde, V.; Hissler, M.; Geffroy, B.; Réau, R. *Adv. Mater.* **2009**, *21*, 1261-1265.
  <u>Abstract:</u>



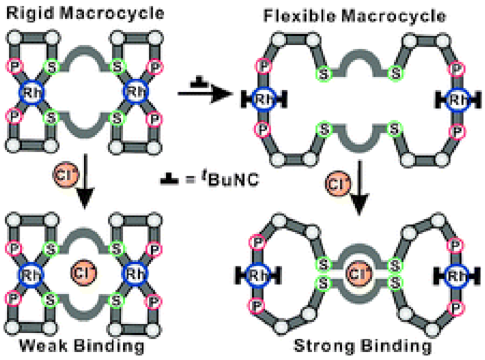
Efficient white-light-emitting LEDs have been constructed by varying the substitution pattern of phosphole derivatives and chemical modification of their P atoms, producing thermally stable derivatives that are used as suitable dopants in a blue-light-emitting host. The devices exhibit high brightness and, due to their simple structures, current-independent CIE coordinates.

- Nanorod-Driven Orientational Control of Liquid Crystal for Polarization-Tailored Electro-Optic Devices
  Acharya, S.; Kundu, S.; Hill, J.P.; Richards, G.J.; Ariga K. *Adv. Mater.* **2009**, *21*, 989-993.
  <u>Abstract:</u>



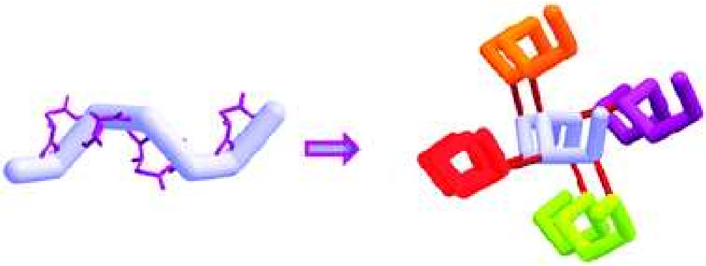
Dispersion of ultranarrow ZnS nanorods of molecular dimensions encapsulated by a fluid-like soft organic layer in the nematic liquid crystal (LC ZLI-4792) results in a novel soft-matter-type blend with previously unachieved electro-optic properties. The local ordering of the nanorods significantly affects the global ordering of the blend, allowing a more rapid response.

- Pseudo-allosteric regulation of the anion binding affinity of a macrocyclic coordination complex.
  Kuwabara, J.; Yoon, H. J.; Mirkin, J. A.; DiPasquale, A. G.; Rheingold, A. L. *Chem. Commun.* **2009**, 4557 – 4559.
  Abstract:



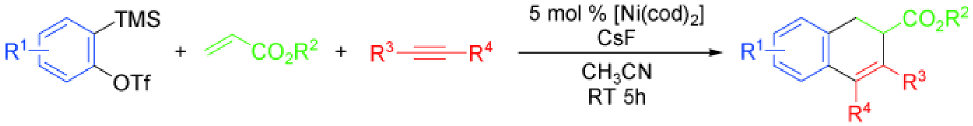
The anion binding affinity of a macrocyclic Rh complex can be allosterically regulated by reaction with a small molecule (an isocyanide), which effects a change in macrocycle size and shape.

- Bulk homochirality of a 3-D inorganic framework: ligand control of inorganic network chirality
  Livage, C.; Guillou, N.; Rabu, P.; Pattison, P.; Marrot, J.; Férey, G. *Chem. Commun.* **2009**, 4551 – 4553.
  Abstract:



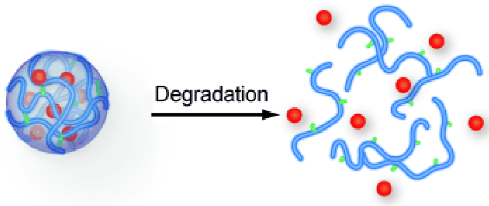
Enantioselective synthesis of a 3-D inorganic net has been achieved leading to metal–organic frameworks built from cobalt-oxide helices in which handedness is controlled by the chirality of the linked ligand.

- Nickel-Catalyzed Three-Component [2+2+2] Cycloaddition Reaction of Arynes, Alkenes, and Alkynes
  Qiu, Z.; Xie, Z. *Angew. Chem. Int. Ed*. **2009**, *48*, 5729 –5732.
  Abstract:



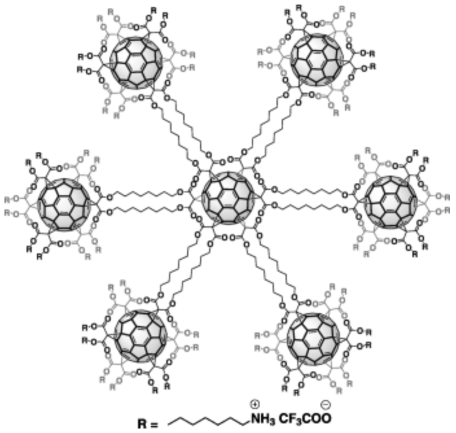
Three in one: Nickel-catalyzed three-component cycloaddition reactions of readily available arynes, activated alkenes, and alkynes gave a series of substituted 1,2-dihydronaphthalenes in moderate to very good yields with excellent chemo- and regioselectivity (see scheme, TMS=trimethylsilyl, cod=1,5-cyclooctadiene).

- Nanogels as Pharmaceutical Carriers: Finite Networks of Infinite Capabilities
  Kabanov, A. V.; Vinogradov, S. V. *Angew. Chem. Int. Ed***. 2009**, *48*, 5418 – 5429.
  Abstract:



Drug protection: Nanogels - swollen nanosized networks of hydrophilic neutral or ionic polymer chains - can spontaneously incorporate low-molecular-mass drugs or biomacromolecules such as oligonucleotides, siRNA, DNA, and proteins. Numerous chemical functionalities can be employed for the introduction of imaging molecules and the targeted release of drugs (see picture).

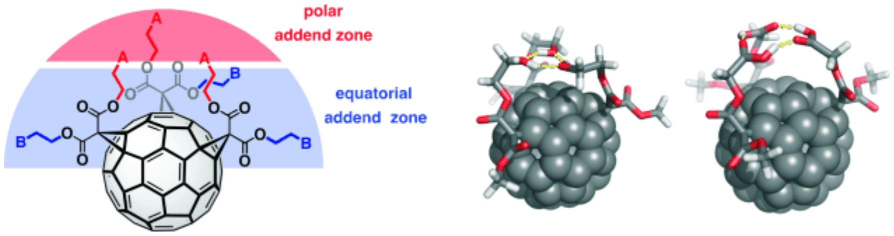
- Large Di- and Heptafullerene Polyelectrolytes Composed of C_{60} Building Blocks Having a Highly Symmetrical Hexakisaddition Pattern
  Witte, P.; Hörmann, F.; Hirsch, A. *Chem. Eur. J.* **2009**, *15*, 7423-7433.
  Abstract:



We report here on the synthesis of three new prototypes (types I-III) of very large fullerene-based polyelectrolytes which can carry up to 60 charges on their periphery. All fullerene moieties incorporated in these macromolecular structures have an octahedral hexakisaddition pattern.

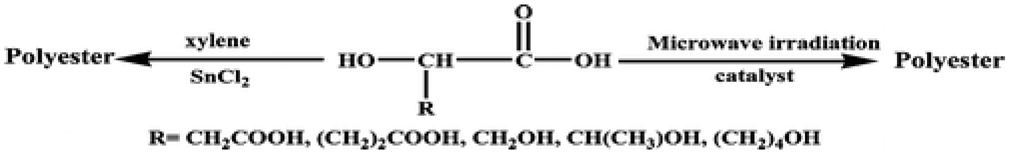
Dumbbell-shaped icosacarboxylate **5** (type I), which can accumulate up to twenty negative charges, is very soluble in methanol as well as in neutral and basic water. On the other hand, Janus dumbbell **13** (type II) contains both positively and negatively chargeable fullerene building blocks and is very soluble in acidic and basic media. However, in the region of the isoelectric point at pH 6.0-6.5 it precipitates as a pale orange solid due to pronounced intermolecular Coulomb interactions. Giant heptafullerene **15** (type III) can store up to 60 positive charges in its periphery and is the largest molecular polyelectrolyte with defined three-dimensional structure.

- Synthesis and Orthogonal Functionalization of [60]Fullerene *e*,*e*,*e*-Trisadducts with Two Spherically Defined Addend Zones
  Beuerle, F.; Hirsch, A. *Chem. Eur. J.* **2009**, *15*, 7434-7446.
  Abstract:



e,*e*,*e*-Trisadducts **13** and **15** have been prepared by a highly regioselective threefold cyclopropanation of tripodal malonates **10** and **12** with C_{60}. The yield and regioselectivity depend on the length and structure of the tethers that connect the malonate units to the focal benzene core of **13**-**15**. As a consequence of the template-directed synthesis, all *e*,*e*,*e*-trisadducts were formed as *in*/*out* isomers exclusively and contain two spherically well-defined addend zones with equatorial and polar orientation, respectively. By variation of the outer malonate termini of the tethers, selective functionalization of the equatorial addend zone could be achieved, thus leading to fine-tuning of intermolecular interactions, such as solubility or aggregation phenomena. After removal of the focal benzene moiety in **14** and **15**, selective functionalization of the polar addend zone could be achieved. Strong intramolecular hydrogen-bonding networks of the polar substituents in the polar addend zone could be observed by ^{1}H NMR spectroscopic analysis. By orthogonal functionalization of both addend zones, fullerene derivatives **44**-**48** could be synthesized as one single *in*/*out* isomer, thus greatly enhancing the potential of *e*,*e*,*e*-trisadducts as building blocks in supramolecular architectures.

- Biodegradable Polyesters Derived from Amino Acids
  Kolitz, M.; Cohen-Arazi, N.; Hagag, I.; Katzhendler, J.; Domb, A.J. *Macromolecules* **2009**, *42*, 4520–4530.
  Abstract:

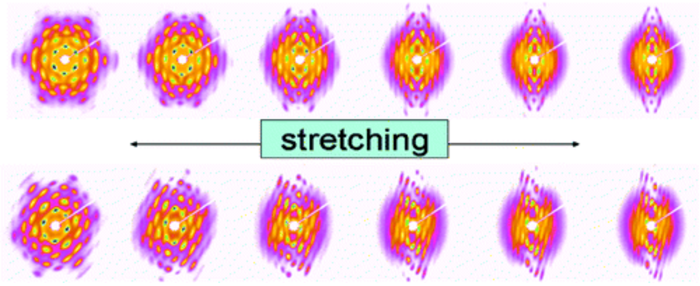


$$\text{Polyester} \xleftarrow[\text{SnCl}_2]{\text{xylene}} \text{HO—}\underset{\text{R}}{\text{CH}}\text{—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—OH} \xrightarrow[\text{catalyst}]{\text{Microwave irradiation}} \text{Polyester}$$

$R = CH_2COOH, (CH_2)_2COOH, CH_2OH, CH(CH_3)OH, (CH_2)_4OH$

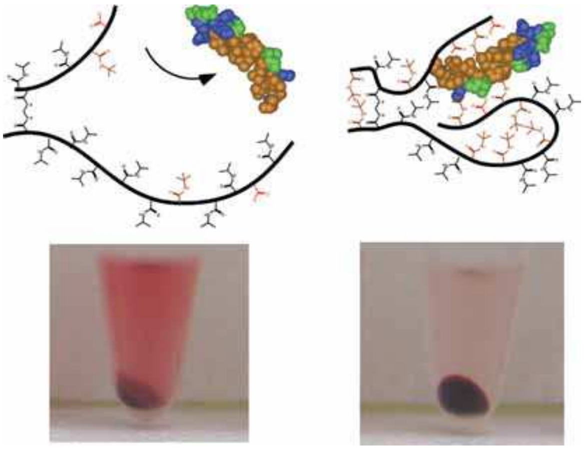
New optically active polyesters derived from amino acids by replacement of the backbone amino groups for hydroxyl residues are presented. The polyesters described are the following: poly(L)HOAsp-(COOH)-OH, poly(L)HOGlu(COOH)-OH, poly(L)HOSer(OH)-OH, poly(L)HOThr(OH)-OH, poly-(L)HOLys(OH)-OH, and poly(HOAa(X)(OH)-co-LA) and some other copolymers of R-hydroxy acids. The polymers were prepared via (a) direct condensation in bulk employing several catalysts as PTSA, boric acid, Mukaiyama’s reagent, stannous chloride dihydrate, (b) acyl halide activation, and (c) microwaveassisted polymerization. The obtained polymers reached a molecular weight between 1000 and 4000. The highest molecular weight attained employing polycondensation methods in solution, was either by utilizing polyacid, or metal catalyst (boric acid and stannous chloride respectively). Applying oxalyl chloride for chain extension also showed to be an efficient method. On the other hand, the microwave-assisted polymerization exhibited significant advantages and polymerization could be implemented with lack of solvent (neat). The polymers were characterized by several methods (GPC, CD, DSC, solubility), and tested for their degradability and biocompatibility to cell growth. Most of the polymers displayed a linear correlation between their calculated log P values and their experimental contact angles parameters. Transition glass temperatures (Tg) of copolymers with various compositions of LA were correlated to either Gordon Taylor equation or to a three parameters modified Kwei equation. The circular dichroism spectra (CD) of several homo and copolymers were measured. In general, CD curves of the homopolymers of HOSer, HOGlu, HOThr, HOAsp, and HOLys(OH) revealed a significant ester maxima approximately at 205-220 nm while the copolymers of HOSer with HOPhe displayed an additional cotton effect band at 200.6-201.5 nm. This is accounted for polymer rotational isomers and not to a different ππ* transition at lower wavelength.

- In Situ Observation of Tensile Deformation Processes of Soft Colloidal Crystalline Latex Fibers. Zhang, J.; Hu, S.; Rieger, J.; Roth, S. V.; Gehrke, R.; Men, Y. *Macromolecules* **2009**, *42*, 4795–4800.
  Abstract:



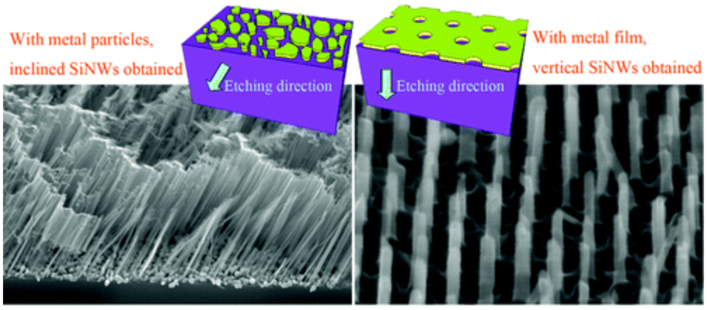
The deformation mechanism of styrene/n-butyl acrylate copolymer latex films with fiber symmetric crystalline structure subjected to uniaxial stretching was studied using synchrotron small-angle X-ray scattering technique. The fibers were drawn at angles of 0, 35, and 55_ with respect to the fiber axis. In all cases, the microscopic deformation within the crystallites was found to deviate from affine deformation behavior with respect to the macroscopic deformation ratio. Moreover, the extent of this deviation is different in the three cases. This peculiar behavior can be attributed to the relative orientation of the (111) plane of the crystals, the plane of densest packing, with respect to the stretching direction in each case. When the stretching direction coincides with the crystallographic (111) plane, which is the case for stretching directions of 0 and 55_ with respect to the fiber axis, the microscopic deformation deviates less from affine behavior than when the stretching direction is arbitrarily oriented with respect to the crystallographic (111) plan. The dependence of tilting angle and d-spacing of selected (111) or (220) planes from the microscopic crystalline draw ratio are fully in accordance with theoretical considerations.

- Design of Synthetic Polymer Nanoparticles that Capture and Neutralize a Toxic Peptide Hoshino, Y.; Urakami, T.; Kodama, T.; Koide, H.; Oku, N.; Okahata, Y.; Shea, K. J. *Small* **2009**, *5*, 1562 – 1568.
  Abstract:



Designed polymer nanoparticles (NPs) capable of binding and neutralizing a biomacromolecular toxin are prepared. A library of copolymer NPs is synthesized from combinations of functional monomers. The binding capacity and affinity of the NPs are individually analyzed. NPs with optimized composition are capable of neutralizing the toxin even in a complex biological milieu. It is anticipated that this strategy will be a starting point for the design of synthetic alternatives to antibodies.

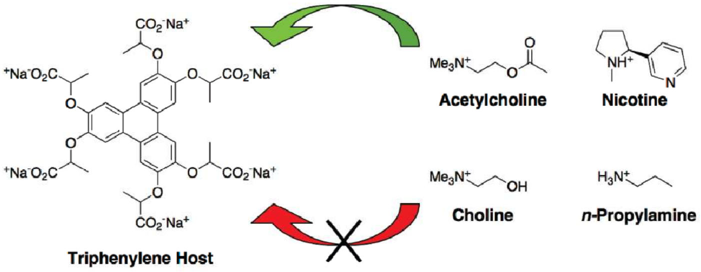
- Ordered Arrays of Vertically Aligned [110] Silicon Nanowires by Suppressing the Crystallographically Preferred <100> Etching Directions
  Huang, Z.; Shimizu, T.; Senz, S.; Zhang, Z.; Zhang, X.; Lee, W.; Geyer, N.; Gösele, U. *Nano Lett.* **2009**, *9*, 2519–2525.
  Abstract:



Morphology-dependent etching of (110) Si substrate

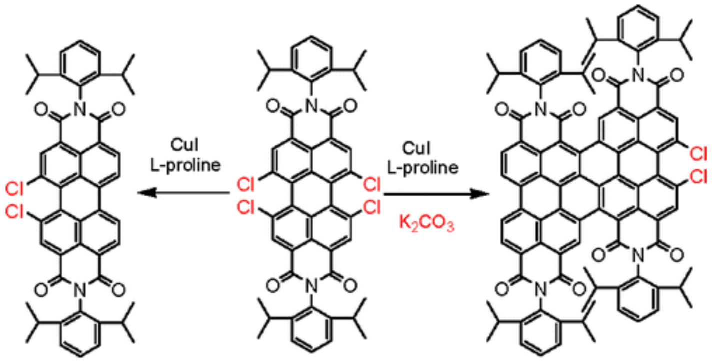
The metal-assisted etching direction of Si(110) substrates was found to be dependent upon the morphology of the deposited metal catalyst. The etching direction of a Si(110) substrate was found to be one of the two crystallographically preferred 〈100〉 directions in the case of isolated metal particles or a small area metal mesh with nanoholes. In contrast, the etching proceeded in the vertical $[\bar{1}\bar{1}0]$ direction, when the lateral size of the catalytic metal mesh was sufficiently large. Therefore, the direction of etching and the resulting nanostructures obtained by metal-assisted etching can be easily controlled by an appropriate choice of the morphology of the deposited metal catalyst. On the basis of this finding, a generic method was developed for the fabrication of wafer-scale vertically aligned arrays of epitaxial [110] Si nanowires on a Si(110) substrate. The method utilized a thin metal film with an extended array of pores as an etching catalyst based on an ultrathin porous anodic alumina mask, while a prepatterning of the substrate prior to the metal depostion is not necessary. The diameter of Si nanowires can be easily controlled by a combination of the pore diameter of the porous alumina film and varying the thickness of the deposited metal film.

- A Hydrosoluble Triphenylene That Preferentially Binds Acetylcholine, Epibatidine, and Nicotine
  Givelet, C.; Buffeteau, T.; Arnaud-Neu, F.; Hubscher-Bruder, V.; Bibal, B. *J. Org. Chem.* **2009**, *74*, 5059–5062.
  Abstract:



Synthesis and binding properties of a new hydrosoluble triphenylene **1b** are reported. Selective recognition of acetylcholine (ACh) against other aliphatic ammoniums is achieved by this flat receptor, which also forms complexes with epibatidine and nicotine. Ionic pairing and hydrophobic effects between host **1b** and ACh are studied by infrared spectroscopy.

- Highly Regiospecific Synthetic Approach to Monobay-Functionalized Perylene Bisimide and Di(perylene bisimide)
  Zhen, Y.; Qian, H.; Xiang, J.; Qu, J.; Wang, Z. *Org. Lett.* **2009**, *11*, 3084-3087.
  Abstract:



Monobay-dichlorinated perylene bisimide and diperylene bisimide have been regiospecifically synthesized from tetrachlorinated perylene bisimide in different copper-mediated reaction conditions, thus opening a new avenue to their monobay-functionalization.