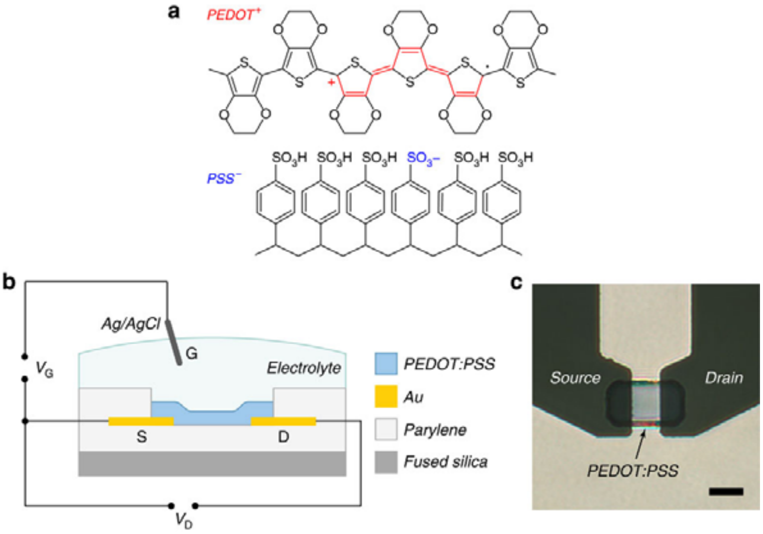
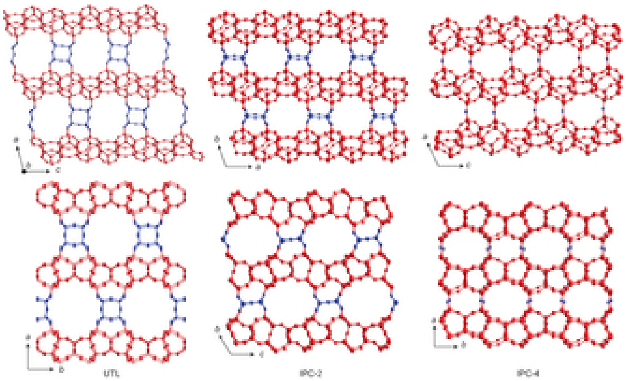
- High transconductance organic electrochemical transistors
  Khodagholy, D.; Rivnay, J.; Sessolo, M.; Gurfinkel, M.; Leleux, P.; Jimison, L. H.; Stavrinidou, E.; Herve, T.; Sanaur, S.; Owens, R. M.; Malliaras, G. G. *Nature Commun.* **2013**, *4*, 2133.
  Abstract:



The development of transistors with high gain is essential for applications ranging from switching elements and drivers to transducers for chemical and biological sensing. Organic transistors have become well-established based on their distinct advantages, including ease of fabrication, synthetic freedom for chemical functionalization, and the ability to take on unique form factors. These devices, however, are largely viewed as belonging to the low-end of the performance spectrum. Here we present organic electrochemical transistors with a transconductance in the mS range, outperforming transistors from both traditional and emerging semiconductors. The transconductance of these devices remains fairly constant from DC up to a frequency of the order of 1 kHz, a value determined by the process of ion transport between the electrolyte and the channel. These devices, which continue to work even after being crumpled, are predicted to be highly relevant as transducers in biosensing applications.

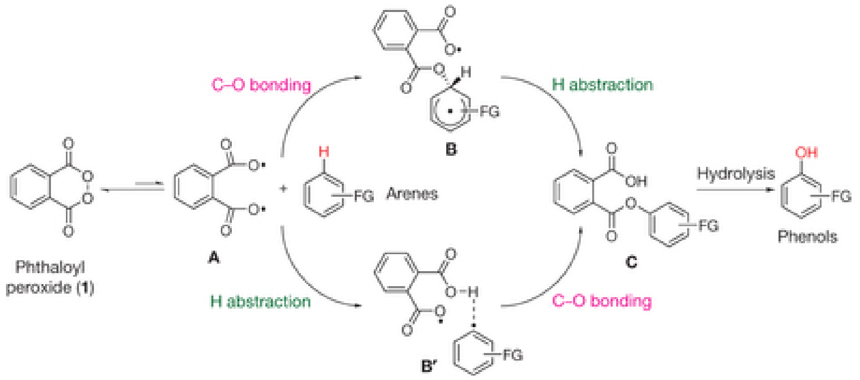
- A family of zeolites with controlled pore size prepared using a top-down method
  Roth, W. J.; Nachtigall, P.; Morris, R. E.; Wheatley, P. S.; Seymour, V. R.; Ashbrook, S. E.; Chlubná, P.; Grajciar, L.; Položij, M.; Zukal, A.; Shvets, O.; Čejka, J. *Nature Chem.* **2013**, *5*, 628–633.
  Abstract:



The properties of zeolites, and thus their suitability for different applications, are intimately connected with their structures. Synthesizing specific architectures is therefore important, but has

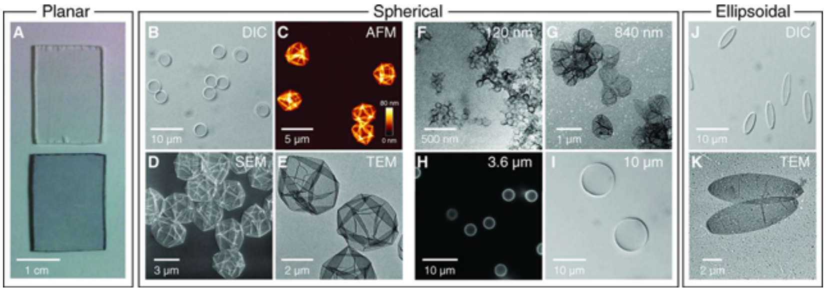
remained challenging. Here we report a top-down strategy that involves the disassembly of a parent zeolite, UTL, and its reassembly into two zeolites with targeted topologies, IPC-2 and IPC-4. The three zeolites are closely related as they adopt the same layered structure, and they differ only in how the layers are connected. Choosing different linkers gives rise to different pore sizes, enabling the synthesis of materials with predetermined pore architectures. The structures of the resulting zeolites were characterized by interpreting the X-ray powder-diffraction patterns through models using computational methods; IPC-2 exhibits orthogonal 12- and ten-ring channels, and IPC-4 is a more complex zeolite that comprises orthogonal ten- and eight-ring channels. We describe how this method enables the preparation of functional materials and discuss its potential for targeting other new zeolites.

- Metal-free oxidation of aromatic carbon–hydrogen bonds through a reverse-rebound mechanism
  Yuan, C.; Liang, Y.; Hernandez, T.; Berriochoa, A.; Houk, K. N.; Siegel, D. *Nature* **2013**, *499*, 192-196.
  Abstract:



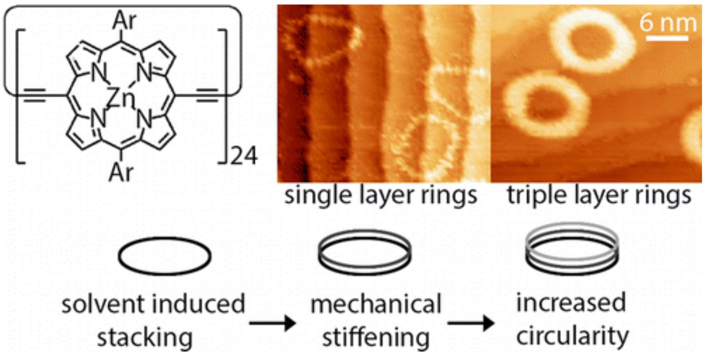
Methods for carbon–hydrogen (C–H) bond oxidation have a fundamental role in synthetic organic chemistry, providing functionality that is required in the final target molecule or facilitating subsequent chemical transformations. Several approaches to oxidizing aliphatic C–H bonds have been described, drastically simplifying the synthesis of complex molecules. However, the selective oxidation of aromatic C–H bonds under mild conditions, especially in the context of substituted arenes with diverse functional groups, remains a challenge. The direct hydroxylation of arenes was initially achieved through the use of strong Brønsted or Lewis acids to mediate electrophilic aromatic substitution reactions with super-stoichiometric equivalents of oxidants, significantly limiting the scope of the reaction. Because the products of these reactions are more reactive than the starting materials, over-oxidation is frequently a competitive process. Transition-metal-catalysed C–H oxidation of arenes with or without directing groups has been developed, improving on the acid-mediated process; however, precious metals are required. Here we demonstrate that phthaloyl peroxide functions as a selective oxidant for the transformation of arenes to phenols under mild conditions. Although the reaction proceeds through a radical mechanism, aromatic C–H bonds are selectively oxidized in preference to activated C_{sp^3}–H bonds. Notably, a wide array of functional groups are compatible with this reaction, and this method is therefore well suited for late-stage transformations of advanced synthetic intermediates. Quantum mechanical calculations indicate that this transformation proceeds through a novel addition–abstraction mechanism, a kind of 'reverse-rebound' mechanism as distinct from the common oxygen-rebound mechanism observed for metal–oxo oxidants. These calculations also identify the origins of the experimentally observed aryl selectivity.

- One-Step Assembly of Coordination Complexes for Versatile Film and Particle Engineering
  Ejima, H.; Richardson, J. J.; Liang, K.; Best, J. P.; van Koeverden, M. P.; Such, G. K.; Cui, J.; Caruso, F. *Science* **2013**, *341*, 154-157.
  <u>Abstract:</u>



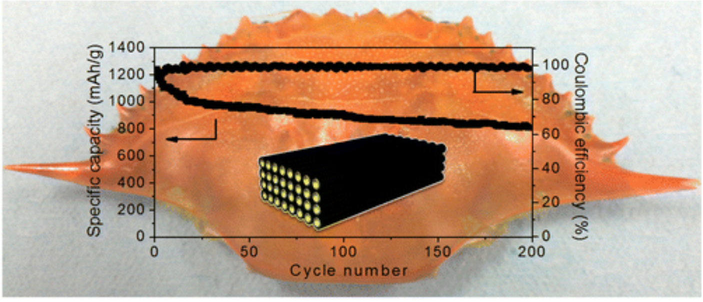
The development of facile and versatile strategies for thin-film and particle engineering is of immense scientific interest. However, few methods can conformally coat substrates of different composition, size, shape, and structure. We report the one-step coating of various interfaces using coordination complexes of natural polyphenols and Fe(III) ions. Film formation is initiated by the adsorption of the polyphenol and directed by pH-dependent, multivalent coordination bonding. Aqueous deposition is performed on a range of planar as well as inorganic, organic, and biological particle templates, demonstrating an extremely rapid technique for producing structurally diverse, thin films and capsules that can disassemble. The ease, low cost, and scalability of the assembly process, combined with pH responsiveness and negligible cytotoxicity, makes these films potential candidates for biomedical and environmental applications.

- Mechanical stiffening of porphyrin nanorings through supramolecular columnar stacking
  Svatek, S. A.; Perdigão, L. M. A.; Stannard, A.; Wieland, M. B.; Kondratuk, D. V.; Anderson, H. L.; O'Shea, J. N.; Beton, P. H. *Nano Lett.* **2013**, *13*, 3391-3395.
  <u>Abstract:</u>



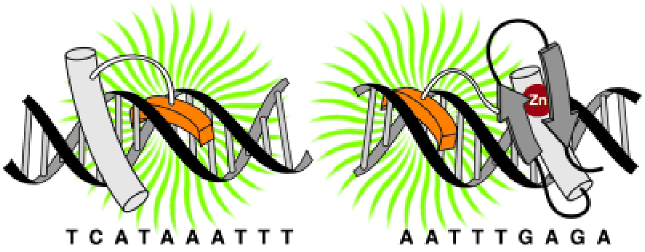
Solvent-induced aggregates of nanoring cyclic polymers may be transferred by electrospray deposition to a surface where they adsorb as three-dimensional columnar stacks. The observed stack height varies from single rings to four stacked rings with a layer spacing of 0.32 ± 0.04 nm as measured using scanning tunneling microscopy. The flexibility of the nanorings results in distortions from a circular shape, and we show, through a comparison with Monte Carlo simulations, that the bending stiffness increases linearly with the stack height. Our results show that noncovalent interactions may be used to control the shape and mechanical properties of artificial macromolecular aggregates offering a new route to solvent-induced control of two-dimensional supramolecular organization.

- Crab shells as sustainable templates from nature for nanostructured battery electrodes
  Yao, H.; Zheng, G.; Li, W.; McDowell, M. T.; Seh, Z.; Liu, N.; Lu, Z.; Cui, Y. *Nano Lett.* **2013**, *13*, 3385-3390.
  Abstract:



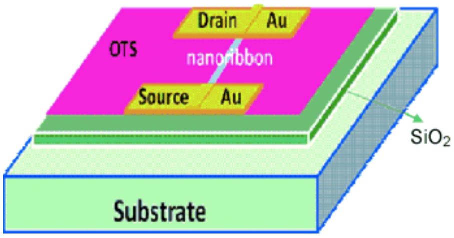
Rational nanostructure design has been a promising route to address critical materials issues for enabling next-generation high capacity lithium ion batteries for portable electronics, vehicle electrification, and grid-scale storage. However, synthesis of functional nanostructures often involves expensive starting materials and elaborate processing, both of which present a challenge for successful implementation in low-cost applications. In seeking a sustainable and cost-effective route to prepare nanostructured battery electrode materials, we are inspired by the diversity of natural materials. Here, we show that crab shells with the unique Bouligand structure consisting of highly mineralized chitin-protein fibers can be used as biotemplates to fabricate hollow carbon nanofibers; these fibers can then be used to encapsulate sulfur and silicon to form cathodes and anodes for Li-ion batteries. The resulting nanostructured electrodes show high specific capacities (1230 mAh/g for sulfur and 3060 mAh/g for silicon) and excellent cycling performance (up to 200 cycles with 60% and 95% capacity retention, respectively). Since crab shells are readily available due to the 0.5 million tons produced annually as a byproduct of crab consumption, their use as a sustainable and low-cost nanotemplate represents an exciting direction for nanostructured battery materials.

- Sequence-Selective DNA Recognition with Peptide–Bisbenzamidine Conjugates
  Sánchez, M. I.; Vázquez, O.; Vázquez, E. M.; Mascareñas, J. L. *Chem. Eur. J.* **2013**, *30*, 9923-9929.
  Abstract:



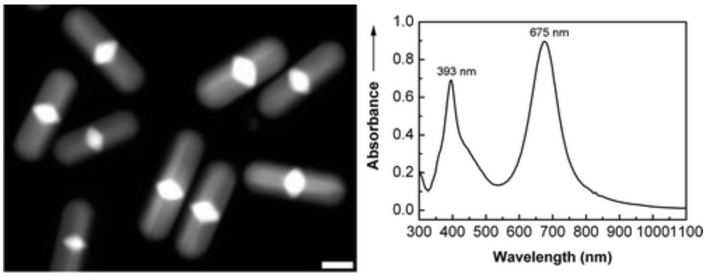
Transcription factors (TFs) are specialized proteins that play a key role in the regulation of genetic expression. Their mechanism of action involves the interaction with specific DNA sequences, which usually takes place through specialized domains of the protein. However, achieving an efficient binding usually requires the presence of the full protein. This is the case for bZIP and zinc finger TF families, which cannot interact with their target sites when the DNA binding fragments are presented as isolated monomers. Herein it is demonstrated that the DNA binding of these monomeric peptides can be restored when conjugated to aza-bisbenzamidines, which are readily accessible molecules that interact with A/T-rich sites by insertion into their minor groove. Importantly, the fluorogenic properties of the aza-benzamidine unit provide details of the DNA interaction that are eluded in electrophoresis mobility shift assays (EMSA). The hybrids based on the GCN4 bZIP protein preferentially bind to composite sequences containing tandem bisbenzamidine–GCN4 binding sites (TCAT·AAATT). Fluorescence reverse titrations show an interesting multiphasic profile consistent with the formation of competitive nonspecific complexes at low DNA/peptide ratios. On the other hand, the conjugate with the DNA binding domain of the zinc finger protein GAGA binds with high affinity (K_D≈12 nM) and specificity to a composite AATTT·GAGA sequence containing both the bisbenzamidine and the TF consensus binding sites.

- Self-Assembled π-Extended Condensed Benzothiophene Nanoribbons for Field-Effect Transistors
  Pan, Z.; Liu, Y.; Fan, F.; Chen, Y.; Li, Y.; Zhan, X.; Song, Y. *Chem. Eur. J.* **2013**, *30*, 9771-9774.
  Abstract:



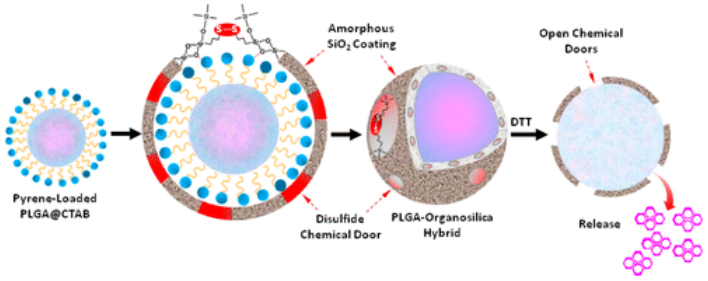
Nanostructures: A new air-stable π-extended condensed benzothiophene was prepared by starting from 4,8-dioctyl-oxybenzo[1,2-b:4,5-b′]dithiophene in about 54 % overall yield. Highly ordered 1D organic nanoribbons of the resultant compound were formed by molecular self-assembly. An individual nanoribbon-based organic field-effect transistor (see figure) exhibited an average mobility of 0.05 $cm^2 V^{-1} s^{-1}$.

- One-Pot Controllable Synthesis of Au@Ag Heterogeneous Nanorods with Highly Tunable Plasmonic Absorption
  Li, C.; Sun, L.; Sun, Y.; Teranishi, T. *Chem. Mater.* **2013**, *25*, 2580-2590.
  Abstract:



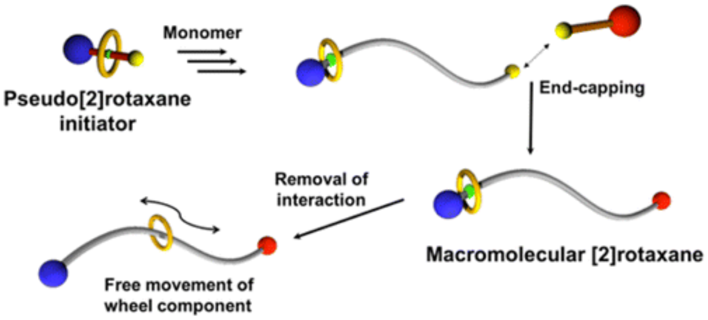
It generally requires a complex workup procedure for the fabrication of Au@Ag heterogeneous nanostructures with an accurate morphology by the present multistep seed-mediated growth approaches. In this paper, we present a new and straightforward method for the controllable synthesis of uniform Au@Ag heterogeneous nanorods (NRs) by coreduction of gold and silver sources in a one-pot polyol reaction. High-quality Au@Ag heterogeneous NRs of various aspect ratios were facilely and selectively produced in high concentration by tuning the initial experimental parameters. Our synthetic approach is highlighted by its simplicity, large-scale production, and controllability of the synthesis. Our study indicates the oxidative etching by O_2/Cl^- pairs plays a key role for the high-yield synthesis of uniform Au@Ag heterogeneous NRs. The size-dependent optical properties of Au@Ag heterogeneous NRs were first and systematically investigated. Our experiments reveal that Au@Ag heterogeneous NRs exhibit two strong absorption peaks that, respectively, originate from the transverse and longitudinal localized surface plasmon resonances (LSPRs). Moreover, the longitudinal LSPR can be facilely tuned from the visible to the near-infrared regions by changing the aspect ratio of Au@Ag heterogeneous NRs. Importantly, Au@Ag heterogeneous NRs synthesized by our method have an excellent stability. They can maintain their optical properties over a long period of time. Au@Ag heterogeneous NRs with an interesting plasmonic property would have fascinating application in surface plasmonics, surface-enhanced Raman scattering, chemical and biological sensing, optical labeling, and information storage.

- Hybrid PLGA-Organosilica Nanoparticles with Redox-Sensitive Molecular Gates
  Quesada, M.; Muniesa, C.; Botella, P. *Chem. Mater.* **2013**, *25*, 2597-2602.
  <u>Abstract:</u>



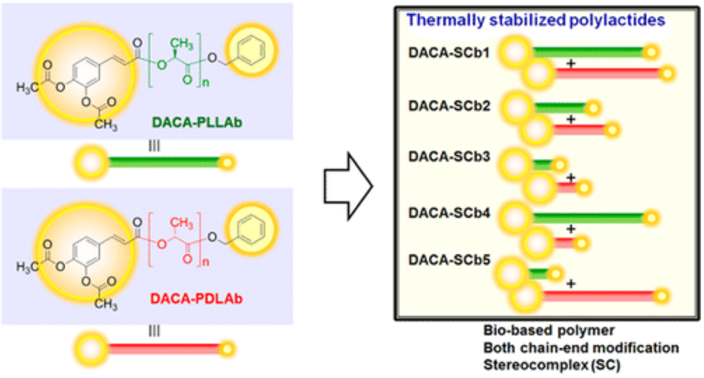
A novel type of hybrid material based on a PLGA nanoparticle core and a redox-responsive amorphous organosilica shell have been successfully synthesized. The outer layer is obtained by self-assembly of silicate ions with a silsesquioxane containing a disulfide bridge. These organic linkers work as molecular gates that can be selectively cleaved by reducing agents. This system is particularly suitable for storage and release of hydrophobic molecules, as the treatment with dithiothreitol leaves open doors that allow for the discharge of encapsulated molecules in the organic matrix. Using pyrene as a probe molecule, it has been shown that after partial disruption of the organic–inorganic coating, the release mechanism from PLGA particles fits pretty well into Higuchi's model, corresponding to a diffusion-mediated process. These nanohybrids impose a better control and slower release of encapsulated molecules than bare PLGA nanoparticles, are reasonably stable in a physiological medium, and show great potential as stimuli-responsive vehicles for drug delivery.

- Macromolecular [2]Rotaxanes: Effective Synthesis and Characterization
  Aoki, D.; Uchida, S.; Nakazono, K.; Koyama, Y.; Takata, T. *ACS Macro Lett.* **2013**, *2*, 461-465.
  <u>Abstract:</u>



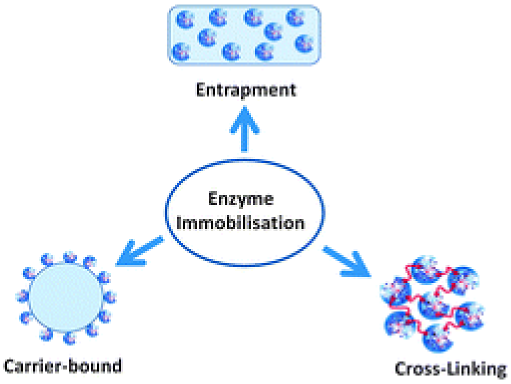
Macromolecular [2]rotaxanes, which consist of a polymer chain threading into a wheel component, were synthesized in high yield and with high purity. The synthesis was achieved by the ring-opening polymerization (ROP) of δ-valerolactone (VL) using a hydroxyl-terminated pseudorotaxane as an initiator with diphenyl phosphate as a catalyst in dichloromethane at room temperature. The ^{1}H NMR, gel permeation chromatography (GPC), and MALDI-TOF-MS measurements of the resulting poly(δ-valerolactone)s clearly indicate the presence of the rotaxane structure with the polymer chain, confirming that the diphenyl phosphate-catalyzed ROP of VL proceeds without deslippage of the wheel component. The obtained macromolecular [2]rotaxane was acetylated to afford a nonionic macromolecular [2]rotaxane, in which only one wheel component is movable from one end to another along the polymer chain.

- Thermally Stabilized Poly(lactide)s Stereocomplex with Bio-Based Aromatic Groups at Both Initiating and Terminating Chain Ends
  Ajiro, H.; Hsiao, Y.-J.; Tran, H. T.; Fujiwara, T.; Akashi, M. *Macromolecules* **2013**, *46*, 5150-5156.
  Abstract:



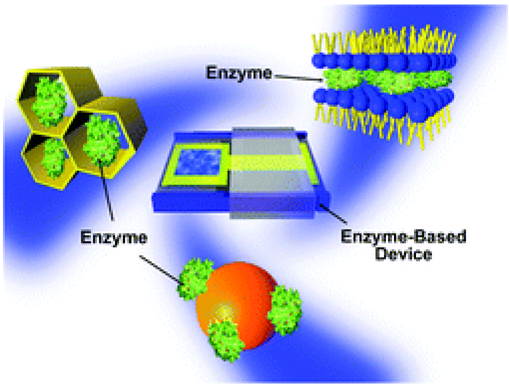
In order to improve the thermal stability of polylactides (PLA), conjugation approaches have been applied to both the terminal and initiating chain end of PLA. We selected benzyl alcohol as the initiator to introduce an aromatic group at one end. The terminal hydroxyl group of the resultant PLAs was conjugated with 3,4-diacetoxycinnamic acid (DACA). The modified polymers showed a dramatic improvement in their thermal decomposing temperature (T_{10}) from 326 to 355 °C. The stereocomplexation of the modified PLAs could be achieved by a variety of molecular weight (M_n) combination. The melting temperature (T_m) increased after stereocomplexation with any size of polymer mixture, but the best improvements on thermal properties in both T_m and T_{10} were obtained by a mixture of specific M_n ranges of enantiomeric PLAs (M_n = 11 400 and 9600). In contrast, the longer and shorter M_n discouraged the simultaneous improvements in the T_m and T_{10}, suggesting that a balance of chain end groups and stereocomplexation efficiency was important.

- Enzyme immobilisation in biocatalysis: why, what and how
  Sheldon, R. A.; Van Pelt, S. *Chem. Soc. Rev.* **2013**, *42*, 6223-6235.
  Abstract:



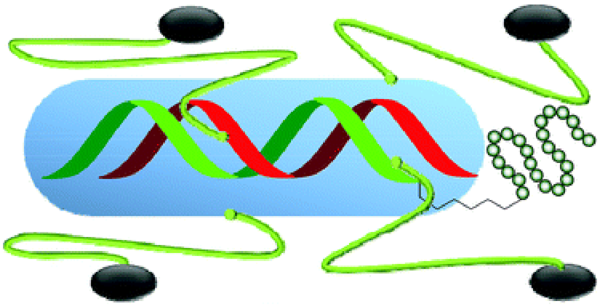
In this tutorial review, an overview of the why, what and how of enzyme immobilisation for use in biocatalysis is presented. The importance of biocatalysis in the context of green and sustainable chemicals manufacture is discussed and the necessity for immobilisation of enzymes as a key enabling technology for practical and commercial viability is emphasised. The underlying reasons for immobilisation are the need to improve the stability and recyclability of the biocatalyst compared to the free enzyme. The lower risk of product contamination with enzyme residues and low or no allergenicity are further advantages of immobilised enzymes. Methods for immobilisation are divided into three categories: adsorption on a carrier (support), encapsulation in a carrier, and cross-linking (carrier-free). General considerations regarding immobilisation, regardless of the method used, are immobilisation yield, immobilisation efficiency, activity recovery, enzyme loading (wt% in the biocatalyst) and the physical properties, *e.g.* particle size and density, hydrophobicity and mechanical robustness of the immobilisate, *i.e.* the immobilised enzyme as a whole (enzyme + support). The choice of immobilisate is also strongly dependent on the reactor configuration used, *e.g.* stirred tank, fixed bed, fluidised bed, and the mode of downstream processing. Emphasis is placed on relatively recent developments, such as the use of novel supports such as mesoporous silicas, hydrogels, and smart polymers, and cross-linked enzyme aggregates (CLEAs).

- Enzyme nanoarchitectonics: organization and device application
  Ariga, K.; Ji, Q.; Mori, T.; Naito, M.; Yamauchi, Y.; Abec, H.; Hillab, J. P. *Chem. Soc. Rev.* **2013**, *42*, 6322-6345.
  Abstract:



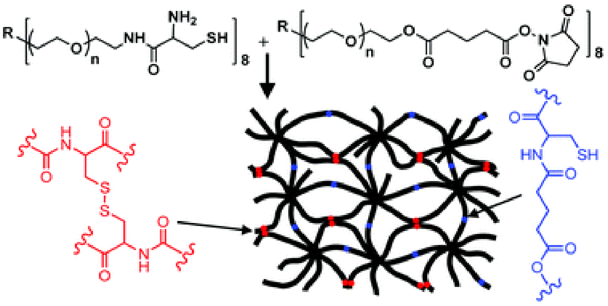
Fabrication of ultrasmall functional machines and their integration within ultrasmall areas or volumes can be useful for creation of novel technologies. The ultimate goal of the development of ultrasmall machines and device systems is to construct functional structures where independent molecules operate as independent device components. To realize exotic functions, use of enzymes in device structures is an attractive solution because enzymes can be regarded as efficient machines possessing high reaction efficiencies and specificities and can operate even under ambient conditions. In this review, recent developments in enzyme immobilization for advanced functions including device applications are summarized from the viewpoint of micro/nano-level structural control, or nanoarchitectonics. Examples are roughly classified as organic soft matter, inorganic soft materials or integrated/organized media. Soft matter such as polymers and their hybrids provide a medium appropriate for entrapment and encapsulation of enzymes. In addition, self-immobilization based on self-assembly and array formation results in enzyme nanoarchitectures with soft functions. For the confinement of enzymes in nanospaces, hard inorganic mesoporous materials containing well-defined channels play an important role. Enzymes that are confined exhibit improved stability and controllable arrangement, which are useful for formation of functional relays and for their integration into artificial devices. Layer-by-layer assemblies as well as organized lipid assemblies such as Langmuir–Blodgett films are some of the best media for architecting controllable enzyme arrangements. The ultrathin forms of these films facilitate their connection with external devices such as electrodes and transistors. Artificial enzymes and enzyme-mimicking catalysts are finally briefly described as examples of enzyme functions involving non-biological materials. These systems may compensate for the drawbacks of natural enzymes, such as their instabilities under harsh conditions. We believe that enzymes and their mimics will be freely coupled, organized and integrated upon demand in near future technologies.

- Biomaterials in RNAi therapeutics: quo vadis?
  Wagner, E. *Biomater. Sci.* **2013**, *1*, 804-809.
  Abstract:



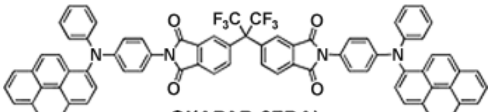
The fifteen years of utilizing RNAi present a surprise story, ranging from the unexpected discovery and publication of RNA interference in 1998, rewarded by the nobel prize in 2006, the introduction of synthetic short siRNAs for the specific gene silencing in mammalian cells in 2001, or the discovery of more than 1600 human microRNAs naturally regulating about one third of our genes. Therapeutic applications started amazingly fast and resulted in the first recent successes in therapy. Synthetic siRNAs are under evaluation for knocking down disease-associated target mRNAs, microRNA mimics for turning on or antagonists (antagomirs) for turning off microRNA activity. Modified oligonucleotides comprise a special class of therapeutics with a new chemical profile; the precise synthetic molecules are much smaller than protein or gene vector drugs, but they are larger than conventional drugs and thus cannot passively diffuse into their target cells. The main current strategies for solving the delivery problem are discussed. We now face the interesting question of alternative future directions: should oligonucleotide molecules be chemically further minimized into small drug-like chemical entities? Or should multiple RNAi molecules be wrapped up into larger virus-like nanoparticles for delivery? Biomaterials in therapeutic RNA interference, *quo vadis*?

- Hydrogels formed by oxo-ester mediated native chemical ligation
  Strehin, I.; Gourevitch, D.; Zhang, Y.; Heber-Katz, E.; Messersmith, P. B. *Biomater. Sci.* **2013**, *1*, 603-613.
  Abstract:

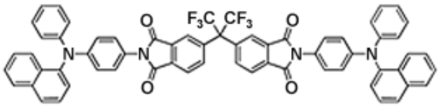


Oxo-ester mediated native chemical ligation (OMNCL) is a variation of the more general native chemical ligation reaction that is widely employed for chemoselective ligation of peptide fragments. While OMNCL has been used for a variety of peptide ligations and for biomolecular modification of surfaces, it is typically practiced under harsh conditions that are unsuitable for use in a biological context. In this report we describe the use of OMNCL for polymer hydrogel formation, *in vitro* cell encapsulation, and *in vivo* implantation. Multivalent polymer precursors containing *N*-hydroxysuccinimide (NHS) activated oxo-esters and *N*-cysteine (*N*-Cys) endgroups were chemically synthesized from branched poly(ethylene glycol) (PEG). Hydrogels formed rapidly at physiologic pH upon mixing of aqueous solutions of NHS and *N*-Cys functionalized PEGs. Quantitative ^{1}H NMR experiments showed that the reaction proceeds through an OMNCL pathway involving thiol capture to form a thioester intermediate, followed by an *S*-to-*N* acyl rearrangement to yield an amide cross-link. pH and temperature were found to influence gelation rate, allowing tailoring of gelation times from a few seconds to a few minutes. OMNCL hydrogels initially swelled before contracting to reach an equilibrium increase in relative wet weight of 0%. This unique behavior impacted the gel stiffness and was attributed to latent formation of disulfide cross-links between network-bound Cys residues. OMNCL hydrogels were adhesive to hydrated tissue, generating a lap shear adhesion strength of 46 kPa. Cells encapsulated in OMNCL hydrogels maintained high viability, and *in situ* formation of OMNCL hydrogel by subcutaneous injection in mice generated a minimal acute inflammatory response. OMNCL represents a promising strategy for chemical cross-linking of hydrogels in a biological context and is an attractive candidate for *in vivo* applications such as wound healing, tissue repair, drug delivery, and tissue engineering.

- Donor–Acceptor Oligoimides for Application in High-Performance Electrical Memory Devices
  Lai, Y.-C.; Kurosawa, T.; Higashihara, T.; Ueda, M.; Chen, W.-C. *Chem. Asian. J.* **2013***, 8,* 1514–1522.
  Abstract:



OI(APAP-6FDA)

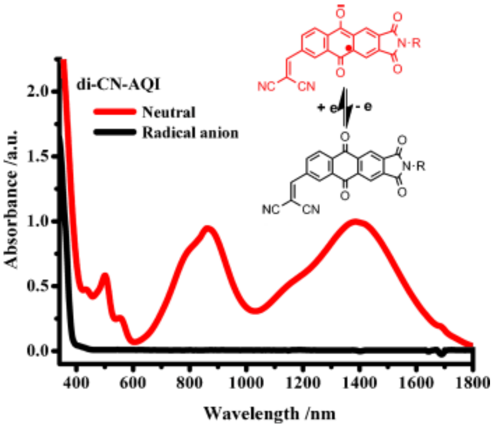


OI(APAN-6FDA)

Two new oligoimides, OI(APAP-6FDA) and OI(APAN-6FDA), which consisted of electron-donating *N*-(4-

*a*minophenyl)-*N*-phenyl-1-aminopyrene (APAP) or *N*-(4-*a*minophenyl)-*N*-phenyl-1-aminonaphthalene (APAN) moieties and electron-accepting 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) moieties, were designed and synthesized for application in electrical memory devices. Such devices, with the indium tin oxide (ITO)/oligoimide/Al configuration, showed memory characteristics, from high-conductance Ohmic current flow to negative differential resistance (NDR), with corresponding film thicknesses of 38 and 48 nm, respectively. The 48 nm oligoimide film device exhibited NDR electrical behavior, which resulted from the diffusion of Al atoms into the oligoimide layer. On further increasing the film thickness to 85 nm, the OI(APAP-6FDA) film device showed a reproducible nonvolatile "write once read many" (WORM) property with a high ON/OFF current ratio (more than $\times 10^4$). On the other hand, the device that was based on the 85 nm OI(APAN-6FDA) film exhibited a volatile static random access memory (SRAM) property. The longer conjugation length of the pyrene unit compared to that of a naphthalene unit was considered to be responsible for the different memory characteristics between these two oligoimides. These experimental results suggested that tunable switching behavior could be achieved through an appropriate design of the donor–acceptor oligoimide structure and controllable thickness of the active memory layer.

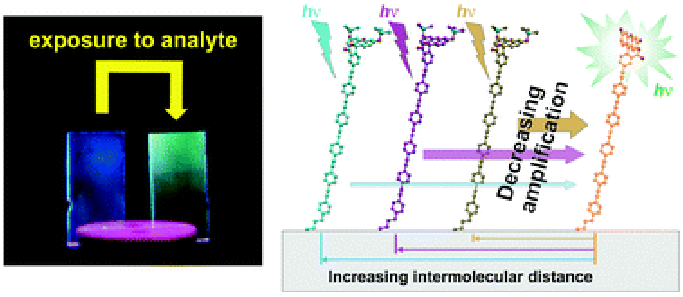
- Colorless to Purple–Red Switching Electrochromic Anthraquinone Imides with Broad Visible/Near-IR Absorptions in the Radical Anion State: Simulation-Aided Molecular Design
  Chen, F.; Zhang, J.; Jiang, H.; Wan, X. *Chem. Asian. J.* **2013***, 8,* 1497 – 1503.
  <u>Abstract:</u>



The large redshift of near-infrared (NIR) absorptions of nitro-substituted anthraquinone imide (Nitro-AQI) radical anions, relative to other AQI derivatives, is rationalized based on quantum chemical calculations. Calculations reveal that the delocalization effects of electronegative substitution in the radical anion states is dramatically enhanced, thus leading to a significant decrease in the HOMO–LUMO band gap in the radical anion states. Based on this understanding, an AQI derivative with an even stronger electron-withdrawing dicyanovinyl (di-CN) substituent was designed and prepared. The resulting molecule, di-CN-AQI, displays no absorption in the Vis/NIR region in the neutral state, but absorbs intensively in the range of λ=700–1000 (λ_{max}≈860 nm) and λ=1100–1800 nm (λ_{max}≈1400 nm) upon one-electron reduction; this is accompanied by a transition from a highly transmissive colorless solution to one that is purple–red. The relationship between calculated radical anionic HOMO–LUMO gaps and the electron-withdrawing capacity of the substituents is also determined by employing Hammett parameter, which could serve as a theoretical tool for further molecular design.

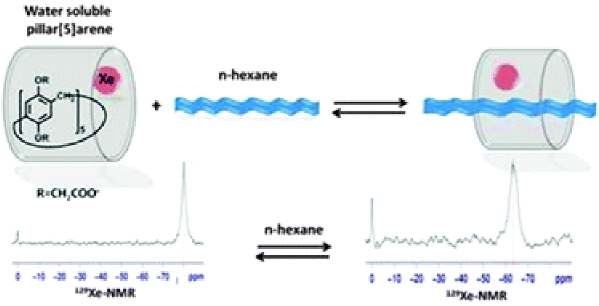
- Thin-film ratiometric fluorescent chemosensors with tunable performance characteristics
  Imsick, B. G.; Acharya, J. R.; Nesterov, E. E. *Chem. Commun*. **2013**, *49*, 7043-7045.

Abstract:



A simple method for tuning the performance characteristics of fluorescent ratiometric sensors based on surface-immobilized monolayers of π-conjugated molecules enabled gradual adjustment of the sensitivity and the analyte detection range of the sensor. This approach has been applied to fine-tune the sensing performance of a prototype ratiometric chemosensor for fluoride ions.

- Potential 129Xe-NMR biosensors based on secondary and tertiary complexes of a water-soluble pillar[5]arene derivative
  Adiri, T.; Marciano, D.; Cohen, Y. *Chem. Commun*. **2013**, *49*, 7082-7084.
  Abstract :

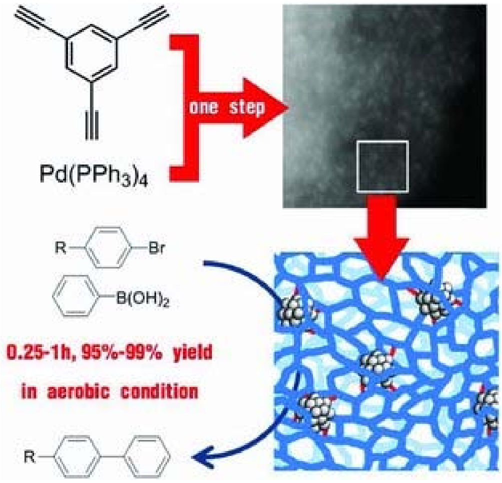


We report on the first secondary and tertiary complexes of the pillar[5]arene derivative 3 with xenon in water. We show that the chemical shift of the encapsulated xenon provides information on the type of the formed complex suggesting that 3 has the potential to be used as a platform for NMR biosensors.

- Smart Nanomachines Based on DNA Self-Assembly
  Song, C.; Wang, Z-G.; Ding, B. *Small* **2013**, *9*, 2382–2392.
  Abstract:

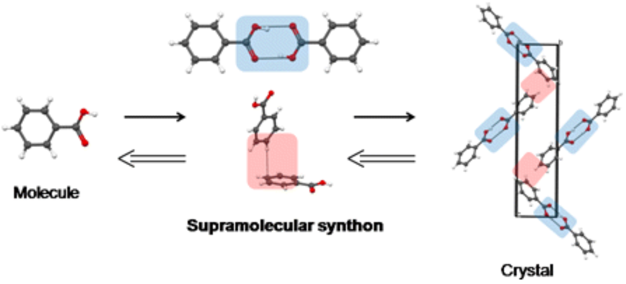
DNA-based nanomachines are self-assembled DNA superstructures that harness chemical free energy to perform mechanical work. The development of DNA machines has benefited greatly from the achievements in both structural and dynamic DNA nanotechnology. In this review, the configurations of DNA machines, fuel systems, and operations are discussed to outline the evolving paths of DNA machines. The focus is on the smart mechanical behavior of DNA machines, from the standpoint of upgrading the complexity of DNA nanostructures, cooperative activation of multimachinary systems, and the establishment of a network of the mechanical states. In the end, the challenges are highlighted and possible solutions are proposed to push forward smart DNA nanomachines, with the goal of creating biomimicking systems. Insights are also provided into the potential applications of the DNA machines with designable intelligence.

- Covalently Stabilized Pd Clusters in Microporous Polyphenylene: An Efficient Catalyst for Suzuki Reactions Under Aerobic Conditions
  Song, Q.; Jia, Y.; Luo, B.; He, H.; Zhi, L. *Small* **2013**, *9*, 2460–2465.
  Abstract:



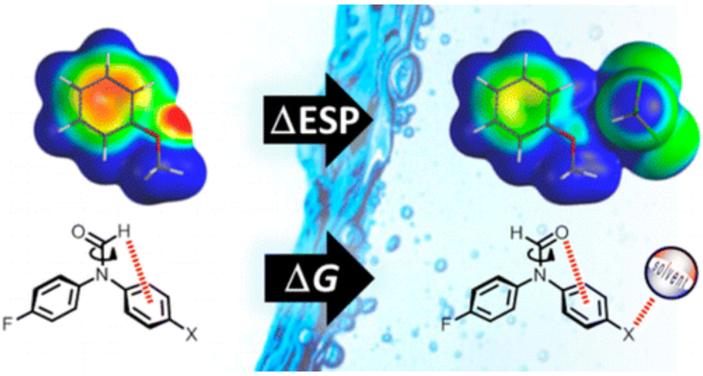
A novel catalyst composed of a microporous polyphenylene network and covalently stabilized Pd clusters (Pd/MPP) for highly efficient Suzuki–Miyaura coupling is synthesized with an in-situ one-pot chemical approach, through the catalytic trimerization of 1,3,5-triethynylbenzene. The unique Pd/MPP cluster exhibits very high catalytic activity for a broad scope of Suzuki–Miyaura reactions with short reaction time, good yield, and high turnover number and turnover frequency values, even in aqueous media under aerobic conditions. The strong covalent interaction between Pd and MPP network prevents the agglomeration or leaching of Pd clusters and enables the catalyst to remain highly active, even after a number of cycles.

- Crystal Engineering: From Molecule to Crystal
  Desiraju, G. R. *J. Am. Chem. Soc.* **2013***, 135*, 9952–9967.
  Abstract:



How do molecules aggregate in solution, and how do these aggregates consolidate themselves in crystals? What is the relationship between the structure of a molecule and the structure of the crystal it forms? Why do some molecules adopt more than one crystal structure? Why do some crystal structures contain solvent? How does one design a crystal structure with a specified topology of molecules, or a specified coordination of molecules and/or ions, or with a specified property? What are the relationships between crystal structures and properties for molecular crystals? These are some of the questions that are being addressed today by the crystal engineering community, a group that draws from the larger communities of organic, inorganic, and physical chemists, crystallographers, and solid state scientists. This Perspective provides a brief historical introduction to crystal engineering itself and an assessment of the importance and utility of the supramolecular synthon, which is one of the most important concepts in the practical use and implementation of crystal design. It also provides a look to the future from the viewpoint of the author, and indicates some directions in which this field might be moving.

- Electrostatic Modulation of Aromatic Rings via Explicit Solvation of Substituents
  Muchowska, K. B.; Adam, C.; Mati, I. K.; Cockroft, S. L. *J. Am. Chem. Soc.* **2013**, *135*, 9976–9979.
  Abstract:



Solvent effects are implicated as playing a major role in modulating electrostatic interactions via through-space and polarization effects, but these phenomena are often hard to dissect. By using synthetic molecular torsion balances and a simple explicit solvation model, we demonstrate that the solvation of substituents substantially affects the electrostatic potential of aromatic rings. Although polarization effects are important, we show that a simple additive through-space model also provides a reasonable account of the experimental data. The results deliver insights into solvent structure and might contribute to the development of computationally inexpensive solvent models.