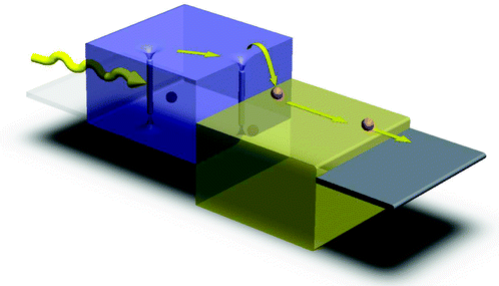
- Strategies for Increasing the Efficiency of Heterojunction Organic Solar Cells: Material Selection and Device Architecture
  Heremans, P.; Cheyns, D.; Rand, B. P. *Acc. Chem. Res.* **2009**, *42*, 1740–1747.
  Abstract:



Thin-film blends or bilayers of donor- and acceptor-type organic semiconductors form the core of heterojunction organic photovoltaic cells. Researchers measure the quality of photovoltaic cells based on their power conversion efficiency, the ratio of the electrical power that can be generated versus the power of incident solar radiation. The efficiency of organic solar cells has increased steadily in the last decade, currently reaching up to 6%. Understanding and combating the various loss mechanisms that occur in processes from optical excitation to charge collection should lead to efficiencies on the order of 10% in the near future.

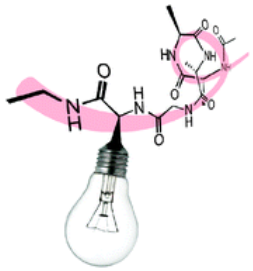
In organic heterojunction solar cells, the generation of photocurrent is a cascade of four steps: generation of excitons (electrically neutral bound electron−hole pairs) by photon absorption, diffusion of excitons to the heterojunction, dissociation of the excitons into free charge carriers, and transport of these carriers to the contacts. In this Account, we review our recent contributions to the understanding of the mechanisms that govern these steps. Starting from archetype donor−acceptor systems of planar small-molecule heterojunctions and solution-processed bulk heterojunctions, we outline our search for alternative materials and device architectures.

We show that non-planar phthalocynanines have appealing absorption characteristics but also have reduced charge carrier transport. As a result, the donor layer needs to be ultrathin, and all layers of the device have to be tuned to account for optical interference effects. Using these optimization techniques, we illustrate cells with 3.1% efficiency for the non-planar chloroboron subphthalocyanine donor. Molecules offering a better compromise between absorption and carrier mobility should allow for further improvements. We also propose a method for increasing the exciton diffusion length by converting singlet excitons into long-lived triplets. By doping a polymer with a phosphorescent molecule, we demonstrate an increase in the exciton diffusion length of a polymer from 4 to 9 nm. If researchers can identify suitable phosphorescent dopants, this method could be employed with other materials.

The carrier transport from the junction to the contacts is markedly different for a bulk heterojunction cell than for planar junction cells. Unlike for bulk heterojunction cells, the open-circuit voltage of planar-junction cells is independent of the contact work functions, as a consequence of the balance of drift and diffusion currents in these systems.

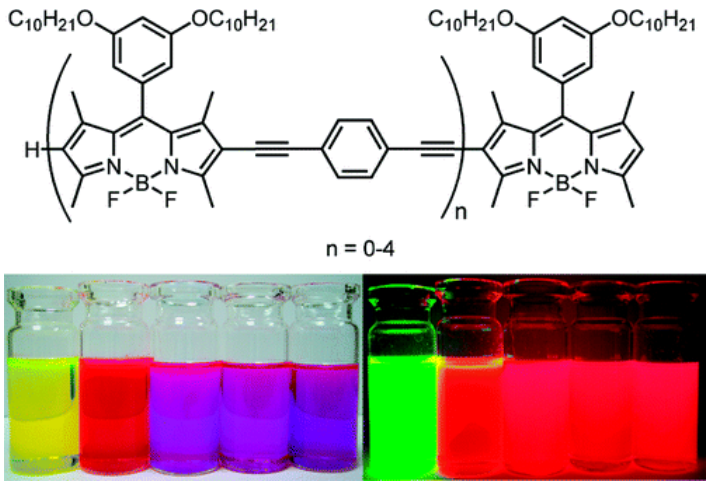
This understanding helps to guide the development of new materials (particularly donor materials) that can further boost the efficiency of single-junction cells to 10%. With multijunction architectures, we expect that efficiencies of 12−16% could be attained, at which point organic photovoltaic cells could become an important renewable energy source.

- Peptide-based fluorescent biosensors
  Pazos, E.; Vázquez, O.; Mascareñas, J. L.; Eugenio, M. Vázquez *Chem. Soc. Rev.* **2009**, *38*, 3348 – 3359.
  Abstract:



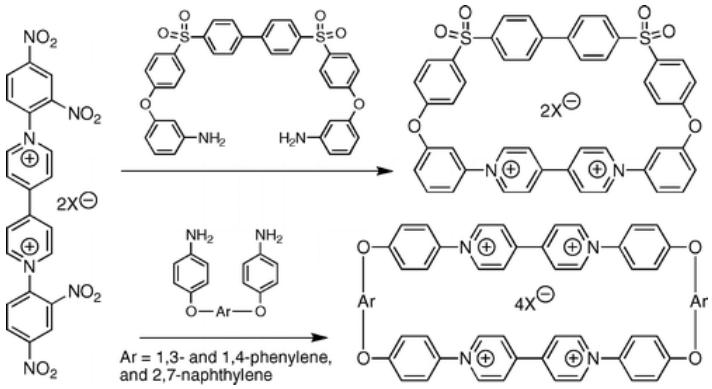
The use of fluorescent techniques in biological research is widespread. Many of the techniques rely on the use of fluorescent genetically-encoded tags (namely GFP and its different variants), but small molecules and nanoparticle-based approaches are being increasingly used. Peptides, owing to their modular nature, synthetic accessibility and biomolecular recognition potential, offer unique possibilities for the development of efficient and selective fluorescent sensors. In this *tutorial review* we present several of the strategies that have been used to develop fluorescent-based peptide sensors and discuss selected applications to biological problems.

- Phenylethynyl-BODIPY Oligomers: Bright Dyes and Fluorescent Building Blocks
  Cakmak, Y.; Akkaya, E. U. *Org. Lett.* **2009**, *11*, 85–88.
  Abstract:



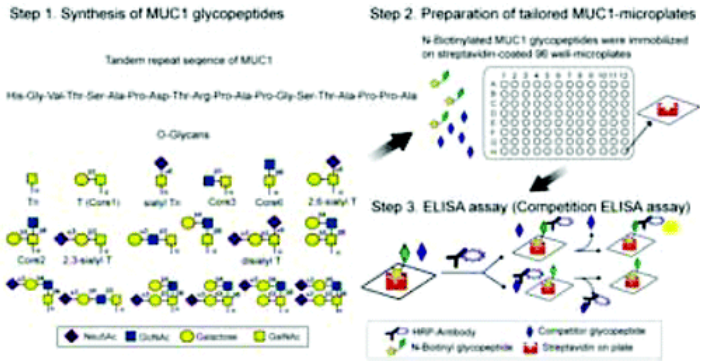
Boradiazaindacene dyes were converted into phenylethynyl-BODIPY oligomers via a cycle of reactions, notably including Sonogashira couplings. As expected, as the number, *n*, of repeating units increases, peak absorption and emission wavelengths are shifted to the red end of the visible spectrum, albeit with smaller increments as *n* increases. Decyl groups help to keep the solubility remarkably high, and in addition to being very bright red-emitting fluorophores, their rigid rod-like structures could allow their use as functional building blocks.

- A General Synthesis of Macrocyclic π-Electron-Acceptor Systems
  Colquhoun, H. M.; Greenland, B. W.; Zhu, Z.; Shaw, J. S.; Cardin, C. J.; Burattini, S.; Elliott, J. M.; Basu, S.; Gasa, T. B.; Stoddart, J. F. *Org. Lett.* **2009**, *11*, 5238–5241.
  Abstract:



Cyclocondensations of aromatic diamines with 1,1′-bis(2,4-dinitrophenyl)-4,4′-bipyridinium salts afford doubly or quadruply charged, macrocyclic, *N*,*N*′-diarylbipyridinium cations. These are tolerant of a wide range of acids, bases, and nucleophiles, although they appear to undergo reversible, one-electron reduction by tertiary amines. Single-crystal X-ray analysis demonstrates the presence of a macrocycle conformation in which the 4,4′-bipyridinium and 4,4′-biphenylenedisulfonyl residues are suitably spaced and aligned for complexation with π-donor arenes, and NMR studies in solution indeed confirm binding to 1,5-bis[hydroxy(ethoxy)ethoxy]naphthalene.

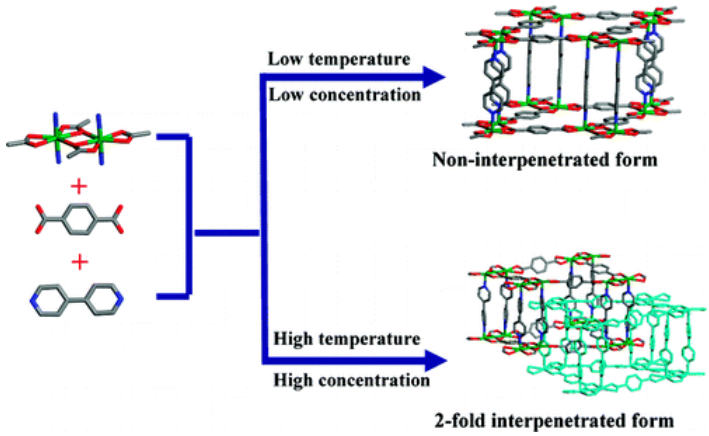
- An Essential Epitope of Anti-MUC1 Monoclonal Antibody KL-6 Revealed by Focused Glycopeptide Library
  Ohyabu, N.; Hinou, H.; Matsushita, T.; Izumi, R.; Shimizu, H.; Kawamoto, K.; Numata, Y.; Togame, H.; Takemoto, H.; Kondo, H.; Nishimura, S. *J. Am. Chem. Soc.* **2009**, *131*, 17102–17109.
  Abstract:



Human serum Krebs von den Lungen-6 (KL-6) antigen, a high-molecular-weight glycoprotein classified as a polymorphic epithelial mucin (MUC1), is a biomarker of diseases such as interstitial pneumonia, lung adenocarcinoma, breast cancer, colorectal adenocarcinoma, and hepatocellular carcinoma. Anti-KL-6 monoclonal antibody (anti-KL-6 MAb) is therefore a potential diagnostic and therapeutic reagent. Although glycosylation at Thr/Ser residues of the tandem-repeating MUC1 peptides appears to determine the disease-associated antigenic structures of KL-6, an essential epitope structure recognized by anti-KL-6 MAb remains unclear. In the present study, a novel compound library of synthetic MUC1 glycopeptides allowed the first rapid and precise evaluation of the specific epitope structure of anti-KL-6 MAb by combined use of a tailored glycopeptides library and common ELISA protocol. We demonstrated that the minimal antigenic structure, an essential epitope, recognized by anti-KL-6 MAb is a heptapeptide sequence Pro-Asp-Thr-Arg-Pro-Ala-Pro (PDTRPAP), in which the Thr residue is modified by Neu5Acα2,3Galβ1,3GalNAcα (2,3-sialyl T antigen, core 1-type O-glycan). Anti-KL-6 MAb did not bind with other tumor-relevant antigens, such as GalNAcα (Tn),

Neu5Acα2,6GalNAcα (STn), and Galβ1,3GalNAcα (T), except for Neu5Acα2,3Galβ1,3(Neu5Acα2,6)GalNAcα (2,3/2,6-disialyl T). However, anti-KL-6 MAb could not differentiate the above minimal antigenic glycopeptide from some core 2-based glycopeptides involving this crucial epitope structure and showed a similar binding affinity toward these compounds, indicating that branching at the O-6 position of GalNAc residue does not influence the interaction of anti-KL-6 MAb with some MUC1 glycoproteins involving an essential epitope. Actually, anti-KL-6 MAb reacts with 2,3/2,6-disialyl T having a 2,3-sialyl T component. This is why anti-KL-6 MAb often reacts with various kinds of tumor-derived MUC1 glycoproteins as well as a clinically important MUC1 glycoprotein biomarker of interstitial pneumonia, namely KL-6, originally discovered as a circulating pulmonary adenocarcinoma-associated antigen. In other words, combined use of anti-KL-6 MAb and some probes that can differentiate the sugars substituted at the O-6 position of the GalNAc residue in MUC1 glycopeptides including the PDTRPAP sequence might be a promising diagnostic protocol for individual disease-specific biomarkers. It was also revealed that glycosylation at neighboring Thr/Ser residues outside the immunodominant PDTRPAP motif strongly influences the interaction between anti-KL-6 MAb and MUC1 glycopeptides involving the identified epitope. Our novel strategy will greatly facilitate the processes for the identification of the tumor-specific and strong epitopes of various known anti-MUC1 MAbs and allow for their practical application in the generation of improved antibody immunotherapeutics, diagnostics, and MUC1-based cancer vaccines.

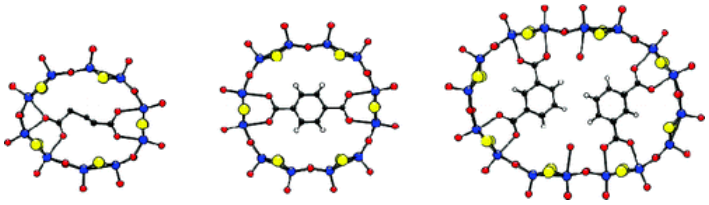
- Temperature and Concentration Control over Interpenetration in a Metal−Organic Material
  Zhang, J.; Wojtas, L.; W. Larsen, R.; Eddaoudi, M.; Zaworotko, M. J. *J. Am. Chem. Soc.* **2009**, *131*, 17040–17041.
  Abstract:



A pillared framework formed from 4,4′-bipyridine (bipy) and sheets of dinuclear Cd2 nodes and 1,4-benzenedicarboxylic acid (bdc) linkers can be prepared in both interpenetrated and noninterpenetrated forms by simply varying the temperature or concentration of the reaction. These results demonstrate that higher temperatures and concentrations favor interpenetration over the corresponding noninterpenetrating structure, an observation that could have broad implications for controlling the synthesis of metal−organic materials.

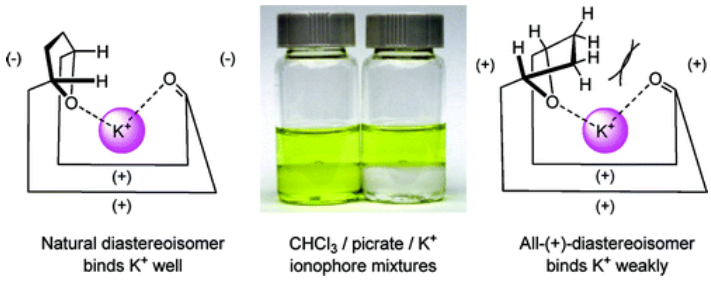
- Molecular Weights of Cyclic and Hollow Clusters Measured by DOSY NMR Spectroscopy
  Floquet, S.; Brun, S.; Lemonnier, J.-F.; Henry, M.; Delsuc, M.-A.; Prigent, Y.; Cadot, E.; Taulelle, F. *J. Am. Chem. Soc.* **2009**, *131*, 17254–17259.

Abstract:



The Stokes−Einstein expression of the diffusion coefficient as a function of the hydrodynamic radius of the diffusing object does not explicitly carry the mass dependency of the object. It is possible to correlate the translational self-diffusion coefficients *D* with the molecular weight *M* for an ensemble of cyclic or hollow clusters ranging from about 200 to 30 000 g·mol^{-1}. From this correlation, the mass of a cluster can be deduced from its diffusion coefficient. Consistency of diffusion as a power law of mass and Stokes−Einstein formulation is completely fulfilled with the selected compounds of this contribution.

- Alternating Pattern of Stereochemistry in the Nonactin Macrocycle Is Required for Antibacterial Activity and Efficient Ion Binding
  Kusche, B. R.; Smith, A. E.; McGuirl, M. A.; Priestley, N. D. *J. Am. Chem. Soc.* **2009**, *131*, 17155–17165.
  Abstract:

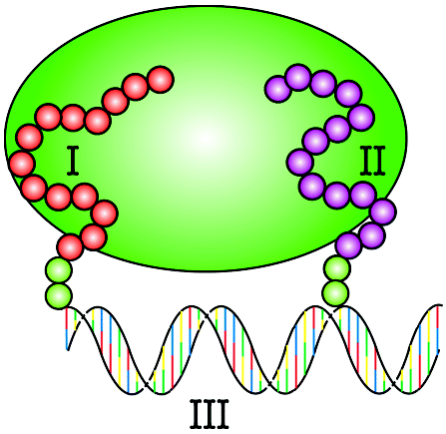


Nonactin is a polyketide antibiotic produced by *Streptomyces griseus* ETH A7796 and is an ionophore that is selective for K^+ ions. It is a cyclic tetraester generated from two monomers of (+)-nonactic acid and two of (−)-nonactic acid, arranged (+)-(−)-(+)-(−) so that nonactin has *S*4 symmetry and is achiral. To understand why achiral nonactin is the naturally generated diastereoisomer, we generated two alternate diastereoisomers of nonactin, one prepared solely from (+)-nonactic acid and one prepared solely from (−)-nonactic acid, referred to here as 'all-(+)-nonactin' and 'all-(−)-nonactin', respectively. Both non-natural diastereoisomers were 500-fold less active against Gram positive organisms than nonactin confirming that the natural stereochemistry is necessary for biological activity. We used isothermal calorimetry to obtain the K_a, Δ*G*, Δ*H*, and Δ*S* of formation for the K^+, Na^+, and NH_4^+ complexes of nonactin and all-(−)-nonactin; the natural diastereoisomer bound K^+ 880-fold better than all-(−)-nonactin. A picrate partitioning assay confirmed that all-(−)-nonactin, unlike nonactin, could not partition K^+ ions into organic solvent. To complement the thermodynamic data we used a simple model system to show that K^+ transport was facilitated by nonactin but not by all-(−)-nonactin. Modeling of the K^+ complexes of nonactin and all-(−)-nonactin suggested that poor steric interactions in the latter complex precluded tight binding to K^+. Overall, the data show that both enantiomers of nonactic acid are needed for the formation of a nonactin diastereoisomer that can act as an ionophore and has antibacterial activity.

- Creating Protein Affinity Reagents by Combining Peptide Ligands on Synthetic DNA Scaffolds

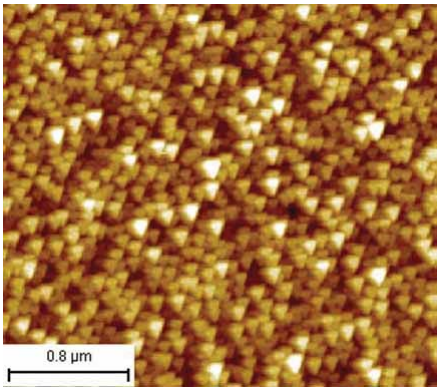
Williams, B. A. R.; Diehnelt, C. W.; Belcher, P.; Greving, M.; Woodbury, N. W.; Johnston, S. A.; Chaput, J. C. *J. Am. Chem. Soc.* **2009**, *131*, 17233–17241.

Abstract:



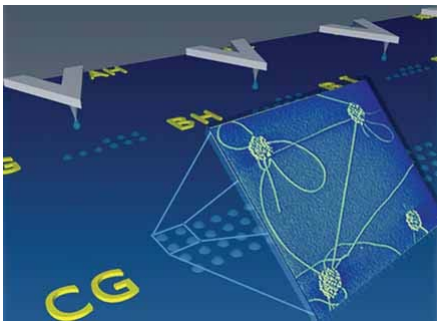
A full understanding of the proteome will require ligands to all of the proteins encoded by genomes. While antibodies represent the principle affinity reagents used to bind proteins, their limitations have created a need for new ligands to large numbers of proteins. Here we propose a general concept to obtain protein affinity reagents that avoids animal immunization and iterative selection steps. Central to this process is the idea that small peptide libraries contain sequences that will bind to independent regions on a protein surface and that these ligands can be combined on synthetic scaffolds to create high affinity bivalent reagents. To demonstrate the feasibility of this approach, an array of 4000 unique 12-mer peptides was screened to identify sequences that bind to nonoverlapping sites on the yeast regulatory protein Gal80. Individual peptide ligands were screened at different distances using a novel DNA linking strategy to identify the optimal peptide pair and peptide pair separation distance required to transform two weaker ligands into a single high affinity protein capture reagent. A synthetic antibody or *synbody* was created with 5 nM affinity to Gal80 that functions in conventional ELISA and pull-down assays. We validated our synthetic antibody approach by creating a second synbody to human transferrin. In both cases, we observed an increase in binding affinity of ~1000-fold ($\Delta\Delta G$ = ~4.1 kcal/mol) between the individual peptides and final bivalent synbody construct.

- Reactive Ion Etching of Gold-Nanoparticle-Modified Pyrolyzed Photoresist Films
  Polsky, R.; Washburn, C. M.; Montano, G.; Liu, H.; Edwards, T. L.; Lopez, D. M.; Harper, J. C.; Brozik, S. M.; Wheeler, D. R. *Small* **2009**, *5*, 2510-2513.
  Abstract:



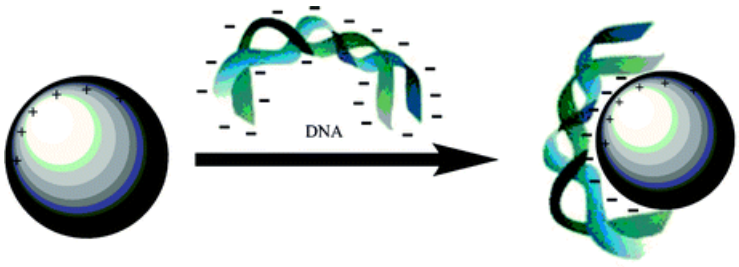
Under similar electrodeposition conditions the unique surface properties of pyrolyzed photoresist films result in smaller gold nanoparticles with a higher density when compared to other common electrode materials. Reactive ion etching of such surfaces results in the formation of unique AuNP-capped pyramidal carbon structures (see image).

- Controllable Patterning and CVD Growth of Isolated Carbon Nanotubes with Direct Parallel Writing of Catalyst Using Dip-Pen Nanolithography
  Kuljanishvili, I.; Dikin, D. A.; Rozhok, S.; Mayle, S.; Chandrasekhar, V. *Small* **2009**, *5*, 2523 – 2527.
  Abstract:



Carbon nanotubes are fabricated using chemical vapor deposition at predetermined locations by patterning catalyst directly on a substrate with nanometer-scale precision using dip-pen nanolithography with multipen cantilevers (see image). The development of new molecular inks for the deposition of the precursor catalyst results in a high yield of isolated carbon nanotubes, ideal for subsequent device fabrication.

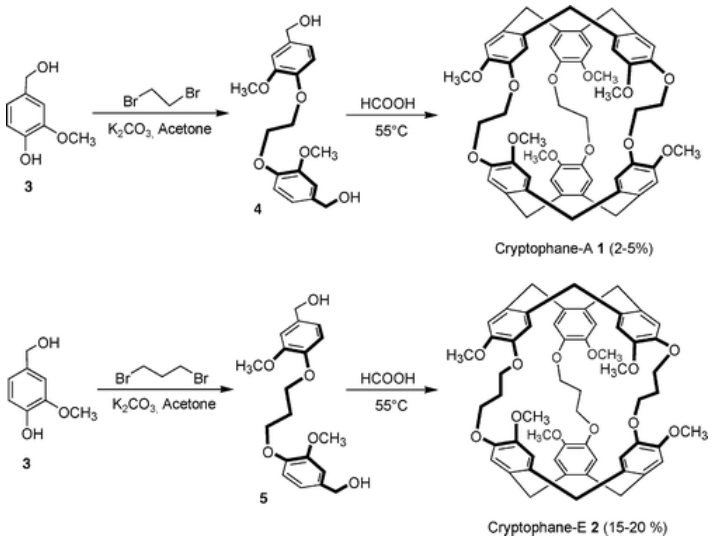
- Dendrimers in Oncology: An Expanding Horizon
  Tekade, R. K.; Kumar, P. V.; Jain, N. K. *Chem. Rev.* **2009***, 109,* 49-87.
  Abstract:



Cancer is a killer disease second only to heart problems. Though there is significant progress in the field of anticancer technology, we are still badly in need of a reliable cure for malignant growths. At present, a variety of drug delivery approaches including polymer microcapsules and microspheres, liposomes, polymer conjugates, and nanoparticles are either FDA-approved or are in clinical development as cancer treatments. The success of novel strategies for cancer therapy relies strongly on the development of reliable delivery devices capable of improving the therapeutic index of biologically active molecules. During the last few decades in particular, medical science has witnessed the exploration of several delivery devices, and along with them a multitalented versatile star named “dendrimers” is now visible on the horizon.
Dendrimers are synthetic macromolecules with a tree-like well-defined branched structure. Their peculiar architecture and flexibility in modifying it in numerous ways has been an active area of

research. Since their introduction the unique characteristics of dendrimers have led to an exponential increase in the number of publications in this innovative field. Recently, progress has been made in the application of biocompatible dendrimers to cancer treatment, including their use as delivery systems for potent anticancer drugs such as cisplatin and doxorubicin. Bifunctional polyamidoamine (PAMAM)-based dendrimers that selectively target cancer cells are described in an issue of *Chemistry and Biology*.

- Cryptophanes and Their Complexes—Present and Future
  Brotin, T.; Dutasta, J.-P. *Chem. Rev.* **2009***, 109,* 88-130.
  Abstract:

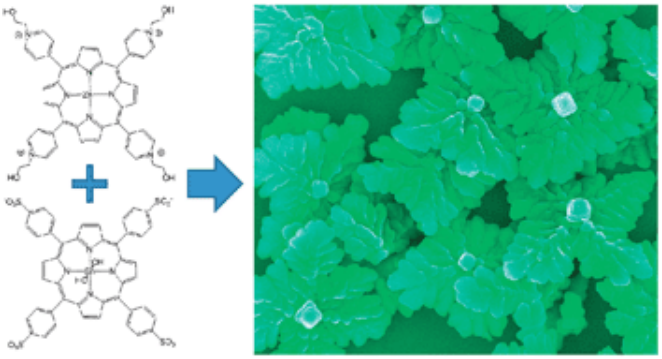


The encapsulation of charged or neutral species in the inner cavity of organic hosts is a fascinating field of research and represents an important challenge for many research laboratories all over the world. The outstanding success of this topic arises mainly from the imagination of the chemists in designing and synthesizing organic hosts with recognition functionality. Since the origin of the concept of host–guest chemistry, a wide variety of synthetic organic compounds have been prepared as molecular receptors, which can form self-organized systems with various degrees of complexity, and have possible applications, including molecular recognition, drug delivery, separation and storage, biosensing, and catalysis (chemical reaction inside the confined space of a molecular nanoreactor). Although, in terms of publications, this field is largely dominated by the supramolecular chemistry of calixarene and cavitand hosts, the synthesis by A. Collet in the early 1980s of original molecules called *cryptophanes* introduced a new source of inspiration for designing molecular cavities. The pioneering work of Collet's group at the Collège de France and after 1988 at the Ecole Normale Supérieure in Lyon concerned the synthesis of cryptophanes and the study of their binding properties with charged or neutral small molecules. Among the most important results published at that time were the complexation of methane by cryptophane-A, the recognition of acetylcholine by cryptophane-O, the chiral discrimination of CHFClBr by enantioenriched cryptophane-C, and the formation of the highly stable Xe@cryptophane-A complex. Reviews on this subject appeared in 1987, 1993, and 1996. The continuing interest in cryptophane hosts has been emphasized again recently by Holman in 2004.

- Self-assembled porphyrin nanostructures

Medforth, C. J.; Wang, Z.; Martin, K. E.; Song, Y.; Jacobsen, J. L.; Shelnutt, J. A. *Chem. Commun.* **2009**, 7261 – 7277.

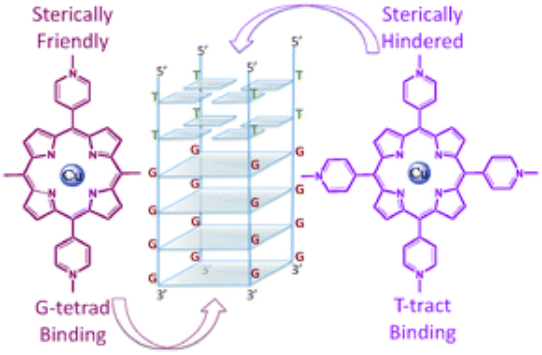
Abstract:



Porphyrins and related tetrapyrroles have been extensively studied because of their importance in biological processes and they are often used in the development of artificial photosynthesis, catalysis, and sensor systems. Challenges in the development of functional nanoscale porphyrin systems are many, including the need to organize the porphyrins (e.g., to facilitate processes such as energy- and electron transfer) and to couple the porphyrin nanostructures to other nanoscale components (e.g., catalytic elements and conductors) to produce multifunctional nanoscale systems. This article summarizes recent advances in the synthesis of discrete self-assembled porphyrin nanostructures with well-defined shapes and sizes. A novel method for growing metal on the porphyrin nanostructures to produce nanocomposites with metal catalysts or interconnects is also described. Current and potential applications of these nanostructures and porphyrin–metal nanocomposites are discussed.

- Steric effects direct the binding of porphyrins to tetramolecular quadruplex DNA
  McGuire, R.; McMillin, Jr. D. R. *Chem. Commun.* **2009**, 7393 – 7395.

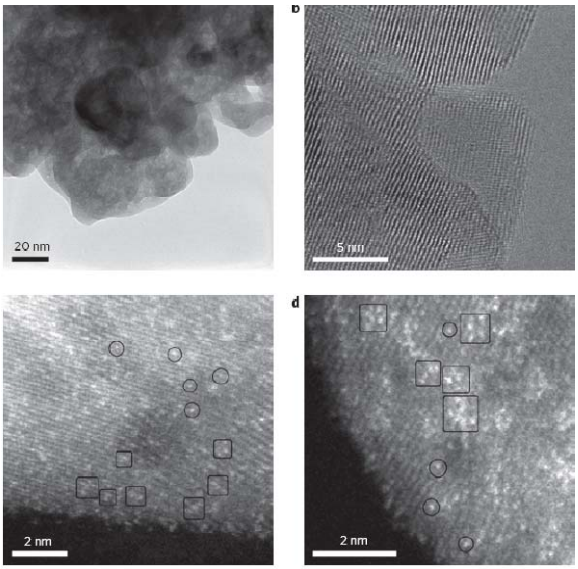
Abstract:



The binding motifs of copper(II) porphyrins with G quadruplex DNA structures vary markedly depending on the steric demands of the ligand and the host structure.

- Identification of active Zr–WOx clusters on a ZrO_2 support for solid acid catalysts
  Zhou, W.; Ross-Medgaarden, E. I.; Knowles, W. V.; Wong, M. S.; Wachs, I. E.; Kiely, C. J. *Nature Chemistry* **2009**, *1*, 722 – 728.

Abstract:

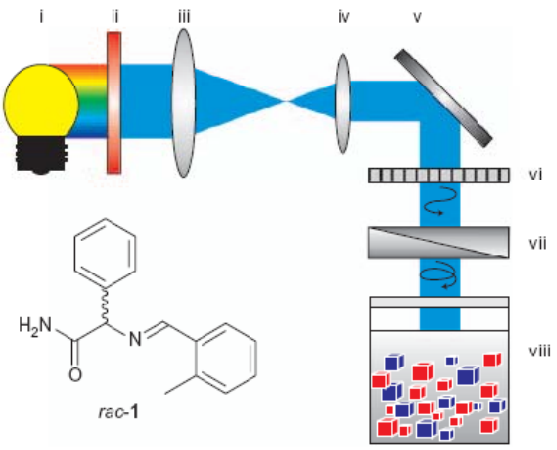


Tungstated zirconia is a robust solid acid catalyst for light alkane (C4–C8) isomerization. Several structural models for catalytically active sites have been proposed, but the topic remains controversial, partly because of the absence of direct structural imaging information on the various supported WOx species. High-angle annular dark-field imaging of WO_3/ZrO_2 catalysts in an aberration-corrected analytical electron microscope allows, for the first time, direct imaging of the various species present. Comparison of the relative distribution of these WOx species in materials showing low and high catalytic activities has allowed the deduction of the likely identity of the catalytic active site—namely, subnanometre Zr–WOx clusters. This information has subsequently been used in the design of new catalysts, in which the activity of a poor catalyst has been increased by two orders of magnitude using a synthesis procedure that deliberately increases the number density of catalytically relevant active species.

- Complete chiral symmetry breaking of an amino acid derivative directed by circularly polarized light

  Noorduin, W. L.; Bode, A. A. C.; van der Meijden, M.; Meekes, H.; van Etteger, A. F.; van Enckevort, W. J. P.; Christianen, P. C. M.; Kaptein, B.; Kellogg, R. M.; Rasing, T.; Vlieg, E. *Nature Chemistry* **2009**, *1*, 729 – 732.

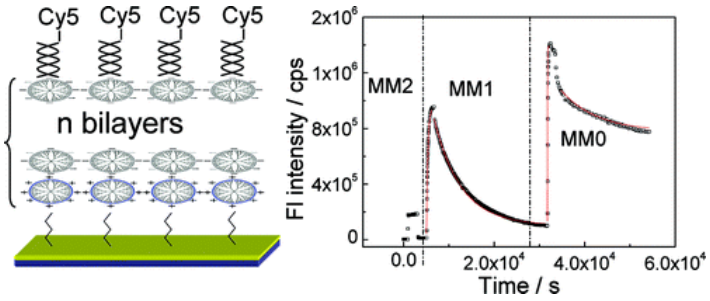
  Abstract:



Circularly polarized light (CPL) emitted from star-forming regions is an attractive candidate as a cause of single chirality in nature. It has remained difficult, however, to translate the relatively small

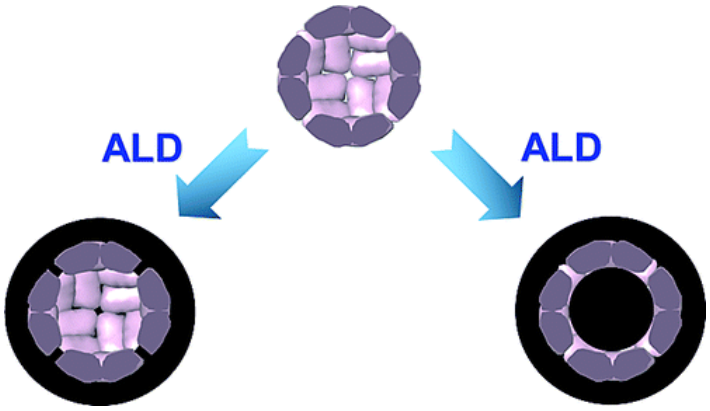
chemical effects observed on irradiation of molecular systems with CPL into high enantiomeric excesses. Here we demonstrate that irradiation of a racemic amino acid derivative with CPL leads to a small amount of chiral induction that can be amplified readily to give an enantiopure solid phase. A racemate composed of equal amounts of left- and right-handed crystals in contact with the irradiated solution is converted completely into crystals of single-handedness through abrasive grinding when racemization is effected in the solution. The rotation sense of the CPL fully determines the handedness of the final solid state. These findings illustrate the potential effectiveness of CPL in the control of molecular asymmetry, which is relevant for the origin of the single chirality inherent to many biological molecules.

- The Detection of DNA Hybridization on Phosphorus Dendrimer Multilayer Films by Surface Plasmon Field Enhanced-Fluorescence Spectroscopy
  Yu, Y.; Feng, C.; Caminade, A.-M.; Majoral, J.-P.; Knoll, W. *Langmuir* **2009**, *25*, 13680–13684.
  Abstract:



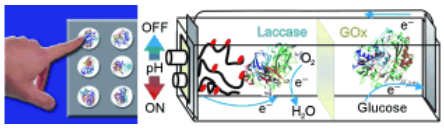
Dendrimer multilayers on gold substrates prepared via layer-by-layer (LbL) assembly technique were characterized and used as substrates forDNAimmobilization/hybridization. The multilayers, built using alternately polycationic and polyanionic phosphorus dendrimers of generation 4, were studied by surface plasmon resonance (SPR) spectroscopy. By varying the concentration of NaCl, the optimized optical thickness of a single dendrimer layer (about 4.5 nm) was achieved. Using the multilayers as the substrate, a high loading ofDNAprobes was obtained through covalent coupling of probe DNA on dendrimer multilayer film. The following hybridization of Cy5-dye labeled complementary target DNAwith immobilized probeDNAwas detected by surface plasmon field-enhanced fluorescence spectroscopy (SPFS).
The limit of detection of target DNA upon hybridization reached 50 pM and 30 pM on 1 bilayer and 4 bilayers, respectively. The phosphorus dendrimer multilayer films display high stability during repeated regeneration and hybridization cycles. The sensitive platforms based on dendrimer multilayers deposited in the presence of NaCl make them attractive candidates for application in DNA sensing.

- Titania Nanostructures Fabricated by Atomic Layer Deposition Using Spherical Protein Cages
  Kim, H.; Pippel, E.; Geosele, U.; Knez, M. *Langmuir* **2009**, *25*, 13284–13289.
  Abstract:



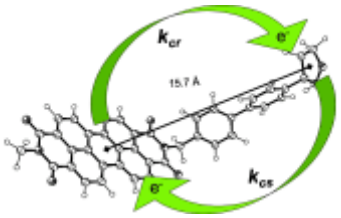
An emerging nanofabrication technology is to synthesize nanoscale inorganic materials with narrow size distribution using biological systems, which are size-constrained, fairly robust, and easily removable. Apoferritin, a spherical and hollow protein complex, was subjected to atomic layer deposition of TiO_2. The growth of TiO_2 on the protein surface was investigated as a function of the precursor exposure and purge length. Thermal pretreatment and osmotic dehydration lead to controllable deposition both on the outer surface and within the inner cavity of apoferritin. Depending on the experimental conditions, either hollow spherical nanoparticles or core-shell nanoparticles comprising TiO_2 were identified.

- Biofuel Cells Controlled by Logically Processed Biochemical Signals: Towards Physiologically Regulated Bioelectronic Devices
  Katz, E.; Pita, M. *Chem. Eur. J.* **2009**, *15*, 12554-12564.
  Abstract:



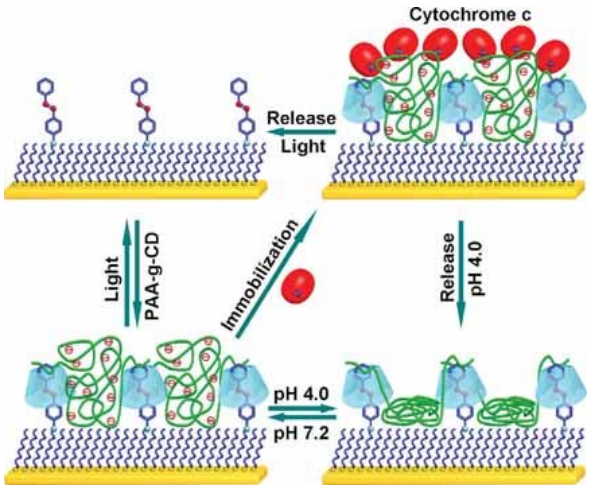
Biofuel cells with a switchable power release controlled by biochemical signals, which can be logically processed by biomolecular computing systems, have been designed. The switchable properties of the biofuel cells were based on the polymer-brush-modified electrodes with the activity dependent on the solution pH value. The pH changes generated in situ by biocatalytic reactions allowed the reversible activation-inactivation of the bioelectrocatalytic interfaces thus affecting the activity of the entire biofuel cells. Boolean logic operations performed by either enzyme- or immune-based systems were functionally integrated with the switchable biocatalytic process allowing logic control over them. Scaling up the complexity of the biocomputing systems to complex multi-component logic networks with a built-in "program" resulted in the control of the bioelectronic systems by multi-signal patterns of biochemical inputs. Future implantable biofuel cells producing electrical power on-demand depending on physiological conditions are feasible, as the result of the present research.

- Light-Driven Charge Separation in Isoxazolidine-Perylene Bisimide Dyads
  Langhals, H.; Obermeier, A.; Floredo, Y.; Zanelli, A.; Flamigni, L. *Chem. Eur. J.* **2009**, *15*, 12733-12744.
  Abstract:



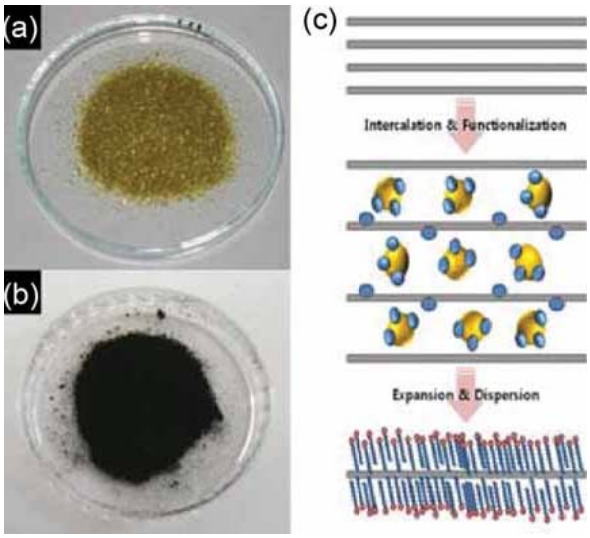
A series of arrays for light-driven charge separation is presented, in which perylene tetracarboxylic bisimide is the light-absorbing chromophore and electron acceptor, whereas isoxazolidines are colourless electron donors, the electron-releasing properties of which are increased with respect to the amino group by means of the α-effect. Charge separation (CS) in toluene over a distance ranging from ≈10 to ≈16 Å, with efficiencies of ≈ 95 to ≈ 50 % and CS lifetimes from 300 ps to 15 ns, are demonstrated. In dichloromethane the charge recombination reaction is faster than charge separation, preventing accumulation of the CS state. The effects of solvent polarity and molecular structure are discussed in the frame of current theories.

- Fabrication of Reactivated Biointerface for Dual-Controlled Reversible Immobilization of Cytochrome c
  Wan, P.; Wang, Y.; Jiang, Y.; Xu, H.; Zhang, X. *Adv. Mater.* **2009**, 4362-4365.
  Abstract:



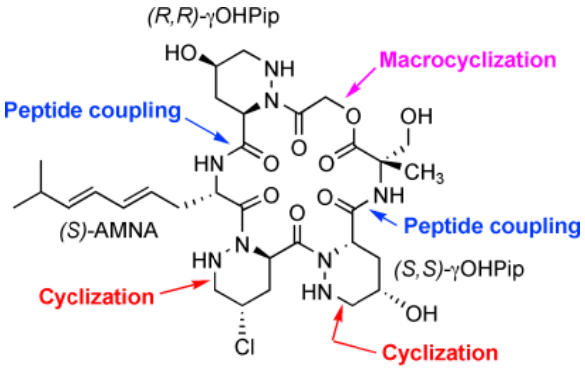
A light or pH dual-responsive reactivated biointerface is fabricated using of photocontrolled reversible inclusion and exclusion reactions between photoresponsive azobenzene-containing self-assembled monolayer and pH-responsive poly(acrylic acid) polymer grafted with cyclodextrins. The dual-controlled reactivated biointerface can be employed for reversible immobilization of redox protein-Cytochrome c, triggered by dual external stimuli-light and pH.

- One-Step Exfoliation Synthesis of Easily Soluble Graphite and Transparent Conducting Graphene Sheets
  Lee, J. H.; Shin, D. W.; Makotchenko, V. G.; Nazarov, A. S.; Fedorov, V. E.; Kim, Y. H.; Choi, J.-Y.; Kim, J. M.; Yoo, J.-B. *Adv. Mater.* **2009,** 4383-4387.
  Abstract:



Easily soluble expanded graphite (see figure) is synthesized in a one-step exfoliation process that can be used for the lowcost mass production of graphene for various applications because of the simplicity and speed of the process. The graphene obtained is sufficiently expanded to be dispersed in aqueous solutions with an ordinary surfactant and in organic solvents.

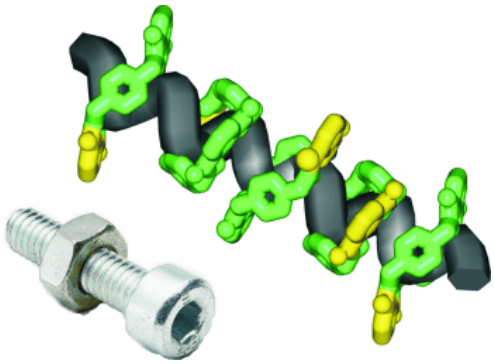
- Total Synthesis of Piperazimycin A: A Cytotoxic Cyclic Hexadepsipeptide
  Li, W.; Gan, J.; Ma, D. *Angew. Chem. Int. Ed*. **2009**, *48*, 8891 –8895.
  Abstract:



1

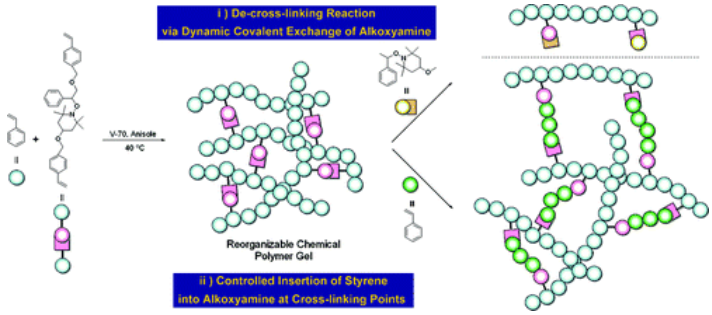
Pied piper: The first total synthesis of the title compound **1**, a potent cytotoxic natural product has been achieved. The key elements include an efficient synthesis of the difficult-to-install (*R*,*S*)-γClPip/(*S*,*S*)-γOHPip dipeptide fragment as well as macrocyclization by an S_N2 reaction of an *N*-2-chloroacetyl moiety with a carboxylate anion.

- A Rigid Helical Peptide Axle for a [2]Rotaxane Molecular Machine
  Moretto, A.; Menegazzo, I.; Crisma, M.; Shotton, E. J.; Nowell, H.; Mammi, S.; Toniolo, C. *Angew. Chem. Int. Ed.* **2009**, *48*, 8986 –8989.
  Abstract:



Spinning around? A series of peptido[2]rotaxanes have been designed which contain a rigid helix as a significant part of their axle. One such rotaxane has been used to construct a reversible molecular device, in which, by virtue of the size of the inner cavity of the wheel relative to the outer diameter of the peptide helix, a rotation of the wheel might occur concomitantly with its translation along the axle (see picture).

- Reorganizable Chemical Polymer Gels Based on Dynamic Covalent Exchange and Controlled Monomer Insertion
  Amamoto, Y.; Kikuchi, M.; Masunaga, H.; Sasaki, S.; Otsuka, H.; Takahara, A. *Macromolecules* **2009**, *42*, 8733–8738.
  Abstract:

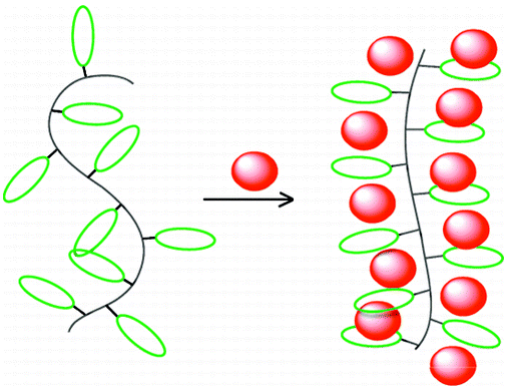


Covalently networked polymer gels were developed with two notable functionalities: de-cross-linking by dynamic covalent exchange based on a radical crossover reaction and insertion of a monomer into the cross-linkers. The network polymer gels were synthesized by free-radical copolymerization of styrene and a bifunctional monomer with an alkoxyamine linker that has two capabilities to exchange with other alkoxyamine derivatives in the radical process and to polymerize styrene in a controlled manner. Three types of network polymers with different cross-linking densities were obtained by changing the ratio of the bifunctional monomer to styrene. The de-cross-linking reaction was carried out by heating the network polymers with excessive alkoxyamine compound in anisole, and it was made clear that the de-cross-linking behavior strongly depended on the cross-linking densities. The insertion of styrene into the alkoxyamine units at the cross-linking points was also performed by heating the network polymers swollen with styrene and anisole, and it was revealed that the mesh sizes grew larger by the insertion of styrene into their skeleton and that the cross-linking density decreased as the reaction proceeded. The variation of the network structures in these reactions was successfully evaluated by small-angle X-ray scattering and dynamic viscoelasticity measurements.

- Ion-Induced Stretching of Low Generation Dendronized Polymers with Crown Ether Branching Units

Ossenbach, A.; Rüegger, H.; Zhang, A.; Fischer, K.; Schlüter, A. D.; Schmidt, M. *Macromolecules* **2009**, *42*, 8781–8793.

Abstract:



Synthesis of the first (G1) and second generation (G2) dendronized macromonomers **MG1** and **MG2** with the dibenzo-24-crown-8 moiety as branching unit is reported. The corresponding dendronized polymers, the polymethacrylates **PG1** and **PG2**, were synthesized by free radical polymerization using AIBN as initiator at 60−80 °C. Static and dynamic light scattering revealed a significant chain expansion upon complexation of these polymers' crown ether side chains with K^+ ions. It is concluded that electrostatic repulsion does not significantly contribute to the chain expansion because of excessive counterion binding even well below the Manning limit, as evidenced by ^{19}F NMR and $^{1}H–^{19}F$ NOE experiments. Rather, the conformational change of the crown ether moieties upon K^+-ion binding plus the short-range interaction between ion pairs formed along the chain cause the observed significant increase in chain stiffness in terms of the Kuhn statistical segment length, l_k, from l_k = 8 to 19 nm and from l_k = 19 to 45 nm for the **PG1** and **PG2** polymers, respectively. At full KPF_6 loading, the effect is as large as to triple the molar mass of the side chains, as evidenced by the similar values of the Kuhn statistical segment length of the fully complexed **PG1** as compared with the noncomplexed **PG2** sample. It is thus demonstrated that steric repulsion induced by host–guest interactions is well suitable to control the conformation of polymers with densely grafted side chains.