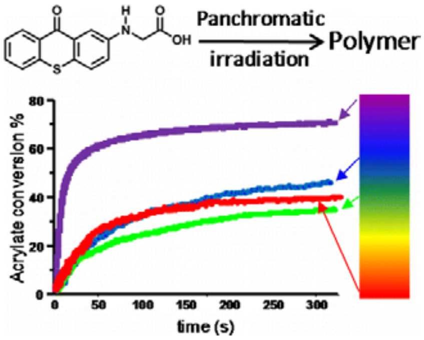
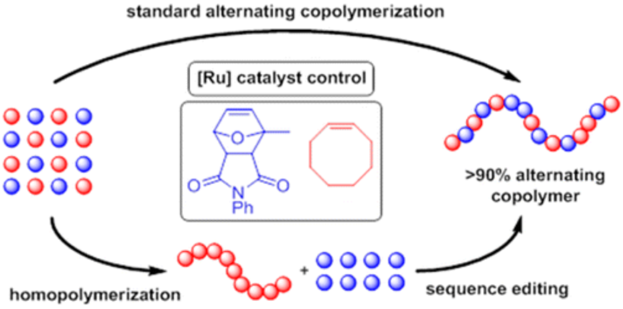
- Panchromatic Type II Photoinitiator for Free Radical Polymerization Based on Thioxanthone Derivatives
  Tar, H.; Esen, D. S.; Aydin, M.; Ley, C.; Arsu, N.; Allonas, X. *Macromolecules* **2013**, *46*, 3266-3272.
  Abstract:



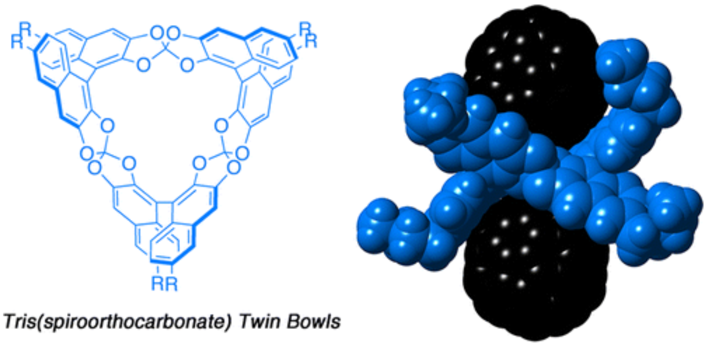
A new photoinitiator for free radical photopolymerization, belonging to the thioxanthone derivatives, was synthesized and characterized. It was found that the compound absorbs over the whole UV-vis spectrum with relatively high absorption coefficients. Fluorescence studies reveal that three different singlet excited states are responsible for this absorption. Phosphorescence and laser flash photolysis evidence the formation of a triplet state from which a photoreduction can occur. Consequently, initiating radicals were formed which are able to initiate the photopolymerization of methyl methacrylate in DMF. Finally, the photopolymerization of acrylates was performed in film at different wavelengths such as 392, 476, 532, and 632 nm, emphasizing the possibility to use this novel photoinitiator when panchromatic irradiation is required.

- Catalyst-Dependent Routes to Ring-Opening Metathesis Alternating Copolymers of Substituted Oxanorbornenes and Cyclooctene
  Daeffler, C. S.; Grubbs, R. H. *Macromolecules* **2013**, *46*, 3288-3292.
  Abstract:



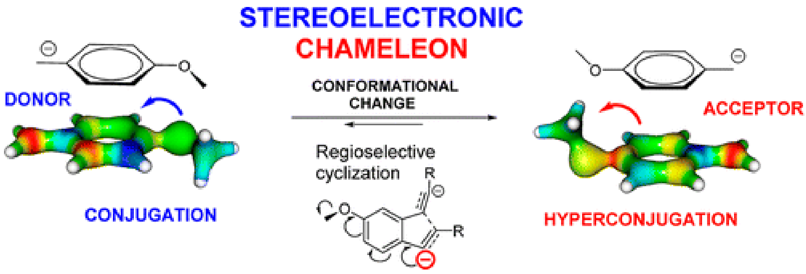
The alternating copolymerization of *cis*-cyclooctene and 1-substituted oxanorbornenes with commercially available ruthenium-based olefin metathesis catalysts was investigated. We determined that RuCl2(CHPh)(PCy3)2 performs a standard alternating copolymerization with these monomers. Unexpectedly, another route to the desired alternating copolymer was revealed. The “sequence editing” route involves the initial polymerization of cis-cyclooctene, followed a ring-opening cross metathesis step that introduces the 1-substituted oxanorbornene monomer in the polycyclooctene chain and largely avoids oxanorborene homopolymerization. Selectivity for alternating diads in the polymer exceeds 90%. Polymer molecular weight can be controlled by linear olefin chain-transfer reagents during sequence editing.

- Preparation of Tris(spiroorthocarbonate) Cyclophanes as Back to Back Ditopic Hosts
  Danjo, H.; Iwaso, K.; Kawahata, M.; Ohara, K.; Miyazawa, T.; Yamaguchi, K. *Org. Lett.* **2013***, 15,* 2164-2167.
  Abstract:



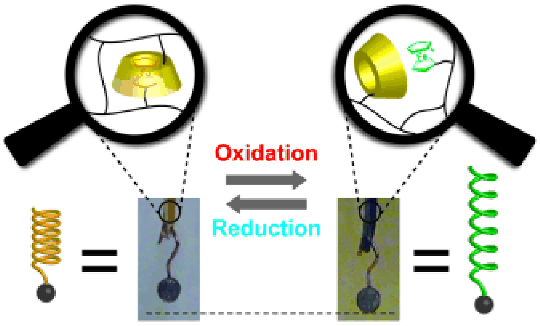
Twin-bowl-shaped tris(spiroorthocarbonate) cyclophanes were designed and prepared as ditopic hosts for electrically neutral or electron-rich guests. Preparation of the desired cyclophanes was achieved by cyclotrimerization of 2,20,3,30-tetrahydroxy-1,10-binaphthyl (THB) via the transesterification of tetraphenyl orthocarbonate or dichlorodiphenoxymethane. In those reactions, bis(spiroorthocarbonate) cyclophane containing two THB units was also formed as the kinetically favored product. The spiroorthocarbonate twin bowl exhibited ditopic molecular recognition toward fullerene C60 in the crystalline state.

- “Stereoelectronic Umpolung”: Converting a p-Donor into a σ-Acceptor via Electron Injection and a Conformational Change
  Peterson, P. W.; Shevchenko, N.; Alabugin, I. V. *Org. Lett.* **2013***, 15,* 2238-2241.
  Abstract:



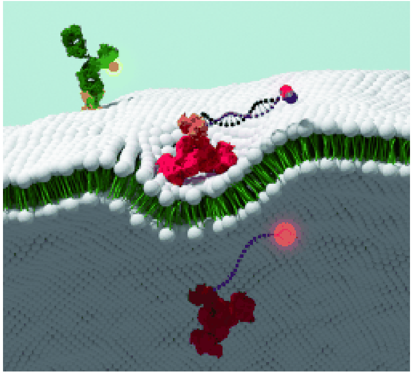
The *para*-OMe functional group, usually regarded as a conjugative p-donor, acts as an efficient hyperconjugative σ-acceptor in reductive cycloaromatization reactions. This apparent reversal of electronic properties is associated with a conformational change that aligns the $\sigma^*_{O\text{–}C}$ orbital with the adjacent aromatic system and provides stabilization to the developing negative charge in the TS of the dianionic cyclization of enediynes. The chameleonic character of the OMe group illustrates the important role of negative hyperconjugation in anionic processes.

- Redox-Generated Mechanical Motion of a Supramolecular Polymeric Actuator Based on Host–Guest Interactions
  Nakahata, M.; Takashima, Y.; Hashidzume, A.; Harada, A. *Angew. Chem. Int. Ed.* **2013**, *52*, 5731–5735.
  Abstract:



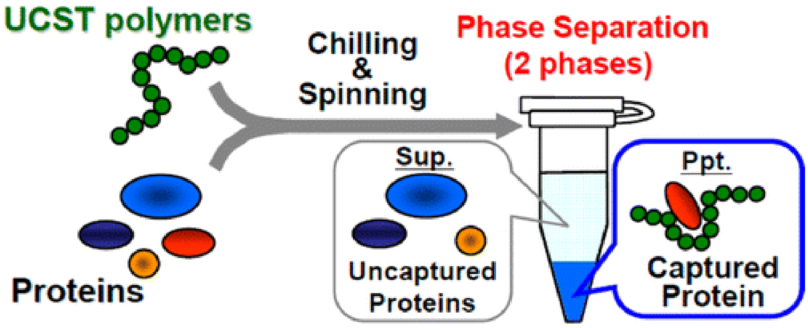
A supramolecular hydrogel is formed by a water-soluble polymer cross-linked with host–guest inclusion complexes between cyclodextrin and ferrocene. Dissociation and re-formation of inclusion complexes by redox stimuli lead to macroscale expansion and contraction of the hydrogel. The gel is utilized as a redox-responsive actuator and the mechanical work done is evaluated.

- A Programmable Sensor to Probe the Internalization of Proteins and Nanoparticles in Live Cells
  Liu, H.; Johnston, A. P. R. *Angew. Chem. Int. Ed*. **2013**, *52*, 5744–5748.
  Abstract:



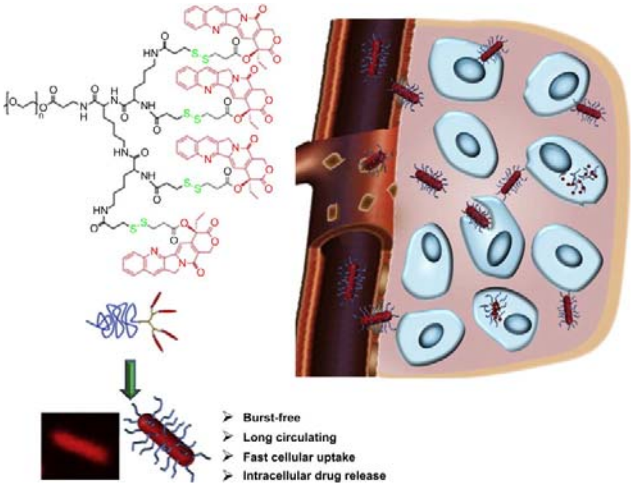
A molecular sensor has been developed to probe the internalization of proteins and nanoparticles into live cells. This simple, high-throughput technique is compatible with cell phenotyping and is independent of the cellular fate of the material.

- Design of UCST Polymers for Chilling Capture of Proteins
  Shimada, N.; Nakayama, M.; Kano, A.; Maruyama, A. *Biomacromolecules* **2013**, *14*, 1452-1457.
  Abstract:



Ureido-derivatized polymers, such as poly(allylurea) (PU) and poly($_\mathrm{L}$-citrulline) derivatives, exhibited upper critical solution temperature (UCST) behavior under physiological buffer conditions as we previously reported. The PU derivatives having amino groups (PU-Am) also showed UCST behavior. In this study, we modified the amino groups of the polymer with succinyl anhydride (PU-Su) or acetyl anhydride (PU-Ac) to determine the effects of these ionic groups on the UCST behavior and to control interactions between the PU derivatives and biocomponents such as proteins and cells. Succinylation of PU-Am resulted in a significant decrease in phase separation temperature (T_p), whereas acetylation of PU-Am resulted in an increase in T_p. As expected, the T_p of PU-Am and PU-Su changed when the pH of the solution was changed. The T_p of PU-Am increased at higher pH, whereas that of PU-Su increased at lower pH, indicating that ionic charge decreases T_p of PU derivatives by increasing osmotic pressure and by increasing hydrophilicity of the polymer chains. Interestingly, these groups did not significantly change UCST when these groups were nonionic. We then examined capture and separation of particular proteins from a protein mixture by cooling-induced phase separation. Selective and rapid capture of particular proteins from protein mixture by PU derivatives was shown, indicating that the ureido-derivatized polymers are potential media for bioseparation under biofriendly conditions.

- Linear-dendritic drug conjugates forming long-circulating nanorods for cancer-drug delivery
  Zhou, Z.; Ma, X.; Jin, E.; Tang, J.; Sui, M.; Shen, Y.; Van Kirk, E. A.; Murdoch, W. J.; Radosz, M. *Biomaterials* **2013**, *34*, 5722-5735.
  Abstract:

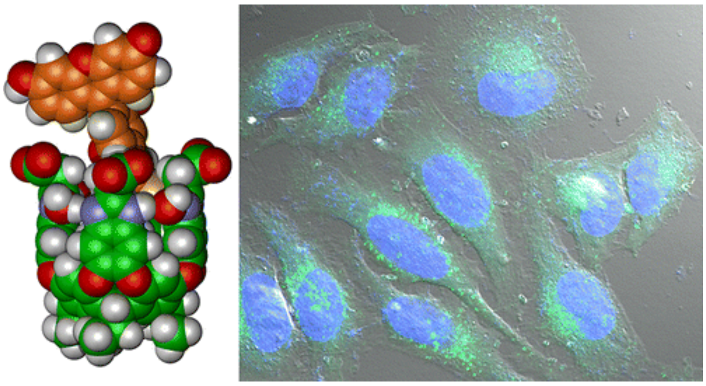


Elongated micelles have many desirable characteristics for cancer-drug delivery, but they are difficult to obtain since amphiphilic polymers form such nanostructures only within narrow composition ranges depending on their own structures. Herein, we demonstrated a facile fabrication of different nanostructures via drug content-controlled self-assembly of amphiphilic linear-dendritic drug conjugates – using the number of the conjugated hydrophobic drug molecule camptothecin (CPT) to tailor the hydrophobicity of amphiphilic PEG-*block*-dendritic polylysine–CPT (PEG–*x*CPT) conjugates and thereby control their self-assembled nanostructures – nanospheres or nanorods of different diameters and lengths. The shape and size of the nanostructures were found to strongly affect their *in vitro* and *in vivo* properties, particularly the blood clearance kinetics, biodistribution and tumor targeting. The nanorods with medium lengths (<500 nm) had a much longer blood circulation and faster cellular uptake than the nanospheres or long nanorods. Thus, polymeric nanorods with proper lengths may be ideal nanocarriers capable of uniting the opposite requirements in cancer-drug delivery.

- Selective Cavitand-Mediated Endocytosis of Targeted Imaging Agents into Live Cells

Ghang, Y.-J.; Schramm, M. P.; Zhang, F.; Acey, R. A.; David, C. N.; Wilson, E. H.; Wang, Y.; Cheng, Q.; Hooley, R. J. *J. Am. Chem. Soc.* **2013**, *135*, 7090–7093.

<u>Abstract:</u>

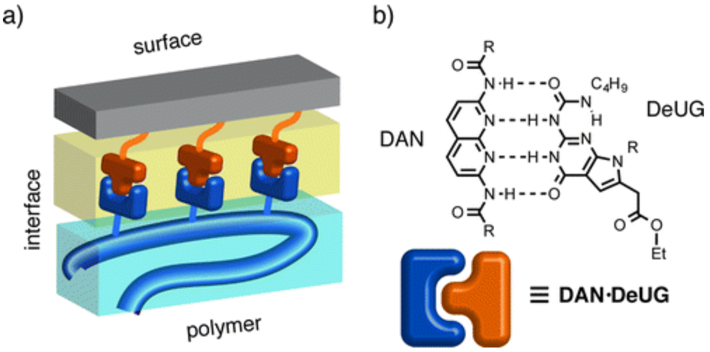


A water-soluble synthetic receptor molecule is capable of selective, controlled endocytosis of a specifically tagged target molecule in different types of living human cells. The presence of suitable choline-derived binding handles is essential for the molecular recognition and transport process, allowing selective guest transport and imaging of cancer cells.

- High-Affinity DNA Base Analogs as Supramolecular, Nanoscale Promoters of Macroscopic Adhesion

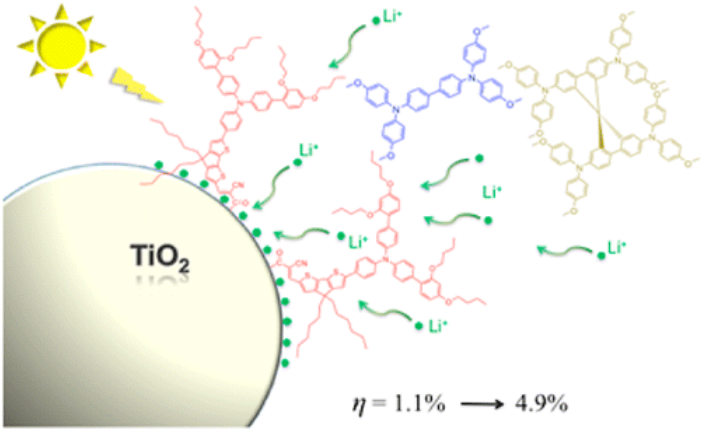
  Anderson, C. A.; Jones, A. R.; Briggs, E. M.; Novitsky, E. J.; Kuykendall, D. W.; Sottos, N. R.; Zimmerman, S. C. *J. Am. Chem. Soc.* **2013**, *135*, 7288–7295.

  <u>Abstract:</u>



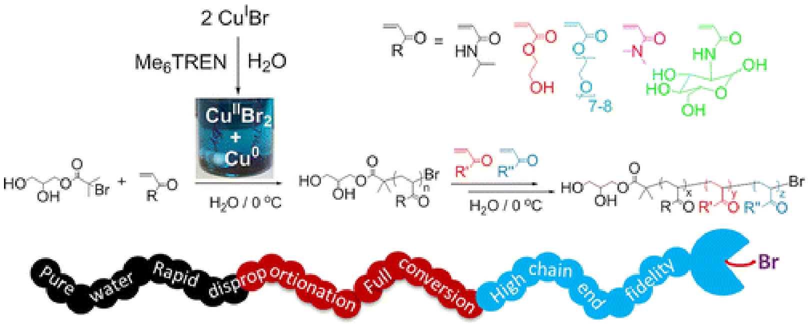
Adhesion phenomena are essential to many biological processes and to synthetic adhesives and manufactured coatings and composites. Supramolecular interactions are often implicated in various adhesion mechanisms. Recently, supramolecular building blocks, such as synthetic DNA base-pair mimics, have drawn attention in the context of molecular recognition, self-assembly, and supramolecular polymers. These reversible, hydrogen-bonding interactions have been studied extensively for their adhesive capabilities at the nano- and microscale, however, much less is known about their utility for practical adhesion in macroscopic systems. Herein, we report the preparation and evaluation of supramolecular coupling agents based on high-affinity, high-fidelity quadruple hydrogen-bonding units (e.g., DAN·DeUG, Kassoc = 108 M–1 in chloroform). Macroscopic adhesion between polystyrene films and glass surfaces modified with 2,7-diamidonaphthyridine (DAN) and ureido-7-deazaguanine (DeUG) units was evaluated by mechanical testing. Structure–property relationships indicate that the designed supramolecular interaction at the nanoscale plays a key role in the observed macroscopic adhesive response. Experiments probing reversible adhesion or self-healing properties of bulk samples indicate that significant recovery of initial strength can be realized after failure but that the designed noncovalent interaction does not lead to healing during the process of adhesion loss.

- Initial Light Soaking Treatment Enables Hole Transport Material to Outperform Spiro-OMeTAD in Solid-State Dye-Sensitized Solar Cells
  Yang, L.; Xu, B.; Bi, D.; Tian, H.; Boschloo, G.; Sun, L.; Hagfeldt, A.; Johansson, E. M. J. *J. Am. Chem. Soc.* **2013**, *135,* 7378–7385.
  Abstract:



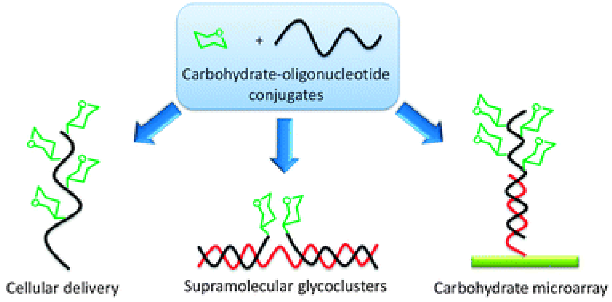
Efficient solid state dye-sensitized solar cells (sDSCs) were obtained using a small hole transport material, MeO-TPD (N,N,N',N'-tetrakis(4-methoxyphenyl)benzidine), after an initial light soaking treatment. It was discovered that the light soaking treatment for the MeO-TPD based solar cells is essential in order to achieve the high efficiency (4.9%), which outperforms spiro-OMeTAD based sDSCs using the same dye and device preparation parameters. A mechanism based on Li+ ion migration is suggested to explain the light soaking effect. It was observed that the electron lifetime for the MeO-TPD based sDSC strongly increases after the light soaking treatment, which explains the higher efficiency. After the initial light soaking treatment the device efficiency remains considerably stable with only 0.2% decrease after around 1 month (unsealed cells stored in dark).

- Aqueous Copper-Mediated Living Polymerization: Exploiting Rapid Disproportionation of CuBr with Me$_6$TREN
  Zhang, Q.; Wilson, P.; Li, Z.; McHale, R.; Godfrey, J.; Anastasaki, A.; Waldron, C.; Haddleton, D. M. *J. Am. Chem. Soc.* **2013**, *135,* 7355–7363.
  Abstract:



A new approach to perform single-electron transfer living radical polymerization (SET-LRP) in water is described. The key step in this process is to allow full disproportionation of CuBr/Me6TREN (TREN = tris(dimethylamino)ethyl amine to Cu(0) powder and CuBr2 in water prior to addition of both monomer and initiator. This provides an extremely powerful tool for the synthesis of functional water-soluble polymers with controlled chain length and narrow molecular weight distributions (polydispersity index approximately 1.10), including poly(N-isopropylacrylamide), N,N-dimethylacrylamide, poly(ethylene glycol) acrylate, 2-hydroxyethyl acrylate (HEA), and an acrylamido glyco monomer. The polymerizations are performed at or below ambient temperature with quantitative conversions attained in minutes. Polymers have high chain end fidelity capable of undergoing chain extensions to full conversion or multiblock copolymerization via iterative monomer addition after full conversion. Activator generated by electron transfer atom transfer radical polymerization of N-isopropylacrylamide in water was also conducted as a comparison with the SET-LRP system. This shows that the addition sequence of l-ascorbic acid is crucial in determining the onset of disproportionation, or otherwise. Finally, this robust technique was applied to polymerizations under biologically relevant conditions (PBS buffer) and a complex ethanol/water mixture (tequila).

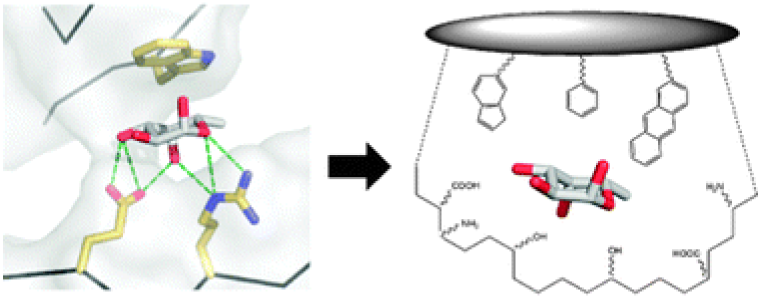
- Glycoclusters on oligonucleotide and PNA scaffolds: synthesis and applications
  Spinelli, N.; Defrancq, E.; Morvan, F. *Chem. Soc. Rev.* **2013**, *42*, 4557-4573.
  Abstract:



Conjugation of oligonucleotides (ONs) to a variety of reporter groups has been the subject of intensive research during the last decade. Conjugation is indeed of great interest because it can be used not only to improve the existing ONs properties but also to impart new ones. In this context tremendous efforts have been made to conjugate carbohydrate moieties to ONs. Indeed carbohydrates play an important role in biological processes such as signal transduction and cell adhesion through the recognition with sugar-binding proteins (*i.e.* lectins) located on the surface of cells. For this reason, carbohydrate–oligonucleotide conjugates (COCs) have been first developed for improving the poor cellular uptake or tissue specific delivery of ONs through receptor-mediated endocytosis. Besides the targeted ONs delivery, carbohydrate–oligonucleotide conjugates (COCs) are also evaluated in the context of carbohydrate biochips in which surface coating with carbohydrates is achieved by using the DNA-directed immobilization strategy (DDI). Peptide nucleic acids (PNAs) have also been extensively investigated as a surrogate of DNA for diverse applications. Therefore attachment of carbohydrate moieties to this class of molecules has been studied. The aforementioned applications of COCs require mimicking of the natural processes, in which the weak individual protein–carbohydrate binding is overcome by using multivalent interactions. This tutorial review focuses on the recent advances in carbohydrate–oligonucleotide conjugates and describes the major synthetic approaches available. In addition, an overview of applications that have been developed using various scaffolds allowing multivalent interactions is provided. Finally recent results on the use of peptide nucleic acids as oligonucleotides surrogate are described.

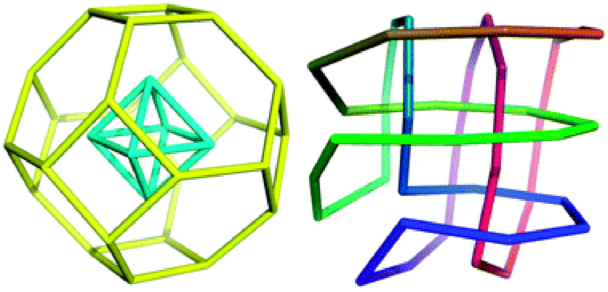
- Binding sugars: from natural lectins to synthetic receptors and engineered neolectins

Arnaud, J.; Audfraya, A.; Imberty, A. *Chem. Soc. Rev.* **2013**, *42*, 4798–4813.
Abstract:



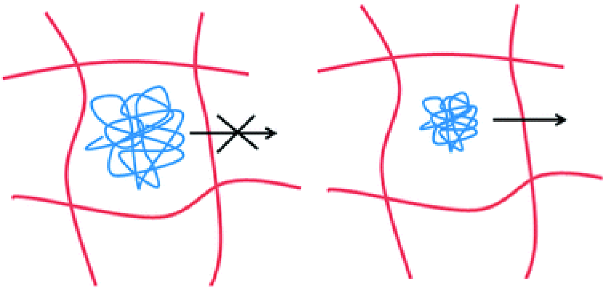
The large diversity and complexity of glycan structures together with their crucial role in many biological or pathological processes require the development of new high-throughput techniques for analyses. Lectins are classically used for characterising, imaging or targeting glycoconjugates and, when printed on microarrays, they are very useful tools for profiling glycomes. Development of recombinant lectins gives access to reliable and reproducible material, while engineering of new binding sites on existing scaffolds allows tuning of specificity. From the accumulated knowledge on protein–carbohydrate interactions, it is now possible to use nucleotide and peptide (bio)synthesis for producing new carbohydrate-binding molecules. Such a biomimetic approach can also be addressed by boron chemistry and supra-molecular chemistry for the design of fully artificial glycosensors.

- Energy landscapes, structural topologies and rearrangement mechanisms in clusters of dipolar particles
  Farrell, J. D.; Lines, C.; Shepherd, J. J.; Chakrabarti, D.; Miller, M. A.; Wales, D. J. *Soft Matter* **2013,** *9*, 5407-5416.
  Abstract:



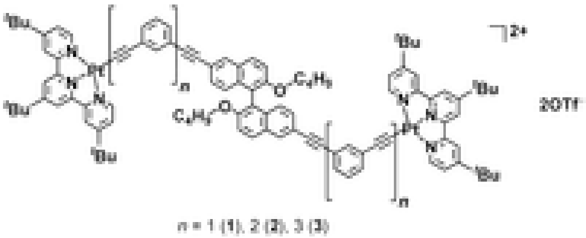
Clusters of spherical particles with isotropic attraction favour compact structures that maximise the number of energetically optimal nearest-neighbour interactions. In contrast, dipolar interactions lead to the formation of chains with a low coordination number. When both isotropic and dipolar interactions are present, the competition between them can lead to intricate knot, link and coil structures. Here, we investigate how these structures may self-organise and interconvert in clusters bound by the Stockmayer potential (Lennard-Jones plus point dipole). We map out the low-lying region of the energy landscape using disconnectivity graphs to follow how it evolves as the strength of the dipolar interactions increases. From comprehensive surveys of isomerisation pathways, we identify a number of rearrangement mechanisms that allow the topology of chain-like structures to interconvert.

- Analysis of the mesh size in a supramolecular hydrogel by PFG-NMR spectroscopy
  Wallace, M.; Adams, D. J.; Iggo, J. A. *Soft Matter* **2013,** *9*, 5483-5491.
  Abstract:



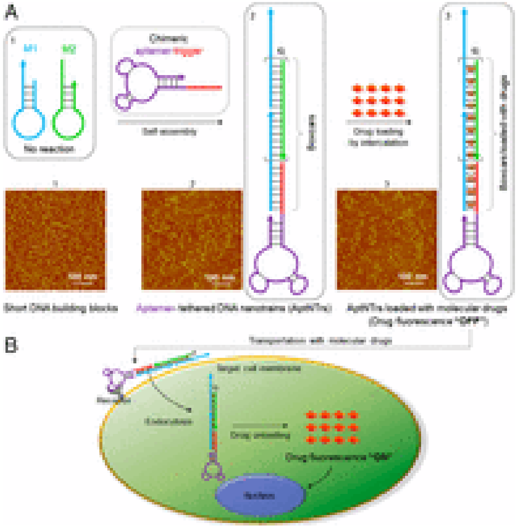
Pulsed field gradient NMR (PFG-NMR) spectroscopy has been used to determine the network mesh size in stable hydrogels formed upon addition of Ca^{2+} to solutions of naphthalene diphenylalanine (2FF). At pH 12, the solutions at 0.55 wt% 2FF comprise worm-like micelles. Addition of Ca^{2+} results in cross-linking of these micelles. The self-diffusion of dextran guests of nominal 6, 40, 70, 100, 500, 670, 1400 and 2000 kDa, possessing hydrodynamic diameters ($2R_h$) similar to the expected pore sizes in these systems, was studied both in the precursor micellar solutions and in the hydrogels. The diffusivity of probes with $2R_h < 40$ nm is restricted to a similar extent in both types of network with diffusion coefficients scaling as $\sim M_r^{-0.5}$, where M_r is the nominal mass of the probe, consistent with relatively unrestricted diffusion. Diffusion coefficients fit well the equation $D_n/D_o = \exp(-R_h/\xi)$, where D_n and D_o are the diffusion coefficients in the presence and absence of network respectively and ξ is the mesh size, giving a mesh size of approximately 40 nm. The heaviest *ca.* 10% of the nominal 2000 kDa dextran fraction having approximate mass and hydrodynamic diameter 3300 kDa and 84 nm respectively was almost immobilised by the gel, consistent with this estimate of the mesh size. The restriction was much weaker in the micellar solution, which is attributed to the transient nature of this micellar network in the absence of Ca^{2+}. Finally, the mesh size for micellar solutions prepared at 1.1 wt% 2FF is smaller than that of micellar solutions prepared at lower concentrations of 2FF. However, the corresponding gels have a larger mesh size than those prepared at lower concentrations of 2FF. We attribute this to increased fibre aggregation at the higher 2FF concentration. This correlates with lower rheological moduli at higher 2FF concentrations.

- Dynamic scaffold of chiral binaphthol derivatives with the alkynylplatinum(II) terpyridine moiety
  Leung, S. Y.-L.; Lam, W. H.; Yam, V. W.-W. *Proc. Nat. Acad. Sci. USA* **2013**, *110*, 7986-7991.
  Abstract:



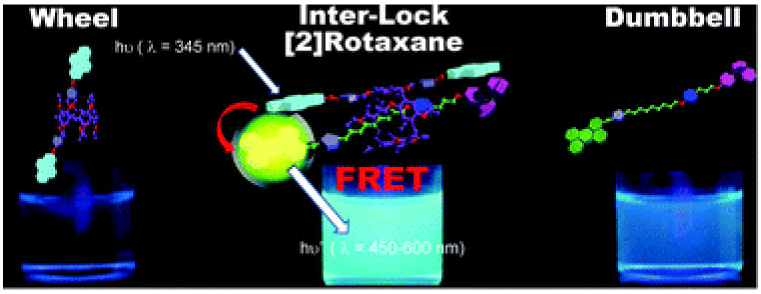
Platinum(II)-containing complexes with inherently chiral binaphthol derivatives display a versatile scaffold between random coils and single-turn helical strands, in which the conformational transition is controlled by the Pt···Pt and π−π interactions of alkynylplatinum(II) terpyridine moiety upon solvent and temperature modulation. The bisignate Cotton effect in the circular dichroism spectra is indicative of the cooperative transformation from random coil state to a compact single-turn *M*- or *P*-helix. More importantly, as revealed by the appearance of new UV-vis absorption and emission bands during conformational change, the self-assembly of the platinum(II)-containing complex into a helical structure is assisted by the metal···metal and π−π interactions of the alkynylplatinum(II) terpyridine moieties. The folded structure with stabilization via metal···metal and π–π interactions has been supported by density functional theory calculations, which provide insights into the folded geometry of these kind of metallo-foldamers.

- Self-assembled, aptamer-tethered DNA nanotrains for targeted transport of molecular drugs in cancer theranostics
  Zhu, G.; Zheng, J.; Song, E.; Donovan, M.; Zhang, K.; Liu, C.; Tan, W. *Proc. Nat. Acad. Sci. USA* **2013**, *110*, 7998-8003.
  Abstract:



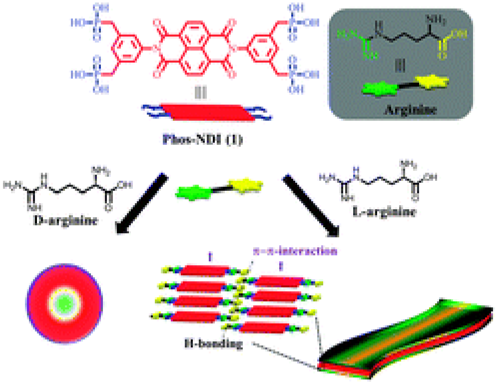
Nanotechnology has allowed the construction of various nanostructures for applications, including biomedicine. However, a simple target-specific, economical, and biocompatible drug delivery platform with high maximum tolerated doses is still in demand. Here, we report aptamer-tethered DNA nanotrains (aptNTrs) as carriers for targeted drug transport in cancer therapy. Long aptNTrs were self-assembled from only two short DNA upon initiation by modified aptamers, which worked like locomotives guiding nanotrains toward target cancer cells. Meanwhile, tandem "boxcars" served as carriers with high payload capacity of drugs that were transported to target cells and induced selective cytotoxicity. aptNTrs enhanced maximum tolerated dose in nontarget cells. Potent antitumor efficacy and reduced side effects of drugs delivered by biocompatible aptNTrs were demonstrated in a mouse xenograft tumor model. Moreover, fluorophores on nanotrains and drug fluorescence dequenching upon release allowed intracellular signaling of nanotrains and drugs. These results make aptNTrs a promising targeted drug transport platform for cancer theranostics.

- Förster resonance energy transfer by formation of a mechanically interlocked [2]rotaxane
  Ogoshi, T.; Yamafuji, D.; Yamagishia, T.; Brouwer, A. M. *Chem. Commun*. **2013**, *49*, 5468-5470.
  Abstract :



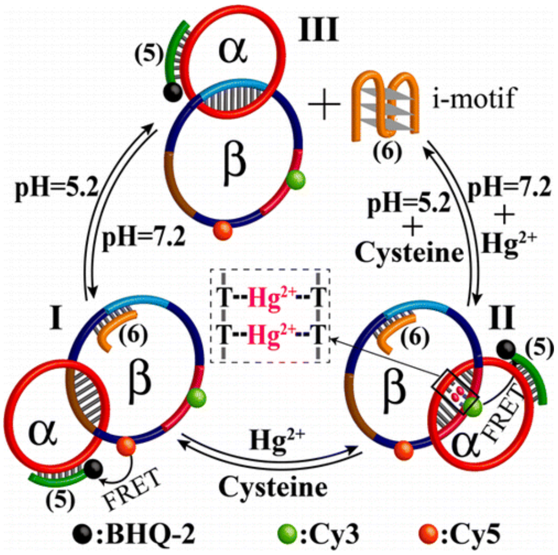
A [2]rotaxane has been constructed from a di-pyrene appended pillar[5]arene wheel, a pyridinium axle, and a perylene stopper. It shows efficient Förster resonance energy transfer from pyrene to perylene by formation of a mechanically interlocked [2]rotaxane.

- A phosphonic acid appended naphthalene diimide motif for self-assembly into tunable nanostructures through molecular recognition with arginine in water
  Nandre, K. P.; Bhosale, S. V.; Krishna, K. V. S. R.; Guptac, A.; Bhosale, S. V. *Chem. Commun*. **2013**, *49*, 5444-5446.
  Abstract:



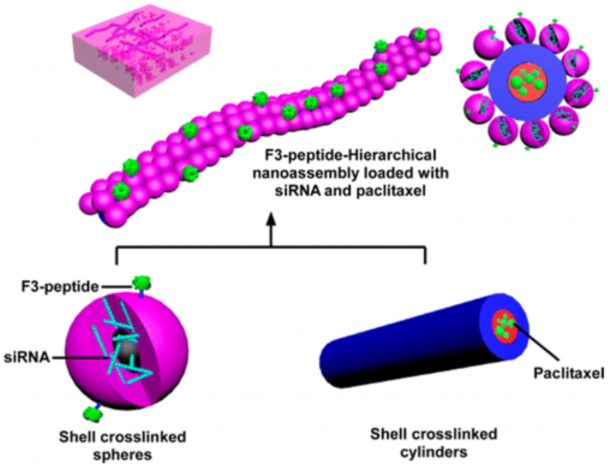
A naphthalene diimide motif bearing phosphonic acid functionalities has been found to be self-assembled with L- and D-arginine through chirality induced molecular recognitions and leads to the formation of micrometre long nanobelts and spherical aggregates at pH 9 in water, respectively.

- A Three-Station DNA Catenane Rotary Motor with Controlled Directionality
  Lu, C.-H.; Cecconello, A.; Elbaz, J.; Credi, A.; Willner, I. *Nano Lett.* **2013**, *13*, 2303-2308.
  Abstract:



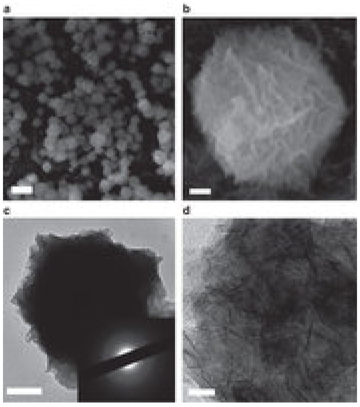
The assembly of DNA machines represents a central effort in DNA nanotechnology. We report on the first DNA rotor system composed of a two-ring catenane. The DNA rotor ring rotates in dictated directions along a wheel, and it occupies three distinct sites. Hg^{2+}/cysteine or pH (H^+/OH^-) act as fuels or antifuels in positioning the rotor ring. Analysis of the kinetics reveals directional clockwise or anticlockwise population of the target-sites (>85%), and the rotor’s direction is controlled by the shortest path on the wheel.

- Multifunctional Hierarchically Assembled Nanostructures as Complex Stage-Wise Dual-Delivery Systems for Coincidental Yet Differential Trafficking of siRNA and Paclitaxel
  Elsabahy, M.; Shrestha, R.; Clark, C.; Taylor, S.; Leonard, J.; Wooley, K. L. *Nano Lett.* **2013**, *13*, 2172-2181.
  Abstract:



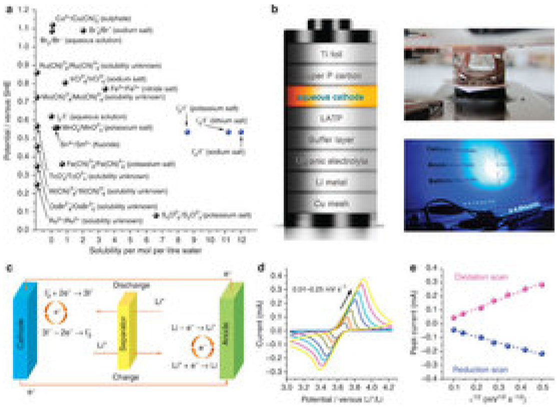
Development of multifunctional nanostructures that can be tuned to codeliver multiple drugs and diagnostic agents to diseased tissues is of great importance. Hierarchically assembled theranostic (HAT) nanostructures based on anionic cylindrical shell cross-linked nanoparticles and cationic shell cross-linked knedel-like nanoparticles (cSCKs) have recently been developed by our group to deliver siRNA intracellularly and to undergo radiolabeling. In the current study, paclitaxel, a hydrophobic anticancer drug, and siRNA have been successfully loaded into the cylindrical and spherical components of the hierarchical assemblies, respectively. Cytotoxicity, immunotoxicity, and intracellular delivery mechanism of the HAT nanostructures and their individual components have been investigated. Decoration of nanoparticles with F3-tumor homing peptide was shown to enhance the selective cellular uptake of the spherical particles, whereas the HAT nanoassemblies underwent an interesting disassembly process in contact with either OVCAR-3 or RAW 264.7 cell lines. The HAT nanostructures were found to “stick” to the cell membrane and “trigger” the release of spherical cSCKs templated onto their surfaces intracellularly, while retaining the cylindrical part on the cell surface. Combination of paclitaxel and cell-death siRNA (siRNA that induces cell death) into the HAT nanostructures resulted in greater reduction in cell viability than siRNA complexed with Lipofectamine and the assemblies loaded with the individual drugs. In addition, a shape-dependent immunotoxicity was observed for both spherical and cylindrical nanoparticles with the latter being highly immunotoxic. Supramolecular assembly of the two nanoparticles into the HAT nanostructures significantly reduced the immunotoxicity of both cSCKs and cylinders. HAT nanostructures decorated with targeting moieties, loaded with nucleic acids, hydrophobic drugs, radiolabels, and fluorophores, with control over their toxicity, immunotoxicity, and intracellular delivery might have great potential for biomedical delivery applications.

- Amorphous nickel hydroxide nanospheres with ultrahigh capacitance and energy density as electrochemical pseudocapacitor materials
  Li, H. B.; Yu, M. H.; Wang, F. X.; Liu, P.; Liang, Y.; Xiao, J.; Wang, C. X.; Tong, Y. X.; Yang, G. W. *Nature Commun.* **2013**, *4*, 1894.
  Abstract:



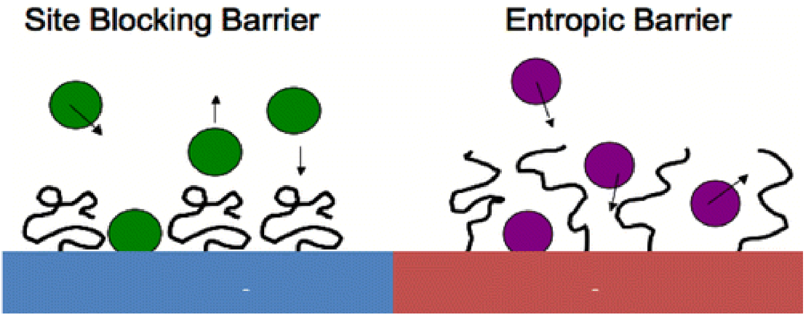
Among numerous active electrode materials, nickel hydroxide is a promising electrode in electrochemical capacitors. Nickel hydroxide research has thus far focused on the crystalline rather than the amorphous phase, despite the impressive electrochemical properties of the latter, which includes an improved electrochemical efficiency due to disorder. Here we demonstrate high-performance electrochemical supercapacitors prepared from amorphous nickel hydroxide nanospheres synthesized via simple, green electrochemistry. The amorphous nickel hydroxide electrode exhibits high capacitance (2,188 F g^{-1}), and the asymmetric pseudocapacitors of the amorphous nickel hydroxide exhibit high capacitance (153 F g^{-1}), high energy density (35.7 W h kg^{-1} at a power density of 490 W kg^{-1}) and super-long cycle life (97% and 81% charge retentions after 5,000 and 10,000 cycles, respectively). The integrated electrochemical performance of the amorphous nickel hydroxide is commensurate with crystalline materials in supercapacitors. These findings promote the application of amorphous nanostructures as advanced electrochemical pseudocapacitor materials.

- High-performance rechargeable lithium-iodine batteries using triiodide/iodide redox couples in an aqueous cathode
  Zhao, Y.; Wang, L.; Byon, H. R. *Nature Commun* **2013**, *4*, 1896.
  <u>Abstract:</u>



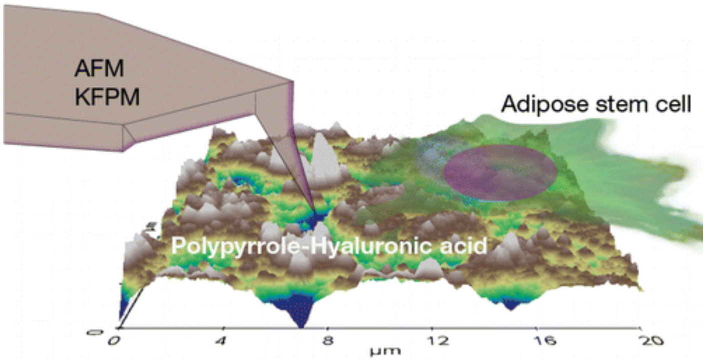
Development of promising battery systems is being intensified to fulfil the needs of long-driving-ranged electric vehicles. The successful candidates for new generation batteries should have higher energy densities than those of currently used batteries and reasonable rechargeability. Here we report that aqueous lithium-iodine batteries based on the triiodide/iodide redox reaction show a high battery performance. By using iodine transformed to triiodide in an aqueous iodide, an aqueous cathode involving the triiodide/iodide redox reaction in a stable potential window avoiding water electrolysis is demonstrated for lithium-iodine batteries. The high solubility of triiodide/iodide redox couples results in an energy density of ~ 0.33 kWh kg^{-1}, approximately twice that of lithium-ion batteries. The reversible redox reaction without the formation of resistive solid products promotes rechargeability, demonstrating 100 cycles with negligible capacity fading. A low cost, non-flammable and heavy-metal-free aqueous cathode can contribute to the feasibility of scale-up of lithium-iodine batteries for practical energy storage.

- Protein Adsorption on Well-Characterized Polyethylene Oxide Brushes on Gold: Dependence on Molecular Weight and Grafting Density
  Taylor, W.; Jones, R. A. L. *Langmuir* **2013**, *29*, 6116–6122.
  Abstract:



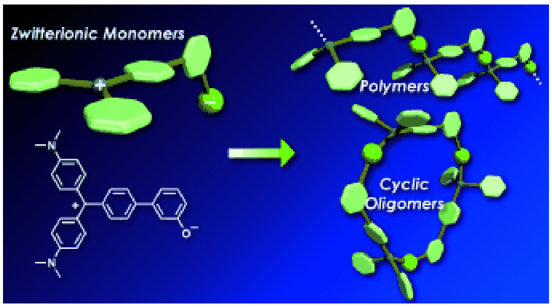
The adsorption of lysozyme protein was measured ex situ on well-characterized gold surfaces coated by end-tethered polyethylene oxide brushes of various molecular weights and controlled grafting densities. The adsorbed amount of protein for different molecular weight brushes was found to collapse onto one master curve when plotted against brush coverage. We interpret this relationship in terms of a model involving site-blocking of the adsorption of proteins at the substrate and discuss the role of the physical attraction of PEO segments to gold. We account for our observation of a simple exponential relationship between protein adsorption and normalized brush coverage with a simple protein adsorption model. In contrast to other studies in similar systems, we do not observe protein adsorption on brushes at high grafting density, and we suggest that this discrepancy may be due to the solubility effects of salt upon the brushes, influencing their protein binding affinity, in the limit of high grafting density and high brush volume fraction.

- Surface Properties and Interaction Forces of Biopolymer-Doped Conductive Polypyrrole Surfaces by Atomic Force Microscopy
  Pelto, J. M.; Haimi, S. P.; Siljander, A. S.; Miettinen, S. S.; Tappura, K. M.; Higgins, M. J.; Wallace, G. G. *Langmuir* **2013**, *29*, 6099–6108.
  Abstract:



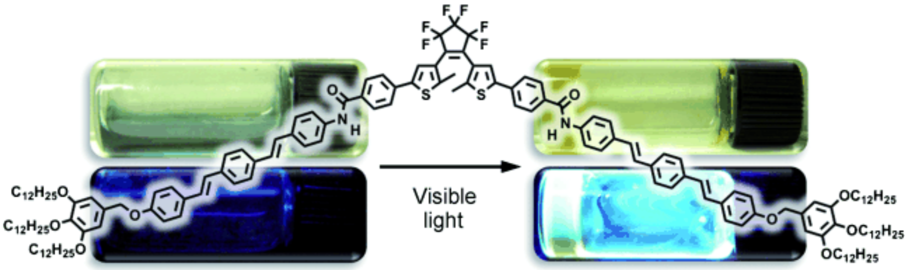
Surface properties and electrical charges are critical factors elucidating cell interactions on biomaterial surfaces. The surface potential distribution and the nanoscopic and microscopic surface elasticity of organic polypyrrole–hyaluronic acid (PPy-HA) were studied by atomic force microscopy (AFM) in a fluid environment in order to explain the observed enhancement in the attachment of human adipose stem cells on positively charged PPy-HA films. The electrostatic force between the AFM tip and a charged PPy-HA surface, the tip–sample adhesion force, and elastic moduli were estimated from the AFM force curves, and the data were fitted to electrostatic double-layer and elastic contact models. The surface potential of the charged and dried PPy-HA films was assessed with Kelvin probe force microscopy (KPFM), and the KPFM data were correlated to the fluid AFM data. The surface charge distribution and elasticity were both found to correlate well with the nodular morphology of PPy-HA and to be sensitive to the electrochemical charging conditions. Furthermore, a significant change in the adhesion was detected when the surface was electrochemically charged positive. The results highlight the potential of positively charged PPy-HA as a coating material to enhance the stem cell response in tissue-engineering scaffolds.

- Formation of Cyclic and Polymeric Structures from Zwitterions
  Komatsu, H.; Oi, W.; Naritani, K.; Takaishi, K.; Uchiyama, M.; Murakana, A.; Maeda, H. *Chem. Eur. J.* **2013**, *22*, 6956-6960.
  Abstract:



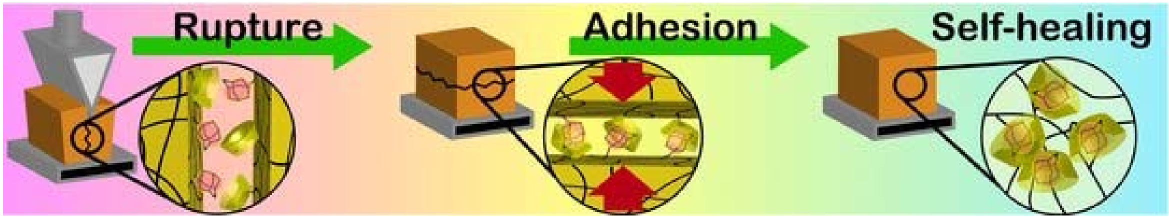
Covalent linkages: Zwitterion-based covalent linkages were observed in cyclic oligomers and in dispersed polymers based on monomers. Addition of acids and bases promoted transitions between monomeric species and the oligomeric and/or polymeric states. Exchange of constituent monomer units in the cyclic oligomers was observed in the solution state, whereas the polymers obtained as precipitates from CH_3CN were not converted to the cyclic oligomers (see scheme).

- Rational Design of Photoresponsive Supramolecular Assemblies Based on Diarylethene
  Yagai, S.; Ishiwatari, K.; Lin, X.; Karatsu, T.; Kitamura, A.; Uemura, S. *Chem. Eur. J.* **2013***, 22*, 6971-6975.
  Abstract:



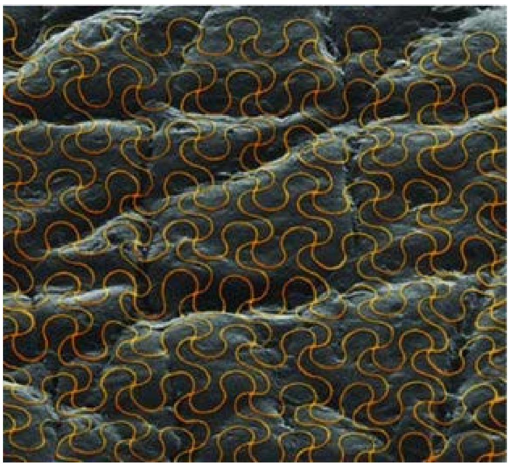
Photochromism: Functionalization of a diarylethene derivative with π-conjugated oligomers resulted in a higher aggregation capability in the open rather than the closed form due to tunable steric hindrance of methyl groups of the diarylethene core (see scheme). Distinct aggregation abilities of the open and the closed isomers in nonpolar solvent and phototunable energy transfer between the two functional units enabled visible-light-triggered formation of fluorescent organogels.

- Preorganized Hydrogel: Self-Healing Properties of Supramolecular Hydrogels Formed by Polymerization of Host–Guest-Monomers that Contain Cyclodextrins and Hydrophobic Guest Groups
  Kakuta, T.; Takashima, Y.; Nakahata, M.; Otsubo, M.; Yamaguchi, H.; Harada, A. *Adv. Mater.* **2013**, *25*, 2849–2853.
  Abstract:



Supramolecular hydrogels formed by a host-guest interaction show self-healing properties. The cube-shaped hydrogels with β-cyclodextrin and adamantane guest molecules mend after being broken. The hydrogels sufficiently heal to form a single gel, and the initial strength is restored. Although contact between a freshly cut and uncut surface does not mend the gels, two freshly cut surfaces selectively mend.

- Multifunctional Epidermal Electronics Printed Directly Onto the Skin
  Yeo, W.-H.; Kim, Y.-S.; Lee, J.; Ameen, A.; Shi, L.; Li, M.; Wang, S.; Ma, R.; Jin, S. H.; Kang, Z.; Huang, Y.; Rogers, J. A. *Adv. Mater.* **2013**, *25*, 2773–2778.
  Abstract:



Materials and designs are presented for electronics and sensors that can be conformally and robustly integrated onto the surface of the skin. A multifunctional device of this type can record various physiological signals relevant to health and wellness. This class of technology offers capabilities in biocompatible, non-invasive measurement that lie beyond those available with conventional, point-contact electrode interfaces to the skin.