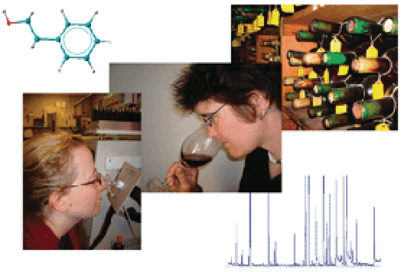
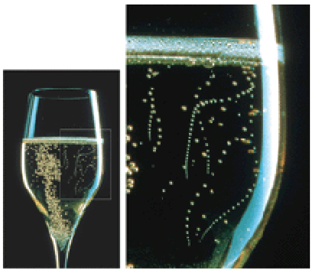
- Wine flavor: chemistry in a glass
  Polášková, P.; Herszage, J.; Ebeler, S. E. *Chem. Soc. Rev.* **2008**, *37*, 2478 – 2489.
  Abstract:



Although hundreds of chemical compounds have been identified in grapes and wines, only a few compounds actually contribute to sensory perception of wine flavor. This *critical review* focuses on volatile compounds that contribute to wine aroma and provides an overview of recent developments in analytical techniques for volatiles analysis, including methods used to identify the compounds that make the greatest contributions to the overall aroma. Knowledge of volatile composition alone is not enough to completely understand the overall wine aroma, however, due to complex interactions of odorants with each other and with other nonvolatile matrix components. These interactions and their impact on aroma volatility are the focus of much current research and are also reviewed here. Finally, the sequencing of the grapevine and yeast genomes in the past ~10 years provides the opportunity for exciting multidisciplinary studies aimed at understanding the influences of multiple genetic and environmental factors on grape and wine flavor biochemistry and metabolism (147 references).

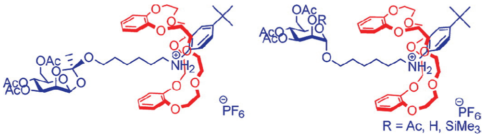
- Recent advances in the science of champagne bubbles
  Liger-Belair, G.; Polidori, G.; Jeandet, P. *Chem. Soc. Rev.* **2008**, *37*, 2490 – 2511.
  Abstract:



The so-called *effervescence* process, which enlivens champagne and sparkling wines tasting, is the result of the fine interplay between CO_2-dissolved gas molecules, tiny air pockets trapped within microscopic particles during the pouring process, and some liquid properties. This *critical review* summarizes recent advances obtained during the past decade concerning the physicochemical processes behind the nucleation, rise, and burst of bubbles found in glasses poured with champagne and sparkling wines. Those phenomena observed in close-up through high-speed photography are often visually appealing. Let’s hope that your enjoyment of champagne will be enhanced after reading this fully illustrated review dedicated to the deep beauties of nature often hidden behind many everyday phenomena (51 references).

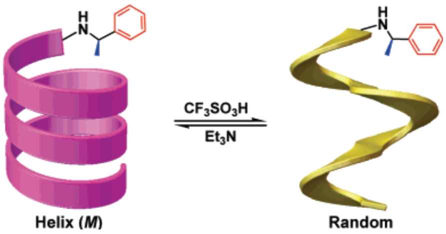
- A Very Efficient Synthesis of a Mannosyl Orthoester [2]Rotaxane and Mannosidic [2]Rotaxanes
  Coutrot F.; Busseron E.; Montero J.-L. *Org. Lett.*, **2008**, *10*, 753-756.

Abstract :



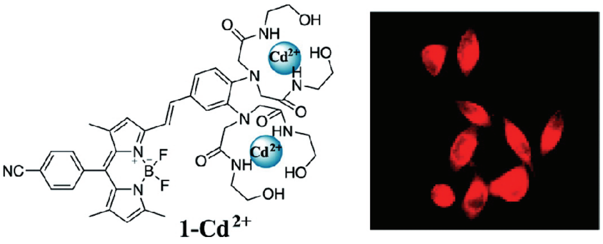
The direct preparation of mannosyl[2]rotaxane derivatives by O-glycosylation from tetra-O-acetyl-α - D-mannosyltrichloroacetimidate and a tertbutylanilinium alcohol in the presence of dibenzo-24-crown-8 is described. The method appears to be very efficient and allows for the preparation of either orthoester or mannosyl rotaxane derivatives, depending on reaction conditions.

- Chiral Induction in Phenanthroline-Derived Oligoamide Foldamers: An Acid- and Base-Controllable Switch in Helical Molecular Strands
  Hu H.-Y.; Xiang J.-F.; Yang Y.; Chen C.-F. *Org. Lett.* **2008**, *10*, 1275-1278.
  Abstract :



A series of phenanthroline-derived oligoamides bearing a chiral (*R*)-phenethylamino end group were synthesized that displayed chiral helical induction and subsequently formed one-hand helical foldamers in solution. Moreover, an acid- and base-controllable switch in the helical molecular strands was observed, which has been demonstrated by NMR, UV-vis, and circular dichroism spectroscopy.

- A Highly Sensitive and Selective OFF-ON Fluorescent Sensor for Cadmium in Aqueous Solution and Living Cell
  Cheng, T.; Xu, X.; Zhang, S.; Zhu, W.; Qian, X.; Duan, L. *J. Am. Chem. Soc.* **2008**, *130*, 16160–16161.
  Abstract:

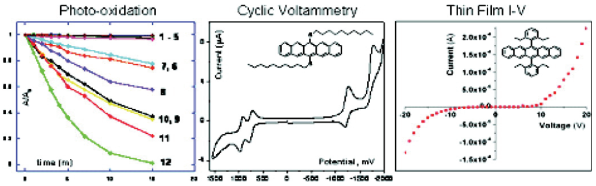


A highly selective and sensitive OFF-ON fluorescent sensor 1, employing the PET mechanism, was designed and synthesized. It could be used to detect Cd^{2+} ion in aqueous solution and to image Cd^{2+} ion in living cells. The fluorescence intensity significantly enhanced about 195-fold and the quantum yield increased almost 100-fold. Moreover the fluorescence intensity of 1 increased linearly with high sensitivity (0−1 μM) toward Cd^{2+}.

- Substituent Effects in Pentacenes: Gaining Control over HOMO−LUMO Gaps and Photooxidative Resistances
  Kaur, I.; Jia,W.; Kopreski, R. P.; S.; Selvarasah, S.; Dokmeci, M. R.; Pramanik, C.; McGrueR, N.

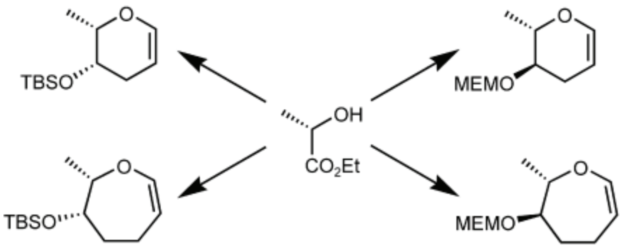
E.; Miller,G. P. *J. Am. Chem. Soc.* **2008**, *130*, 16274–16286.

Abstract:



A combined experimental and computational study of a series of substituted pentacenes including halogenated, phenylated, silylethynylated and thiolated derivatives is presented. Experimental studies include the synthesis and characterization of six new and six known pentacene derivatives and a kinetic study of each derivative under identical photooxidative conditions. Structures, HOMO−LUMO energies and associated gaps were calculated at the B3LYP/6-311+G**//PM3 level while optical and electrochemical HOMO−LUMO gaps were measured experimentally. The combined results provide for the first time a quantitative assessment of HOMO−LUMO gaps and photooxidative resistances for a large series of pentacene derivatives as a function of substituents. The persistence of each pentacene derivative is impacted by a combination of steric resistance and electronic effects as well as the positional location of each substituent. Silylethynyl-substituted pentacenes like TIPS-pentacene possess small HOMO−LUMO gaps but are not the longest lived species under photooxidative conditions, contrary to popular perception. A pentacene derivative with both chlorine substituents in the 2,3,9,10 positions and o-alkylphenyl substituents in the 6,13 positions is longer lived than TIPS-pentacene. Of all the derivatives studied, alkylthio- and arylthio-substituted pentacenes are most resistant to photooxidation, possess relatively small HOMO−LUMO gaps and are highly soluble in a variety of organic solvents. These results have broad implications for the field of organic molecular electronics where OFET, OLED, and other applications can benefit from highly persistent, solution processable pentacene derivatives.

- The Tandem Ring-Closing Metathesis-Isomerization Approach to 6-Deoxyglycals
  Schmidt, B.; Biernat, A. *Chem. Eur. J.* **2008**, *14*, 6135-6141.
  Abstract:

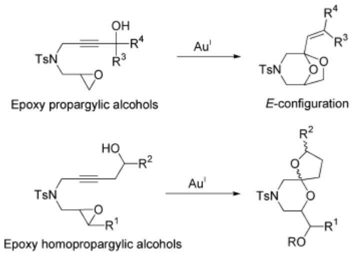


Protected 3,6-dideoxyglycals have been synthesized de novo as single isomers starting from ethyl lactate by using the tandem RCM-isomerization reaction as the key step. Different relative configurations become accessible by addition of vinyl- or allyl-metal compounds to protected lactaldehydes under Cram-chelate or Felkin-Anh control. The concept is exemplified for glycals of **L**-rhodinose and **L**-amicetose, as well as for ring-expanded non-natural analogues thereof. This novel approach to glycals is also applicable to the synthesis of disaccharide glycals via a reiterative strategy, as exemplified for the dimer of **L**-rhodinose and its non-natural ring expanded analogue.

- A Gold(I)-Catalyzed Intramolecular Reaction of Propargylic/Homopropargylic Alcohols with Oxirane

Dai, L.-Z.; Shi, M. *Chem. Eur. J.* **2008**, *14*, 7011-7018.

Abstract:

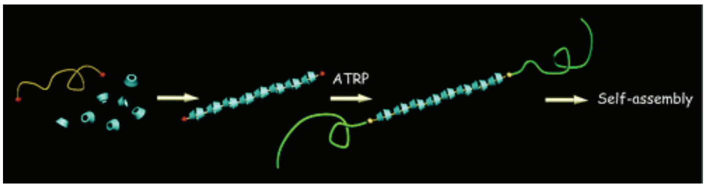


The gold(I)-catalyzed cycloisomerization of epoxy alkynes in the presence of a nucleophile is an efficient protocol to provide ketal skeletons with high stereoselectivity. An intramolecular reaction of propargylic/homopropargylic alcohols with oxirane to produce ketal/spiroketals in moderate yields under mild conditions has been reported. Moreover, the mechanism of this kind of reaction has been discussed on the basis of a series of control and ^{18}O tracer experiments.

- Supramolecular ABA Triblock Copolymer with Polyrotaxane as B Block and Its Hierarchical Self-Assembly

  Ren, L.; Ke, F.; Chen, Y.; Liang, D.; Huang, J. *Macromolecules* **2008**, *41*, 5295-5300.

  Abstract :

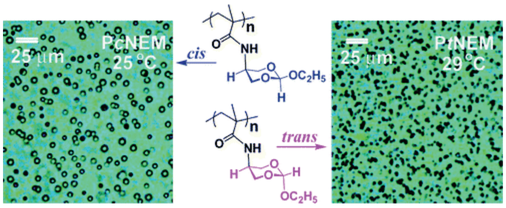


A series of novel well-defined supramolecular ABA triblock copolymers of polyrotaxane are synthesized via atom transfer radical polymerization (ATRP) of 2-(dimethylamino)ethyl methacrylate (DMA) initiated by a polypseudorotaxane initiator of R-cyclodextrins (R-CDs) and PEG. The molecular structure of the ABA triblock copolymer with a polyrotaxane as B block, poly(2-(dimethylamino)ethyl methacrylate)-*b*-PEG[included by R-CDs]-*b*-poly(2-(dimethylamino)ethyl methacrylate) (DMA-*b*-PEGCD-*b*-DMA), was confirmed by two-dimensional rotating frame Overhauser effect spectroscopy (2D ROESY) and X-ray diffraction (XRD) analyses. Self-assembly behaviors of the copolymers in water solution were studied by dynamic light scattering (DLS), static light scattering (SLS), and transmission electron microscopy (TEM). Different from the model triblock copolymer without R-CDs and the polypseudorotaxanes composed of homo-PEG and R-CDs, the supramolecular triblock copolymers in water self-assembled into spheres with an amorphous core. Furthermore, the block copolymers at an acidic aqueous solution where the flanking chains were protonated generated the particles with a core of hexagonally packed polyrotaxanes. It is interesting to notice that the particles further aggregated into large disks induced by the solvent evaporation.

- Stereochemical Effect of *Trans*/*Cis* Isomers on the Aqueous Solution Properties of Acid-Labile Thermoresponsive Polymers.

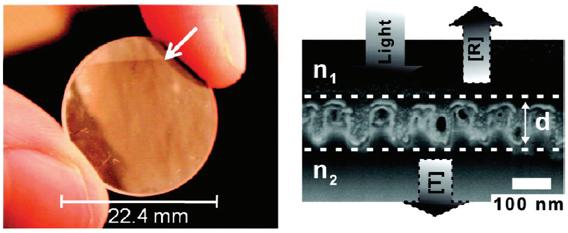
  Huang, X.; Du, F.; Liang, D.; Lin, S.-S.; Li, Z. *Macromolecules* **2008**, *41*, 5433-5440.

  Abstract :



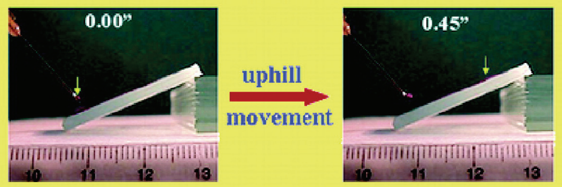
Two acid-labile, thermoresponsive poly(methacrylamide)s with the pendant cyclic orthoester moieties of *trans* and *cis* configurations, P*t*NEM and P*c*NEM, were synthesized via free radical polymerization of the corresponding *trans* and *cis* isomers of *N*-(2-ethoxy-1,3-dioxan-5-yl)methacrylamide (NEM). The thermally induced phase transition/separation behaviors of both polymers as well as the aqueous solution properties below and above their phase transition temperatures were investigated by means of turbidimetry, DSC, 1H NMR, microscopy, fluorescence probe, and dynamic light scattering. Both P*t*NEM and P*c*NEM showed aggregation behaviors below their respective LCSTs, and the former formed more hydrophobic microdomains which had greater capability to solvate pyrene molecules compared with P*c*NEM. These two polymers exhibited thermally induced sensitive and reversible phase transitions in aqueous solution. P*t*NEM showed a little lower cloud point but much greater phase transition enthalpy compared to P*c*NEM. The results of DSC, 1H NMR, and microscopy measurements revealed that P*c*NEM exhibited a liquid-liquid phase separation while P*t*NEM likely underwent a liquid-solid transition. Furthermore, the pH-dependent hydrolyses of both polymers were studied by the 1H NMR and turbidimetric approaches. The results indicated that both P*t*NEM and P*c*NEM showed acid-triggered hydrolysis behaviors, and the hydrolysis products were affected by the configurations of the pendant cyclic groups. On the basis of these results, we can conclude that the stereochemical structures of the pendant cyclic orthoester groups in these poly(methacrylamide)s greatly affect their aqueous solution properties as well as their hydrolysis behaviors.

- Biomimetic Interfaces for High-Performance Optics in the Deep-UV Light Range
  Lohmüller, T.; Helgert, M.; Sundermann, M.; Brunner, R.; Spatz, J. P. *Nano Lett.* **2008**, *8*, 1429-1433.
  Abstract:



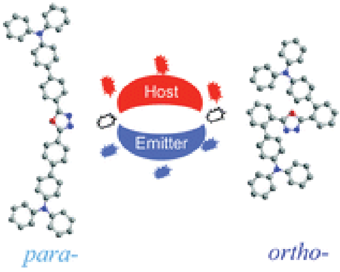
We report an innovative approach for the fabrication of highly light transmissive, antireflective optical interfaces. This is possible due to the discovery that metallic nanoparticles may be used as a lithographic mask to etch nonstraightforward structures into fused silica, which results in a quasihexagonal pattern of hollow, pillar-like protuberances. The far reaching optical performance of these structures is demonstrated by reflection and transmission measurements at oblique angles of incidence over a broad spectral region ranging from deep-ultraviolet to infrared light.

- Shape-Gradient Composite Surfaces: Water Droplets Move Uphill
  Zhang, J.; Han, Y. *Langmuir* **2007**, *23*, 6136-6141.
  Abstract:



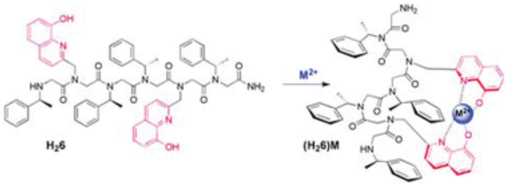
The approach of water droplets self-running horizontally and uphill without any other forces was proposed by patterning the shape-gradient hydrophilic material (i.e., mica) to the hydrophobic matrix (i.e., wax or low-density polyethylene (LDPE)). The shape-gradient composite surface is the best one to drive water droplet self-running both at the high velocity and the maximal distance among four different geometrical mica/wax composite surfaces. The driving force for the water droplets self-running includes: (1) the great difference in wettability of surface materials, (2) the low contact angle hysteresis of surface materials, and (3) the space limitation of the shape-gradient transportation area. Furthermore, the average velocity and the maximal distance of the self-running were mainly determined by the gradient angle (R), the droplet volume, and the difference of the contact angle hysteresis. Theoretical analysis is in agreement with the experimental results.

- Multifunctional bipolar triphenylamine/oxadiazole derivatives: highly efficient blue fluorescence, red phosphorescence host and two-color based white OLEDs
  Tao, Y.; Wang, K.; Shang, Y.; Yang, C.; Ao, L.; Qin, J.; Ma, D.; Shuai, Z. *Chem. Commun.* **2009**, 77 – 79.
  <u>Abstract :</u>



Two simple triphenylamine/oxadiazole derivatives were synthesized and fully characterized; their multifunctionality as highly efficient non-doped blue fluorescence, excellent red phosphorescent host and single-doped two-color based white OLEDs has been demonstrated.

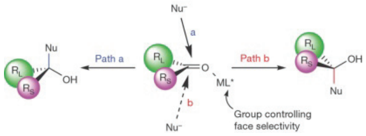
- Metallopeptoids
  Maayan, G.; Ward, M. D.; Kirshenbaum K. *Chem. Commun.* **2009**, 56 – 58.
  <u>Abstract :</u>



N-substituted glycine peptoid oligomers bearing hydroxyquinoline ligands form complexes with Cu(II) and Co(II) in which the chiral helical secondary structure of the foldamers is enhanced upon metal binding and establishes a stereogenic environment for metal coordination.

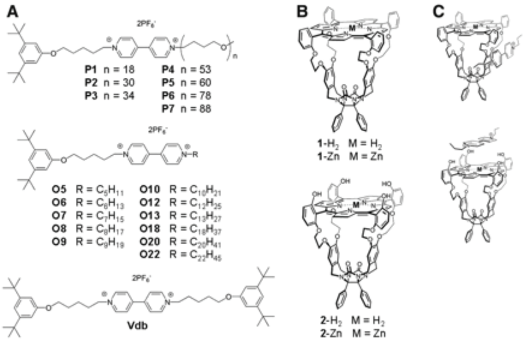
- Enantiodivergent conversion of chiral secondary alcohols into tertiary alcohols
  Stymiest, J. L.; Bagutski, V.; French, R. M.; Aggarwal, V. K. *Nature* **2008**, *456*, 778-782.

Abstract:



From receptors in the nose to supramolecular biopolymers, nature shows a remarkable degree of specificity in the recognition of chiral molecules, resulting in the mirror image arrangements of the two forms eliciting quite different biological responses. It is thus critically important that during a chemical synthesis of chiral molecules only one of the two three-dimensional arrangements is created. Although certain classes of chiral molecules (for example secondary alcohols) are now easy to make selectively in the single mirror image form, one class—those containing quaternary stereogenic centres (a carbon atom with four different non-hydrogen substituents)—remains a great challenge. Here we present a general solution to this problem which takes easily obtainable secondary alcohols in their single mirror image form and in a two-step sequence converts them into tertiary alcohols (quaternary stereogenic centres). The overall process involves removing the hydrogen atom (attached to carbon) of the secondary alcohol and effectively replacing it with an alkyl, alkenyl or aryl group. Furthermore, starting from a single mirror image form of the secondary alcohol, either mirror image form of the tertiary alcohol can be made with high levels of stereocontrol. Thus, a broad range of tertiary alcohols can now be easily made by this method with very high levels of selectivity. We expect that this methodology could find widespread application, as the intermediate tertiary boronic esters can potentially be converted into a range of functional groups with retention of configuration.

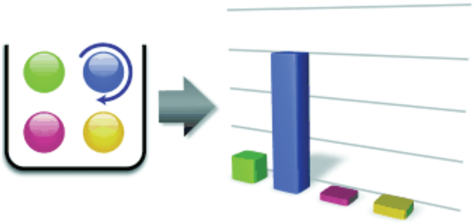
- Mechanism of Threading a Polymer Through a Macrocyclic Ring
  Deutman, A. B. C.; Monnereau, C.; Elemans, J. A. A. W.; Ercolani, G.; Nolte,R. J. M.; Rowan, A. E. *Science* **2008**, *322*, 1668 – 1671.
  Abstract :



The translocation of biopolymers through pores and channels plays a fundamental role in numerous biological processes. We describe here the mechanism of the threading of a series of polymer chains through a synthetic macrocycle, which mimics these natural processes. The threading of polymers involves a kinetically favorable "entron" effect, which is associated with the initial filling of the cavity by the end of the polymer. A preassociation between the outside of the macrocycle and the polymer induces a process in which the polymer end loops back into the cavity of the macrocycle. This looping mechanism results in accelerated threading rates and unidirectional motion and is reminiscent of the protein translocation through membrane pores.

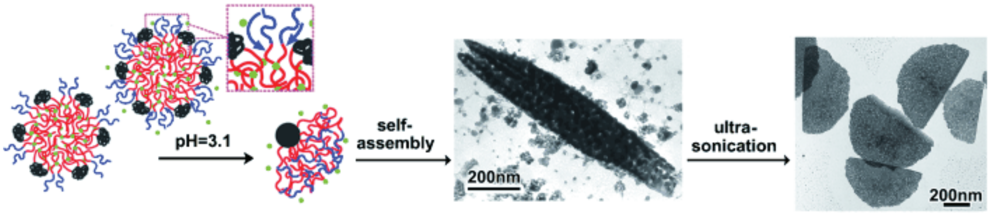
- A Simple Synthetic Replicator Amplifies Itself from a Dynamic Reagent Pool

Sadownik, J. W.; Philp, D. *Angew. Chem. Int. Ed.* **2008**, *47*, 9965–9970.
Abstract:



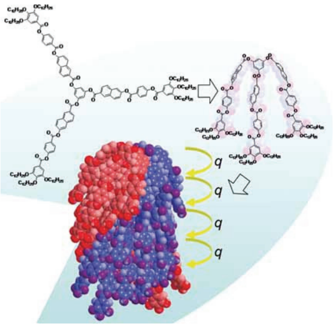
The fate of a dynamic combinatorial library is determined by coupling the exchange processes to a synthetic replicator. The replicating template is capable of exploiting and dominating the exchanging pool of reagents in order to amplify its own formation at the expense of other species (see picture) through the non-linear kinetics inherent in minimal replication.

- Nanoscale Tubular and Sheetlike Superstructures from Hierarchical Self-Assembly of Polymeric Janus Particles
  Cheng, L.; Zhang, G.; Zhu, L.; Chen, D.; Jiang, M. *Angew. Chem. Int. Ed.* **2008**, *47*, 10171 – 10174.
  Abstract:



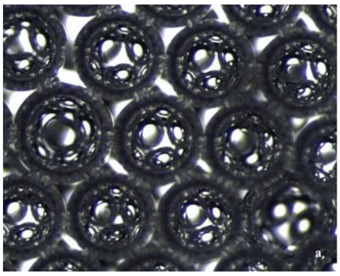
Two faces: Starting from mixed shell micelles, amphiphilic Janus particles with opposite hydrophobic and hydrophilic complex sides were obtained by intramicellar complexation between the mixed shell and the core at pH 3.1 (see picture). Hierarchical self-assembly of these Janus particles in water resulted in a nanoscale tubular superstructure, which was then converted into regular nanosheets upon ultrasonication.

- Columnar Mesophases with 3D Order from New Functional Nonconventional Star-Shaped Mesogens
  Lehmann, M.; Jahr, M.; Grozema, F. C.; Abellon, R. D.; Siebbeles, L. D. A.; Müller, M. *Adv. Mater*. **2008**, *20*, 4414-4418.
  Abstract :



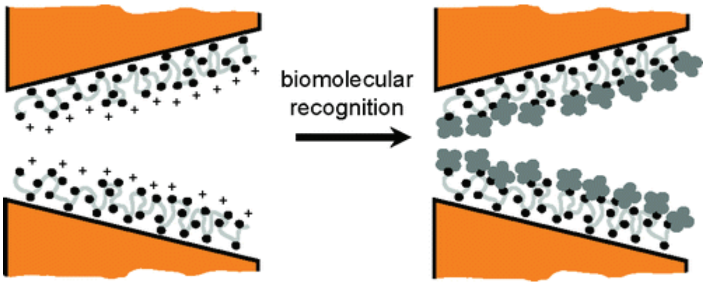
Star-shaped oligobenzoates with naphthalene chromophores assemble in columnar mesophases. In the low-temperature phases, mesogens self-organize helically along the columns, leading to columnar liquid crystal phases with 3D order (see image). The formation of these structures is driven by optimization of space-filling and nanosegregation. Naphthalene chromophores are segregated in the center of the columns and operate as hopping sites for charges.

- Aerodynamically Assisted Jets: A Paradigm for Directly Microbubbling and Microfoaming Combinations of Advanced Materials
  Arumuganathar, S.; Suter, N.; Jayasinghe, S. N. *Adv. Mater*. **2008**, *20*, 4419-4422.
  Abstract :



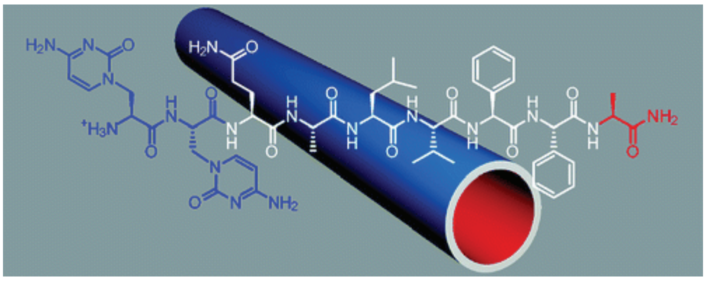
This Communication elucidates the ability to directly microbubble and microfoam suspensions containing structural, functional and/or biological materials. Structural entities such as these having functional gradation could potentially be explored in a plethora of applications within the physical and life sciences.

- Biosensing and Supramolecular Bioconjugation in Single Conical Polymer Nanochannels. Facile Incorporation of Biorecognition Elements into Nanoconfined Geometries
  Ali, M.; Yameen, B.; Neumann, R.; Ensinger, W.; Knoll, W.; Azzaroni, O. *J. Am. Chem. Soc.* 2008, *130*, 16351–16357.
  Abstract:



There is a growing quest for tailorable nanochannels or nanopores having dimensions comparable to the size of biological molecules and mimicking the function of biological ion channels. This interest is based on the use of nanochannels as extremely sensitive single molecule biosensors. The biosensing capabilities of these nanochannels depend sensitively on the surface characteristics of their inner walls to achieve the desired functionality of the biomimetic system. Nanoscale control over the surface properties of the nanochannel plays a crucial role in the biosensing performance due to the chemical groups incorporated on the inner channel walls that act as binding sites for different analytes and interact with molecules passing through the channel. Here we report a new approach to incorporate biosensing elements into polymer nanochannels by using electrostatic self-assembly. We describe a facile strategy based on the use of bifunctional macromolecular ligands to electrostatically assemble biorecongnition sites into the nanochannel wall, which can then be used as recognition elements for constructing a nanobiosensor. The experimental results demonstrate that the ligand-functionalized nanochannels are very stable and the biorecognition event (protein conjugation) does not promote the removal of the ligands from the channel surface. In addition, control experiments indicated that the electrostatically assembled nanochannel surface displays good biospecificity and nonfouling properties. Then, we demonstrate that this approach also enables the creation of supramolecular multilayered structures inside the nanopore that are stabilized by strong ligand−receptor interactions. We envision that the formation of multilayered supramolecular assemblies inside solid-state nanochannels will play a key role in the further expansion of the toolbox called “soft nanotechnology”, as well as in the construction of new multifunctional biomimetic systems.

- Nucleobase-Directed Amyloid Nanotube Assembly
  Liu, P.; Ni, R.; Mehta, A. K.; Childers, W. S.; Lakdawala, A.; Pingali, S. V.; Thiyagarajan, P.; Lynn, D. G. *J. Am. Chem. Soc.* **2008**, *130*, 16867–16869.
  Abstract:



Cytosine nucleobases were successfully incorporated into the side chain of the self-assembling amyloid peptide fragment HHQALVFFA to give ccAQLVFFA. At a pH range of 3−4, where cytosine is expected to be partially protonated, small-angle X-ray scattering analyses revealed the nucleobase peptide assembles to be well-defined nanotubes with an outer diameter of 24.8 nm and wall thicknesses of 3.3 nm. FT-IR and X-ray diffraction confirmed β-sheet-rich assembly with the characteristic cross-β architecture of amyloid. The β-sheet registry, determined by measuring ^{13}CO−^{13}CO backbone distances with solid-state NMR and linear dichroism, placed the cytosine bases roughly perpendicular to the nanotube axis, resulting in a model where the complementary interactions between the cytosine bases increases β-sheet stacking to give the nanotube architecture. These scaffolds then extend the templates used to encode biological information beyond the nucleic acid duplexes and into covalent networks whose self-assembly is still defined by a precise complementarity of the side-chain registry.