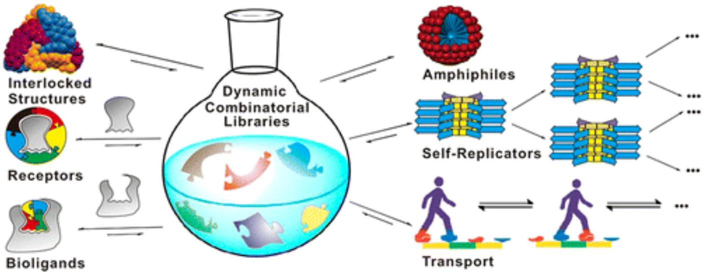
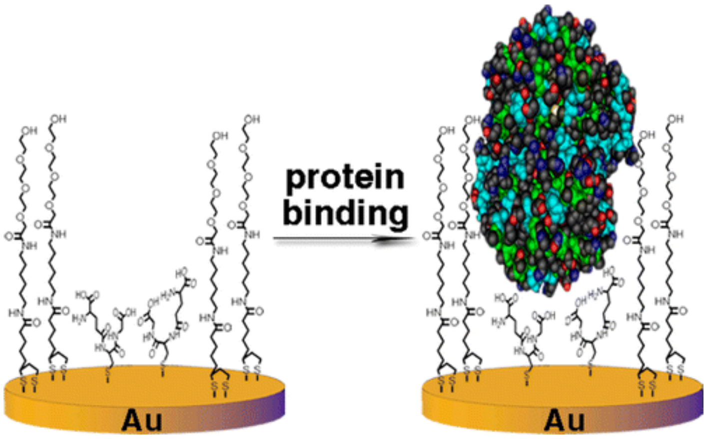
- Dynamic Combinatorial Libraries: From Exploring Molecular Recognition to Systems Chemistry
  Li , J.; Nowak, P.; Otto, S. *J. Am. Chem. Soc.* **2013**, *135*, 9222–9239.
  Abstract:



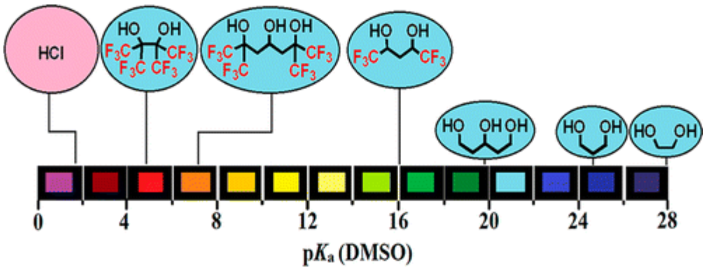
Dynamic combinatorial chemistry (DCC) is a subset of combinatorial chemistry where the library members interconvert continuously by exchanging building blocks with each other. Dynamic combinatorial libraries (DCLs) are powerful tools for discovering the unexpected and have given rise to many fascinating molecules, ranging from interlocked structures to self-replicators. Furthermore, dynamic combinatorial molecular networks can produce emergent properties at systems level, which provide exciting new opportunities in systems chemistry. In this perspective we will highlight some new methodologies in this field and analyze selected examples of DCLs that are under thermodynamic control, leading to synthetic receptors, catalytic systems, and complex self-assembled supramolecular architectures. Also reviewed are extensions of the principles of DCC to systems that are not at equilibrium and may therefore harbor richer functional behavior. Examples include self-replication and molecular machines.

- Creating Protein-Imprinted Self-Assembled Monolayers with Multiple Binding Sites and Biocompatible Imprinted Cavities
  Zhang , X.; Du, X.; Huang, X.; Lv, Z. *J. Am. Chem. Soc.* **2013**, *135*, 9248–9251.
  Abstract:



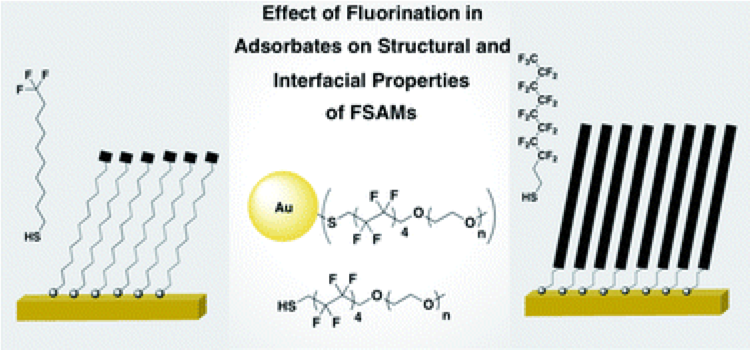
Imprinted monolayers have several advantages over bulk imprinted polymers such as excellent mass transfer of molecules into and out of imprinted sites and transduction of binding signals detected in real time. Protein-imprinted self-assembled monolayers (SAMs) were created with multiple binding sites and biocompatible imprinted cavities from functional thiols and novel disulfide compounds containing an oligoethylene glycol (OEG) terminal moiety and two amide groups incorporated in the chain (DHAP) in a biologically benign solution. DHAP played an important role in the formation of multiple binding sites and biocompatible cavities in addition to resisting nonspecific protein binding. The created protein-imprinted SAMs exhibited the excellent ability of specific binding of target proteins determined by multiple binding sites and imprinted cavities. The strategy generates tailor-made monolayer surfaces with specific protein binding and opens the possibility of controlled assembly of intellectual biomaterials and preparation of biosensors.

- Electron-Withdrawing Trifluoromethyl Groups in Combination with Hydrogen Bonds in Polyols: Brønsted Acids, Hydrogen-Bond Catalysts, and Anion Receptors
  Shokri, A.; Wang, X.-B.; Kass, S. R. *J. Am. Chem. Soc.* **2013***, 135,* 9525–9530.
  Abstract:



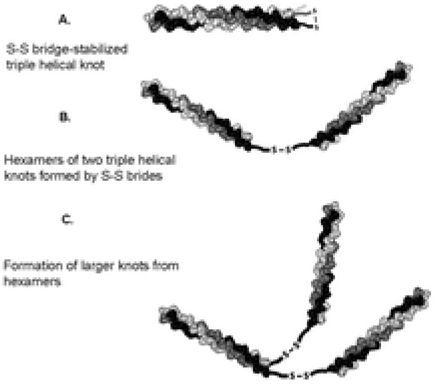
Electron-withdrawing trifluoromethyl groups were characterized in combination with hydrogen-bond interactions in three polyols (i.e., $CF_3CH(OH)CH_2CH(OH)CF_3$, **1**; $(CF_3)_2C(OH)C(OH)(CF_3)_2$, **2**; $((CF_3)_2C(OH)CH_2)_2CHOH$, **3**) by p$K_a$ measurements in DMSO and H_2O, negative ion photoelectron spectroscopy and binding constant determinations with Cl^-. Their catalytic behavior in several reactions were also examined and compared to a Brønsted acid (HOAc) and a commonly employed thiourea ($(3,5\text{-}(CF_3)_2C_6H_3NH)_2CS$). The combination of inductive stabilization and hydrogen bonds was found to afford potent acids which are effective catalysts. It also appears that hydrogen bonds can transmit the inductive effect over distance even in an aqueous environment, and this has far reaching implications.

- The impact of fluorination on the structure and properties of self-assembled monolayer films
  Zenasni, O.; Jamison, A. C.; Lee, T. R. *Soft Matter* **2013,** *9*, 6356-6370.
  Abstract:



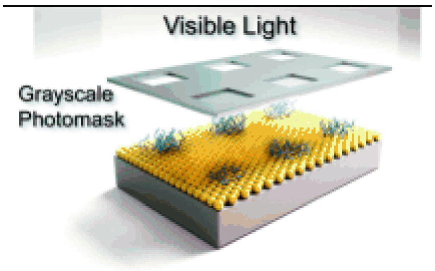
The adsorption of partially fluorinated amphiphiles on metal/metal oxide surfaces allows for the generation of specifically fluorinated thin-film interfaces. Such surfaces are often compared to polytetrafluoroethylene (PTFE), which exhibits a low surface energy, accompanied by biological and chemical inertness, making perfluorinated interfaces applicable to a wide range of technologies. In thin-film research, self-assembled monolayers derived from fluorinated alkanethiols (FSAMs) serve as well-defined systems that can be used to evaluate the physical and chemical properties of interfaces produced with varying degrees of fluorination. The characteristics of these surfaces have been attributed to both the chemical composition of the individual molecular adsorbates and the consequent structural features associated with monolayers formed from these unique partially fluorinated adsorbates. Specifically, this review seeks to correlate the structural and interfacial properties of FSAMs on gold with the structure/composition of the fluorinated moiety present in the adsorbed molecules and to highlight how the degree of fluorination influences the interfacial ordering of the individual alkanethiolate chains and the vacuum energy levels of the modified metal substrate. Additionally, the thermal stability of these organic thin films is analyzed as a function of adsorbate structure. Included are highlights of some of the studies in which FSAMs, formed from a variety of new types of surfactants, were used to modify colloidal systems, to generate anti-adhesive materials, and to enhance the stability of fluorinated thin films toward low-energy electron degradation.

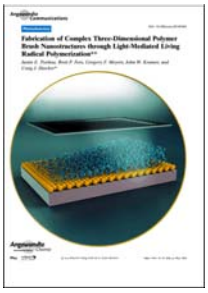
- Disulfide bond-stabilized physical gels of an asymmetric collagen-inspired telechelic protein polymer
  Pham, T. T. H.; Skrzeszewska, P. J.; Werten, M. W. T.; Rombouts, W. H.; Cohen Stuart, M. A.; de Wolf, F. A.; van der Gucht, J. *Soft Matter* **2013,** *9*, 6391-6397.
  Abstract:



We designed and produced an asymmetric collagen-inspired telechelic protein polymer with end blocks that can form triple helices of different thermal stabilities. Both end blocks consist of a motif that can form triple helices at low temperature, but one of these blocks carries an additional cysteine residue at the end. The cysteine residues can form disulfide bridges under oxidizing conditions, leading to dimer formation. This effectively stabilizes the triple helices, resulting in a double melting peak in differential scanning calorimetry: one corresponding to helices without disulfide bridges and one at significantly higher temperature, corresponding to stabilized helices. Under reducing conditions, the disulfide bridges are broken and the molecule behaves similarly to the symmetric variant. We find that these disulfide bridges also lead to an increase of the elastic modulus of the helical polymer network, probably because the number of helices in the system increases and also the disulfide bridges can crosslink different triple helical nodes.

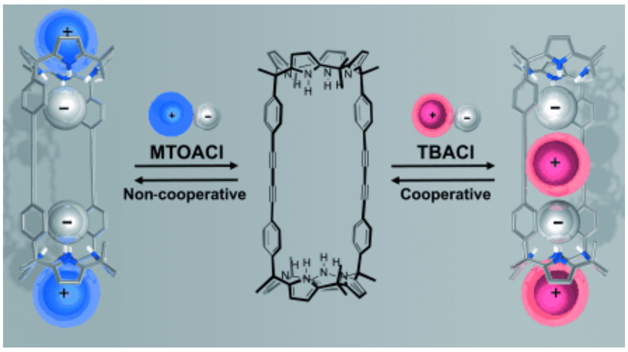
- Fabrication of Complex Three-Dimensional Polymer Brush Nanostructures through Light-Mediated Living Radical Polymerization
  Poelma, J. E.; Fors, B. P.; Meyers, G. F.; Kramer, J. W.; Hawker, C. J. *Angew. Chem. Int. Ed.* **2013**, *52*, 6844–6848.
  Abstract:





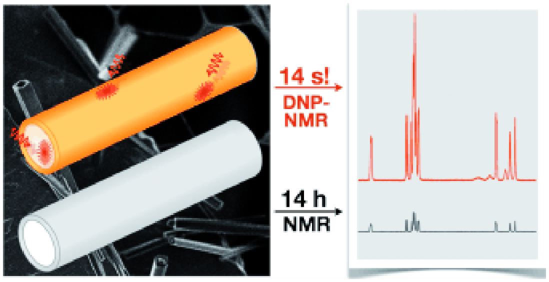
A facile approach to unique 3D, patterned polymer brushes is based on visible-light-mediated controlled radical polymerization. The temporal and spatial control of the polymerization allows the patterning of polymer brushes from a uniform initiating layer using a simple photomask (see picture). Furthermore, gradient polymer brushes, patterned block copolymers, and complex 3D structures can be obtained by modulating light intensity.

- Highly Cooperative Binding of Ion-Pair Dimers and Ion Quartets by a Bis(calix[4]pyrrole) Macrotricyclic Receptor
  Valderrey, V.; Escudero-Adán, E. C.; Ballester, P. *Angew. Chem. Int. Ed.* **2013**, *52*, 6898–6902.
  Abstract:



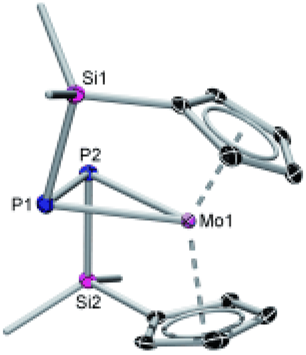
Connect four: A macrotricyclic receptor equipped with two convergent calix[4]pyrrole units features unprecedented binding properties towards two ion pairs. A highly cooperative binding process is observed for pairs of tetrabutylammonium (TBA) salts. MTOA=methyltrioctylammonium.

- Towards Structure Determination of Self-Assembled Peptides Using Dynamic Nuclear Polarization Enhanced Solid-State NMR Spectroscopy
  Takahashi, H.; Viverge, B.; Lee, D.; Rannou, P.; De Paëpe, G. *Angew. Chem. Int. Ed.* **2013**, *52*, 6979–6982.
  Abstract:



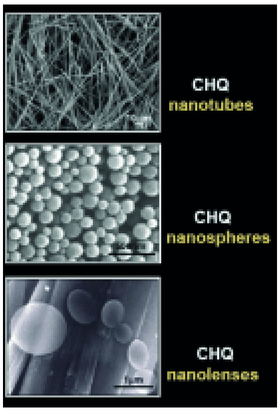
Supra-sensitivity: Dynamic nuclear polarization (DNP) enhanced solid-state NMR spectroscopy was performed on self-assembled peptide nanotubes. This approach yields significant experimental time savings (about five orders of magnitude; see picture) and was used to exemplify the feasibility of supramolecular structural studies of organic nanoassemblies at an atomic scale using DNP-enhanced solid-state NMR spectroscopy.

- Simultaneous Fragmentation and Activation of White Phosphorus
  Arnlod, T.; Braunschweig, H.; Jimenez-Halla, J. O. C.; Radacki, K.; Sen, S. S. *Chem. Eur. J.* **2013**, *28*, 9114-9117.
  Abstract:



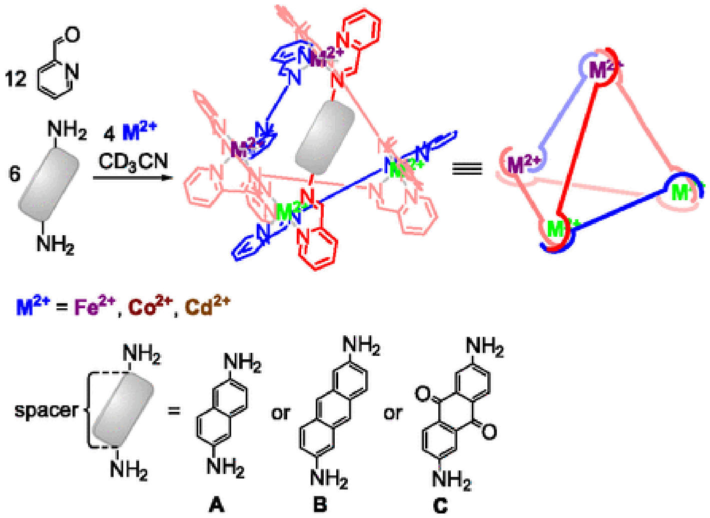
Mo and Si in concert: Fragmentation and simultaneous activation of white phosphorus was achieved by a complex featuring reactive main-group-element and transition-metal sites. The unusual electronic structure of the resulting tricyclic molybdenum complex (see figure) was elucidated experimentally and computationally.

- Tuning Molecular Self-Assembly Toward Intriguing Nanomaterial Architectures
  Lee, J. Y.; Hong, B. H.; Kim, D. Y.; Mason, D. R.; Lee, J. W.; Chun, Y.; Kim, K. S. *Chem. Eur. J.* **2013**, *28*, 9118-9122.
  Abstract:



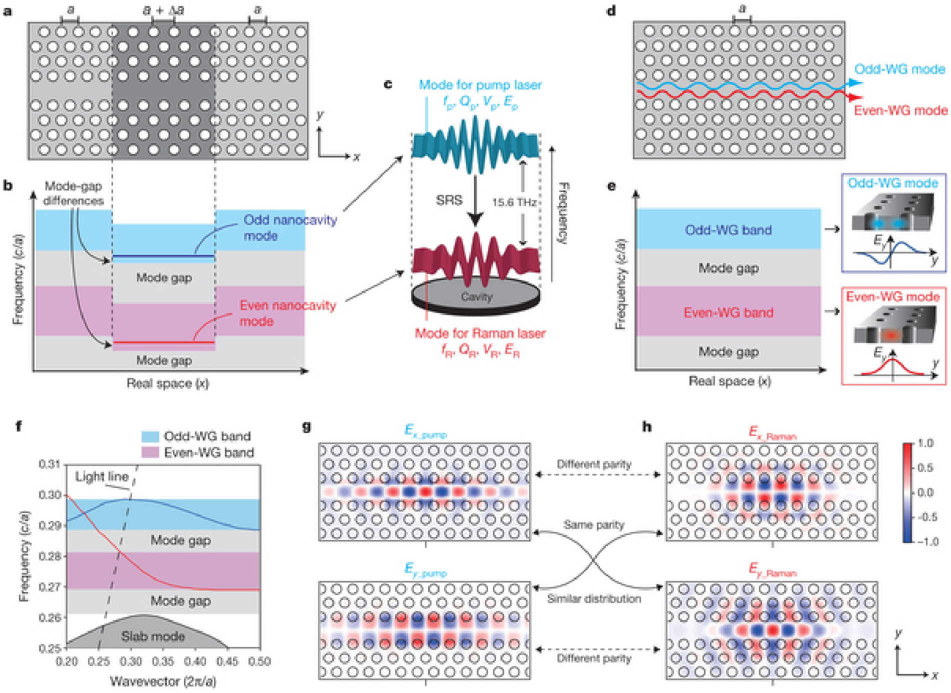
Taking shape nicely: The shaping of electro- and photochemically active calix[4]hydroquinone (CHQ) into nanoplates, -polygons and -tubes and their dynamic conversion into nanospheres and -hemispheres is demonstrated (see figure). CHQ nanostructures can be used to produce nanoshells and -cups with diverse shapes and sizes for a range of noble-metal- coated highly tunable plasmonic materials, generated without additional reducing agent.

- Symmetry breaking in self-assembled M_4L_6 cage complexes
  Meng, W.; Ronson, T. K.; Nitschke, J. R. *Proc. Nat. Acad. Sci. USA* **2013**, *110*, 10531-10535.
  Abstract:



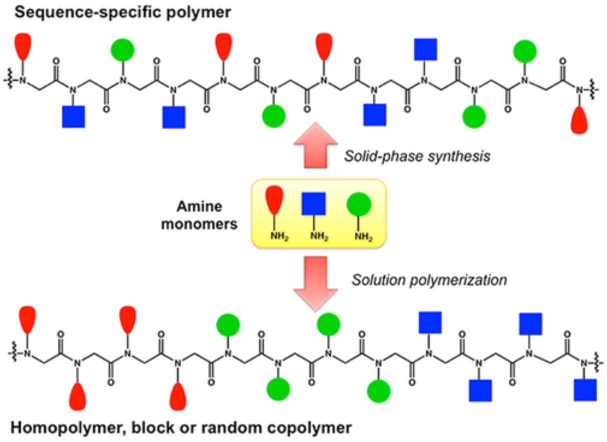
Here we describe the phenomenon of symmetry breaking within a series of M_4L_6 container molecules. These containers were synthesized using planar rigid bis-bidentate ligands based on 2,6-substituted naphthalene, anthracene, or anthraquinone spacers and Fe^{II} ions. The planarity of the ligand spacer favors a stereochemical configuration in which each cage contains two metal centers of opposite handedness to the other two, which would ordinarily result in an S_4-symmetric, achiral configuration. Reduction of symmetry from S_4 to C_1 is achieved by the spatial offset between each ligand's pair of binding sites, which breaks the S_4 symmetry axis. Using larger Cd^{II} or Co^{II} ions instead of Fe^{II} resulted, in some cases, in the observation of dynamic motion of the symmetry-breaking ligands in solution. NMR spectra of these dynamic complexes thus reflected apparent S_4 symmetry owing to rapid interconversion between energetically degenerate, enantiomeric C_1-symmetric conformations.

- A micrometre-scale Raman silicon laser with a microwatt threshold
  Takahashi, Y.; Inui, Y.; Chihara, M.; Asano, T.; Terawaki, R.; Noda, S. *Nature* **2013**, *498*, 470-474.
  Abstract:



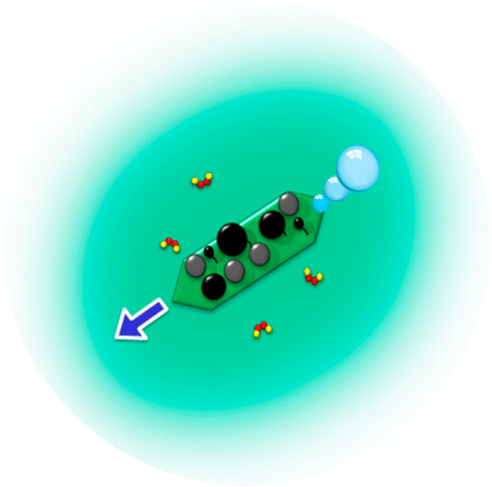
The application of novel technologies to silicon electronics has been intensively studied with a view to overcoming the physical limitations of Moore's law, that is, the observation that the number of components on integrated chips tends to double every two years. For example, silicon devices have enormous potential for photonic integrated circuits on chips compatible with complementary metal–oxide–semiconductor devices, with various key elements having been demonstrated in the past decade. In particular, a focus on the exploitation of the Raman effect has added active optical functionality to pure silicon, culminating in the realization of a continuous-wave all-silicon laser. This achievement is an important step towards silicon photonics, but the desired miniaturization to micrometre dimensions and the reduction of the threshold for laser action to microwatt powers have yet to be achieved: such lasers remain limited to centimetre-sized cavities with thresholds higher than 20 milliwatts, even with the assistance of reverse-biased p–i–n diodes. Here we demonstrate a continuous-wave Raman silicon laser using a photonic-crystal, high-quality-factor nanocavity without any p–i–n diodes, yielding a device with a cavity size of less than 10 micrometres and an unprecedentedly low lasing threshold of 1 microwatt. Our nanocavity design exploits the principle that the strength of light–matter interactions is proportional to the ratio of quality factor to the cavity volume and allows drastic enhancement of the Raman gain beyond that predicted theoretically. Such a device may make it possible to construct practical silicon lasers and amplifiers for large-scale integration in photonic circuits.

- Peptoid polymers: a highly designable bioinspired material
  Sun, J.; Zuckermann, R. N. *ACS Nano* **2013**, *7*, 4715-4732.
  <u>Abstract:</u>



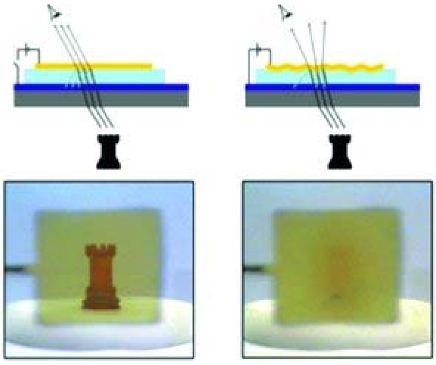
Bioinspired polymeric materials are attracting increasing attention due to significant advantages over their natural counterparts: the ability to precisely tune their structures over a broad range of chemical and physical properties, increased stability, and improved processability. Polypeptoids, a promising class of bioinspired polymer based on a N-substituted glycine backbone, have a number of unique properties that bridge the material gap between proteins and bulk polymers. Peptoids combine the sequence specificity of biopolymers with the simpler intra/intermolecular interactions and robustness of traditional synthetic polymers. They are highly designable because hundreds of chemically diverse side chains can be introduced from simple building blocks. Peptoid polymers can be prepared by two distinct synthetic techniques offering access to two material subclasses: (1) automated solidphase synthesis which enables precision sequence control and near absolute monodispersity up to chain lengths of ≈50 monomers, and (2) a classical polymerization approach which allows access to higher molecular weights and larger-scale yields, but with less control over length and sequence. This combination of facile synthetic approaches makes polypeptoids a highly tunable, rapid polymer prototyping platform to investigate new materials that are intermediate between proteins and bulk polymers, in both their structure and their properties. In this paper, we review the methods to synthesize peptoid polymers and their applications in biomedicine and nanoscience, as both sequence-specific materials and as bulk polymers.

- Directed self-assembly of nanoparticles for nanomotors
  Dong, B.; Zhou, T.; Zhang, H.; Li, C. Y. *ACS Nano* **2013**, *7*, 5192-5198.
  Abstract:



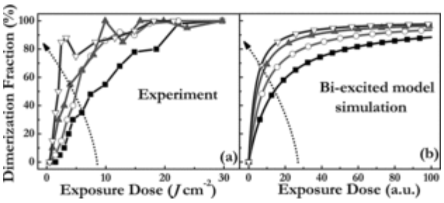
We report, for the first time, the design and fabrication of a nanoparticle-based nanomotor system by directly self-assembling nanoparticles onto functional, nanometer-thin lamellae, such as polymer single crystals. Tens of thousands of judiciously selected nanoparticles (gold, iron oxide, and platinum nanoparticles) with sizes ranging from <5 to a few tens of nanometers have been introduced into a single nanomotor via directed self-assembly. The resulting nanomotor realizes functions such as autonomous movement, remote control, and cargo transportation by utilizing the advantages offered by nanoparticles, such as the small size, surface plasmon resonance, catalytic and magnetic properties. Because of the structural and functional versatility of nanoparticles, the facile fabricating procedure, and the potential for mass production, our strategy shows a key step toward the development of next generation multifunctional nanomotors.

- Voltage-Controlled Surface Wrinkling of Elastomeric Coatings
  van den Ende, D.; Kamminga, J.-D.; Boersma, A.; Andritsch, T.; Steeneken, P. G. *Adv. Mater.* **2013**, *25*, 3438–3442.
  Abstract:



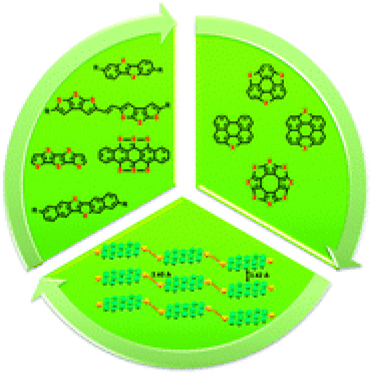
Wrinkling of elastomeric coatings by an electric field is reported. The associated changes in the coating's optical properties yield switchable mirrors and windows. The field E_c needed to induce wrinkling is a factor of 4.4 lower than the theoretically predicted value, which is attributed to space-charge injection.

- Photochemical Transformation of Fullerenes
  Wang, J.; Enevold, J.; Edman, L. *Adv. Funct. Mater.* **2013**, *23*, 3220–3225.
  Abstract:



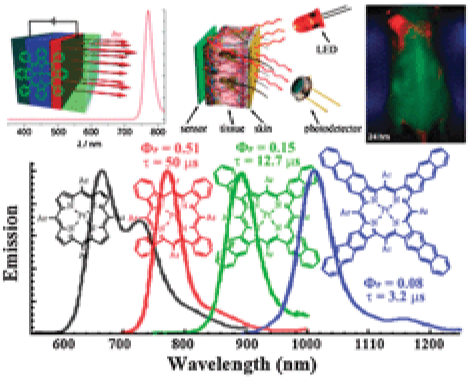
Experimental findings and associated theoretical insights regarding the photochemical transformation of fullerenes are reported, which challenge the conventional wisdom in the field and point out a viable path towards improved fullerene-based electronic devices. It is shown that the efficiency of the photochemical monomer-to-dimer transformation of the fullerene [6,6′]-phenyl-C_{61}-butyric acid methyl ester (PCBM) is strongly dependent on the light intensity, and this is utilized to demonstrate that direct patterning of an electroactive PCBM film can be effectuated by sub-second UV-light exposure followed by development in a tuned developer solution. By straightforward analytical reasoning, it is demonstrated that the observed intensity-dependent monomer-to-dimer transformation dictates that a significant back-reaction to the ground state must be in effect, which presumably originates from the excited-triplet state. By a combination of numerical modeling and analytical argumentation, it is further shown that the final dimer formation must constitute a bi-excited reaction between two neighboring monomers photo-excited to the triplet state.

- Heteroarenes as high performance organic semiconductors
  Jiang, W.; Lia, Y.; Wang, Z. *Chem. Soc. Rev.* **2013**, *42*, 6113-6127.
  Abstract:



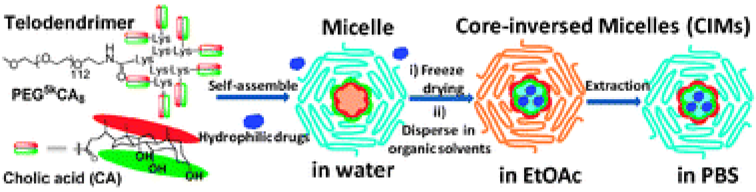
The design, synthesis, and characterization of new organic semiconductors (OSCs) are important aspects for the development of next-generation optoelectronic devices. Structurally, organic semiconductors based on π-conjugated molecules can be easily modified *via* rational synthesis to tune multi-level self-assembled structures and discover novel chemical, optical, and electronic properties. Heteroarenes, which contain chalcogens and nitrogens in fused aromatic rings, are being developed as promising semiconducting materials for applications in a variety of electronic devices due to their outstanding optoelectronic properties. We highlight recent approaches toward realizing high performance p-channel field effect transistors based on linear heteroacenes and heteroatom annulated polycyclic aromatics (PAHs) as key functional components. These comprehensive, but carefully orchestrated approaches simultaneously address (i) practical synthesis, (ii) tunable self-assembled packing arrangement as well as (iii) high electronic performance.

- Near-infrared phosphorescence: materials and applications
  Xiang, H.; Cheng, J.; Ma, X.; Zhoua, X.; Chruma, J. J. *Chem. Soc. Rev.* **2013**, *42*, 6128-6185.
  Abstract:



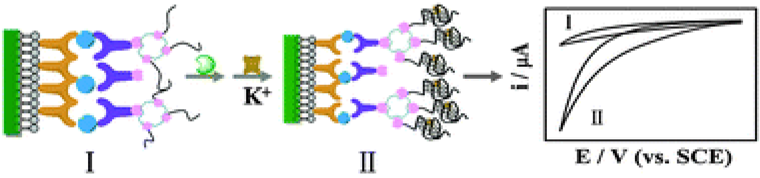
Room-temperature phosphorescent materials that emit light in the visible (red, green, and blue; from 400 to 700 nm) have been a major focus of research and development during the past decades, due to their applications in organic light-emitting diodes (OLEDs), light-emitting electrochemical cells, photovoltaic cells, chemical sensors, and bio-imaging. In recent years, near-infrared (NIR) phosphorescence beyond the visible region (700–2500 nm) has emerged as a new, promising, and challenging research field with potential applications toward NIR OLEDs, telecommunications, night vision-readable displays. Moreover, NIR phosphorescence holds promise for *in vivo* imaging, because cells and tissues exhibit little absorption and auto-fluorescence in this spectral region. This review describes the overall progress made in the past ten years on NIR phosphorescent transition-metal complexes including Cu(I), Cu(II), Cr(III), Re(I), Re(III), Ru(II), Os(II), Ir(III), Pt(II), Pd(II), Au(I), and Au(III) complexes, with a primary focus on material design complemented with a selection of optical, electronic, sensory, and biologic applications. A critical comparison of various NIR phosphorescent materials reported in the literature and a blueprint for future development in this field are also provided.

- The core-inversible micelles for hydrophilic drug delivery
  Huang, W.; Shi, C.; Shao, Y.; Lamb, K. S.; Luo, J. *Chem. Commun*. **2013**, *49*, 6674-6676.
  Abstract:



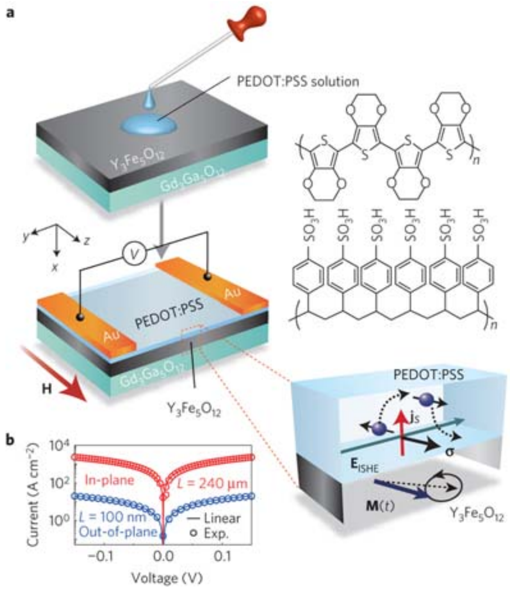
A unique core-inversible micelle (CIM) was formed via PEG5kCA8 for hydrophilic drug delivery. An amyloid-fibril-inhibiting water-soluble molecule, congo red (CR), has been loaded into the hydrophilic core of CIMs. The targeting folate-CIMs significantly enhanced the intracellular delivery of hydrophilic CR in a folate receptor-expressing cell line.

- A dual-functional electrochemical biosensor for the detection of prostate specific antigen and telomerase activity
  Liu, J.; Lu, C.; Zhou, H.; Xu, J.; Wang, Z.-H.; Chen, H.-Y. *Chem. Commun*. **2013**, *49*, 6602-6604.
  Abstract :



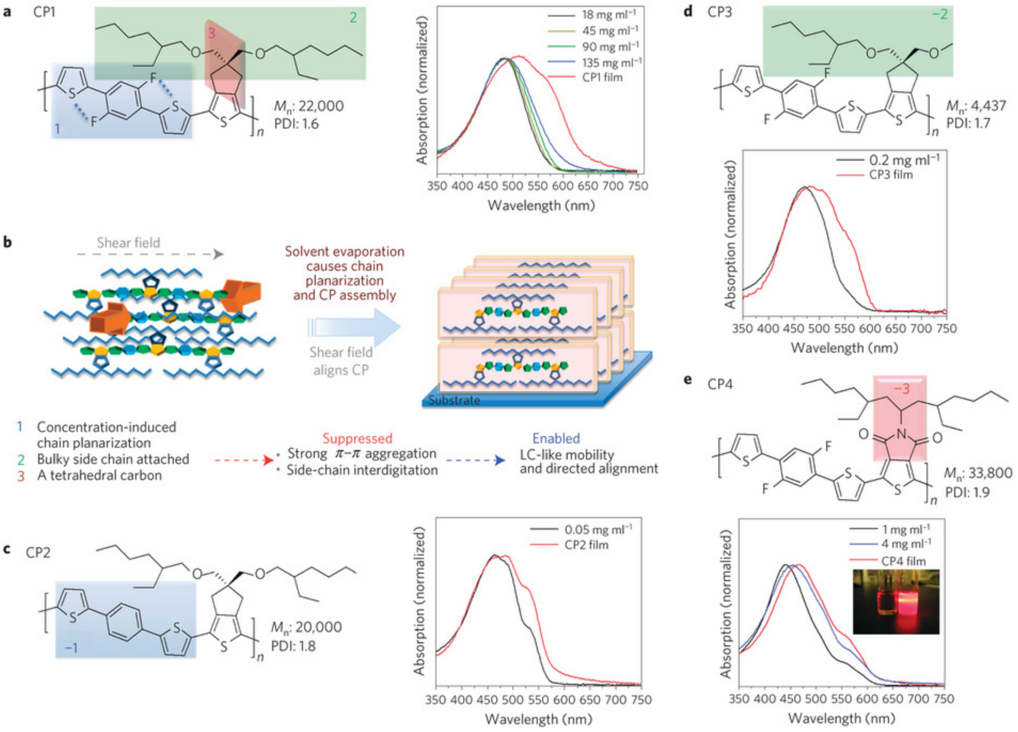
A new dual-functional electrochemical biosensor for the detection of prostate specific antigen (PSA) and telomerase activity was successfully developed based on a sandwich immunobinding format and telomerization assisted hemin–G-quadruplex-based DNAzyme as a biolabel.

- Solution-processed organic spin–charge converter
  Ando, K.; Watanabe, S.; Mooser, S.; Saitoh, E.; Sirringhaus, H. *Nature Mater* **2013**, *12*, 622–627.
  Abstract:



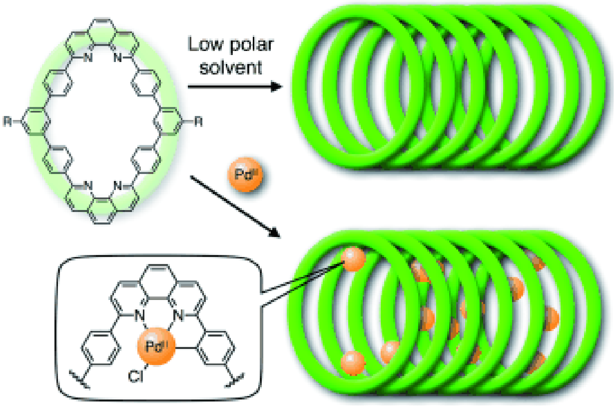
Conjugated polymers and small organic molecules are enabling new, flexible, large-area, low-cost optoelectronic devices, such as organic light-emitting diodes, transistors and solar cells. Owing to their exceptionally long spin lifetimes, these carbon-based materials could also have an important impact on spintronics where carrier spins play a key role in transmitting, processing and storing information. However, to exploit this potential, a method for direct conversion of spin information into an electric signal is indispensable. Here we show that a pure spin current can be produced in a solution-processed conducting polymer by pumping spins through a ferromagnetic resonance in an adjacent magnetic insulator, and that this generates an electric voltage across the polymer film. We demonstrate that the experimental characteristics of the generated voltage are consistent with it being generated through an inverse spin Hall effect in the conducting polymer. In contrast with inorganic materials, the conducting polymer exhibits coexistence of high spin-current to charge-current conversion efficiency and long spin lifetimes. Our discovery opens a route for a new generation of molecular-structure-engineered spintronic devices, which could lead to important advances in plastic spintronics.

- A molecular design principle of lyotropic liquid-crystalline conjugated polymers with directed alignment capability for plastic electronics
  Kim, B.-G.; Jeong, E. J.; Chung, J. W.; Seo, S.; Koo, B.; Kim, J. *Nature Mater.* **2013**, *12*, 659–664.
  Abstract:



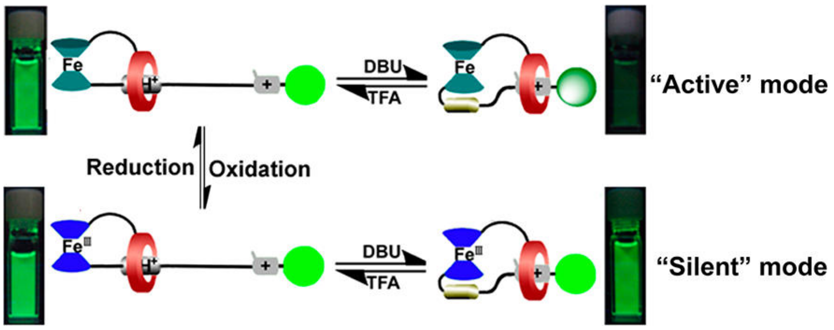
Conjugated polymers with a one-dimensional p-orbital overlap exhibit optoelectronic anisotropy. Their unique anisotropic properties can be fully realized in device applications only when the conjugated chains are aligned. Here, we report a molecular design principle of conjugated polymers to achieve concentration-regulated chain planarization, self-assembly, liquid-crystal-like good mobility and non-interdigitated side chains. As a consequence of these intra- and intermolecular attributes, chain alignment along an applied flow field occurs. This liquid-crystalline conjugated polymer was realized by incorporating intramolecular sulphur–fluorine interactions and bulky side chains linked to a tetrahedral carbon having a large form factor. By optimizing the polymer concentration and the flow field, we could achieve a high dichroic ratio of 16.67 in emission from conducting conjugated polymer films. Two-dimensional grazing-incidence X-ray diffraction was performed to analyse a well-defined conjugated polymer alignment. Thin-film transistors built on highly aligned conjugated polymer films showed more than three orders of magnitude faster carrier mobility along the conjugated polymer alignment direction than the perpendicular direction.

- Organic and Organometallic Nanofibers Formed by Supramolecular Assembly of Diamond-Shaped Macrocyclic Ligands and Pd^{II} Complexes
  Kuritani, M.; Tashiro, S.; Shionoya, M. *Chem. Asian J.* **2013**, *8*, 1368-1371.
  Abstract:



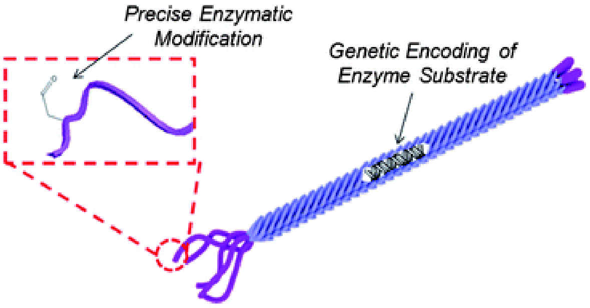
A diamond-shaped macrocycle with two inward phenanthroline ligands and outward long alkyl chains, and its Pd^{II}complex form organic and organometallic fibrous aggregates, respectively, as revealed by NMR, UV/Vis, AFM, and TEM measurements. The most likely structures are face-to-face stacked macrocycles, generating nanotubes

- Dual-Mode Operation of a Bistable [1]Rotaxane with a Fluorescence Signal
  Li, H.; Zhang, J.-N.; Zhou, W.; Zhang, H.; Zhang, Q.; Qu, D.-H.; Tian, H. *Org. Lett.* **2013***, 15,* 3070-3073.
  Abstract:



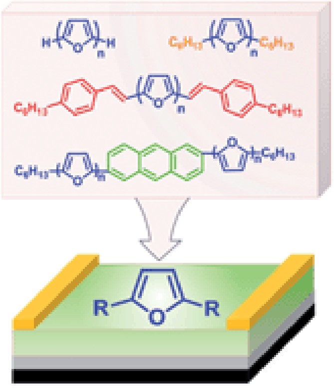
We report the operation of a ferrocene-based bistable [1]rotaxane that can work in two parallel platforms. In an "active" signal mode, the relative mechanical movement of its ring and thread in response to external acidbase-stimuli can result in a remarkable fluorescence signal output observed by the naked eye, whereas no obvious fluorescence change occurred in a "silent" signal mode after oxidation. Its fluorescence responses to the different combinations of DBU and/or $Fe(ClO_4)_3$ corresponds to an INHIBIT logic gate.

- Controlled surface immobilization of viruses *via* site-specific enzymatic modification
  Kwak, E.-A.; Jaworski, J. *J. Mater. Chem. B* **2013**, *1*, 3486-3493.
  Abstract:



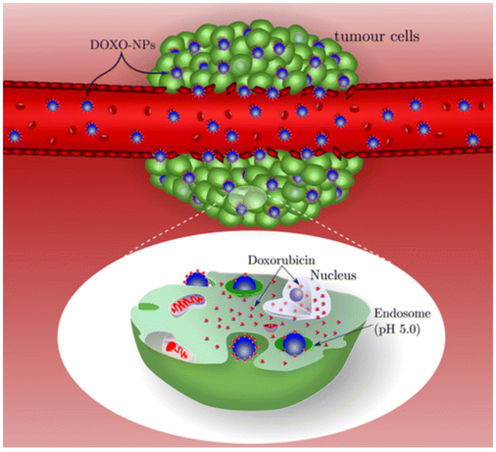
A unique method for the controlled attachment of viruses (or other protein based materials) to a range of surfaces is revealed through site-specific linkages engineered at the fd phage p3 protein coat. After genetic encoding of the virus coat position that is to be engineered, enzymatic modification with a formylglycine generating enzyme (FGE) affords the conversion of a single amino acid at a precise location to yield a reactive aldehyde group. By implementing this modification at a specific p3 coat position, we demonstrate the ability to control the directed immobilization of the virus selectively onto amine exposed surfaces including APTES treated glass, polymeric supports, and protein coated magnetic beads. While the immobilized virus remains stable for even a month, we also show by controlled release from the surface that liberated viruses retain their infectivity. The adaptability of this modification strategy for virus engineering is demonstrated showing great potential for bioconjugation with a range of amine functionalized chemical targets. This is expected to greatly enhance the possibilities for future virus based materials and related technologies.

- Oligofuran-containing molecules for organic electronics
  Gidron, O.; Dadvand, A.; Sun, E. W.-H.; Chung, I.; Shimon, L. J. W.; Bendikov, M.; Perepichka, D. F. *J. Mater. Chem. C* **2013**, *1*, 4358-4367.
  Abstract:



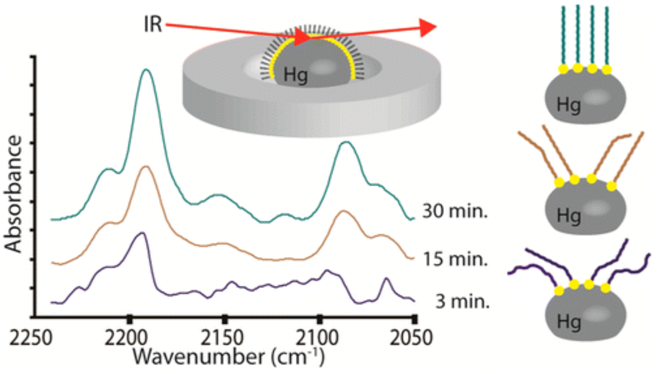
We describe the synthesis, characterization and field effect transistor (FET) properties of a series of furan-based conjugated oligomers such as unsubstituted, hexyl- and styryl-capped linear oligofurans and oligofuran-substituted anthracene derivatives. All studied oligofurans show high fluorescence and good thermal stability. Top contact organic FETs (OFETs) fabricated with oligofurans as the active layer show hole mobilities (~0.01 to 0.07 $cm^2\ V^{-1}\ s^{-1}$) and on/off ratios (10^4 to 10^6) on a par with the corresponding oligothiophene analogues, while the threshold voltages displayed by oligofuran-based OFETs are significantly reduced due to higher HOMO energies as compared to those of oligothiophenes. Electroluminescence observed in oligofuran-based OFETs in a bottom-contact geometry is limited by electron injection. Overall, we find that furan building blocks are excellent candidates for replacing thiophene in optoelectronic materials.

- pH-Responsive Delivery of Doxorubicin from Citrate–Apatite Nanocrystals with Tailored Carbonate Content
  Rodríguez-Ruiz, I.; Delgado-López, J. M.; Durán-Olivencia, M. A.; Lafisco, M.; Tampieri, A.; Colangelo, D.; Prat, M.; Gómez-Morales, J. *Langmuir* **2013**, *29*, 8213–8221.
  Abstract:



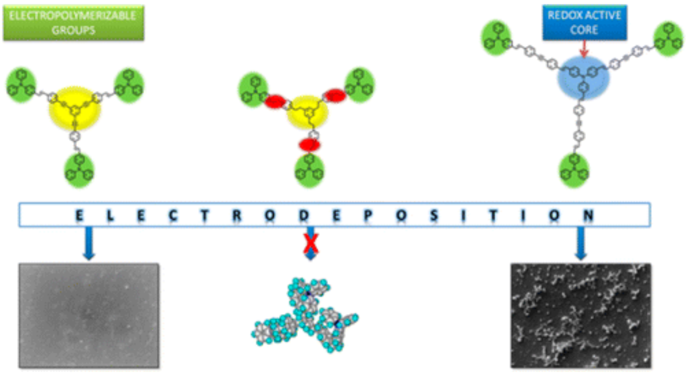
In this work, the efficiency of bioinspired citrate-functionalized nanocrystalline apatites as nanocarriers for delivery of doxorubicin (DOXO) has been assessed. The nanoparticles were synthesized by thermal decomplexing of metastable calcium/citrate/phosphate solutions both in the absence (Ap) and in the presence (cAp) of carbonate ions. The presence of citrate and carbonate ions in the solution allowed us to tailor the size, shape, carbonate content, and surface chemistry of the nanoparticles. The drug-loading efficiency of the two types of apatite was evaluated by means of the adsorption isotherms, which were found to fit a Langmuir–Freundlich behavior. A model describing the interaction between apatite surface and DOXO is proposed from adsorption isotherms and ζ-potential measurements. DOXO is adsorbed as a dimer by means of a positively charged amino group that electrostatically interacts with negatively charged surface groups of nanoparticles. The drug-release profiles were explored at pHs 7.4 and 5.0, mimicking the physiological pH in the blood circulation and the more acidic pH in the endosome-lysosome intracellular compartment, respectively. After 7 days at pH 7.4, cAp-DOXO released around 42% less drug than Ap-DOXO. However, at acidic pH, both nanoassemblies released similar amounts of DOXO. In vitro assays analyzed by confocal microscopy showed that both drug-loaded apatites were internalized within GTL-16 human carcinoma cells and could release DOXO, which accumulated in the nucleus in short times and exerted cytotoxic activity with the same efficiency. cAp are thus expected to be a more promising nanocarrier for experiments in vivo, in situations where intravenous injection of nanoparticles are required to reach the targeted tumor, after circulating in the bloodstream.

- Evolution of Conformational Order During Self-Assembly of n-Alkanethiols on Hg Droplets: An Infrared Spectromicroscopy Study
  Babayco, C. B.; Chang, P. J.; Land, D. P.; Kiehl, R. A.; Parikh, A. N. *Langmuir* **2013**, *29*, 8203–8207.
  <u>Abstract:</u>



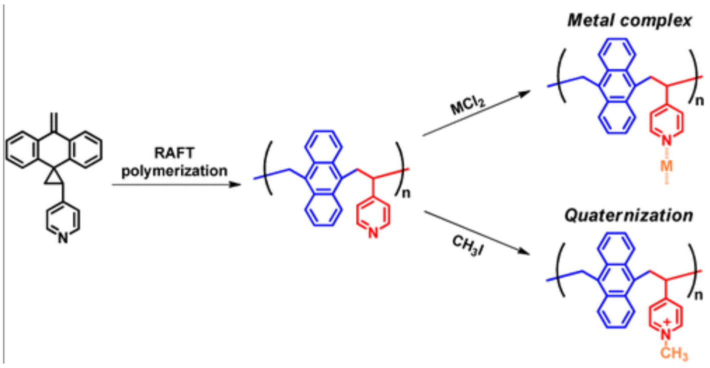
This Letter describes Fourier-transform infrared spectroscopy evidence for the evolution of conformational order and coverage during the formation of n-alkanethiol monolayers on microdroplets of mercury from the solution phase. At the highest coverages obtained by self-assembly, the monolayer is characterized by predominantly all-trans conformational order. For partial monolayers obtained at arbitrarily quenched incubation periods, we find a continuous evolution of the chain conformational order with monolayer coverage. Analyzing these results in light of previously reported models from X-ray scattering reveals a complex self-assembly process in which the density-dependent evolution of the chain conformational order is coupled with that of molecular orientation and density.

- Electrogenerated Conductive Polymers from Triphenylamine End-Capped Dendrimers
  Mangione, M. I.; Spanevello, R. A.; Rumbero, A.; Heredia, D.; Marzari, G.; Fernandez, L.; Otero, L.; Fungo, F. *Macromolecules* **2013**, *46*, 4754-4763.
  Abstract:



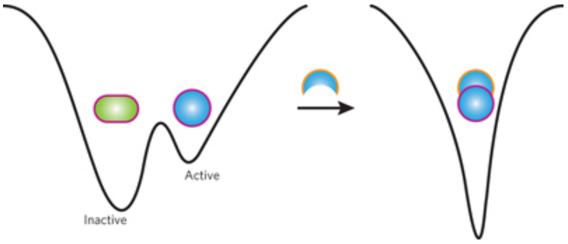
Electroactive end-capped dendritic macromolecules were designed and synthesized. Their structures contain triphenylamine moieties as part of the core or dendrons. The electrogenerated films produced with these monomers behaved as conductive dendritic polymers that can be reversible charged, both in the core and in the peripheral units. The design of dendrimer structures with the introduction of systematic changes allows to establish relationships between their electro-optical properties with molecular structural parameters. The films of polymeric material hold good electrical conductivity, reversible electrochemical processes and chemical stability. The results indicate that the use of conjugated and rigid structures in dendritic macromolecules is an important factor in order to obtain electropolymeric films. This work provides a model to design starburst dendrimers capable to form electrochemically active polymers with potential applications in electronic and optoelectronic devices.

- Polymers Composed of Alternating Anthracene and Pyridine Containing Units by Radical Ring-Opening Polymerization: Controlled Synthesis, Optical Properties, and Metal Complexes
  Nakabayashi, K.; Inoue, S.; Abiko, Y.; Mori, H. *Macromolecules* **2013**, *46*, 4790-4798.
  Abstract:



Novel polymers composed of alternating anthracene and pyridine containing units were synthesized by radical ring-opening polymerization of pyridine-containing cyclic monomers via reversible addition-fragmentation chain transfer (RAFT) process. The ring-opening polymerization proceeded predominantly to afford well-defined polymers (Mw/Mn~1.30), which exhibited the characteristic absorption and fluorescence due to the anthracene unit. On the other hand, fluorescence quenching was observed in chloroform and acidic aqueous solutions. The quenching was explained by charge transfer from the excited anthracene units to the coordinated or protonated pyridine units. Additionally, fluorescence quenching independent of external ambient conditions was conducted by quaternization. In the thin film state, the obtained polymers exhibited fluorescence due to the formation of excimers. The formation of complexes between the anthracene-containing polymers and metal species (Zn, Cu, and Co) led to the change in the optical properties compared to those of pristine polymers. These results demonstrate that the unique optical properties could be developed under various conditions due to the interactions between the anthracene and pyridine units in the well-defined polymers.

- Allosteric inhibition through suppression of transient conformational states
  Tzeng, S.-R.; Kalodimos, C. G. *Nature Chem. Biol.* **2013**, *9*, 462–465.
  Abstract:



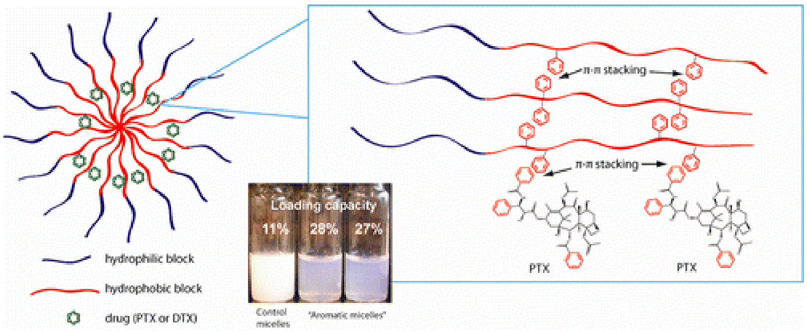
The ability to inhibit binding or enzymatic activity is key to preventing aberrant behaviors of proteins. Allosteric inhibition is desirable as it offers several advantages over competitive inhibition, but the mechanisms of action remain poorly understood in most cases. Here we show that allosteric inhibition can be effected by destabilizing a low-populated conformational state that serves as an on-pathway intermediate for ligand binding, without altering the protein's ground-state structure. As standard structural approaches are typically concerned with changes in the ground-state structure of proteins, the presence of such a mechanism can go easily undetected. Our data strongly argue for the routine use of NMR tools suited to detect and characterize transiently formed conformational states in allosteric systems. Structure information on such important intermediates can ultimately result in more efficient design of allosteric inhibitors.

- Π–Π Stacking Increases the Stability and Loading Capacity of Thermosensitive Polymeric

Micelles for Chemotherapeutic Drugs

Shi, Y.; van Steenbergen, M. J.; Teunissen, E. A.; Novo, L.; Gradmann, S.; Baldus, M.; van Nostrum, C. F.; Hennink, W. E. *Biomacromolecules* **2013**, *14*, 1826-1837.

Abstract:



Thermosensitive amphiphilic block copolymers self-assemble into micelles above their lower critical solution temperature in water, however, the micelles generally display mediocre physical stability. To stabilize such micelles and increase their loading capacity for chemotherapeutic drugs, block copolymers with novel aromatic monomers were synthesized by free radical polymerization of *N*-(2-benzoyloxypropyl methacrylamide (HPMAm-Bz) or the corresponding naphthoyl analogue (HPMAm-Nt), with *N*-(2-hydroxypropyl) methacrylamide monolactate, using a polyethylene glycol based macroinitiator. The critical micelle temperatures and critical micelle concentrations decreased with increasing the HPMAm-Bz/Nt content. The micelles of 30–50 nm were prepared by heating the polymer aqueous solutions from 0 to 50 °C and were colloidally stable for at least 48 h at pH 7.4 and 37 °C. Paclitaxel and docetaxel encapsulation was performed by mixing drug solutions in ethanol with polymer aqueous solutions and heating from 0 to 50 °C. The micelles had a drug loading capacity up to 34 wt % for docetaxel, which is among the highest loadings reported for polymeric micelles, with loaded micelle sizes ranging from 60 to 80 nm. The micelles without aromatic groups almost completely released loaded paclitaxel in 10 days, whereas the HPMAm-Bz/Nt containing micelles released 50% of the paclitaxel at the same time, which showed a better retention for the drug of the latter micelles. ^{1}H solid-state NMR spectroscopy data are compatible with π–π stacking between aromatic groups. The empty micelles demonstrated good cytocompatibility, and paclitaxel-loaded micelles showed high cytotoxicity to tumor cells. In conclusion, the π–π stacking effect introduced by aromatic groups increases the stability and loading capacity of polymeric micelles.