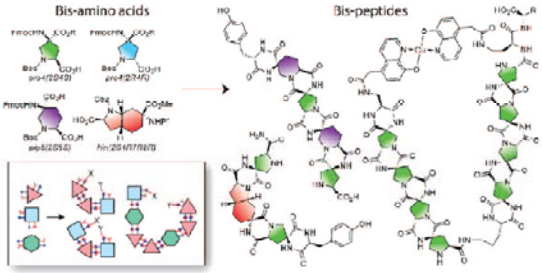
- Shape-Programmable Macromolecules
  Schafmeister, C. E.; Brown, Z. Z.; Gupta, S. *Acc. Chem. Res.* **2008**, *41*, 1387–1398.
  Abstract :

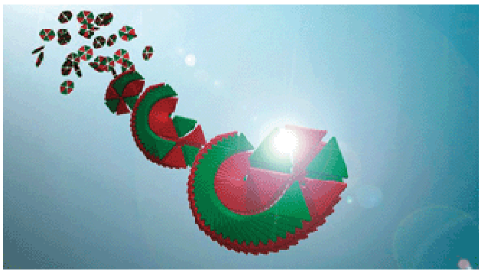


Proteins catalyze specific chemical reactions and carry out highly selective molecular recognition because they adopt well-defined three-dimensional structures and position chemically reactive functional groups in specific constellations. Proteins attain these well-defined structures through the complex process of protein folding. We seek to emulate these protein functions by constructing macromolecules that are easier to engineer by avoiding folding altogether.

Toward that goal, we have developed an approach for the synthesis of macromolecules with programmable shapes. As described in this Account, we have constructed synthetic building blocks called bis-amino acids that we then couple through pairs of amide bonds to create water-soluble, spiroladder oligomers (bis-peptides) with well-defined three-dimensional structures. Bis-peptides use the conformational preferences of fused rings, stereochemistry, and strong covalent bonds to define their shape, unlike natural proteins and synthetic foldamers, which depend on noncovalent interactions and an unpredictable folding process to attain structure.

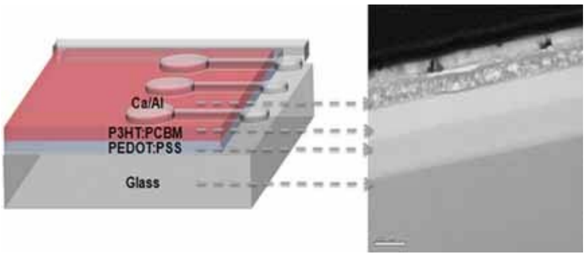
Using these bis-amino acid monomers, we have built and characterized a number of bis-peptide nanostructures. We also constructed a molecular actuator that undergoes a large change in conformation under the control of metal exchange; the first application of bis-peptides. We are currently developing further approaches to functionalize bis-peptides as scaffolds to present well-defined constellations of functional groups. Such macromolecules could facilitate multifunctional catalysis and molecular recognition and lead to nanoscale molecular devices.

- Recent advances in photoresponsive supramolecular self-assemblies
  Yagai, S.; Kitamura, A. *Chem. Soc. Rev.* **2008**, *37*, 1520-1529.
  Abstract :



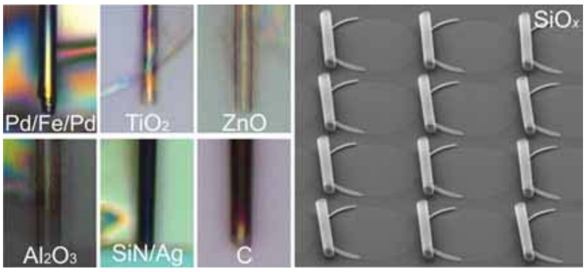
Construction of supramolecular self-assemblies whose self-assembling process and self-assembled architectures can be controlled by external stimuli is a fascinating and challenging topic for supramolecular chemists. The modification of photochromic molecules with noncovalent interaction sites or the incorporation of photochromic molecules into self-assembling modules makes light an ideal external input, providing high-performance photoresponsive multicomponent self-assemblies. Among such systems, in this *tutorial review* we deal with several photoresponsive supramolecular self-assemblies showing a unique mechanism and/or type of photoresponse. These examples illustrate that we would be able to produce further new photoresponsive molecular ensembles if one can elaborately hybridize photochromic molecules to specifically-designed supramolecular self-assemblies. We believe that the accumulation of insight into the construction principle, mechanism and concept of such smart supramolecular self-assemblies should realize practical smart functional materials.

- Efficient and Flexible ITO-Free Organic Solar Cells Using Highly Conductive Polymer Anodes
  Na, S.-I.; Kim, S.-S.; Jo, J.; Kim, D.-Y. *Adv. Mater.* **2008**, *20*, 4061-4067.
  <u>Abstract:</u>



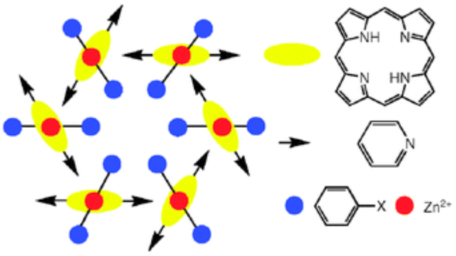
ITO-free organic solar cells are fabricated on glass and on flexible substrates. The efficiencies of these cells on glass and plastic substrates (3.27% and 2.8%, respectively) were comparable to those of ITO-based devices (3.66% and 2.9%, respectively). Furthermore, in the flexibility test the ITO-free cells on flexible substrates manifested superior mechanical robustness compared with ITO-based cells.

- Versatile Approach for Integrative and Functionalized Tubes by Strain Engineering of Nanomembranes on Polymers
  Mei, Y.; Huang, G.; Solovev, A. A.; Bermúdez Ureña, E.; Mönch, I.; Ding, F.; Reindl, T.; Fu, R. K. Y.; Chu, P. K.; Schmidt, O. G. *Adv. Mater.* **2008**, *20*, 4085-4090.
  <u>Abstract:</u>



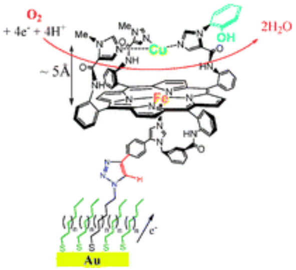
We have developed a generic approach to engineer tubular micro-/nanostructures out of many different materials (see figure) with tunable diameters and lengths by precisely releasing and rolling up functional nanomembranes on polymers. The technology spans across different scientific fields ranging from photonics to biophysics and we demonstrate optical ring resonators, magneto-fluidic sensors, remotely controlled microjets and 2D confined channels for cell growth guiding.

- Molecular tectonics: control of pore size and polarity in 3-D hexagonal coordination networks based on porphyrins and a zinc cation
  Kühn, E.; Bulach, V.; Hosseini, M. W. *Chem. Commun.* **2008**, 5104-5106.
  <u>Abstract:</u>



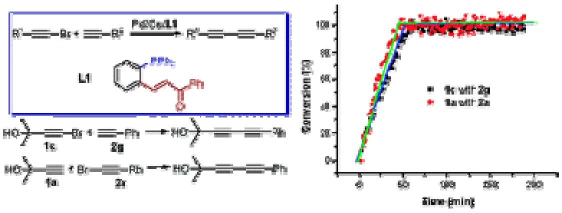
In the crystalline phase, porphyrin derivatives based on two 4-pyridyl units at the 5 and 15 *meso* positions and two 4-aryl moieties bearing various groups (CN, OMe, OH and CF_3) at the 10 and 20 *meso* positions lead, in the presence of a zinc dication, to the formation of robust 3-D networks presenting hexagonal channels: both the size and the polarity of the pores were tuned by the nature of the substituents attached to the two aryl groups.

- Functional biomimetic models for the active site in the respiratory enzyme cytochrome c oxidase
  Collman, J. P.; Decréau, R. A. *Chem. Commun.* **2008**, 5065-5076.
  <u>Abstract:</u>



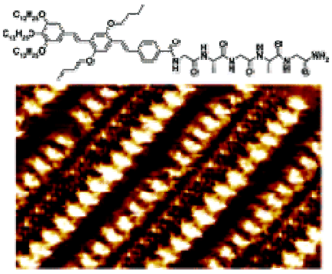
A functional analog of the active site in the respiratory enzyme, cytochrome c oxidase (CcO) reproduces every feature in CcO's active site: a myoglobin-like heme (heme *a3*), a distal tridentate imidazole copper complex (Cu_B), a phenol (Tyr244), and a proximal imidazole. When covalently attached to a liquid-crystalline SAM film on an Au electrode, this functional model continuously catalyzes the selective four-electron reduction of dioxygen at physiological potential and pH, under rate-limiting electron flux (as occurs in CcO).

- Investigation of an Efficient Palladium-Catalyzed C(sp)−C(sp) Cross-Coupling Reaction Using Phosphine−Olefin Ligand: Application and Mechanistic Aspects
  Shi, W.; Luo, Y.; Luo, X.; Chao, L.; Zhang, H.; Wang, J.; Lei, A. *J. Am. Chem. Soc.* **2008**, *130*, 14713–14720.
  <u>Abstract:</u>



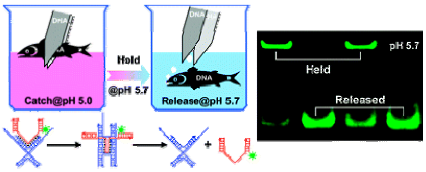
A π-acceptor phosphine−electron-deficient olefin ligand was found effective in promoting Pd-catalyzed C(sp)−C(sp) cross-coupling reactions. The new protocol realized the cross-coupling of a broad scope of terminal alkynes and haloalkynes in good to excellent yields with high selectivities. Electron-rich alkynes, which are normally difficult substrates in Glaser couplings, could be employed as either nucleophiles or electrophiles. Alkynes bearing similar substituents, such as n-C_5H_{11}CCBr and *n*-C_4H_9CCH, which usually suffer from homocoupling side reactions under Cadiot−Chodkiewicz conditions, were successfully cross-coupled in the system. Preliminary kinetic studies revealed that the reaction rate was zero-order in the concentrations of both haloalkynes and terminal alkynes and first order in the loading of $Pd(dba)_2$ and exhibited no obvious dependence on the loading of the copper salt. Control experiments with other phosphines such as PPh_3 and DPPF as the ligand were carried out. All the kinetic evidence indicated that the phosphine−olefin ligand facilitated the reductive elimination in the catalytic cycle.

- Oligo(*p*-phenylenevinylene)−Peptide Conjugates: Synthesis and Self-Assembly in Solution and at the Solid−Liquid Interface
  Matmour, R.; De Cat, I.; George, S. J.; Adriaens, W.; re, P.; Bomans, P. H. H.; Sommerdijk, N. A. J. M.; Gielen, J. C.; Christianen, P. C. M.; Heldens, J. T.; van Hest, J. C. M.; wik, D. W. P. M.; De Feyter, S.; Meijer, E. W.; Schenning, A. P. H. J. *J. Am. Chem. Soc.* **2008**, *130*, 14576–14583.
  Abstract:



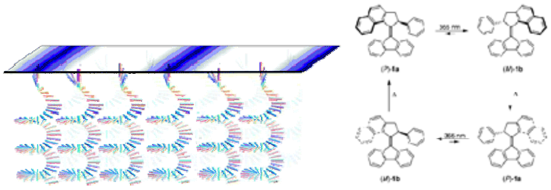
Two oligo(*p*-phenylenevinylene)−peptide hybrid amphiphiles have been synthesized using solid- and liquid-phase strategies. The amphiliphiles are composed of a π-conjugated oligo(*p*-phenylenevinylene) trimer (OPV) which is coupled at either a glycinyl-alanyl-glycinyl-alanyl-glycine (GAGAG) silk-inspired β-sheet or a glycinyl-alanyl-asparagyl-prolyl-asparagy-alanyl-alanyl-glycine (GANPNAAG) β-turn forming oligopeptide sequence. The solid-phase strategy enables one to use longer peptides if strong acidic conditions are avoided, whereas the solution-phase coupling gives better yields. The study of the two-dimensional (2D) self-assembly of OPV−GAGAG by scanning tunneling microscopy (STM) at the submolecular level demonstrated the formation of bilayers in which the molecules are lying antiparallel in a β-sheet conformation. In the case of OPV−GANPNAAG self-assembled monolayers could not be observed. Absorption, fluorescence, and circular dichroism studies showed that OPV−GAGAG and OPV−GANPNAAG are aggregated in a variety of organic solvents. In water cryogenic temperature transmission electron microscopy (cryo-TEM), atomic force microscopy (AFM), light scattering, and optical studies reveal that self-assembled nanofibers are formed in which the helical organization of the OPV segments is dictated by the peptide sequence.

- Catch and Release: DNA Tweezers that Can Capture, Hold, and Release an Object under Control
  Han, X.; Zhou, Z.; Yang, F.; Deng, Z. *J. Am. Chem. Soc.* **2008**, *130*, 14414–14415.
  Abstract:



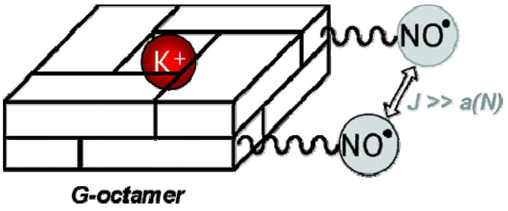
A pair of DNA tweezers are constructed, which are capable of capturing, holding and releasing a DNA object by playing with the open and close actions of the tweezers assisted by pH switchings. The object is captured between the tweezers' arms at pH 5.0 through Hoogsteen hydrogen bonding and can be stably held even when the pH is increased to 5.7 after the tweezers are closed. Upon introducing a DNA unlocker strand, the tweezers are opened and the object gets released. This capture-hold-release process can be easily cycled without losing much of its efficiency.

- Photoinduced Reorganization of Motor-Doped Chiral Liquid Crystals: Bridging Molecular Isomerization and Texture Rotation
  Bosco, A.; Jongejan, M. G. M.; Eelkema, R.; Katsonis, N.; Lacaze, E.; Ferrarini, A.; Feringa, B. L. *J. Am. Chem. Soc.* **2008**, *130*, 14615–14624.
  Abstract:



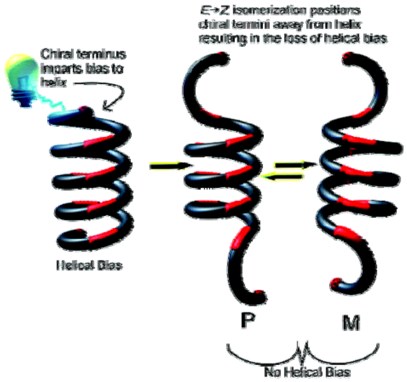
We recently reported that the photoisomerization of molecular motors used as chiral dopants in a cholesteric liquid crystal film induces a rotational reorganization which can be observed by optical microscopy and produces the motion of microscopic objects placed on top of the film (Feringa, B. L.; et al. *Nature* **2006**, *440*, 163; *J. Am. Chem. Soc.* **2006**, *128*, 14397). The mechanism underlying the mesoscopic manifestation of the molecular process was not fully understood, and here we present a joint theoretical and experimental investigation, which provides a detailed insight into the mechanism of texture rotation. This description allows us to identify the interplay between the chemical structure of the chiral dopant and the material properties of the liquid crystal host, and to quantify their role in the observed dynamic phenomenon. We have found that a crucial role is played by the hybrid anchoring of the liquid crystal, with the director parallel to the substrate and perpendicular to the interface with air; in this configuration an almost unperturbed cholesteric helix, with its axis normal to the substrate, is present in most of the film, with strong deformations only close to the free interface. The texture rotation observed in the experiment reflects the rotation of the director during the unwinding of the cholesteric helix, produced by the change in shape of the chiral dopant under photoisomerization. The rotational reorganization is controlled by the photochemical process, via the coupling between the chirality of the dopant and the elastic properties of the liquid crystal host.

- A Cation-Directed Switch of Intermolecular Spin-Spin Interaction of Guanosine Derivatives Functionalized with Open-Shell Units
  Graziano, C.; Masiero, S.; Pieraccini, S.; Lucarini, M.; Spada, G. P. *Org. Lett.* **2008**, *10*, 1739-1742.
  Abstract:



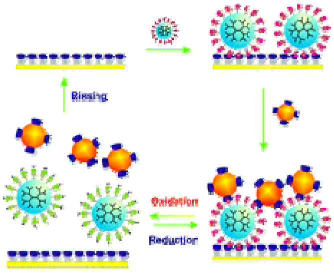
The guanosine derivative 1 functionalized with the persistent radical unit 4-carbonyl-2,2,6,6-tetramethylpiperidin-1-oxyl in solution has no particular intermolecular spin−spin interactions; however, in the presence of potassium ions this compound can form a D_4-symmetric octameric assembly $[1_8K]^+$ in which the nitroxyl moieties show a weak electron spin−spin exchange interaction. Since the relative geometry of the radicals is the outcome of K^+-directed self-assembly, the spin−spin interaction can be suppressed by removing the alkaline ion.

- Photomodulated Chiral Induction in Helical Azobenzene Oligomers
  King, E. D.; Tao, P.; Sanan, T. T.; Hadad, C. M.; Parquette, J. R. *Org. Lett.* **2008**, *10*, 1671-1674.
  Abstract:



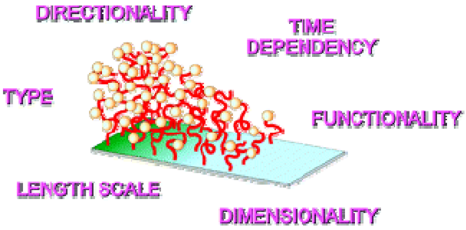
Appending L-alanine to the terminal positions of a helical azobenzene oligomer produced a *P* helical bias, which increased with oligomer length. Irradiation gave rise to *E* → *Z* isomerization of the terminal azo linkages, which displaced the stereogenic center of L-Ala from the helix backbone and suppressed chiral induction. Theoretical simulations of the CD spectrum of the *P* helical conformation are in qualitative agreement with the experimental spectra.

- Reversible Attachment at Molecular Printboards through Supramolecular Glue
  Ling, X. Y.; Reinhoudt, D. N.; Huskens, J. *Chem. Mater.* **2008**, *20*, 3574-3578.
  Abstract:



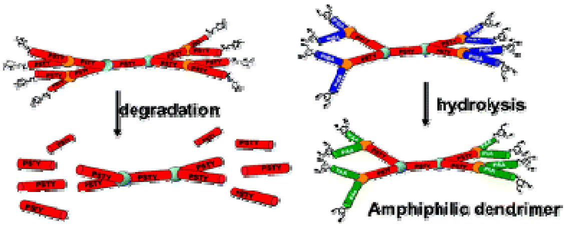
Regenerable surfaces and reversible attachment of nanostructures onto them is an important aim in nanotechnology. Reversible attachment of nanostructures at molecular printboards was illustrated by the adsorption and desorption of β-cyclodextrin (β-CD)-functionalized nanoparticles onto and from stimuli-responsive preadsorbed ferrocenyl-functionalized poly(propylene imine) dendrimers at a β-CD self-assembled monolayer (SAM). Electrochemical oxidation of the ferrocenyl endgroups was employed to induce desorption of nanostructures from the β-CD SAMs. A combined surface plasmon resonance spectroscopy and electrochemistry setup was used to monitor the in situ adsorption and desorption of ferrocenyl dendrimers and β-CD-functionalized Au nanoparticles (CD-Au, *d*~ 2.8 nm) onto and from the molecular printboard. In the case of the larger β-CD-functionalized silica nanoparticles (CD-SiO_2, *d*~ 60 nm), ultrasonication was used to reduce the desorption time. By electrochemical oxidation applied to a specific area of a nanoparticle layer, local desorption of nanoparticles was observed. In the nonoxidized area, nanoparticles remained robustly attached to the surface, whereas nanoparticles on the electrochemically oxidized area were completely removed.

- Surface-Bound Soft Matter Gradients
  Genzer, J.; Bhat, R. R. *Langmuir* **2008***, 24*, 2294 -2317.
  Abstract:



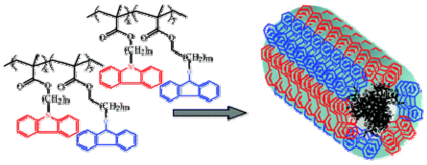
This feature article describes the progress realized over the past half century in the field of surface-bound gradient structures created on or from soft materials (oligomers and/or polymers), or those enabling the study of the behavior of soft materials. By highlighting our work in the field and accounting for the contribution of other groups, we emphasize the exceptional versatility of gradient assemblies in facilitating fast screening of physicochemical phenomena, acting as "recording media" for monitoring a process, and playing a key role in the design and fabrication of surface-bound molecular and macromolecular motors capable of directing a transport phenomenon.

- Self-Assembly of Amphiphilic Polymeric Dendrimers Synthesized with Selective Degradable Linkages
  Urbani, C. N.; Bell, C. A.; Lonsdale, D.; Whittaker, M. R.; Monteiro, M. J. *Macromolecules* **2008**, *41*, 76–86.
  Abstract:



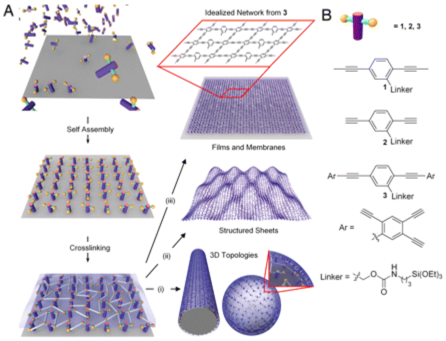
Enhancing the structural complexity and functionality of building blocks allows the design and synthesis of complex macromolecular architectures. In this work, we use a combination of atom transfer radical polymerization to produce polymers with well-defined chain length and telechelic end group functionality and "click" reactions to quantitatively couple these polymer chains together to form functional second- and third-generation dendrimers. Importantly, this methodology provides starting polymers in combination with linkers and end group protecting chemistries to design dendrimers with degradable linkages between the desired generations and incorporates functionality at the polymer chain ends of each generation. We have synthesized second- and third-generation homo- and amphiphilic diblock copolymer dendrimers and specifically designed third-generation dendrimers in pure form such that the peripheral generational layer could be selectively cleaved off from the second-generation. The degradation of the peripheral polymer layer is a useful feature in biomedical delivery devices for slow and controlled release of its payload. These dendrimers also have either "free" or protected hydroxyl groups on the peripheral ends, which are useful for further chemical modification or chemical coupling to important biomolecules. The amphiphilic dendrimers self-assemble in water to form well-defined micelles of near identical size (18.2 nm, PDI = 1.04), each consisting of approximately 19 individual dendrimers. The dense core of the spherical micelles found from sizing measurements supports the postulate that these amphiphilic dendrimers have no mutual interpenetration and thus pack uniformly to form the micelles.

- Synthesis and Self-Assembly of Copolymers with Pendant Electroactive Units
  Barik, S.; Valiyaveettil, S. *Macromolecules* **2008**, *41*, 6376–6386.
  Abstract:



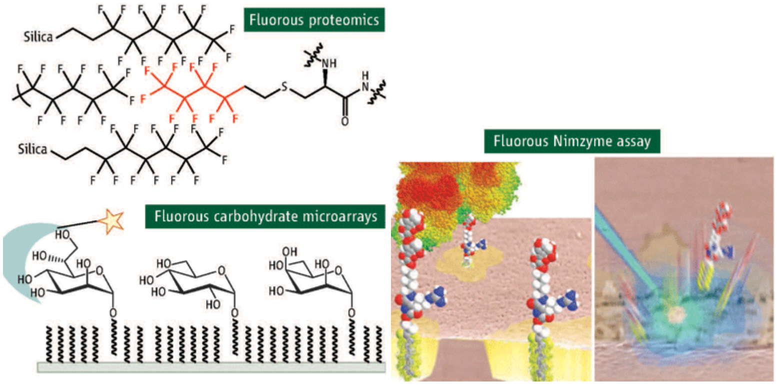
The methacrylic copolymers incorporated with electroactive groups such as thiophene, carbazole, and fluorene moieties on the side chain were synthesized. Our approach consists of incorporating multiple electroactive functional groups onto a polymer backbone that can be used to develop functional materials. All copolymers were characterized, and a systematic structure–property relationship study was established. The structure and morphology of supramolecular self-assembly of copolymers were studied using transmission electron microscopy, wide-angle X-ray diffraction, and atomic force microscopy. Polymers can be patterned using an atomic force microscope, and nanosized lines or dots can be drawn on the polymer films. Polymer nanotubes obtained through self-assembly can be further stabilized by electropolymerization of the side chains.

- Synthesis of linked carbon monolayers: Films, balloons, tubes, and pleated sheets
  Schultz, M. J.; Zhang, X.; Unarunotai, S.; Khang, D.-Y.; Cao, Q.; Wang, C.; Lei, C.; MacLaren, S.; Soares, J. A. N. T.; Petrov, I.; Moore, J. S.; Rogers, J. A. *PNAS* **2008**, *105,* 7353-7358.
  Abstract:



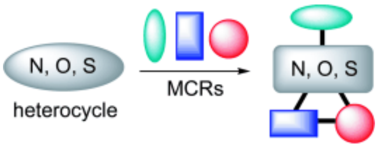
Because of their potential for use in advanced electronic, nanomechanical, and other applications, large two-dimensional, carbon-rich networks have become an important target to the scientific community. Current methods for the synthesis of these materials have many limitations including lack of molecular-level control and poor diversity. Here, we present a method for the synthesis of two-dimensional carbon nanomaterials synthesized by Mo- and Cu-catalyzed cross-linking of alkyne-containing self-assembled monolayers on SiO_2 and Si_3N_4. When deposited and cross-linked on flat surfaces, spheres, cylinders, or textured substrates, monolayers take the form of these templates and retain their structure on template removal. These nanomaterials can also be transferred from surface to surface and suspended over cavities without tearing. This approach to the synthesis of monolayer carbon networks greatly expands the chemistry, morphology, and size of carbon films accessible for analysis and device applications.

- Fluorous Tags Unstick Messy Chemical Biology Problems
  Curran, D. P. *Science* **2008**, *321*, 1645−1646.
  Abstract:



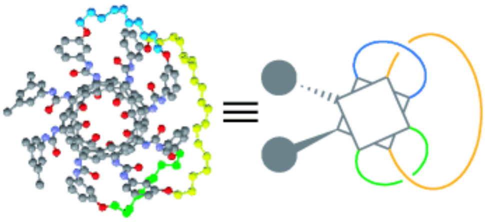
Separation and identification of biological molecules from complex mixtures can be made easier with fluorinated labeling groups and separation media.

- Heterocycles as Key Substrates in Multicomponent Reactions: The Fast Lane towards Molecular Complexity
  Isambert, N.; Lavilla, R. *Chem. Eur. J.* **2008**, *14*, 8444-8454.
  Abstract:



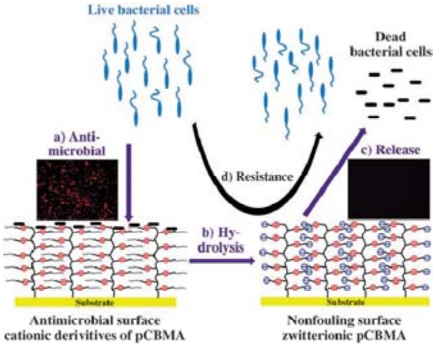
Heterocycles display an intrinsic reactivity which enables rich, versatile and productive transformations. Taking into account their ubiquitous presence in natural products and drugs, the development of new, fast and efficient preparative protocols for these structures remains an urgent task in Organic Synthesis. Multicomponent reactions using heterocyclic chemistry offer new possibilities to exploit this exclusive reactivity. Recent results show relevant examples of such transformations. Several approaches which allow the construction of complex heterocyclic compounds from simple starting materials using this principle have been analyzed.

- Molecules with New Topologies Derived from Hydrogen-Bonded Dimers of Tetraurea Calix[4]arenes
  Bogdan, A.; Bolte, M.; Böhmer, V. *Chem. Eur. J.* **2008**, *14*, 8514-8520.
  Abstract:



Tetraurea calix[4]arenes **2** have been synthesized in which two adjacent aryl urea residues are connected to a loop by an aliphatic chain -O-$(CH_2)_n$-O-. The remaining urea residues have a bulky 3,5-di-*tert*-butylphenyl residue and an ω-alkenyloxyphenyl residue. Since this bulky residue cannot pass through the loop, only one homodimer (**2**·**2**) is formed in apolar solvents, for steric reasons, in which the two alkenyl residues penetrate the two macrocyclic loops. Covalent connection of these alkenyl groups by olefin metathesis followed by hydrogenation creates compounds **3**, which consist of molecules with hitherto unknown topology. Their molecular structure was confirmed by ^{1}H NMR spectroscopy and ESIMS, and for one example by single-crystal X-ray analysis.

- A Switchable Biocompatible Polymer Surface with Self-Sterilizing and Nonfouling Capabilities
  Cheng, G.; Xue, H.; Zhang, Z.; Chen, S.; Jiang, S. *Angew. Chem. Int. Ed.* **2008**, *47*, 8831 –8834.
  Abstract:



Trap, kill, and release: An antimicrobial cationic surface can effectively kill bacterial cells and switch to a nonfouling zwitterionic surface which releases dead microorganisms upon hydrolysis (see picture). This biocompatible nonfouling surface can prevent further attachment of proteins and microorganisms and the formation of a biofilm on the surface.