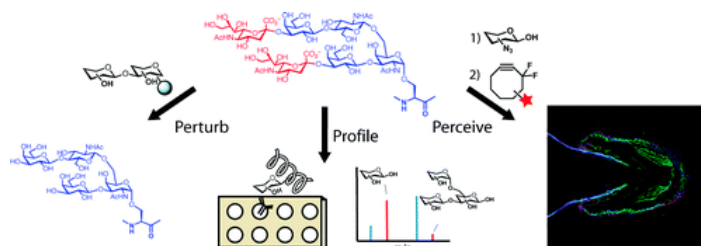


- Chemical Approaches To Perturb, Profile, and Perceive Glycans  
Agard, N. J.; Bertozzi, C. R. *Acc. Chem. Res.* **2009**, *42*, 788–797.

Abstract:



Glycosylation is an essential form of post-translational modification that regulates intracellular and extracellular processes. Regrettably, conventional biochemical and genetic methods often fall short for the study of glycans, because their structures are often not precisely defined at the genetic level. To address this deficiency, chemists have developed technologies to perturb glycan biosynthesis, profile their presentation at the systems level, and perceive their spatial distribution. These tools have identified potential disease biomarkers and ways to monitor dynamic changes to the glycome in living organisms. Still, glycosylation remains the underexplored frontier of many biological systems. In this Account, we focus on research in our laboratory that seeks to transform the study of glycan function from a challenge to routine practice.

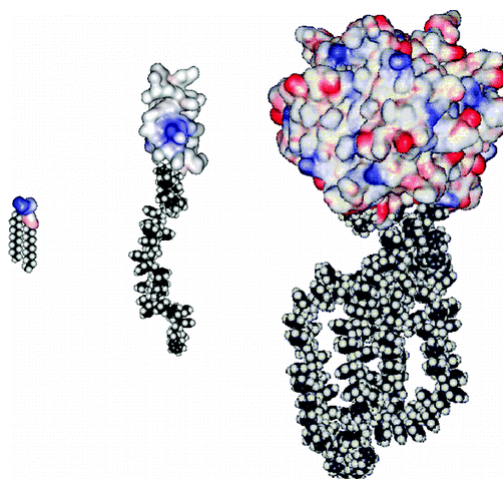
In studies of proteins and nucleic acids, functional studies have often relied on genetic manipulations to perturb structure. Though not directly subject to mutation, we can determine glycan structure–function relationships by synthesizing defined glycoconjugates or by altering natural glycosylation pathways. Chemical syntheses of uniform glycoproteins and polymeric glycoprotein mimics have facilitated the study of individual glycoconjugates in the absence of glycan microheterogeneity. Alternatively, selective inhibition or activation of glycosyltransferases or glycosidases can define the biological roles of the corresponding glycans. Investigators have developed tools including small molecule inhibitors, decoy substrates, and engineered proteins to modify cellular glycans. Current approaches offer a precision approaching that of genetic control.

Genomic and proteomic profiling form a basis for biological discovery. Glycans also present a rich matrix of information that adapts rapidly to changing environs. Glycomic and glycoproteomic analyses via microarrays and mass spectrometry are beginning to characterize alterations in glycans that correlate with disease. These approaches have already identified several cancer biomarkers. Metabolic labeling can identify recently synthesized glycans and thus directly track glycan dynamics. This approach can highlight changes in physiology or environment and may be more informative than steady-state analyses. Together, glycomic and metabolic labeling techniques provide a comprehensive description of glycosylation as a foundation for hypothesis generation.

Direct visualization of proteins via the green fluorescent protein (GFP) and its congeners has revolutionized the field of protein dynamics. Similarly, the ability to perceive the spatial organization of glycans could transform our understanding of their role in development, infection, and disease progression. Fluorescent tagging in cultured cells and developing organisms has revealed important insights into the dynamics of these structures during growth and development. These results have highlighted the need for additional imaging probes.

- Synthesis of Polymer–Biohybrids: From Small to Giant Surfactants  
Reynhout, I. C.; Cornelissen, J. J. L. M.; Nolte, R. J. M. *Acc. Chem. Res.* **2009**, *42*, 681–692.

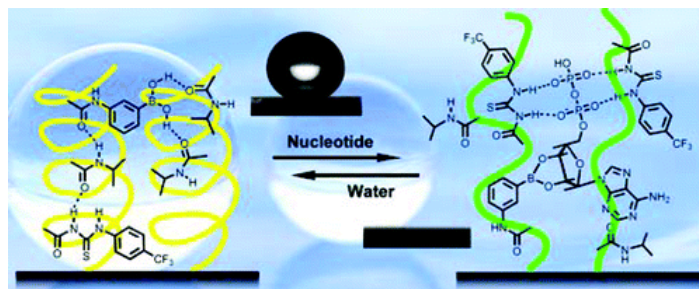
Abstract:



Amphiphiles or surfactants, more popularly known as soaps, are among the oldest known chemical compounds used by man. Written text on a clay tablet dated to 2200 B.C. indicates that the Babylonians were familiar with soap-like substances. According to the Ebers papyrus (1550 B.C.), the ancient Egyptians bathed regularly in a mixture of animal oils, vegetable extracts, and alkaline salts, and a soap factory with bars of scented soap was found in the ruins of Pompeii (79 A.D.). In modern times, the use of soap has become universal, and we now understand reasonably well what happens when soap molecules are dispersed in aqueous solution and how the cleaning properties of soap work. The latter is related to the surface-active behavior of soap molecules, which is a result of their amphiphilic, also called amphipathic, character. Although the cleaning aspect is still an important issue, scientists are increasingly focusing on other properties of soaps, for example, self-assembling behavior and how this can be used in the design and non-covalent synthesis of new (macro)molecular architectures. These new molecules can be employed in nanotechnology and drug delivery, among other applications.

This Account will focus on three different classes of amphiphiles. The first is the low molecular weight amphiphiles, also called classical amphiphiles in this context. A short overview will be given on the research carried out by our group and others on the self-assembly behavior and properties of these compounds; in particular, we focus on the ones that can be stabilized by polymerization (polymerized vesicles). Next, we will introduce the still relatively young field of superamphiphiles, macromolecules consisting of a hydrophobic and a hydrophilic polymeric block. Finally, and this constitutes the main part of this Account, we will provide an overview of a new class of amphiphiles, the so-called giant amphiphiles. These macromolecules have an enzyme or protein as the polar head group and a hydrophobic polymer as a tail. We will finish the Account with conclusions and an outlook to the future.

- Nucleotide-Responsive Wettability on a Smart Polymer Surface  
Qing, G.; Wang, X.; Fuchs, H.; Sun, T. *J. Am. Chem. Soc.* **2009**, *131*, 8370–8371.  
Abstract:

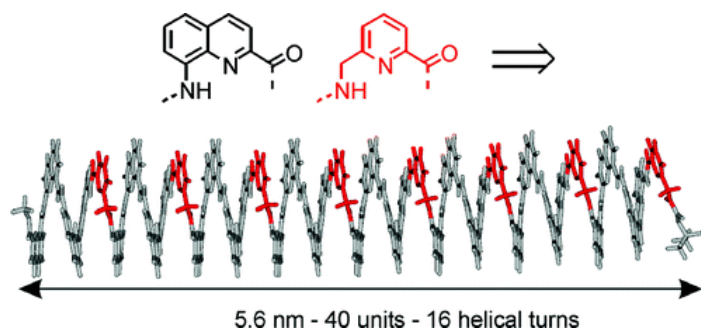


A smart copolymer film that is sensitive to nucleotide species in solution was developed. The film exhibits an excellent reversible wettability response to nucleotide solutions, which is accompanied by a phase change and the corresponding swell and shrinkage of the copolymer.

- Nanosized Hybrid Oligoamide Foldamers: Aromatic Templates for the Folding of Multiple Aliphatic Units

Garcia, D. S.; Kauffmann, B.; Kawanami, T.; Ihara, H.; Takafuji, M.; Delville, M. H.; Huc, I. *J. Am. Chem. Soc.* **2009**, *131*, 8642-8648.

Abstract:



Oligoamide sequences comprised of both 8-amino-2-quinolinecarboxylic acid "Q" and 6-aminomethyl-2-pyridinecarboxylic acid "P" have been synthesized. It was found that the aliphatic amine of P greatly facilitates amide couplings, as opposed to the aromatic amine of Q, which enabled us to prepare sequences having up to 40 units. The conformation and conformational stability of these oligomers were characterized in the solid state using X-ray crystallography and in solution using NMR and various chromatographic techniques. Q<sub>n</sub> oligomers adopt very stable helically folded conformations whereas P<sub>n</sub> oligomers do not fold and impart conformational preferences distinct from those of Q units. When a P<sub>n</sub> segment is attached at the end of a Q<sub>n</sub> segment, a couple P units appear to follow the folding pattern imposed by the Q<sub>n</sub> segment, but P units remote from the Q<sub>n</sub> segment do not fold. When a P<sub>n</sub> segment is inserted between two Q<sub>4</sub> segments, the P<sub>n</sub> segment adopts the canonical helical conformation imposed by the Q units at least up to two full helical turns ( $n = 5$ ). However, the overall stability of the helix tends to decrease as the number of P units increases. When noncontiguous P units separated by Q<sub>4</sub> segments are incorporated in a sequence, they all adopt the helical conformation imposed by Q monomers and the overall helix stability increases when helix length increases. For example, a 40mer with a sequence (PQ<sub>4</sub>)<sub>8</sub> folds into a rod-like helix spanning over 16 turns with a length of 5.6 nm. This investigation thus demonstrates that remarkably long (nanometers) yet well-defined foldamers can be efficiently synthesized stepwise and that their helical stability may be continuously tuned upon controlling the ratio and sequence of P and Q monomers.

- Radical Reactions with Double Memory of Chirality ( $^2$ MOC) for the Enantiospecific Synthesis of Adjacent Stereogenic Quaternary Centers in Solution: Cleavage and Bonding Faster than Radical Rotation

Resendiz, M. J. E.; Family, F.; Fuller, K.; Campos, L. M.; Khan, S. I.; Lebedeva, N. V.; Forbes, M. D. E.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2009**, *131*, 8425–8433.

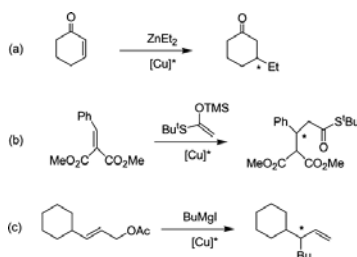
Abstract:



The solution photochemistry of bis(phenylpyrrolidinonyl)ketones (*R,R*)-**1b** and (*S,S*)-**1b** exhibited a remarkably high memory of chirality. Stereospecific decarbonylation to products (*R,R*)-**3b** and (*S,S*)-**3b**, respectively, occurred with an ee of ca. 80%. The reaction is thought to occur along the single state manifold by sequential Norrish type-I  $\alpha$ -cleavage, decarbonylation, and radical–radical combination in a time scale that is comparable to that required for the radical intermediate to expose its other enantiotopic face by rotation about an axis perpendicular to that of the p orbital (ca. 3–7 ps). The absolute configuration of a key intermediate and that of ketone (*R,R*)-**1b** were determined by single-crystal X-ray diffraction and the ee values of the photochemical products with the help of chiral shift reagent (+)-Eu(tfc)<sub>3</sub> and chiral LC-MS/MS. On the basis of the ee and de values at 25 °C, it could be determined that ca. 70% of the bond forming events occur with double memory of chirality, ca. 21% occur after rotation of one radical to form the meso product (*R,S*)-**3b**, and only 9% occur after double rotation to form the opposite enantiomer. This report represents the first example of a doubly enantiospecific Norrish type-I and decarbonylation reaction in solution and illustrates potentially efficient ways to obtain compounds with adjacent stereogenic quaternary centers.

- Enantioselective Copper-Catalyzed Conjugate Addition and Allylic Substitution Reactions  
Alexakis, A.; Bäckvall, J. E.; Krause, N.; Pàmies, O.; Diéguez, M. *Chem. Rev.* **2008**, *108*, 2796–2823.

Abstract:



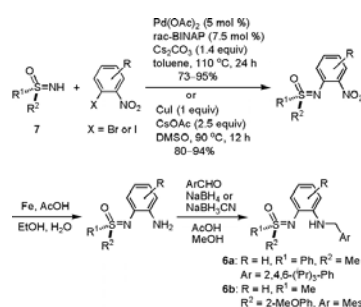
Enantioselective copper-catalyzed conjugate addition and allylic substitution are two of the most powerful carbon–carbon bond-forming reactions for construction of enantioenriched synthons for biological active and natural compounds. Significant advantages of these processes are the high compatibility with many functional groups, low cost of the copper salts, and the often high regio- and enantioselectivities. In the copper-catalyzed asymmetric conjugate addition an  $\alpha,\beta$ -unsaturated compound is attacked by a carbon nucleophile (nonstabilized, or stabilized) to form a new stereogenic carbon center. In the copper-catalyzed asymmetric allylic substitution the new

stereogenic carbon center is formed by the attack of a nonstabilized carbon nucleophile to an allylic substrate. In the past few years impressive results have been obtained in the development of highly efficient new copper catalytic systems by exploring several ligand types, copper sources, and reaction conditions. Remarkable efforts have been made to enlarge the scope of substrates and nucleophiles, increasing the possibilities for their use in the synthesis of more complex chiral organic molecules. This review covers the literature reports on enantioselective copper-catalyzed conjugate additions and allylic substitution reactions in the most emerging period in these areas of research. Particular emphasis is given to the results published in the last five years (2002–2007).

- Asymmetric Synthesis of Tertiary Alcohols and  $\alpha$ -Tertiary Amines via Cu-Catalyzed C–C Bond Formation to Ketones and Ketimines

Shibasaki, M.; Kanai, M. *Chem. Rev.* **2008**, *108*, 2853-2873.

Abstract:



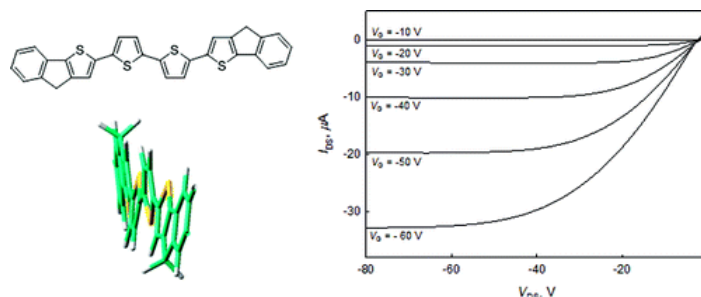
Chiral tertiary alcohols and  $\alpha$ -tertiary amines are important building blocks of naturally occurring and artificial biologically active molecules. Although there are catalytic asymmetric oxidation and amination reactions to access these chiral building blocks, the catalytic asymmetric addition of carbon nucleophiles to ketones and ketimines, which can simultaneously construct a carbon skeleton and tetrasubstituted stereogenic center, is synthetically more efficient. Realizing the catalytic asymmetric addition to ketones and ketimines (tetrasubstituted carbon synthesis), however, is generally more challenging than addition to aldehydes or aldimines (trisubstituted carbon synthesis) for two main reasons: (1) ketones and ketimines are significantly less reactive than aldehydes and aldimines; (2) enantio-face differentiation of ketones and ketimines is more difficult due to the smaller steric and electronic differences between the two substituents on prochiral carbons. Therefore, asymmetric catalysts that promote C–C bond-formation to ketones and ketimines should have high catalyst activity and enantioselectivity.

In this review, Cu-catalyzed asymmetric tetrasubstituted carbon-forming reactions via the addition of carbon nucleophiles to ketones and ketimines are discussed, classified by the nucleophiles.

- Quaterthiophenes with Terminal Indeno[1,2-*b*]thiophene Units as *p*-Type Organic Semiconductors

Pouchain, L.; Alévêque, O.; Nicolas, Y.; Oger, A.; Le Régent, C.-H.; Allain, M.; Blanchard, P.; Roncali, J. *J. Org. Chem.* **2009**, *74*, 1054–1064.

Abstract:

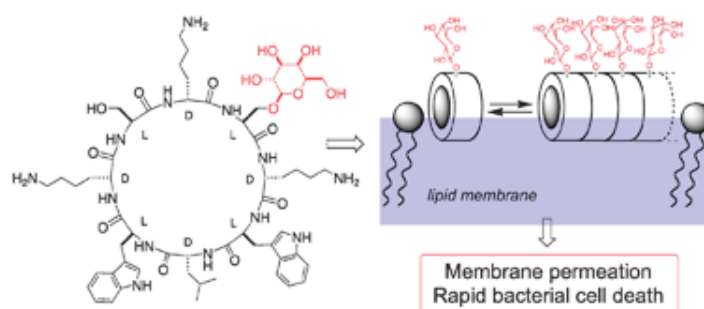


Quaterthiophenes **4T**, **Oct-4T**, and **Tol-4T** based on a central 2,2'-bithiophene core  $\alpha,\omega$ -terminated with 4,4-unsubstituted and 4,4-disubstituted *n*-octyl or *p*-tolyl indeno[1,2-*b*]thiophene have been synthesized by Stille or Miyaura–Suzuki couplings. Compound **4T** was also synthesized by an alternative route involving a soluble precursor bearing solubilizing trimethylsilyl groups which have been eliminated in the last step. The electronic properties of the compounds have been analyzed by cyclic voltammetry, UV–vis absorption and fluorescence emission spectroscopy. Thermal evaporation of **4T** and **Oct-4T** leads to crystalline thin films and UV–vis absorption and X-ray diffraction data for these films suggest that the molecules adopt a quasi-vertical orientation onto the substrate. Strong  $\pi$ - $\pi$  intermolecular interactions have been observed for **4T** but not for molecules **Oct-4T** due to the presence of *n*-octyl chains. Sublimed thin films of **Tol-4T** show an amorphous character. The characterization of field-effect transistors fabricated from these three materials gave a hole-mobility of  $2.2 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  with an on/off ratio of  $2.2 \times 10^4$  for **4T** while no field-effect was observed for **Oct-4T** and **Tol-4T**.

- Antibacterial cyclic D,L--glycopeptides.

Motiei, L.; Rahimpour, S.; Thayer, D. A.; Wong, C. H.; Ghadiri, M. R. *Chem. Commun.* **2009**, 3693 – 3695.

Abstract:

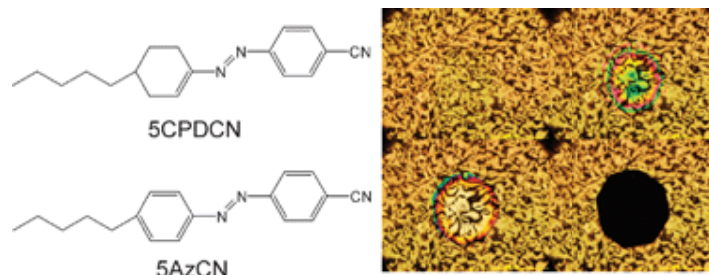


We report the design, synthesis, membrane activity, biophysical characterization, and in vitro antibacterial activities of cationic cyclic D,L-glycopeptides bearing D-glucosamine (GlcNH<sub>2</sub>), D-galactose (Gal), or D-mannose (Man) glycosyl side chains.

- A photoresponsive liquid crystal based on (1-cyclohexenyl)phenyldiazene as a close analogue of azobenzene.

Sato, M.; Nagano, S.; Seki, T. *Chem. Commun.* **2009**, 3792 – 3794.

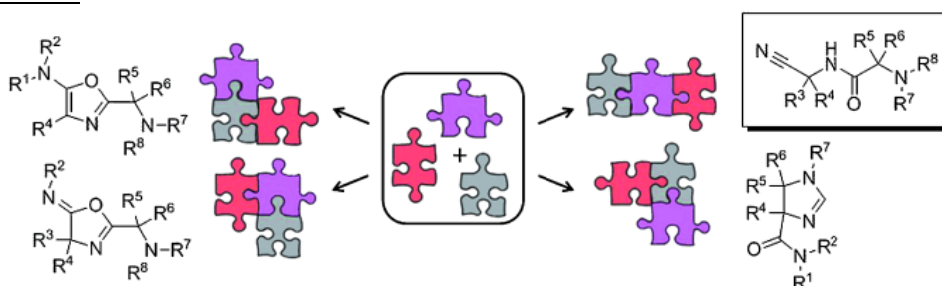
Abstract:



A new photoresponsive calamitic liquid crystal molecule possessing (1-cyclohexenyl)phenyldiazeno as a close analogue of azobenzene was synthesized and a comparative study with the corresponding azobenzene analogue carried out.

- A Multicomponent Reaction Towards *N*-(Cyanomethyl)amides  
Elders, N.; Ruijter, E.; de Kanter, F. J. J.; Janssen, E.; Lutz, M.; Spek, A. L.; Orru, R. V. A. *Chem. Eur. J.* **2009**, *15*, 6096-6099.

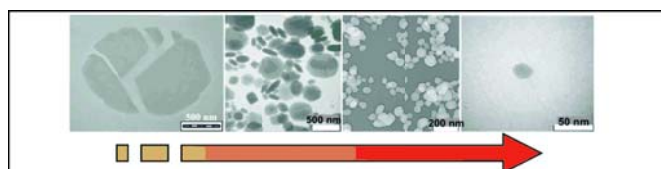
Abstract:



**Diversity-oriented synthesis:** The multicomponent reaction of  $\alpha$ -isocyanamides, aldehydes or ketones, and amines affords *N*-(cyanomethyl)amides, presenting the fourth class of products from this combination of reagents (see scheme). The scope of the reaction is very broad and various functional groups are tolerated. The outcome of the reaction can also be directed to the formation of 2*H*-2-imidazolines by Ag<sup>I</sup> catalysis.

- Nanoparticles of [Fe(NH<sub>2</sub>-trz)<sub>3</sub>]Br<sub>2</sub>·3 H<sub>2</sub>O (NH<sub>2</sub>-trz=2-Amino-1,2,4-triazole) Prepared by the Reverse Micelle Technique: Influence of Particle and Coherent Domain Sizes on Spin-Crossover Properties  
Forestier, T.; Kaiba, A.; Pechev, S.; Denux, D.; Guionneau, P.; Etrillard, C.; Daro, N.; Freysz, E.; Létard, J.-F. *Chem. Eur. J.* **2009**, *15*, 6122-6130.

Abstract:



**By changing the surfactant/water ratio**, nanoparticles of the iron(II) spin crossover material, [Fe(NH<sub>2</sub>-trz)<sub>3</sub>]Br<sub>2</sub>·3 H<sub>2</sub>O (with NH<sub>2</sub>-trz=4-amino-1,2,4-triazole), have been synthesised from 1 μm down to 30 nm (see figure). Magnetic and reflectivity experiments indicate that the critical size for observing a thermal hysteresis in this 1D polymer family is around 50 nm, and powder X-ray diffraction shows that particles of about 30 nm are constituted by about one coherent domain.

This paper describes the synthesis of iron(II) spin-crossover nanoparticles prepared by the reverse micelle technique by using the non-ionic surfactant Lauropal (Ifralan D0205) from the

polyoxyethylenic family. By changing the surfactant/water ratio, the size of the particles of  $[\text{Fe}(\text{NH}_2\text{-trz})_3]\text{Br}_2 \cdot 3\text{H}_2\text{O}$  (with  $\text{NH}_2\text{trz}$ =4-amino-1,2,4-triazole) can be controlled. On the macroscopic scale this complex exhibits cooperative thermal spin crossovers at 305 and 320 K. We find that when the size is reduced down to 50 nm, the spin transition becomes gradual and no hysteresis can be detected. For our data it seems that the critical size, for which the existence of a thermal hysteresis can be detected, is around 50 nm. Interestingly, the change of the particle size induces almost no change in the temperature of the thermal spin transition. A systematic determination of coherent domain size carried out on the nanoparticles by powder X-ray diffraction indicates that at approximately 30 nm individual particles consist of one coherent domain.

- Direct Condensation Method for the Preparation of Organic-Nanoparticle Dispersions  
Köstler, S.; Rudorfer, A.; Haase, A.; Satzinger, V.; Jakopic, G.; Ribitsch, V. *Adv. Mater.* **2009**, *21*, 2505–2510.

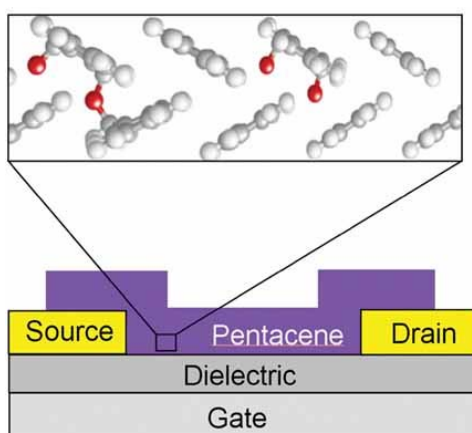
Abstract:



**Organic nanoparticle dispersions are prepared** via a versatile technique. Particles are formed by evaporation of aromatic hydrocarbons (like pentacene, rubrene, and tetracene) in an inert atmosphere and condensation of the vapor in a liquid medium. This allows the preparation of stable and concentrated dispersions of organic nanoparticles, showing interesting optical properties and potential applications in organic electronics and sensors.

- Electric-Field-Induced Gap States in Pentacene  
Knipp, D.; Northrup, J. E. *Adv. Mater.* **2009**, *21*, 2511–2515.

Abstract:



**Electrical measurements of a pentacene (Pn) thin-film transistor** reveal that oxygen exposure under certain bias voltages results in the formation of Pn gap states, whose influence on transistor properties is relevant to the development of organic electronics. A model explaining the origin of



these states is presented, and the current/voltage characteristics of the transistor are simulated using results from pseudopotential density functional theory.

- **Ultrasmall Liquid Droplets on Solid Surfaces: Production, Imaging, and Relevance for Current Wetting Research**

Méndez-Vilas, A.; Jódar-Reyes, A.-B.; González-Martín, M. L. *Small* **2009**, *5*, 1366 – 1390.

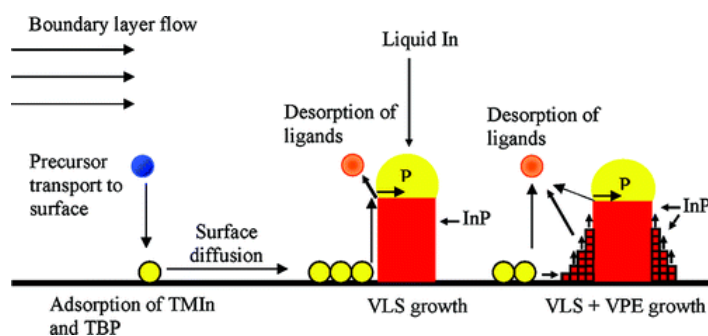
Abstract:



**Wetting:** The current interest in advancing the knowledge of the behavior of ultrasmall droplets (see image; courtesy of Dr. Luis Labajos-Broncano) on solid surfaces in a variety of different fields and applications is highlighted. The achievements in the field are reviewed and the technical advances that are thought to circumvent the current limitations in the coming years are discussed.

- **Kinetic Control of Self-Catalyzed Indium Phosphide Nanowires, Nanocones, and Nanopillars**  
Woo, R. L.; Gao, L.; Goel, N.; Hudait, M. K.; Wang, K. L.; Kodambaka, S.; Hicks, R. F. *Nano Lett.* **2009**, *9*, 2207–2211.

Abstract:



The morphological phase diagram is reported for InP nanostructures grown on InP (111)B as a function of temperature and V/III ratio. Indium droplets were used as the catalyst and were generated in situ in the metalorganic vapor-phase epitaxy reactor. Three distinct nanostructures were observed: wires, cones, and pillars. It is proposed that the shape depends on the relative rates of indium phosphide deposition via the vapor–liquid–solid (VLS) and vapor-phase epitaxy (VPE) processes. The rate of VLS is relatively insensitive to temperature and results in vertical wire growth starting at 350 °C. By contrast, the rate of VPE accelerates with temperature and drives the lateral growth of cones at 385 °C and then pillars at 400 °C.

- **Chirally Twisted Oligo(phenyleneethynylene) by Cyclization with  $\alpha$ -Helical Peptide**  
Nakayama, H.; Kimura, S. *J. Org. Chem.* **2009**, *74*, 3462–3468.

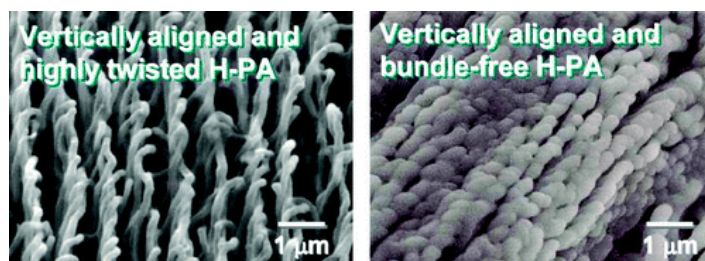
Abstract:

A novel cyclic conjugate of a helical decapeptide and oligo(phenyleneethynylene) (OPE), **C-OPE10**, was synthesized. The conformation and the optical properties of the cyclic conjugate were studied by circular dichroism (CD), absorption, and emission spectroscopies. In the cyclic conjugate, the rotational motion around the molecular axis of the OPE moiety was hindered to take a chirally twisted conformation, which is a distorted form from the coplanar conjugated structure, as revealed by observation of an induced negative Cotton effect of the OPE moiety. Molecular simulation using time dependent-density functional theory indicated a right-handed twist conformation of the OPE moiety for the negative Cotton effect.

This conjugate therefore provides a new way to obtain a  $\pi$ -conjugated compound having main-chain chirality. The optical properties of the OPE moiety taking the twist conformation in the cyclic conjugate are also discussed in depth.

- Macroscopically Aligned Helical Conjugated Polymers in Orientation-Controllable Chiral Nematic Liquid Crystal Field.

Mori, T.; Sato, T.; Kyotani, M.; Akagi, K. *Macromolecules* **2009**, *42*, 1817-1823.

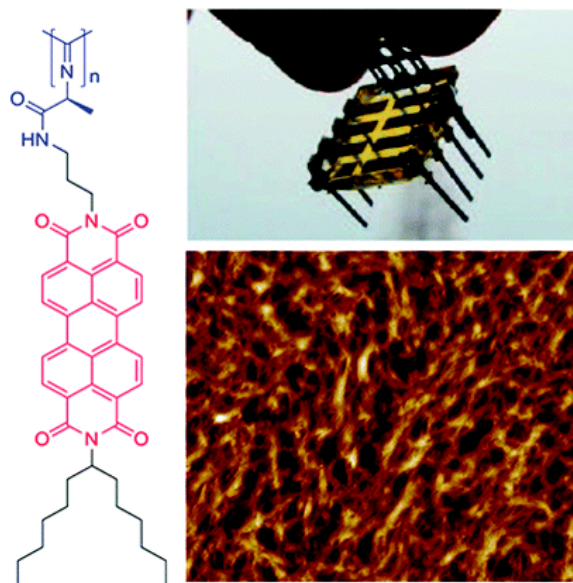
Abstract:

Horizontally and vertically aligned helical polyacetylenes (H-PAs) are synthesized by using orientation-controlled chiral nematic liquid crystals ( $N^*$ -LCs) consisting of vertical orientation inducers, chiral dopants and parent N-LC. The chemically graspable pictures of horizontal and vertical  $N^*$ -LCs and the corresponding macroscopically aligned H-PAs are put forward as a guideline of the syntheses of the  $N^*$ -LCs and H-PAs. It is found that the present  $N^*$ -LCs show horizontal and vertical orientations, although they include the vertical orientation inducer. Systematic examinations indicate that the horizontal or vertical orientation of the  $N^*$ -LC sensitively depends on (i) the relative concentrations of the vertical orientation inducer and the chiral dopant, (ii) the miscibility of the vertical orientation inducer to the parent N-LC, and (iii) the helical twisting power of the chiral dopant. In other words, the balance in effective strength between the vertical orientation inducer and the chiral dopant dominates the macroscopic orientation of the  $N^*$ -LC and hence the morphological alignment of the H-PA.

- Improved Performance of Perylene-Based Photovoltaic Cells Using Polyisocyanopeptide Arrays.

Foster, S.; Finlayson, C. E.; Keivanidis, P. E.; Huang, Y.-S.; Hwang, I.; Friend, R. H.; Otten, M. B. J.; Lu, L.-P.; Schwartz, E.; Nolte, R. J. M.; Rowan, A. E. *Macromolecules* **2009**, *42*, 2023-2030.

Abstract:



Photovoltaic devices incorporating perylene-substituted polyisocyanide materials have been demonstrated, using blend systems with polythiophene- and polyfluorene-based conjugated polymers. Prototypical structures with nominal (1:1) blend weight ratios of the polyisocyanide with poly(3-hexylthiophene) (P3HT) and poly(9,9'-dioctylfluorene-*co*-bis(*N,N'*-(4-butylphenyl))-bis(*N,N'*-phenyl)-1,4-phenyldiamine) PFB) readily showed an order of magnitude improvement in power conversion efficiency, as compared to analogous blend architectures using a perylene (PDI) monomer, whereas the performance of strongly phase-separated F8BT (poly(9,9-dioctylfluorene-*co*-benzothiadiazole) blend devices showed no such improvement. We propose that the use of polyisocyanide chains as a molecular template offers a method by which the morphology and connectivity of photovoltaic blends can be modified and enhanced.