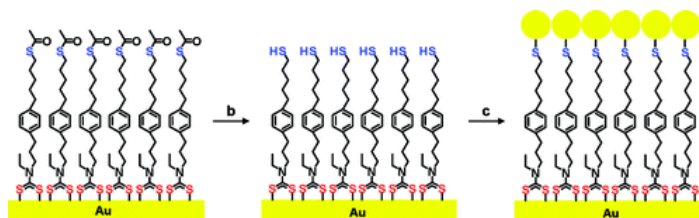


- Fabrication of Asymmetric Molecular Junctions by the Oriented Assembly of Dithiocarbamate Rectifiers

1

Gao, D.; Scholz, F.; Nothofer, H.-G.; Ford, W. E.; Scherf, U.; Wessels, J. M.; Yasuda, A.; von Wrochem, F. *J. Am. Chem. Soc.* **2011**, *133*, 5921–5930.

Abstract:

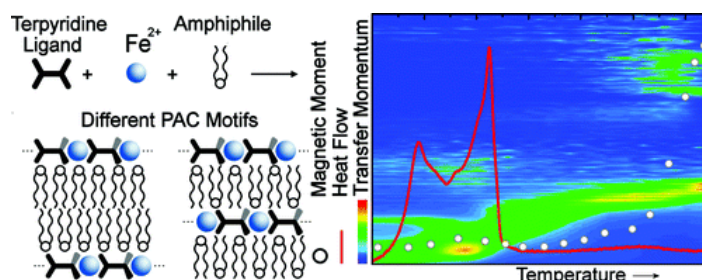


The oriented assembly of molecules on metals is a requirement for rectification in planar metal–molecule–metal junctions. Here, we demonstrate how the difference in adsorption kinetics between dithiocarbamate and thioacetate anchor groups can be utilized to form oriented assemblies of asymmetric molecules that are bound to Au through the dithiocarbamate moiety. The free thioacetate group is then used as a ligand to bind Au nanoparticles and to form the desired metal–molecule–metal junction. Besides allowing an asymmetric coupling to the electrodes, the molecules exhibit an asymmetric molecular backbone where the length of the alkyl chains separating the electrodes from a central, *para*-substituted phenyl ring differs by two methylene units. Throughout the junction fabrication, the layers were characterized by photoelectron spectroscopy, infrared spectroscopy, and scanning tunneling microscopy. Large area junctions using a conducting polymer interlayer between a mercury-drop electrode and the self-assembled monolayer prove the relationship between electrical data and molecular structure.

- Tuning the Structure and the Magnetic Properties of Metallo-supramolecular Polyelectrolyte–Amphiphile Complexes

Schwarz, G.; Bodenthin, Y.; Tomkowicz, Z.; Haase, W.; Geue, T.; Kohlbrecher, J.; Pietsch, U.; Kurth, D. G. *J. Am. Chem. Soc.* **2011**, *133*, 547–558.

Abstract:

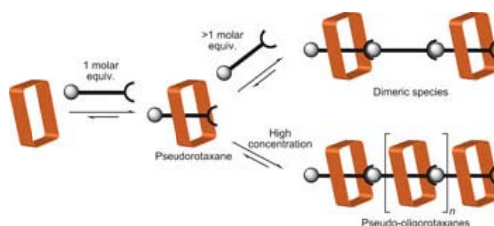


Self-assembly of Fe^{2+} ions and the rigid ditopic ligand 1,4-bis(2,2':6',2''-terpyridin-4'-yl)benzene results in metallo-supramolecular coordination polyelectrolytes (MEPE). Sequential self-assembly of MEPE and dialkyl phosphoric acid esters of varying chain length via electrostatic interactions leads to the corresponding polyelectrolyte–amphiphile complexes (PAC), which have liquid–crystalline properties. The PACs have a stratified architecture where the MEPE is embedded in between the amphiphile layers. Upon heating above room temperature, the PACs show either a reversible or an irreversible spin-crossover (SCO) in a temperature range from 360 to 460 K depending on the architecture of the amphiphilic matrix. As the number of amphiphiles per metal ion is increased in the sequence 1:2, 1:4, and 1:6, the temperature of the SCO is shifted to higher values whereas the amphiphile chain length does not have a significant impact on the SCO temperature. In summary, we describe in this article

how the structure and the magnetic response function of PACs can be tailored through the design of the ligand and the composition. To investigate the structure and the magnetic behavior, we use X-ray scattering, X-ray absorption spectroscopy, differential scanning calorimetry, faraday-balance, and superconducting quantum interference measurements in combination with molecular modeling.

- A ‘Texas-sized’ molecular box that forms an anion-induced supramolecular necklace
Gong, H.-Y.; Rambo, B. M.; Karnas, E.; Lynch, V. M.; Sessler, J. L. *Nature Chem.* **2010**, *2*, 406-409.

Abstract:



The ‘blue box’ (cyclobis(paraquat-*p*-phenylene) or CBPQT⁴⁺), developed by Stoddart and colleagues, forms effective charge transfer complexes with a variety of electron-rich species and has been used to support the formation of a wide range of interlocked structures. However, little effort seems to have been devoted to generalizing the blue box concept. We describe a new flexible tetracationic macrocycle—a ‘Texas-sized’ molecular box. This positively charged receptor is capable of binding the mono-terephthalate anion, forming pseudorotaxanes. These pseudorotaxanes self-assemble into short supramolecular pseudo-oligorotaxanes in solution and more extended pseudo-polyrotaxanes in the solid state. The supramolecular oligomers formed in solution are environmentally responsive; they undergo deaggregation as the overall concentration of the cationic and anionic constituents is reduced, the temperature is increased, or the protonation state of the threading mono-terephthalate anion is changed.

- Ion-triggered spring-like motion of a double helicate accompanied by anisotropic twisting
Miwa, K.; Furusho, Y.; Yashima, E. *Nature Chem.*, **2010**, *2*, 444-449.

Abstract:



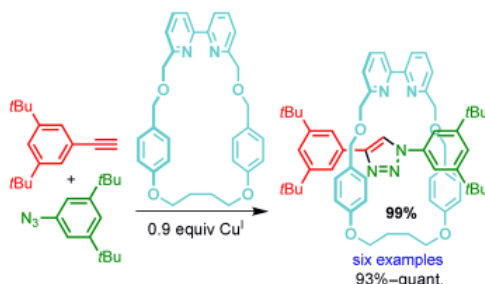
Molecules that extend and contract under external stimuli are used to build molecular machines with nanomechanical functions. But although common in biological systems, such extension and contraction motions with helical molecules have rarely been accompanied by unidirectional twisting in synthetic systems. Here we show that sodium ions can trigger the reversible anisotropic twisting of an enantiomeric double-stranded helicate, without racemization. An optically active helicate consisting of two tetraphenol strands bridged by two spiroborate groups sandwiches a sodium ion. On removal of the central sodium—through addition of a cryptand [2.2.1] in solution—the double helicate extends. Crystallographic and nuclear magnetic resonance studies reveal that the extended helicate is over twice as long as the initial molecule, and is twisted in the right-handed direction. Circular dichroism analysis suggests that the twisting doesn't affect the helicate's handedness. This

anisotropic extension–contraction process is reversibly triggered by the successive addition and removal of sodium ions in solution.

- Macrocycle Size Matters: “Small” Functionalized Rotaxanes in Excellent Yield Using the CuAAC Active Template Approach

Lahlali, H.; Jobe, K.; Watkinson, M.; Goldup, S. M. *Angew. Chem. Int. Ed.* **2011**, *50*, 4151–4155.

Abstract:

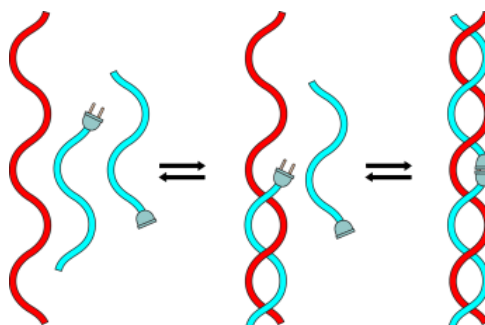


By shrinking the macrocycle in the CuAAC active template reaction not only is it demonstrated to be possible to use smaller macrocycles, but, surprisingly, that smaller macrocycles lead to higher yields of rotaxane product (see scheme). The synthesis of “small” functionalized [2]rotaxanes showcases this as a method for the production of materials with potential applications in molecular electronics, drug delivery, sensing, and enantioselective catalysis.

- Dynamic and Programmable DNA-Templated Boronic Ester Formation

Martin, A. R.; Barvik, I.; Luvino, D.; Smietana, M.; Vasseur, J.-J. *Angew. Chem. Int. Ed.* **2011**, *50*, 4193–4196.

Abstract:

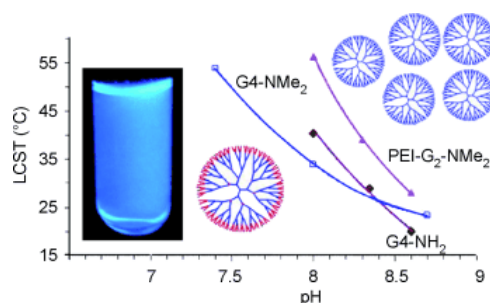


Plug and play: A helix with a boronate ester linkage was constructed by DNA- or RNA-templated assembly through the plugging together of appropriately designed half-sequences, one with a boronic acid at its 5' end, the other with a ribonucleotide at its 3' end. The two hybridization steps in the three-component assembly (see picture) could be controlled reversibly by external stimuli, including an acid or base, cyanide ions, or fructose.

- Degradable Dual pH- and Temperature-Responsive Photoluminescent Dendrimers

Shen, Y.; Ma, Y.; Zhang, B.; Zhou, Z.; Sun, Q.; Jin, E.; Sui, M.; Tang, J.; Wang, J.; Fan, M. *Chem. Eur. J.* **2011**, *17*, 5319–5326.

Abstract:

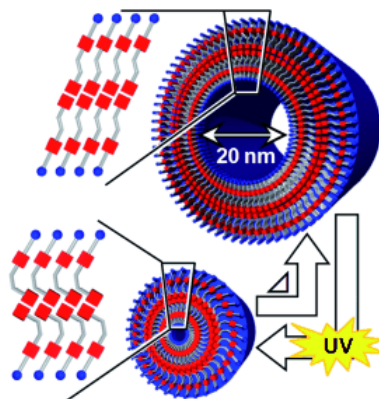


Poly(β -aminoester) dendrimers have been prepared. These systems represent the first degradable dual pH- and temperature-responsive dendrimers displaying photoluminescence. The pH/temperature sensitivities are interrelated; the lower critical solution temperature of the dendrimer decreases as the pH of the solution is increased. The sensitivities are mainly due to phase changes of the surface groups with changes in pH or temperature. These dual-responsive dendrimers are very useful in drug delivery. They may be loaded with a hydrophobic drug at low temperature without using organic solvents. The loaded drug is released very slowly and steadily at 37 °C and physiological pH, but can be quickly released at acidic pH, for example the lysosomal pH (pH 4–5), for intracellular drug release. These dendrimers also display strong photoluminescence, which can be exploited for monitoring drug loading and release. Thus, poly(β -aminoester) dendrimers constitute ideal drug carriers since their thermal sensitivity allows the loading of drugs without using organic solvents, their pH sensitivity permits fast intracellular drug release, and their photoluminescence provides a means of monitoring drug loading and release.

- Photoresponsive Soft Nanotubes for Controlled Guest Release

Kameta, N.; Tanaka, A.; Akiyama, H.; Minamikawa, H.; Masuda, M.; Shimizu, T. *Chem. Eur. J.* **2011**, *17*, 5251-5255.

Abstract:

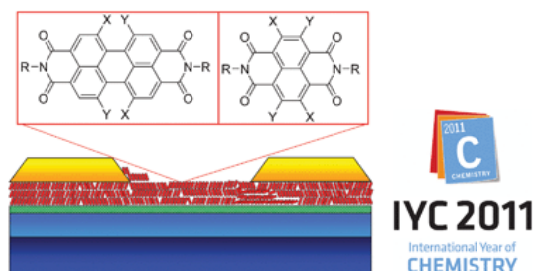


Light, transformation, release! Self-assembly of a simple amphiphile with an azobenzene unit produced an organic nanotube with 20 nm inner diameter. The *trans*-to-*cis* photoisomerization of the azobenzene unit within the solid bilayer membranes of the nanotube induced the transformation to cylindrical nanofibers (see graphic). This way, the nanotube was able to precisely release encapsulated guest molecules as a response to photostimulus.

- Naphthalene and perylene diimides for organic transistors

Würthner, F.; Stolte, M. *Chem. Commun.* **2011**, *47*, 5109-5115.

Abstract:

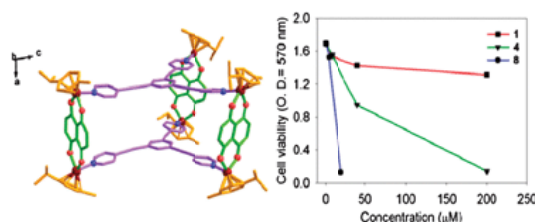


This highlight article gives an overview on the development of highly promising ambient stable n-channel organic thin film transistors (OTFTs) based on naphthalene and perylene tetracarboxylic diimides during the last decade.

- Hexanuclear self-assembled arene-ruthenium nano-prismatic cages: potential anticancer agents

Vajpayee, V.; Yang, Y. J.; Kang, S. C.; Kim, H.; Kim, I. S.; Wang, M.; Stang, P. J.; Chi, K.-W. *Chem. Commun.* **2011**, 47, 5184-5186.

Abstract:

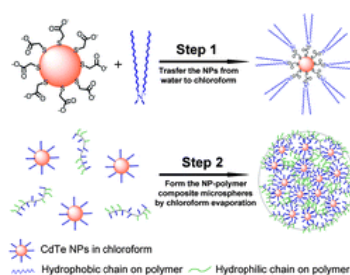


Two novel molecular prismatic cages were prepared *via* the self-assembly of a tripodal donor with metallic acceptors and their antitumor activity was screened against various cancer cell lines. The cytotoxicity of nano cage 8 was found to be considerably stronger than that of cisplatin.

- Versatile fabrication of water-dispersible nanoparticle–amphiphilic copolymer composite microspheres with specific functionalities

Ning, Y.; Zhang, H.; Han, J.; Yang, C.; Liu, Y.; Zhou, D.; Yang, B. *J. Mater. Chem.*, **2011**, 21, 6837-6843.

Abstract:

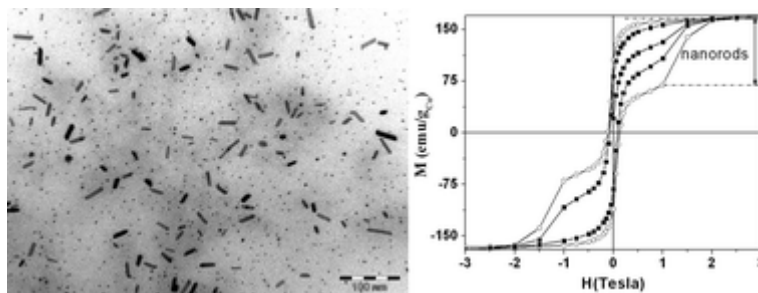


In this paper, we demonstrated a versatile approach for fabricating water-dispersible nanoparticle (NP)–polymer composite microspheres from amphiphilic poly(ethylene glycol) diglycidyl-grafted poly(maleic anhydride-*alt*-octadecene) (PMAO-*g*-PEG) and various NPs with specific functionalities. Depending on the surface polarity of the NPs, the microspheres were fabricated either *via* two step phase transfers for water soluble NPs or one step phase transfer for oil-soluble ones. For example, aqueous luminescent CdTe NPs were first transferred to chloroform by dimethyldioctadecylammonium bromide modification, and subsequently transferred back to water using PMAO-*g*-PEG, thus producing luminescent microspheres. Due to the protection of the polymer,

the luminescence stability of the NPs under acidic conditions was significantly improved, permitting the detection of Ag^+ and Cu^{2+} over a broader pH range.

- *In situ* synthesis of cobalt nanoparticles in functionalized liquid crystalline polymers
Zadoina, L.; Soulantica, K.; Ferrere, S.; Lonetti, B.; Respaud, M.; Mingotaud, A.-F.; Falqui, A.; Genovese, A.; Chaudret, B.; Mauzac, M. *J. Mater. Chem.*, **2011**, *21*, 6988-6994.

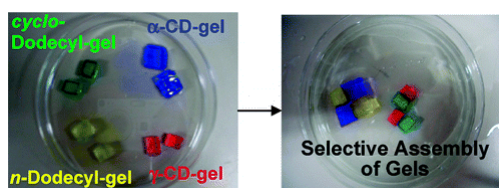
Abstract:



Magnetic hybrid liquid crystal composites have been obtained by thermal decomposition of a cobalt coordination precursor in the presence of a liquid crystal polymer and functional molecules (acid or amine) interacting with the precursor. The final materials contain anisotropic and/or spherical nanoparticles depending on the reaction conditions. They are all mesomorphous and ferromagnetic at ambient temperature. The role of the macromolecular chains as stabilizers of the nanoparticles has been examined. Apart from stabilizing, the polymer chains also prevent the easy access of the functional molecules to the surface of the nanoparticles, necessary to obtain anisotropic objects. Last but not least, the ferromagnetic behavior of the nanoobjects is shown to be enhanced by the presence of the liquid crystal phase: the nano-objects easily align by application of a 3 T magnetic field.

- Self-Assembly of Gels through Molecular Recognition of Cyclodextrins: Shape Selectivity for Linear and Cyclic Guest Molecules
Yamaguchi, H.; Kobayashi, R.; Takashima, Y.; Hashidzume, A.; Harada, A. *Macromolecules* **2011**, *44*, 2395–2399.

Abstract:

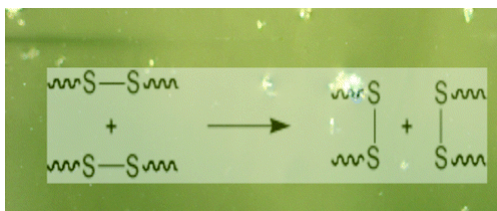


Herein we demonstrated that molecular recognition of CDs for linear and cyclic guest moieties attached to the gels could lead to the specific assembly of gels, which are on the millimeter/centimeter scale. α -CD-gel bound a gel containing linear alkyl groups to give an association, although α -CD-gel did not bind a cyclic alkyl-gel at all. In contrast, β -CD- or γ -CD-gel bound the cyclic alkyl-gel strongly, although it did not bind the linear alkyl-gel. This is the first example to visualize specific molecular recognition of CDs for linear and cyclic alkyl guests on a macroscopic scale. The assembly of host-gels with guest-gels was found to be reversible. The mechanical strength of the assembled gel could be regulated by the mole content of guest moiety in the guest gels.

- Self-Healing Materials Based on Disulfide Links

Canadell, J.; Goossens, H.; Klumperman, B. *Macromolecules* **2011**, *44*, 2536–2541.

Abstract:

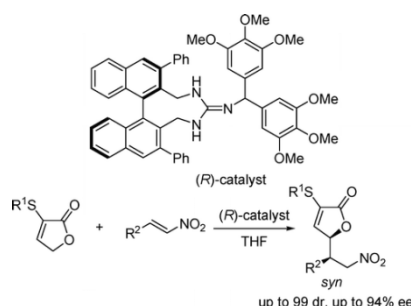


Autonomous healing of damage is a common phenomenon in living organisms but is hardly ever encountered in synthetic materials. Disulfide chemistry is used to introduce a self-healing ability in a covalently cross-linked rubber. Autonomous healing of a cut takes place at moderate temperatures and leads to full recovery of mechanical properties. This result is achieved by introducing disulfide groups in the network that are able to exchange, leading to renewal of cross-links across the damaged surfaces. The healing process can be repeated many times. The combination of their unique self-healing properties and applicability for a large variety of polymers makes this approach ideal for coatings.

- Enantioselective Direct Vinylogous Michael Addition of Functionalized Furanones to Nitroalkenes Catalyzed by an Axially Chiral Guanidine Base

Terada, M.; Ando, K. *Org. Lett.* **2011**, *13*, 2026–2029.

Abstract:

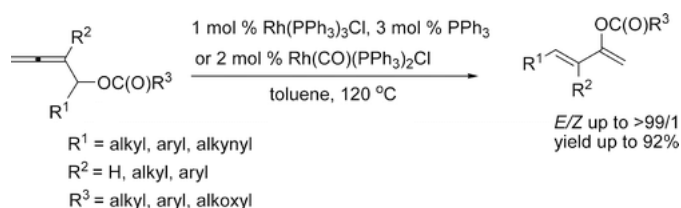


The highly *syn*-diastereo- and enantioselective direct vinylogous Michael addition of α -thio substituted furanones with conjugate nitroalkenes was demonstrated using an axially chiral guanidine base catalyst. The method provides facile access to enantioenriched α,γ -functionalized butenolides that can be further manipulated, thereby rendering them useful synthetic intermediates.

- Highly Stereoselective Facile Synthesis of 2-Acetoxy-1,3(*E*)-alkadienes via a Rh(I)-Catalyzed Isomerization of 2,3-Allenyl Carboxylates

Zhang, X.; Fu, C.; Ma, S. *Org. Lett.* **2011**, *13*, 1920–1923.

Abstract:

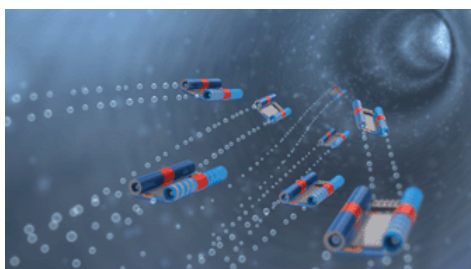


A highly stereoselective Rh(I)-catalyzed 1,3-acetoxy rearrangement of 1,2-allen-3-yl carboxylates leading to 2-acetoxy-1,3(*E*)-alkadienes has been developed. In addition to the high catalytic efficiency and the scope, the excellent *E*-selectivity of the double bond is remarkable.

- Rolled-up nanotech on polymers: from basic perception to self-propelled catalytic microengines

Mei, Y.; Solovev, A. A.; Sanchez, S.; Schmidt, O. G. *Chem. Soc. Rev.* **2011**, *40*, 2109–2119.

Abstract:

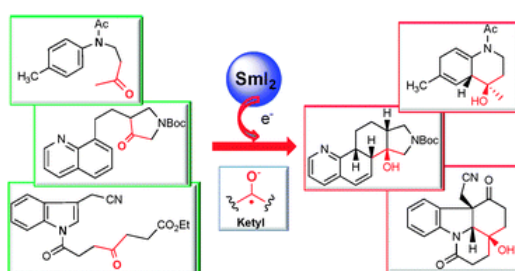


In this *tutorial review* we describe the recent progress on catalytic microtubular engines fabricated by rolled-up nanotech on polymers. We summarize the technical aspects of the technology and the basic principles that cause the catalytic microengines to self-propel in fuel solutions. The control over speed, directionality and interactions of the microengines to perform tasks such as cargo transportation is also discussed. We compare this technology to other fabrication techniques of catalytic micro-/nanomotors and outline challenges and opportunities for such engines in future studies. Since rolled-up nanotech on polymers can easily integrate almost any type of inorganic material, huge potential and advanced performance such as high speed, cargo delivery, motion control, and dynamic assembly are foreseen—ultimately promising a practical way to construct versatile and intelligent catalytic tubular microrobots.

- Samarium diiodide induced ketyl-(het)arene cyclisations towards novel N-heterocycles

Beemelmans, C.; Reissig, H.-U. *Chem. Soc. Rev.* **2011**, *40*, 2199–2210.

Abstract:



In this *tutorial review* we discuss recent advances in the field of ketyl-(het)arene cyclisations promoted by samarium diiodide and related processes. Couplings of samarium ketyls with carbon–carbon multiple bonds are perhaps the most useful reactions to create carbocycles and heterocycles of various ring sizes. They have also successfully been exploited for the synthesis of biologically active compounds or natural products. In this article we intend to summarise our diversity orientated approaches towards nitrogen heterocycles and emphasize other approaches with SmI_2 as well as electrochemical cyclisation methods providing similar N-heterocycles. We also briefly discuss our recently published formal total synthesis of strychnine employing a new samarium diiodide induced cascade reaction as key step. All these examples demonstrate the high synthetic potential of

samarium ketyl-(het)arene cyclisations for the preparation of various types of important heterocyclic compounds.