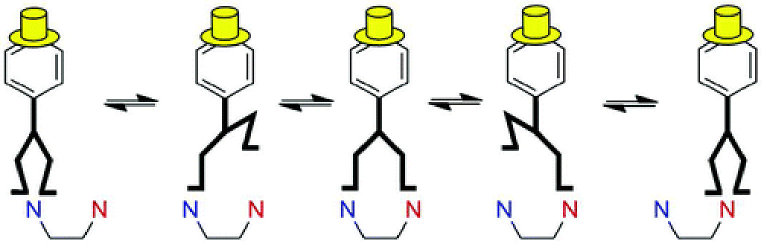
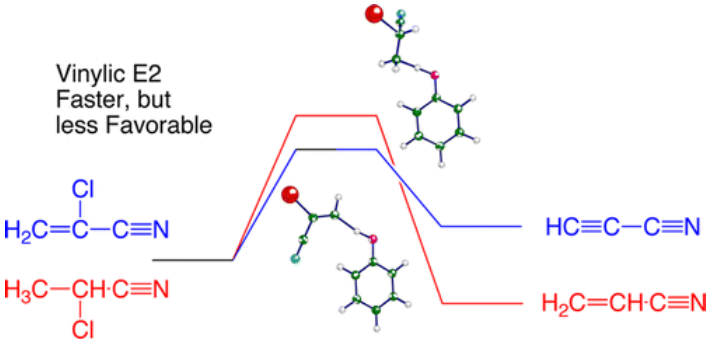
- Merging Constitutional and Motional Covalent Dynamics in Reversible Imine Formation and Exchange Processes
  Kovaříček, P.; Lehn, J.-M. *J. Am. Chem. Soc.* **2012**, *134*, 9446–9455.
  Abstract:



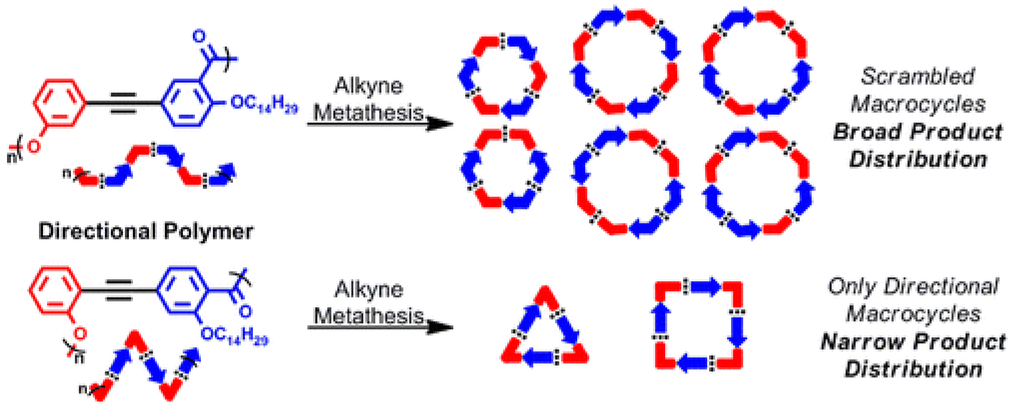
The formation and exchange processes of imines of salicylaldehyde, pyridine-2-carboxaldehyde, and benzaldehyde have been studied, showing that the former has features of particular interest for dynamic covalent chemistry, displaying high efficiency and fast rates. The monoimines formed with aliphatic α,ω-diamines display an internal exchange process of self-transimination type, inducing a local motion of either "stepping-in-place" or "single-step" type by bond interchange, whose rate decreases rapidly with the distance of the terminal amino groups. Control of the speed of the process over a wide range may be achieved by substituents, solvent composition, and temperature. These monoimines also undergo intermolecular exchange, thus merging motional and constitutional covalent behavior within the same molecule. With polyamines, the monoimines formed execute internal motions that have been characterized by extensive one-dimensional, two-dimensional, and EXSY proton NMR studies. In particular, with linear polyamines, nondirectional displacement occurs by shifting of the aldehyde residue along the polyamine chain serving as molecular track. Imines thus behave as simple prototypes of systems displaying relative motions of molecular moieties, a subject of high current interest in the investigation of synthetic and biological molecular motors. The motional processes described are of dynamic covalent nature and take place without change in molecular constitution. They thus represent a category of dynamic covalent motions, resulting from reversible covalent bond formation and dissociation. They extend dynamic covalent chemistry into the area of molecular motions. A major further step will be to achieve control of directionality. The results reported here for imines open wide perspectives, together with other chemical groups, for the implementation of such features in multifunctional molecules toward the design of molecular devices presenting a complex combination of motional and constitutional dynamic behaviors.

- The Impact of Substituents on the Transition States of SN2 and E2 Reactions in Aliphatic and Vinylic Systems: Remarkably Facile Vinylic Eliminations
  Nettey, S.; Swift, C. A.; Joviliano, R.; Noin, D. O.; Gronert, S. *J. Am. Chem. Soc.* **2012**, *134*, 9303–9310.
  Abstract:



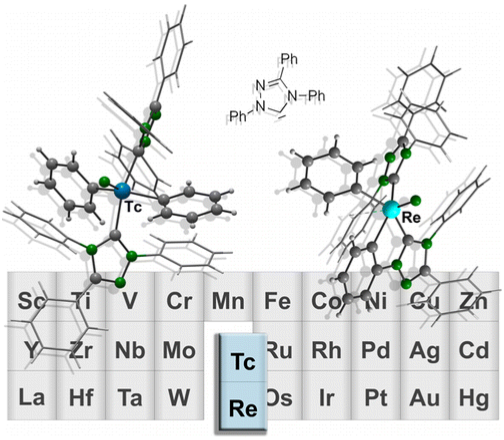
For a series of α and β substituted haloethanes and haloethenes, gas-phase experiments and computational modeling have been used to characterize their nucleophilic substitution and elimination reactions. Despite being less thermodynamically favorable, the vinylic eliminations have rate constants and computed barriers that are similar to those of analogous aliphatic eliminations. This is the result of the vinylic systems shifting to more E1_{cb}-like transition states and exploiting the inherent greater acidity of vinylic hydrogens. In general, the α-substituents have a greater impact on the S_N2 pathways and stabilize the transition states via field and polarizability effects. Substantial stabilization is also provided to the E2 transition states by the α-substituents, but they have surprisingly little impact on the geometries of the transition states of either pathway. The β-substituents generally lead to a strong bias toward elimination and greatly affect the synchronicity of the elimination (more E1_{cb}-like) as well as its location on the reaction coordinate (early). The experimental and computational data are in good accord, and the full data set provides a comprehensive picture of substituent effects on solvent-free S_N2 and E2 processes.

- Directional Cyclooligomers via Alkyne Metathesis
  Sisco, S. W.; Moore, J. S. *J. Am. Chem. Soc.* **2012**, *134*, 9114–9117.
  Abstract:



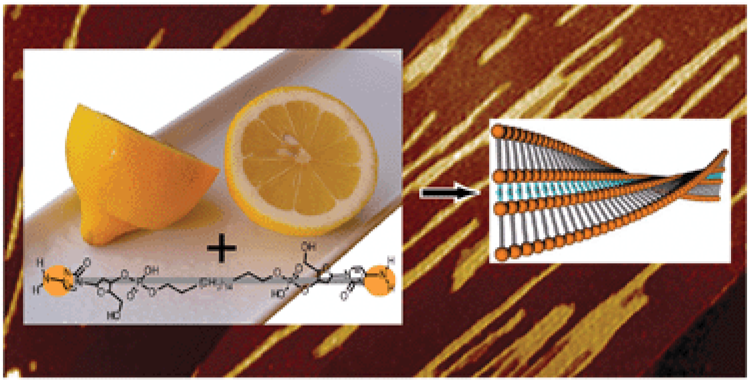
Macrocyclic oligomers possessing direction-defining ester linkages were synthesized via metathesis of the nondirectional alkyne functional group. Alkyne metathesis is expected to scramble the relative orientation of adjacent ester groups, potentially leading to a complex mixture of macrocyclic products. We wondered whether a narrow product distribution would be achievable with a proper choice of the building block structure. Here we show that the shape of the building block determines whether the macrocyclic products are directionally uniform or scrambled. Specifically, two isomeric arylene-ethynylene polyesters afforded significantly different product distributions upon being subjected to depolymerization–macrocyclization. These results underscore the importance of learning how the shape and geometry of the building blocks affect the macrocyclization energy landscape.

- Aryl and NHC Compounds of Technetium and Rhenium
  Oehlke, E.; Kong, S.; Arciszewski, P.; Wiebalck, S.; Abram, U. *J. Am. Chem. Soc.* **2012**, *134*, 9118–9121.
  Abstract:



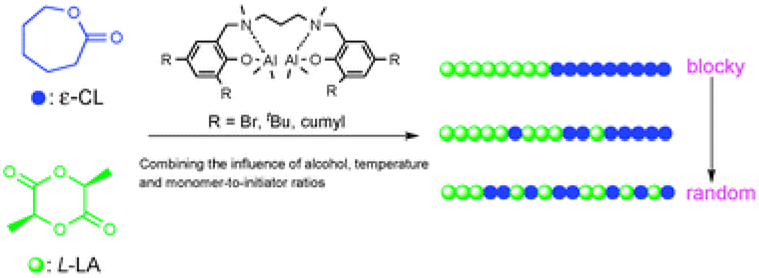
Air- and water-stable phenyl complexes with nitridotechnetium(V) cores can be prepared by straightforward procedures. $[TcNPh_2(PPh_3)_2]$ is formed by the reaction of $[TcNCl_2(PPh_3)_2]$ with PhLi. The analogous N-heterocyclic carbene (NHC) compound $[TcNPh_2(HL^{Ph})_2]$, where HL^{Ph} is 1,3,4-triphenyl-1,2,4-triazol-5-ylidene, is available from $(NBu_4)[TcNCl_4]$ and HL^{Ph} or its methoxo-protected form. The latter compound allows the comparison of different Tc–C bonds within one compound. Surprisingly, the Tc chemistry with such NHCs does not resemble that of corresponding Re complexes, where CH activation and orthometalation dominate.

- Construction of supramolecular helical nanofibers using renewable biomaterials: self-assembly of a cytidylic acid-appended bolaamphiphile in lemon juice
  Iwaura, R.; Kameyama, M. O. *Chem. Commun.* **2012**, *48*, 6633-6635.
  Abstract:



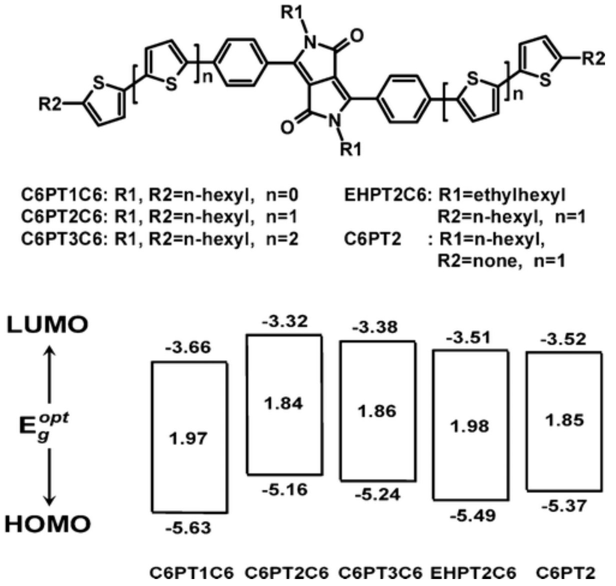
Left-handed helical nanofibers were produced from the self-assembly of nucleotide-appended bola-shape molecules in lemon juice.

- Exploitation of dinuclear salan aluminum complexes for versatile copolymerization of ε-caprolactone and L-lactide
  Wang, Y.; Ma, H. *Chem. Commun.* **2012**, *48*, 6729-6731.
  Abstract:



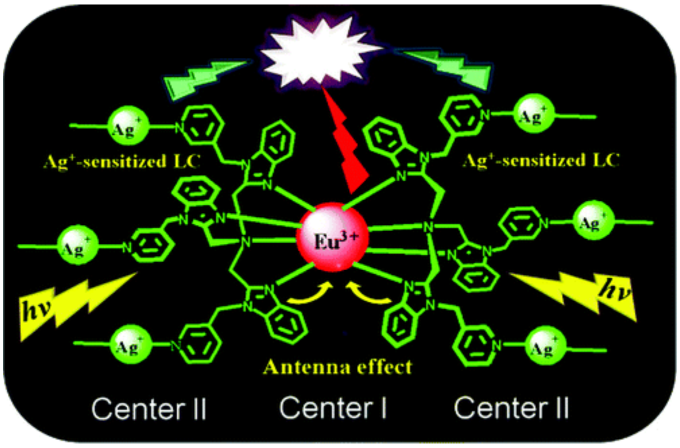
By combining the influence of excess alcohol, temperature and monomer-to-initiator ratios in the feed, dinuclear salan aluminum complexes copolymerized L-LA and ε-CL to produce blocky, gradient, tapered and random copolymers.

- Influence of Structural Variation on the Solid-State Properties of Diketopyrrolopyrrole-Based Oligophenylenethiophenes: Single-Crystal Structures, Thermal Properties, Optical Bandgaps, Energy Levels, Film Morphology, and Hole Mobility
  Kim, C.; Liu, J.; Lin, J.; Tamayo, A. B.; Walker, B.; Wu, G.; Nguyen, T.-Q.; Wang, Z.; Hu, R.; Xie, N.; Kwok, H. S.; Zhang, Y.; Sun, J. Z.; Tang, B. Z. *Chem. Mater.* **2012**, *24*, 1699–1709.
  Abstract:



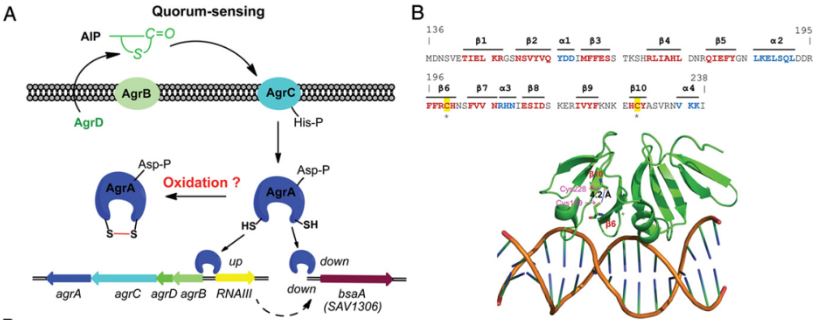
Five new compounds, based on diketopyrrolopyrrole (DPP) and phenylene thiophene (PT) moieties, were synthesized to investigate the effect of structural variations on solid state properties, such as single-crystal structures, optical absorption, energy levels, thermal phase transitions, film morphology, and hole mobility. The molecular structures were modified by means of (i) backbone length by changing the number of thiophenes on both sides of DPP, (ii) alkyl substitution (n-hexyl or ethylhexyl) on DPP, and (iii) the presence of an n-hexyl group at the end of the molecular backbone. These DPP-based oligophenylenethiophenes were systematically characterized by UV–visible spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), cyclic voltammetry (CV), ultraviolet photoelectron spectroscopy (UPS), atomic force microscopy (AFM), and hole-only diodes. Single-crystal structures were provided to probe insight into structure–property relationships at a molecule level resolution. This work demonstrates the significance of alkyl substitution as well as backbone length in tuning material's solid-state properties.

- Dual-Emission from a Single-Phase Eu–Ag Metal–Organic Framework: An Alternative Way to Get White-Light Phosphor
  Liu, Y.; Pan, M.; Yang, Q.-Y.; Fu, L.; Li, K.; Wei, S.-C.; Su, C.-Y. *Chem. Mater.* **2012**, *24*, 1954–1960.
  Abstract:



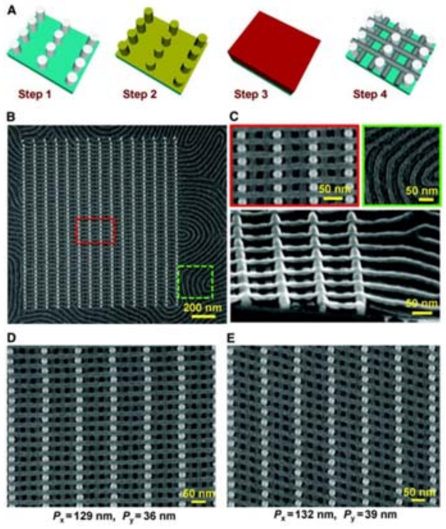
A new bifunctional NTB (tris(benzimidazol-2-ylmethyl)amine)-type ligand incorporating coordination discriminable tripodal benzimidazolyl and monodentate pyridyl groups, tris((pyridin-3-ylmethyl)benzoimidazol-2-ylmethyl)amine (3-TPyMNTB), has been prepared to assemble 4d–4f heterometallic three-dimensional metal–organic frameworks (MOFs) in a stepwise route: (1) direct reaction of 3-TPyMNTB with Ln$(ClO_4)_3$ affords monomeric complexes [Eu(3-TPyMNTB)$_2$]$(ClO_4)_3\cdot$2.5MeCN (**1**-**Eu**) and [Gd(3-TPyMNTB)$_2$]$(ClO_4)_3\cdot$2MeCN$\cdot$2$CHCl_3$ (**1**-**Gd**), and (2) assembly of the precursors **1**-**Eu** and **1**-**Gd** with $AgClO_4$ gives rise to infinite MOFs [EuAg$_3$(3-TPyMNTB)$_2$(H_2O)(MeCN)]$(ClO_4)_6\cdot$4MeCN (**2**-**Eu**-**Ag**) and [GdAg$_3$(3-TPyMNTB)$_2$(H_2O)(MeCN)]$(ClO_4)_6\cdot$4MeCN (**2**-**Gd**-**Ag**), respectively. In monomer **1**-**Eu**, the ligand shows an antenna effect to transfer absorbed energy to Eu^{3+} center to emit characteristic red luminescence, while in 4d–4f heterometallic MOF **2**-**Eu**-**Ag**, the ligand centered emission is resensitized by Ag^+ ions to generate dual emissions, coming up with the direct white-light emission from a single crystal. The detailed photoluminescent study has been carried out in both solid state and solution to elucidate the emission nature.

- Quorum-sensing agr mediates bacterial oxidation response via an intramolecular disulfide redox switch in the response regulator AgrA.
  Sun, F.; Liang, H.; Kong, X.; Xie, S.; Cho, H.; Deng, X.; Jia, Q.; Zhang, H.; Alvarez, S.; Hicks, L. M.; Bae, T.; Luo, C.; Jiang, H.; He, C. *Proc. Nat. Acad. Sci. USA* **2012**, *109*, 9095-9100.
  Abstract:



Oxidation sensing and quorum sensing significantly affect bacterial physiology and host-pathogen interactions. However, little attention has been paid to the cross-talk between these two seemingly orthogonal signaling pathways. Here we show that the quorum-sensing agr system has a built-in oxidation-sensing mechanism through an intramolecular disulfide switch possessed by the DNA-binding domain of the response regulator AgrA. Biochemical and mass spectrometric analysis revealed that oxidation induces the intracellular disulfide bond formation between Cys-199 and Cys-228, thus leading to dissociation of AgrA from DNA. Molecular dynamics (MD) simulations suggest that the disulfide bond formation generates a steric clash responsible for the abolished DNA binding of the oxidized AgrA. Mutagenesis studies further established that Cys-199 is crucial for oxidation sensing. The oxidation-sensing role of Cys-199 is further supported by the observation that the mutant *Staphylococcus aureus* strain expressing AgrAC199S is more susceptible to H_2O_2 owing to repression of the antioxidant *bsaA* gene under oxidative stress. Together, our results showthat oxidation sensing is a component of the quorum-sensing *agr* signaling system, which serves as an intrinsic checkpoint to ameliorate the oxidation burden caused by intense metabolic activity and potential host immune response.

- Templating Three-Dimensional Self-Assembled Structures in Bilayer Block Copolymer Films.
  Tavakkoli, A. K. G.; Gotrik, K. W.; Hannon, A. F.; Alexander-Katz, A.; Ross, C. A.; Berggren, K. K.
  Science **2012**, *336*, 1294-1297.
  Abstract:

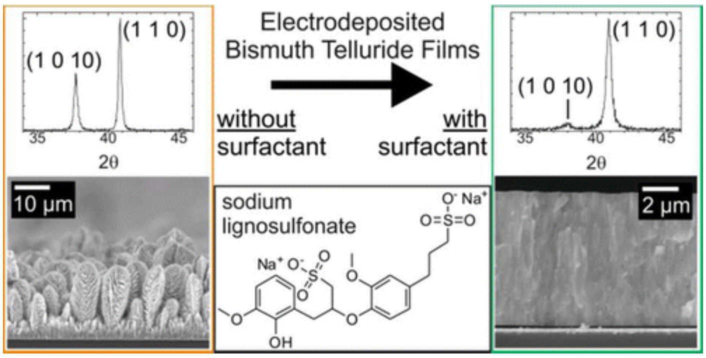


The registration and alignment of a monolayer of microdomains in a self-assembled block copolymer thin film can be controlled by chemical or physical templating methods. Although planar patterns are useful for nanoscale device fabrication, three-dimensional multilevel structures are required for some applications. We found that a bilayer film of a cylindrical-morphology block copolymer, templated by an array of posts functionalized with a brush attractive to the majority block, can form a rich variety of three-dimensional structures consisting of cylinder arrays with controllable angles, bends, and junctions whose geometry is controlled by the template periodicity and arrangement. This technique allows control of microdomain patterns and the ability to route and connect microdomains in specific directions.

- Surfactant-Mediated Electrodeposition of Bismuth Telluride Films and Its Effect on Microstructural Properties

Naylor, A. J.; Koukharenko, E.; Nandhakumar, I. S.; White, N. M. *Langmuir* **2012**, *28*, 8296-8299.

Abstract:

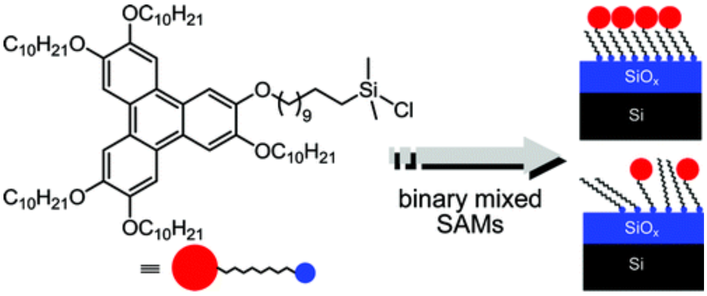


We report the synthesis of highly crystallographically textured films of stoichiometric bismuth telluride (Bi_2Te_3) in the presence of a surfactant, sodium lignosulfonate (SL), that resulted in the improved alignment of films in the (110) plane and offered good control over the morphology and roughness of the electrodeposited films. SL concentrations in the range 60–80 mg dm^{-3} at a deposition potential of −0.1 V vs SCE (saturated calomel electrode) were found to yield the most improved crystallinity and similar or superior thermoelectric properties compared with results reported in the literature.

- Triphenylene Silanes for Direct Surface Anchoring in Binary Mixed Self-Assembled Monolayers

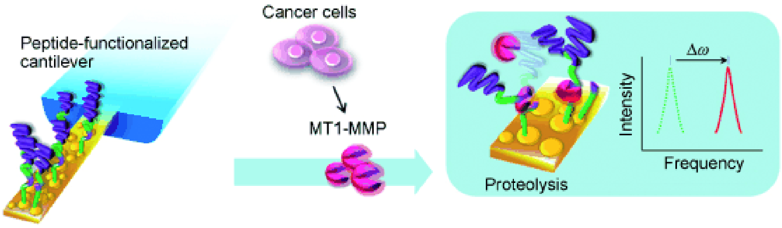
Mansueto, M.; Sauer, S.; Butschies, M.; Kaller, M.; Baro, A.; Woerner, R.; Hauke Hansen, N.; Tovar, G.; Pflaum, J.; Laschat, S. *Langmuir* **2012**, *28*, 8399-8407.

Abstract:



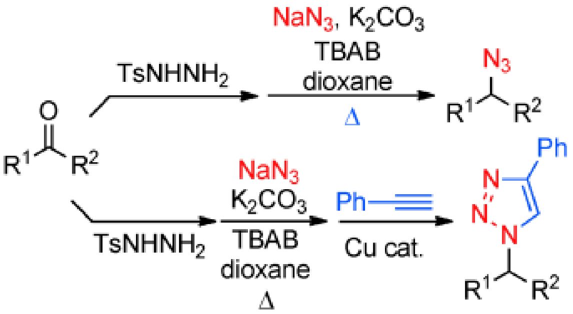
New triphenylene-based silanes 2-(ω-(chlorodimethylsilyl)-*n*-alkyl)-3,6,7,10,11-penta-*m*-alkoxytriphenylene **4 (T*m*-C*n*)** with *n* = 8 or 9 and *m* = 7, 8, 9, 10, or 11 were synthesized, and their self-assembly behavior in the liquid state and at glass and silicon oxide surfaces was investigated. The mesomorphic properties of triphenylene silanes **4 (T*m*-C*n*)** and their precursors **3 (T*m*-C*n*)** were determined by differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffraction. From the small-angle X-ray scattering (SAXS) regime, a preferential discotic lamellar mesophase can be deduced, and wide-angle X-ray scattering (WAXS) highlights the liquid-like characteristics of the alkyl side chains. To transfer these bulk structural properties to thin films, self-assembled monolayers (SAMs) were obtained by adsorption from solution and characterized by water contact angle measurements, null ellipsometry, and atomic force microscopy (AFM). Employing the concentration as an additional degree of freedom, binary SAMs of 2-(ω-(chlorodimethylsilyl)-undecyl)-3,6,7,10,11-penta-decyloxytriphenylene **4 (T10-C11)** were coassembled with chlorodecyldimethylsilane or chlorodimethyloctadecylsilane, and their capability as model systems for organic templating was evaluated. The structure of the resulting binary mixed SAMs was analyzed by water contact angle measurements, null ellipsometry, and X-ray reflectivity (XRR) in combination with theoretical modeling by a multidimensional Parratt algorithm and AFM. The composition dependence of film thickness and roughness can be explained by a microscopic model including the steric hindrance of the respective molecular constituents.

- Real-Time Quantitative Monitoring of Specific Peptide Cleavage by a Proteinase for Cancer Diagnosis
  Li, Lee, G.; Eom, K.; Park, J.; Yang, J.; Haam, S.; Huh, Y.-M.; Ryu, J. K.; Kim, N. H.; Yook, J. I.; Lee, S. W.; Yoon, D. S.; Kwon, T. *Angew. Chem. Int. Ed.* **2012**, *51*, 5837-5841.;
  Abstract:



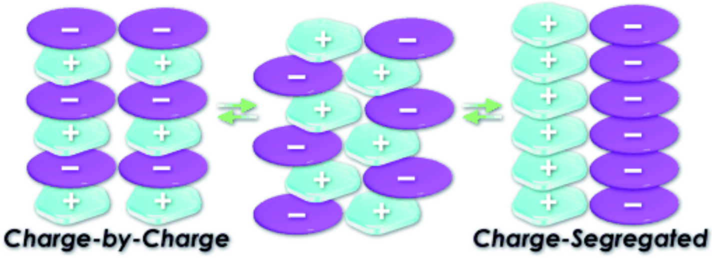
Good vibrations: A bioassay using a resonant peptide-functionalized microcantilever enables the quantitative characterization of the proteolytic activity of membrane type-1 matrix metalloproteinase (MT1-MMP). In this assay, shifts in the frequency of the cantilever after specific proteolytic cleavage of the target peptides by MT1-MMP are measured (see picture).

- Reductive Azidation of Carbonyl Compounds via Tosylhydrazone Intermediates Using Sodium Azide
  Barluenga, J.; Tomás-Gamasa, M.; Valdés, C. *Angew. Chem. Int. Ed.* **2012**, *51*, 5950-5952.
  Abstract:



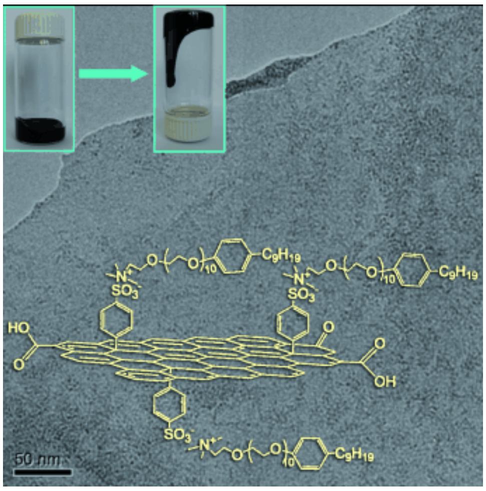
Simple and direct: Aldehydes and ketones can be transformed into alkyl azides through a reductive coupling of the corresponding tosylhydrazones in a process that takes place simply in the presence of K2CO3, tetrabutylammonium bromide (TBAB), and NaN3 (top of scheme). The application of this methodology followed by the Cu-catalyzed azide–alkyne cycloaddition allows the direct transformation of carbonyl compounds into triazoles (bottom of scheme).

- Ion Materials Comprising Planar Charged Species
  Haketa, Y.; Honsho, Y.; Seki, S.; Maeda, H. *Chem. Eur. J.* **2012**, *18*, 7016–7020.
  Abstract:



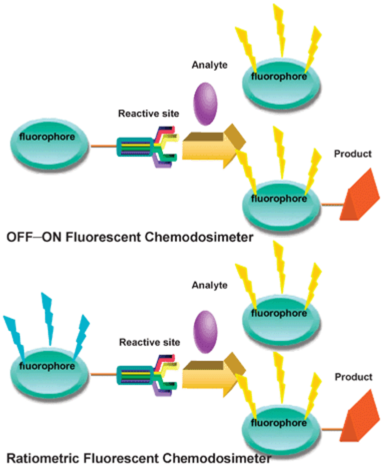
Assemblies of planar ions: Anion complexes of appropriately designed pyrrole-based π-conjugated molecules provided liquid crystalline materials by combination with a planar cation based on charge-by-charge and charge-segregated assemblies (see figure). The series of charge-based assemblies exhibited well-balanced ambipolar charge carrier transport behavior with relatively high mobilities.

- Self-Unfolded Graphene Sheets
  Li, Q.; Dong, L.; Sun, F.; Huang, J.; Xie, H.; Xiong, C. *Chem. Eur. J.* **2012**, *18*, 7055–7059.
  Abstract:



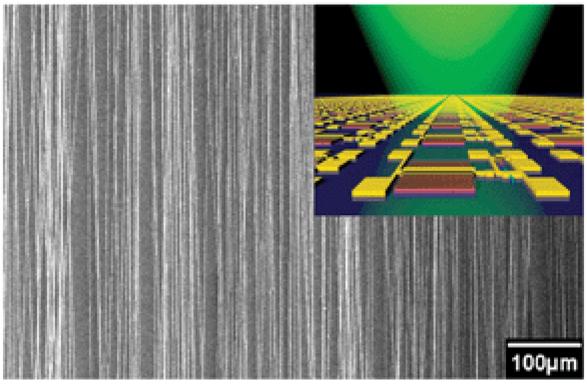
Do it yourself! Self-unfolded graphene sheets were prepared by treatment of exfoliated graphene oxide (GO) with aryl diazonium salts with concomitant reduction, followed by ion exchange with oligomeric quaternary ammonium salts. The self-driven unfolding behavior is very convenient for the large-scale production of graphene sheets with superior properties relating to the extremely extended configuration (see figure).

- Fluorescent chemodosimeters using “mild” chemical events for the detection of small anions and cations in biological and environmental media
  Du, J.; Hu, M.; Fan, J.; Peng, X. *Chem. Soc. Rev.* **2012**, *41*, 4511-4535.
  Abstract:



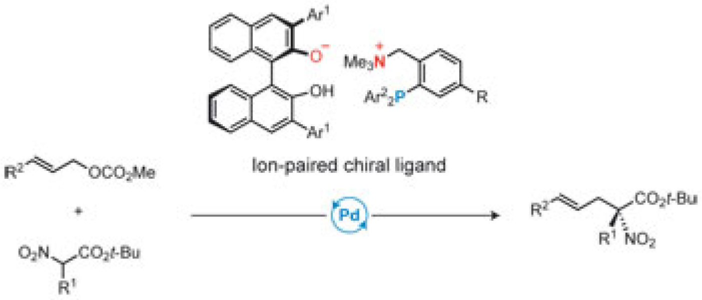
Mild chemical processes of various analytes and detection methods involving revolutionary strategies in the fields of analytical chemistry, biology and environmental sciences have been extensively developed. This *critical review* focuses on representative examples of mild chemical processes that can be used in fluorescent chemodosimeters for ion sensing (anions and cations). A systematisation according to the type of reaction mechanism is established. Numerous examples including extensions combined with catalytic and material sciences applicable in fluorescence imaging and water treatment are also discussed (151 references).

- Recent advances in large-scale assembly of semiconducting inorganic nanowires and nanofibers for electronics, sensors and photovoltaics
  Long, Y.-Z.; Yu, M.; Sun, B.; Gu, C.-Z.; Fan, Z. *Chem. Soc. Rev.* **2012**, *41*, 4560-4580.
  Abstract:



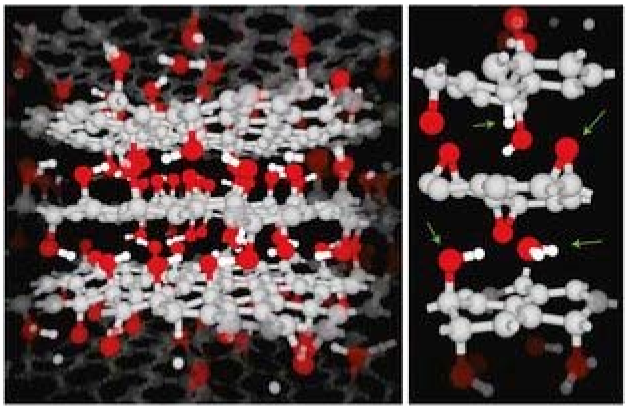
Semiconducting inorganic nanowires (NWs), nanotubes and nanofibers have been extensively explored in recent years as potential building blocks for nanoscale electronics, optoelectronics, chemical/biological/optical sensing, and energy harvesting, storage and conversion, *etc.* Besides the top-down approaches such as conventional lithography technologies, nanowires are commonly grown by the bottom-up approaches such as solution growth, template-guided synthesis, and vapor–liquid–solid process at a relatively low cost. Superior performance has been demonstrated using nanowires devices. However, most of the nanowire devices are limited to the demonstration of single devices, an initial step toward nanoelectronic circuits, not adequate for production on a large scale at low cost. Controlled and uniform assembly of nanowires with high scalability is still one of the major bottleneck challenges towards the materials and device integration for electronics. In this review, we aim to present recent progress toward nanowire device assembly technologies, including flow-assisted alignment, Langmuir–Blodgett assembly, bubble-blown technique, electric/magnetic-field-directed assembly, contact/roll printing, planar growth, bridging method, and electrospinning, *etc.* And their applications in high-performance, flexible electronics, sensors, photovoltaics, bioelectronic interfaces and nano-resonators are also presented.

- Ion-paired chiral ligands for asymmetric palladium catalysis
  Ohmatsu, K.; Ito, M.; Kunieda, T.; Ooi, T. *Nature Chemistry* **2012**, *4*, 473 – 477.
  Abstract:



Conventional chiral ligands rely on the use of a covalently constructed, single chiral molecule embedded with coordinative functional groups. Here, we report a new strategy for the design of a chiral ligand for asymmetric transition-metal catalysis; our approach is based on the development of an achiral cationic ammonium–phosphine hybrid ligand paired with a chiral binaphtholate anion. This ion-paired chiral ligand imparts a remarkable stereocontrolling ability to its palladium complex, which catalyses a highly enantioselective allylic alkylation of α-nitrocarboxylates. By exploiting the possible combinations of the achiral onium entities with suitable coordinative functionalities and readily available chiral acids, this approach should contribute to the development of a broad range of metal-catalysed, stereoselective chemical transformations.

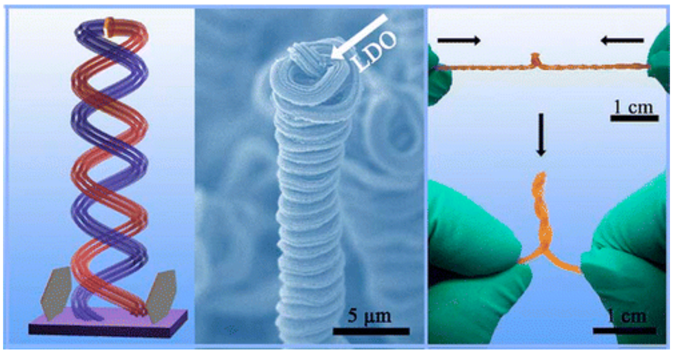
- Room-temperature metastability of multilayer graphene oxide films
  Kim, S.; Zhou, S.; Hu, Y.; Acik, M.; Chabal, Y. J.; Berger, C.; Heer, W.; Bongiorno, A.; Riedo, E. *Nature Materials* **2012**, *11*, 544–549.
  Abstract:



Graphene oxide potentially has multiple applications. The chemistry of graphene oxide and its response to external stimuli such as temperature and light are not well understood and only approximately controlled. This understanding is crucial to enable future applications of this material. Here, a combined experimental and density functional theory study shows that multilayer graphene oxide produced by oxidizing epitaxial graphene through the Hummers method is a metastable material whose structure and chemistry evolve at room temperature with a characteristic relaxation

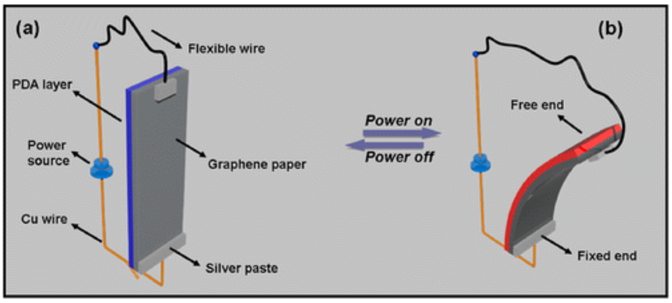
time of about one month. At the quasi-equilibrium, graphene oxide reaches a nearly stable reduced O/C ratio, and exhibits a structure deprived of epoxide groups and enriched in hydroxyl groups. Our calculations show that the structural and chemical changes are driven by the availability of hydrogen in the oxidized graphitic sheets, which favours the reduction of epoxide groups and the formation of water molecules.

- Space Confinement and Rotation Stress Induced Self-Organization of Double-Helix Nanostructure: A Nanotube Twist with a Moving Catalyst Head
  Zhao, M.-Q.; Zhang, Q.; Tian, G.-L.; Huang, J.-Q.; Wei, F. *ACS Nano* **2012**, *6*, 4520-4529.
  Abstract:



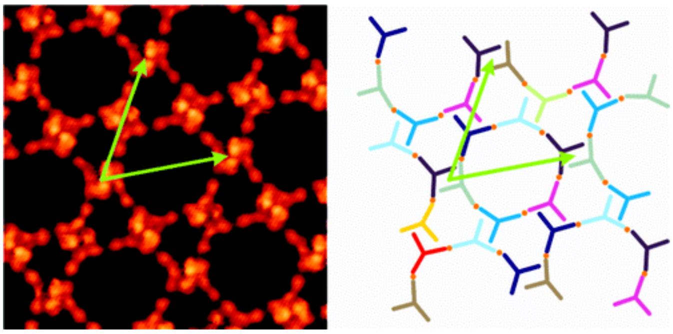
Inorganic materials with double-helix structure have attracted intensive attention due to not only their elegant morphology but also their amazing morphology-related potential applications. The investigation on the formation mechanism of the inorganic double-helix nanostructure is the first step for the fundamental studies of their materials or physical properties. Herein, we demonstrated the space confinement and rotation stress induced self-organization mechanism of the carbon nanotube (CNT)-array double helices under scanning electron microscopy by directly observing their formation process from individual layered double hydroxide flakes, which is a kind of hydrotalcite-like material composed of positively charged layers and charge-balancing interlayer anions. Space confinement is considered to be the most important extrinsic factor for the formation of CNT-array double helices. Synchronous growth of the CNT arrays oppositely from LDH flakes with space confinement on both sides at the same time is essential for the growth of CNT-array double helices. Coiling of the as-grown CNT arrays into double helices will proceed by self-organization, tending to the most stable morphology in order to release their internal rotation stress. Based on the demonstrated mechanism, effective routes were carried out to improve the selectivity for CNT-array double helices. The work provides a promising method for the fabrication of double-helix nanostructures with their two helices connected at the end by self-assembly.

- Electromechanical Actuator with Controllable Motion, Fast Response Rate, and High-Frequency Resonance Based on Graphene and Polydiacetylene
  Liang, J.; Huang, L.; Li, N.; Huang, Y.; Wu, Y.; Fang, S.; Oh, J.; Kozlov, M.; Ma, Y.; Li, F.; Baughman, R.; Chen, Y. *ACS Nano* **2012**, *6*, 4508-4519.
  Abstract:



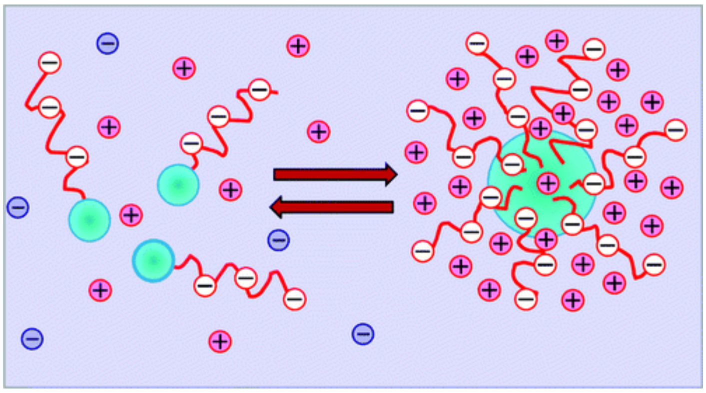
Although widely investigated, novel electromechanical actuators with high overall actuation performance are still in urgent need for various practical and scientific applications, such as robots, prosthetic devices, sensor switches, and sonar projectors. In this work, combining the properties of unique environmental perturbations-actuated deformational isomerization of polydiacetylene (PDA) and the outstanding intrinsic features of graphene together for the first time, we design and fabricate an electromechanical bimorph actuator composed of a layer of PDA crystal and a layer of flexible graphene paper through a simple yet versatile solution approach. Under low applied direct current (dc), the graphene–PDA bimorph actuator with strong mechanical strength can generate large actuation motion (curvature is about 0.37 cm^{-1} under a current density of 0.74 A/mm^2) and produce high actuation stress (more than 160 MPa/g under an applied dc of only 0.29 A/mm^2). When applying alternating current (ac), this actuator can display reversible swing behavior with long cycle life under high frequencies even up to 200 Hz; significantly, while the frequency and the value of applied ac and the state of the actuators reach an appropriate value, the graphene–PDA actuator can produce a strong resonance and the swing amplitude will jump to a peak value. Moreover, this stable graphene–PDA actuator also demonstrates rapidly and partially reversible electrochromatic phenomenon when applying an ac. Two mechanisms—the dominant one, electric-induced deformation, and a secondary one, thermal-induced expansion of PDA—are proposed to contribute to these interesting actuation performances of the graphene–PDA actuators. On the basis of these results, a mini-robot with controllable direction of motion based on the graphene–PDA actuator is designed to illustrate the great potential of our discoveries for practical use. Combining the unique actuation mechanism and many outstanding properties of graphene and PDA, this novel kind of graphene–PDA actuator exhibits compelling advantages to traditional electromechanical actuation technology and may provide a new avenue for actuation applications.

- Two-Dimensional Short-Range Disordered Crystalline Networks from Flexible Molecular Modules
  Ecija, D.; Vijayaraghavan, S.; Auwärter, W.; Joshi, S.; Seufert, K.; Aurisicchio, C.; Bonifazi, D.; Barth, J. V. *ACS Nano* **2012**, *6*, 4258-4265.
  <u>Abstract:</u>



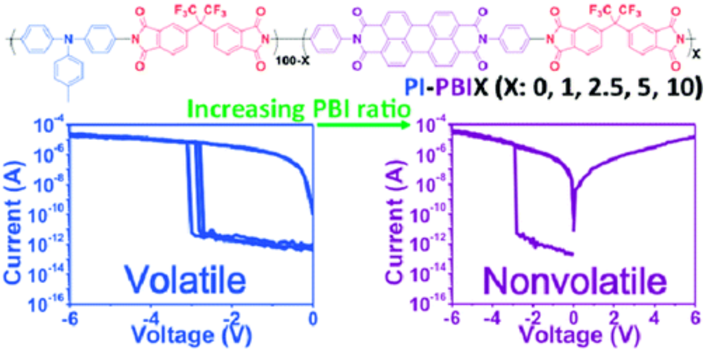
Studies of complex condensed matter systems have led to the discovery of materials of unexpected spatial organization as glasses, glassy crystals, quasicrystals, and protein and virus crystals. Here, we present *two-dimensional (2D) short-range disordered molecular crystalline networks*, which, regarding spatial organization, can be considered as surface analogues of 3D glassy crystals. In particular, the deposition of a flexible molecular module on Cu(111) gives rise to distinct phases whose characteristics have been examined in real space by scanning tunneling microscopy: a 2D short-range distortional disordered crystalline network and a 2D short-range orientational disordered crystalline network, respectively. Both phases exhibit a random arrangement of nanopores that are stabilized by the simultaneous presence of metal–organic and pyridyl–pyridyl interactions. The 2D short-range distortional disordered crystalline network displayed intriguing flexibility, as probed by the STM tip that modifies the pore shape, a prerequisite for adaptive behavior in host–guest processes.

- Theory of Block Polymer Micelles: Recent Advances and Current Challenges
  Zhulina, E. B.; Borisov, O. V. *Macromolecules* **2012**, *45*, 4429–4440.
  Abstract:



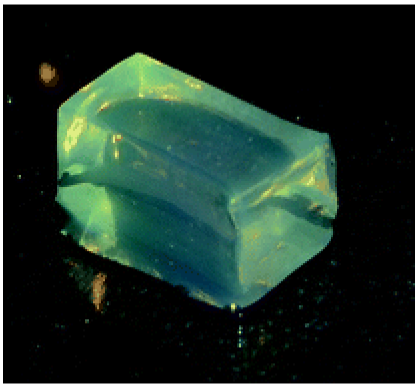
We present an overview of existing theories of block polymer micelles. We focus here on the equilibrium structure of nanoaggregates formed by solvophobic/solvophilic diblock copolymers in a dilute solution and briefly address the association behavior of triblock terpolymer. We outline recent advances in the field and some challenging problems for theoretical developments.

- Tuning the Electrical Memory Characteristics from Volatile to Nonvolatile by Perylene Imide Composition in Random Copolyimides
  Kurosawa, T.; Lai, Y.-C.; Higashihara, T.; Ueda, M.; Liu, C.-L.; Chen, W.-C. *Macromolecules* **2012**, *45*, 4556–4563.
  Abstract:



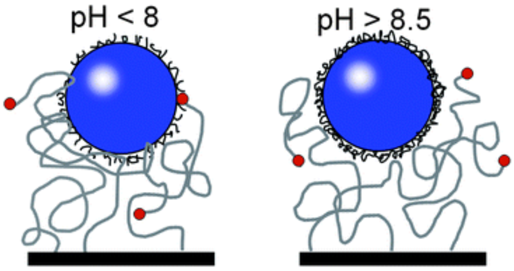
Random copolyimides, **PI–PBIX**, with different compositions of 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (**6FDA**), *N*,*N*′-bis(4-aminophenyl)-3,4,9,10-perylenebis(dicarboximide) (**PBI**), and 4,4′-diamino-4″-methyltriphenylamine (**AMTPA**) were designed and synthesized for resistive-switching memory device applications. By varying the feeding ratio of monomers, **PI–PBIX** (where **X** = 0, 1, 2.5, 5, and 10 for molar composition of repeating units containing **PBI**) showed tunable optical and electronic properties through the charge transfer between **AMTPA** and **PBI**. Also, the memory devices prepared from **PI–PBIX** sandwiched between ITO and Al electrodes exhibited the tunable electrical bistability from the volatile to nonvolatile write once read many-times (WORM) memory characteristics as the **PBI** composition increased. The OFF/ON electrical switching transition was mainly attributed to the charge-transfer mechanism for charge-separated high conductance, based on the analysis of density function theory. Also, the volatility of **PI–PBIX** device depended on the stability of charge-transfer complex and charge trapping sites. The deep LUMO energy level of the **PBI** moiety increased the back-charge-transfer energy barrier and prevented recombination of segregated charges even through applying the high negative and positive voltage. The study revealed that the memory characteristics could be tailored from the donor–acceptor composition in the random copolyimides.

- Dipeptide hydrogel formation triggered by boronic acid–sugar recognition
  Grigoriou, S.; Johnson, E. K.; Chen, L.; Adams, D. J.; James, T. D.; Cameron, P. J. *Soft Matter* **2012**, *8,* 2788-2791.
  Abstract:



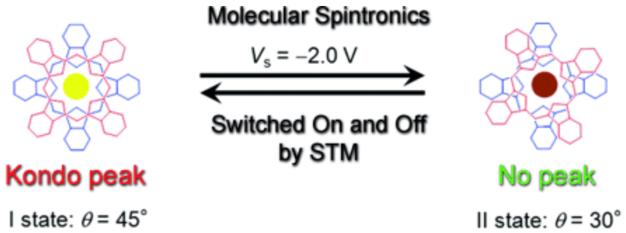
The pH drop associated with sugar recognition and binding by boronic acids has been used to initiate the formation of gels from dipeptide gelators. Gels formed in the presence of fructose, but not glucose which has a weaker binding constant to boronic acids.

- Diffusive behaviour of PLL–PEG coated colloids on λ-DNA brushes – tuning hydrophobicity
  Yanagishima, T.; Di Michele, L.; Kotar, J.; Eiser, E. *Soft Matter* **2012, *8,*** 2792-2798.
  Abstract:



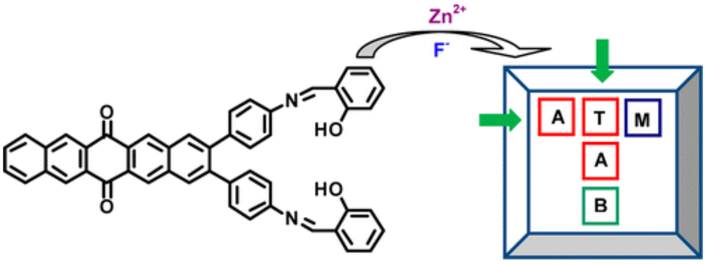
We find 'sticky' 2D diffusion of poly-L-lysine–polyethylene glycol (PLL–PEG) coated silica colloids sedimented onto a brush of long, double stranded λ-DNA. The interaction is hypothesised to be hydrophobic, due to known physical properties of single and double stranded DNA and the systematic elimination of other known forces. The colloids are found to have variable affinity to the surface when prepared at different pH, even when the electrostatic environment of the brush is kept identical. Varied diffusive behaviour is observed: the diffusivity increases when the incubation pH is higher, and fewer beads are stuck to the brush surface. This sensitivity is found to agree with a simple model for the adsorption conditions of the PLL on the silica spheres. The significance of hydrophobicity is confirmed by capping the ssDNA 'sticky' end of the DNA, leading to a drastic enhancement of diffusivity of the particles on the brush.

- Molecular Spintronics Based on Single-Molecule Magnets Composed of Multiple-Decker Phthalocyaninato Terbium(III) Complex
  Katoh, K.; Isshiki, H.; Komeda, T.; Yamashita, M. *Chem. Asian J.* **2012**, *7*, 1154–1169.
  Abstract:



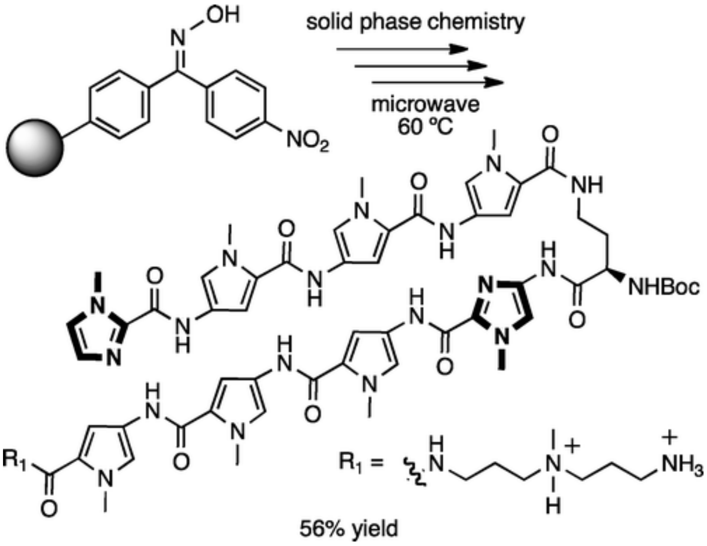
Unlike electronics, which is based on the freedom of the charge of an electron whose memory is volatile, spintronics is based on the freedom of the charge, spin, and orbital of an electron whose memory is non-volatile. Although in most GMR, TMR, and CMR systems, bulk or classical magnets that are composed of transition metals are used, this Focus Review considers the growing use of single-molecule magnets (SMMs) that are composed of multinuclear metal complexes and nanosized magnets, which exhibit slow magnetic-relaxation processes and quantum tunneling. Molecular spintronics, which combines spintronics and molecular electronics, is an emerging field of research. Using molecules is advantageous because their electronic and magnetic properties can be manipulated under specific conditions. Herein, recent developments in [LnPc]-based multiple-decker SMMs on surfaces for molecular spintronic devices are presented. First, we discuss the strategies for preparing single-molecular-memory devices by using SMMs. Next, we focus on the switching of the Kondo signal of [LnPc]-based multiple-decker SMMs that are adsorbed onto surfaces, their characterization by using STM and STS, and the relationship between the molecular structure, the electronic structure, and the Kondo resonance of [$TbPc_2$]. Finally, the field-effect-transistor (FET) properties of surface-adsorbed [$LnPc_2$] and [Ln_2Pc_3] cast films are reported, which is the first step towards controlling SMMs through their spins for applications in single-molecular memory and spintronics devices.

- Fluoride Triggered Fluorescence "Turn On" Sensor for Zn^{2+} Ions Based on Pentaquinone Scaffold That Works as a Molecular Keypad Lock
  Bhalla, V.; Roopa, Kumar, M. *Org. Lett.* **2012,** *14*, 2802-2805.
  Abstract:



A pentaquinone based compound **3a** has been synthesized which exhibits pronounced fluorescence enhancement in the presence of Zn^{2+} ions under a F^- triggered synergistic effect. Derivative **3a** also behaves as a molecular keypad lock with sequential chemical inputs of Zn^{2+} and F^- ions.

- Microwave Assisted Synthesis of Py-Im Polyamides
  Puckett, J. W.; Green, J. T.; Dervan, P. B. *Org. Lett.* **2012,** *14*, 2774-2777.
  Abstract:



Microwave synthesis was utilized to rapidly build Py-Im polyamides in high yields and purity using Boc-protection chemistry on Kaiser oxime resin. A representative polyamide targeting the 5′-WGWWCW-3′ (W = A or T) subset of the consensus Androgen and Glucocorticoid Response Elements was synthesized in 56% yield after 20 linear steps and HPLC purification. It was confirmed by Mosher amide derivatization of the polyamide that a chiral α-amino acid does not racemize after several additional coupling steps.