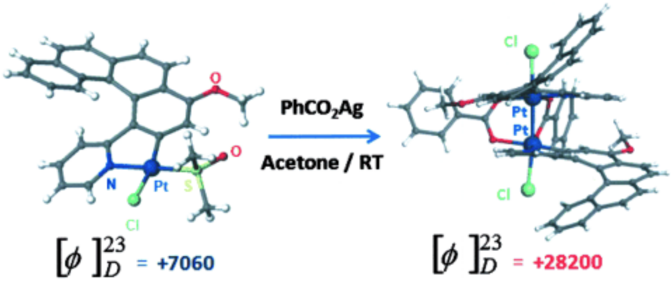
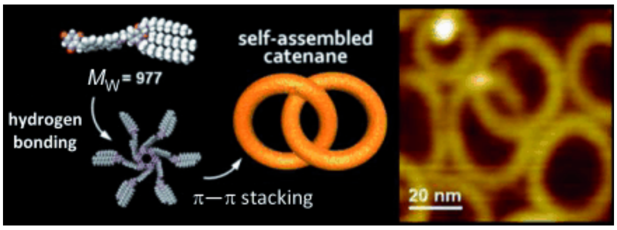
- Multifunctional and Reactive Enantiopure Organometallic Helicenes : Tuning Chiroptical Properties by Structural Variations of Mono- and Bis(platinahelicene)s
  Anger, E.; Rudolph, M.; Norel, L.; Zrig, S.; Shen, C.; Vanthuyne, N.; Toupet, L.; Williams, J. A. G.; Roussel, C.; Autschbach, J.; Crassous, J.; Réau R. *Chem. Eur. J.* **2011**, *17*, 14178-14198.
  Abstract:



Acetylacetonato-platina[6]- and -platina[7]helicenes have been prepared from 2-pyridyl-substituted benzophenanthrene ligands by following a two-step cycloplatination reaction. The photophysical properties (UV-visible absorption and emission behavior) and chiroptical properties (circular dichroism and molar rotation) of the resolved enantiomers have been measured. These metallahelicenes constitute a novel family of easily accessible helicene derivatives that exhibit large and tuneable chiroptical properties that can be rationalized theoretically and compared to the parent [6]- and [7]carbohelicenes. Furthermore, they are red phosphors at room temperature and their large chiroptical properties can be modulated by oxidation of the metal center to PtIV. Hetero- and homochiral diastereomeric bis(metallahelicene)s that possess a rare PtIIIPtIII scaffold bridged by benzoato ligands have also been prepared. It is shown that the heterochiral (P,M)-bis(PtIII–[6]helicene) 9�a1 can isomerize into the homochiral (P,P)- and (M,M)-bis(PtIII–[6]helicene) 9�a2. Spectral assignments and an analysis of the optical rotation of these systems were made with the help of time-dependent density functional theory. The calculations highlight the contributions of the metal centers to the chiroptical properties. For 9�a1 and 9�a2, σ–π conjugation between the helicenes and the PtPt moiety may contribute strongly to the optical rotation and electronic circular dichroism.

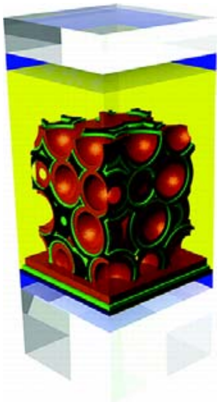
- Catenation of Self-Assembled Nanorings
  Yagai, S.; Got, Y.; Karatsu, T.; Kitamura, A.; Kikkawa, Y. *Chem. Eur. J.* **2011**, *17*, 13657-13660.
  Abstract:



Till death do us part: Catenation of toroidal nanostructures (nanorings), self-assembled from more than 1000 small molecular building blocks in solution, occurs when aggregation takes place under high solution concentrations. The formation of interlocked circular nanostructures is prima facie visual evidence for the existence of self-assembled nanorings in solution (see AFM image).

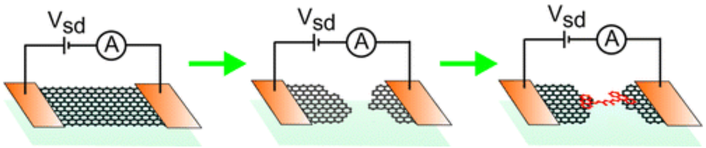
- High-Efficiency Dye-Sensitized Solar Cell with Three-Dimensional Photoanode
  Tétreault, N.; Arsenault,E.; Heiniger, L. P.; Soheilnia, N.; Brillet, J.; Moehl,T.; Zakeeruddin, S.; Ozin, G. A.; Grätzel, M. *Nano Lett.* **2011***, 11, 4579–4584*

Abstract:



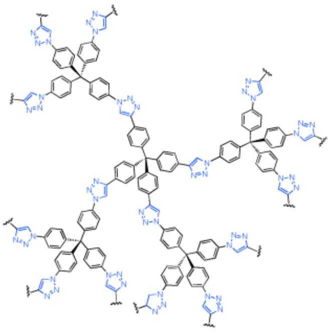
Herein, we present a straightforward bottom-up synthesis of a high electron mobility and highly light scattering macroporous photoanode for dye-sensitized solar cells. The dense three-dimensional Al/ZnO, SnO_2, or TiO_2 host integrates a conformal passivation thin film to reduce recombination and a large surface-area mesoporous anatase guest for high dye loading. This novel photoanode is designed to improve the charge extraction resulting in higher fill factor and photovoltage for DSCs. An increase in photovoltage of up to 110 mV over state-of-the-art DSC is demonstrated.

- Room-Temperature Gating of Molecular Junctions Using Few-Layer Graphene Nanogap Electrodes
  Prins, F.; Barreiro, A.; Ruitenberg, J. W.; Seldenthuis, J. S.; Alcalde, N. A.; Vandersypen, L. M. K.; van der Zant, S. J. *Nano Lett.* **2011**,*11,* 4607–4611.
  Abstract:



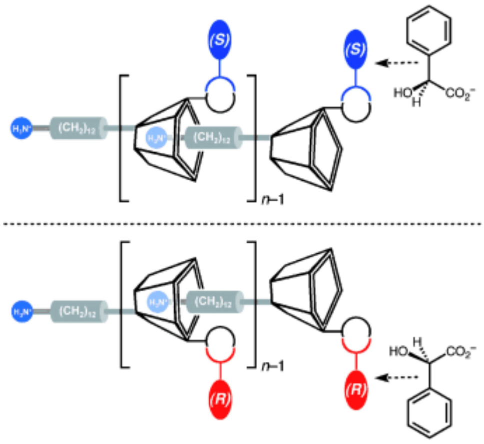
We report on a method to fabricate and measure gateable molecular junctions that are stable at room temperature. The devices are made by depositing molecules inside a few-layer graphene nanogap, formed by feedback controlled electroburning. The gaps have separations on the order of 1–2 nm as estimated from a Simmons model for tunneling. The molecular junctions display gateable *I*–*V*-characteristics at room temperature.

- Click Chemistry Finds Its Way into Covalent Porous Organic Materials
  Muller, T.; Bräse, S. *Angew. Chem. Int. Ed.* **2011**, 50, *11*, 11844–11845.
  Abstract:



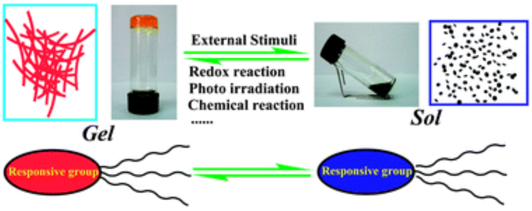
Click the CMPs and POPs: The Huisgen 1,3-dipolar cycloaddition reaction can be used to generate covalent porous organic materials such as conjugated microporous polymers (CMPs) and porous organic polymers (POPs). A triazole-linked network based on complementary tetrahedral monomers has been prepared by means of click chemistry.

- Anion-Assisted Supramolecular Polymerization: From Achiral AB-Type Monomers to Chiral Assemblies
  Capici, C.; Cohen, Y.; D'Urso, A.; Gattuso, G.; Notti, A.; Pappalardo, A.; Pappalardo, S.; Parisi, M. F.; Purrello, R.; Slovak, S.; Villari, V. *Angew. Chem. Int.* Ed. **2011**, *50*, 11956–11961.
  Abstract:



Anions do make a difference! Counterions released during the acid-promoted self-assembly of AB-type monomer precursors dock into designated ancillary binding sites and thus facilitate the polymerization process while transferring their molecular properties to the entire supramolecular structure (see picture).

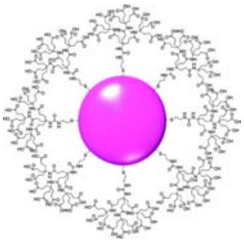
- Stimuli responsive gels based on low molecular weight gelators
  Yang, X.; Zhang, G.; Zhang, D. *J. Mater. Chem*. **2011**, *22*, 38-50.
  Abstract:



In this feature article we summarize the recent developments of stimuli responsive gels based on low molecular weight gelators (LMWGs) for which the gel-sol transitions can be triggered by other stimuli besides heating. These include gels responsive to redox reactions and light irradiations. Chemoresponsive gels are also introduced, including those for which the gel-sol transitions can be induced by reactions with neutral molecules and those for which the gel strength is improved following the addition of neutral molecules. Perspectives for such stimuli responsive gels are discussed with regard to their potential applications and remaining challenging issues.

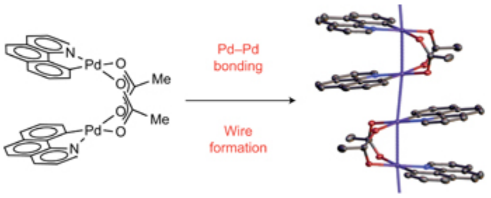
- Newkome-Type Dendron-Stabilized Gold Nanoparticles : Synthesis,Reactivity, and Stability
  Cho, T. J.; Zangmeister, R. A.; MacCuspie, R. I.; Patri, A. K.; Hackley, V. A. *Chem. Mater*. **2011,** *23*, 2665-2676.

Abstract:



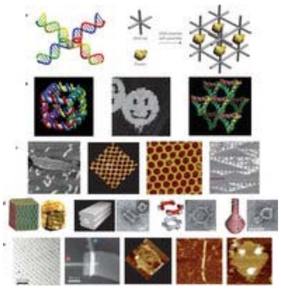
We report the synthesis and evaluation of four Newkome-type dendrons, G1-COOH, G2-COOH, SH-G1-COOH, and TA-G1-COOH, and their respective gold-dendron conjugates, where GX represents the generation number. G1- and G2-COOH are two-directional symmetric dendrons that have cystamine cores containing a disulfide group. SH-G1-COOH was prepared by treatment of G1-COOH with dithioerythritol to yield a free thiol group to replace the disulfide linkage. TA-G1-COOH has a thioctic acid moiety, which is a five-membered ring containing a disulfide group that cleaves to produce two anchoring thiols to bond with the gold surface. All dendrons have peripheral carboxylate groups to afford hydrophilicity and functionality. Gold nanoparticle conjugates were prepared by reaction of each dendron solution with a suspension of gold colloid (nominally 10 nm diameter) and purified by stirred cell ultrafiltration. Chemical structures were confirmed by 1H and 13C nuclear magnetic resonance spectroscopy and matrix assisted laser desorption/ionization time-of-flight mass spectrometry. Particle size and surface plasmon resonance of the conjugates were characterized by dynamic light scattering (DLS) and UV-vis spectroscopy, respectively. X-ray photoelectron spectroscopy (XPS) was utilized to confirm covalent bonding between the thiols on the dendron and the gold surface. XPS also revealed changes in the S/Au intensity ratio as a function of the dendron chemical structure, suggesting steric effects play a role in the reaction and/or conformation of dendrons on the gold surface. The colloidal and chemical stability of the conjugates as a function of temperature, pH, and suspending medium, and with respect to chemical resistance toward KCN, was investigated using DLS and UV-vis absorption.

- Synthesis and structure of solution-stable one-dimensional palladium wires
  Campbell, M. G.; Powers, D. C.; Raynaud, J.; Graham, M. J.; Xie, P.; Lee, E.; Ritter, T. *Nature Chem.* **2011**, *3*, 949-953.
  Abstract:



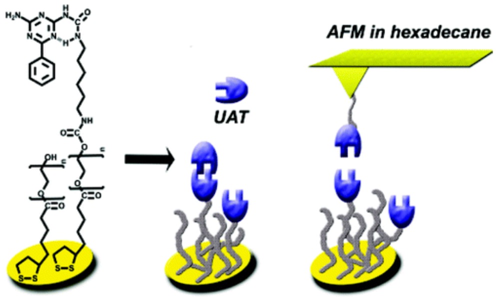
One-dimensional metal wires are valuable materials because of their optical and electronic anisotropy, and they have potential utility in devices such as photovoltaic cells and molecular sensors. However, despite more than a century of research, only a few examples exist of well-defined one-dimensional (1D) metal wires that allow for the rational variation of conductivity. Herein we describe the first examples of 1D molecular wires supported by Pd–Pd bonds, the thin-film conductive properties of which can be altered by controlled molecular changes. Wires based on Pd(III) give semiconducting films with a modifiable bandgap, whereas wires based on Pd(2.5) give films that display metallic conductivity above 200 K: a metallic state has not been reported previously for any polymer composed of 1D metal wires. The wires are infinite in the solid state and maintain 1D structures in solution with lengths of up to 750 nm. Solution stability enables thin film coating, a requisite for device fabrication using molecular wires.

- Challenges and opportunities for structural DNA nanotechnology
  Pinheiro, A. V.; Han, D.; Shih, W. M.; Yan, H. *Nature Nanotech.* **2011**, *6*, 763-772.
  Abstract:



DNA molecules have been used to build a variety of nanoscale structures and devices over the past 30 years, and potential applications have begun to emerge. But the development of more advanced structures and applications will require a number of issues to be addressed, the most significant of which are the high cost of DNA and the high error rate of self-assembly. Here we examine the technical challenges in the field of structural DNA nanotechnology and outline some of the promising applications that could be developed if these hurdles can be overcome. In particular, we highlight the potential use of DNA nanostructures in molecular and cellular biophysics, as biomimetic systems, in energy transfer and photonics, and in diagnostics and therapeutics for human health.

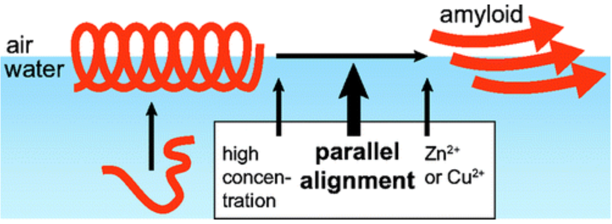
- Self-Complementary Recognition of Supramolecular Urea–Aminotriazines in Solution and on Surfaces
  Embrechts, A.; Velders, A. H.; Schönherr, H.; Vancso, G. J. *Langmuir* **2011**, *27*, 14272-14278.
  Abstract:



The recognition of self-complementary quadruple urea–aminotriazine (UAT)-based hydrogen-bonded arrays was investigated in solution and at surfaces. For this purpose, an UAT-based donor–acceptor–donor–acceptor (DADA) array and complementary receptors were synthesized. Two-dimensional proton nuclear magnetic resonance (^{1}H NMR) measurements in $CDCl_3$ pointed at an intramolecular hydrogen-bond stabilization of the UAT, which promotes a planar molecular geometry and, thereby, results in a significant stabilization of the dimeric complex. The bond strength of the UAT dimers at surfaces was determined by atomic force microscopy-based single molecule force spectroscopy (AFM–SMFS) in hexadecane. The UAT receptor was immobilized on gold surfaces using an ultrathin layer of ethylene glycol terminated lipoic acid and isocyanate chemistry. The layers obtained and the reversible self-complementary recognition were thoroughly characterized with contact angle measurements, grazing angle Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and AFM. Loading rate-dependent SMFS measurements yielded a barrier width

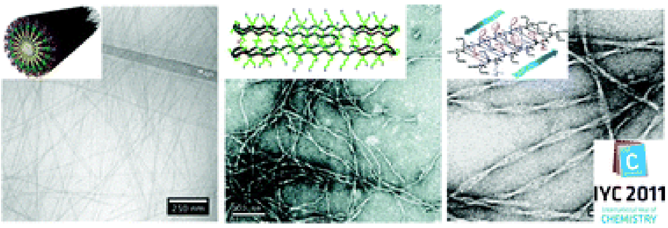
x_β and a bond lifetime at zero force $t_{off}(0)$ of 0.29 ± 0.02 nm and 100 ± 80 ms, respectively. The value of the corresponding off-rate constant k_{off} suggests a substantially larger value of the dimerization constant compared to theoretical predictions, which is fully in line with the additional intramolecular hydrogen-bond stabilization detected in solution by ^{1}H NMR spectroscopy.

- Triggers for β-Sheet Formation at the Hydrophobic–Hydrophilic Interface : High Concentration, In-Plane Orientational Order, and Metal Ion Complexation
  Hoernke, M.; Falenski, J. A.; Schwieger, C.; Koksch, B.; Brezesinski, G. *Langmuir* **2011**, *27*, 14218-14231.
  <u>Abstract:</u>



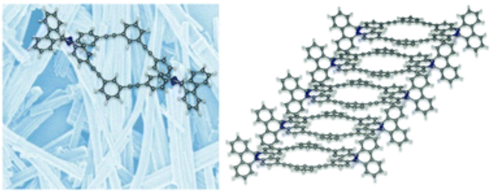
Amyloid formation plays a causative role in neurodegenerative diseases such as Alzheimer's disease or Parkinson's disease. Soluble peptides form β-sheets that subsequently rearrange into fibrils and deposit as amyloid plaques. Many parameters trigger and influence the onset of the β-sheet formation. Early stages are recently discussed to be cell-toxic. Aiming at understanding various triggers such as interactions with hydrophobic–hydrophilic interfaces and metal ion complexation and their interplay, we investigated a set of model peptides at the air–water interface. We are using a general approach to a variety of diseases such as Alzheimer's disease, Parkinson's disease, and type II diabetes that are connected to amyloid formation. Surface sensitive techniques combined with film balance measurements have been used to assess the conformation of the peptides and their orientation at the air–water interface (IR reflection–absorption spectroscopy). Additionally, the structures of the peptide layers were characterized by grazing incidence X-ray diffraction and X-ray reflectivity. The peptides adsorb to the air–water interface and immediately adopt an α-helical conformation. This helical intermediate transforms into β-sheets upon further triggering. The factors that result in β-sheet formation are dependent on the peptide sequence. In general, the interface has the strongest effect on peptide conformation compared to high concentrations or metal ions. Metal ions are able to prevent aggregation in bulk but not at the interface. At the interface, metal ion complexation has only minor effects on the peptide secondary structure, influencing the in-plane structure that is formed in two dimensions. At the air–water interface, increased concentrations or a parallel arrangement of the α-helical intermediates are the most effective triggers. This study reveals the role of various triggers for β-sheet formation and their complex interplay. Our main finding is that the hydrophobic–hydrophilic interface largely governs the conformation of peptides. Therefore, the present study implies that special care is needed when interpreting data that may be affected by different amounts or types of interfaces during experimentation.

- Self-assembling peptide scaffolds for regenerative medicine
  Matson J. B.; Stupp, S. I. *Chem. Commun.* **2012**, *48*, 26-33.
  <u>Abstract:</u>



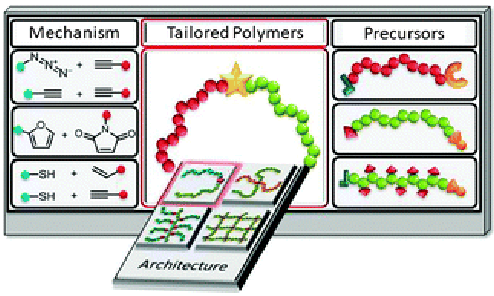
Biomaterials made from self-assembling, short peptides and peptide derivatives have great potential to generate powerful new therapies in regenerative medicine. The high signaling capacity and therapeutic efficacy of peptidic scaffolds has been established in several animal models, and the development of more complex, hierarchical structures based on peptide materials is underway. This highlight discusses several classes of self-assembling peptide-based materials, including peptide amphiphiles, Fmoc-peptides, self-complementary ionic peptides, hairpin peptides, and others. The self-assembly designs, bioactive signalling strategies, and cell signalling capabilities of these bioactive materials are reported. The future challenges of the field are also discussed, including short-term goals such as integration with biopolymers and traditional implants, and long term goals, such as immune system programming, subcellular targeting, and the development of highly integrated scaffold systems.

- Columnar self-assembly of rhomboid macrocyclic molecules via step-like intermolecular interaction. Crystal formation and gelation
  Ide, T.; Takeuchi, D.; Osakada, K. *Chem. Commun.* **2012,** *48*, 278-280.
  <u>Abstract:</u>



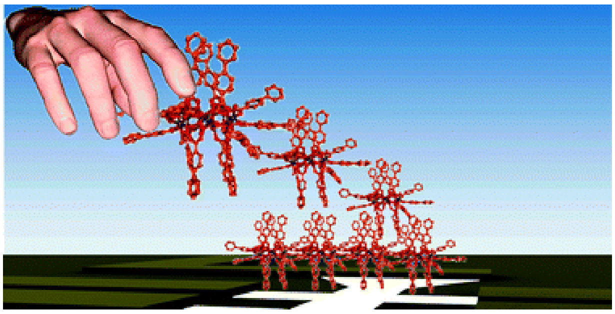
Two macrocyclic compounds with a rhomboid molecular shape, composed of a π-conjugated framework and an imine or amine functionality, were synthesized. The amine-containing macrocycle crystallizes with step-like interaction of each molecule, forming a columnar arrangement, although dispersion of the imine gelates upon ultrasonification.

- "Clicking" on/with polymers: a rapidly expanding field for the straightforward preparation of novel macromolecular architectures
  Kempe, K.; Krieg, A.; Becer, C. R. ; Schubert, *U. S. Chem. Soc. Rev.* **2012**, *41*, 176-191.
  <u>Abstract:</u>



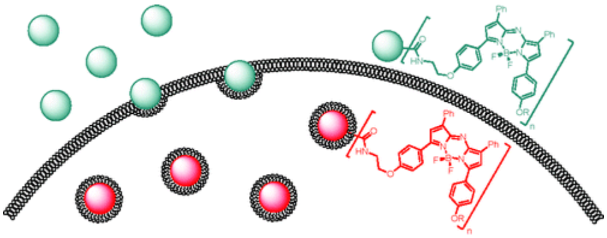
The combination of controlled polymerization techniques and "click" reactions form an efficient platform for the preparation of polymers in various architectures. In this *critical review*, an update of our 2007 review in *Chem. Soc. Rev.*, we focus on the "click" reactions that have been used widely in the last four years to create new polymer architectures. Not only block copolymers and star-shaped polymers but also cyclic and dendritic macromolecules could be synthesized using these robust “click” reactions (205 references).

- Advances on structuring, integration and magnetic characterization of molecular nanomagnets on surfaces and devices
  Domingo, N.; Bellido, E.; Ruiz-Molina, D. *Chem. Soc. Rev.* **2012**, *41*, 258-302.
  Abstract:



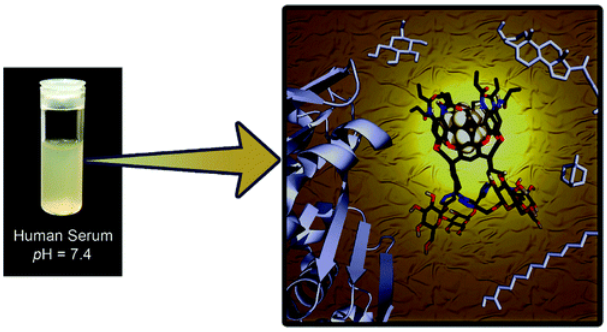
This *critical review* represents a concise revision of the different experimental approaches so far followed for the structuration of molecular nanomagnets on surfaces, since the first reports on the field more than ten years ago. Afterwards, a presentation of the different experimental approaches followed for their integration in sensors is described. Such work involves mainly two families of sensors and devices, microSQUIDs sensors and three-terminal devices for single-molecule detection. Finally the last section is devoted to a detailed revision of the different experimental techniques that can be used for the magnetic characterization of these systems on surfaces, ranging from magnetic circular dichroism to magnetic force microscopy. The use of these techniques to characterize other nanostructured magnetic materials, such as nanoparticles, is also revised. The aim is to give a broad overview of the last advances achieved with these techniques and their potential and evolution over the next years.

- Cellular Uptake Mediated Off/On Responsive Near-Infrared Fluorescent Nanoparticles
  Palma, A.; Alvarez, L. A.; Scholz,D.; Frimannsson, D. O.; Grossi,M.; Quinn, S. J.; O’Shea, D. F. *J. Am. Chem. Soc.* **2011**, *133*, 19618-19621.
  Abstract:



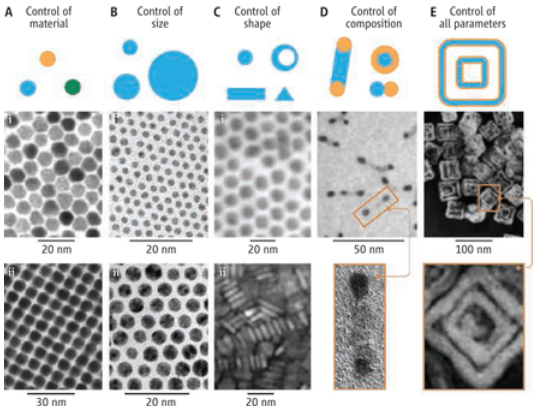
Fluorescence imaging, utilizing molecular fluorophores, often acts as a central tool for the investigation of fundamental biological processes and offers huge future potential for human imaging coupled to therapeutic procedures. An often encountered limitation with fluorescence imaging is the difficulty in discriminating nonspecific background fluorophore emission from a fluorophore localized at a specific region of interest. This limits imaging to individual time points at which background fluorescence has been minimized. It would be of significant advantage if the fluorescence output could be modulated from *off* to *on* in response to specific biological events as this would permit imaging of such events in real time without background interference. Here we report our approach to achieve this for the most fundamental of cellular processes, i.e. endocytosis. We describe a new near-infrared *off* to *on* fluorescence switchable nanoparticle construct that is capable of switching its fluorescence on following cellular uptake but remains switched off in extracellular environments. This permits continuous real-time imaging of the uptake process as extracellular particles are nonfluorescent. The principles behind the fluorescence off/on switch can be understood by encapsulation of particles in cellular organelles which effect a microenvironmental change establishing a fluorescence signal.

- A Carbohydrate-Conjugated Deep Cavitand Permits Observation of Caviplexes in Human Serum
  Ryan, D. A.; Rebek, J. Jr. *J. Am. Chem. Soc.* **2011**, *133*, 19653-19655.
  Abstract:



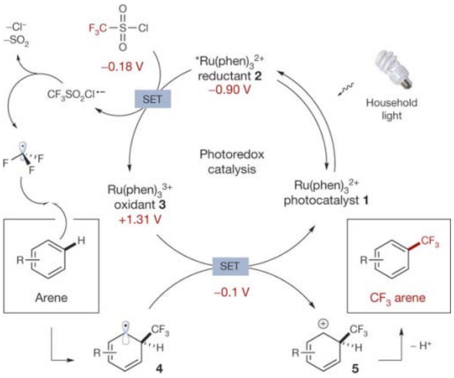
A deep cavitand was covalently modified with carbohydrates to provide solubility in biologically relevant environments and to investigate its receptor function. Specifically, a tetrakis(β-d-glucosyl) cavitand (**1**) that was soluble in neutral water or acid/base-buffered solutions was synthesized, and it formed complexes with hydrophobic small molecules. Extraction of the cavitand into aqueous sodium dodecyl sulfate micelles as simple membrane mimetics increased the scope of guests bound by **1** beyond that observed in only aqueous media. Complex formation was also detected in human serum. The findings show the functional compatibility of the receptor in both micelle-bound and serum-soluble forms.

- Complex Colloidal Assembly
  Parak, W. J. *Science* **2011,** *334*, 1359-1360.
  Abstract:



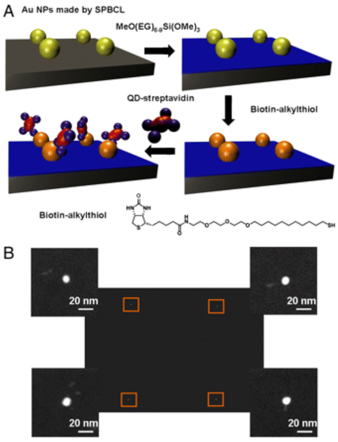
Since the popularization of nanotechnology almost two decades ago, the public has been fascinated by the prospect of a “nano-assembler” for the construction of complex three-dimensional (3D) objects. Such a device would assemble objects atom-by-atom or molecule-by-molecule. Indeed, small objects have been assembled on a 2D surface by picking up individual atoms and molecules with the tip of a scanning tunneling microscope or an atomic force microscope, respectively (1, 2). However, it is not only the action of gripping an object that presents a challenge, but also its release at the designated position. The Nobel laureate Richard Smalley described this as a problem of “sticky fingers” (3). There is, however, an alternative approach for bottom-up assembly on the nanometer scale that originates from colloidal chemistry. On page 1377 of this issue, González et al. (4) report on the synthesis of complex 3D colloidal nanoparticles, a route that may circumvent the problem of the sticky nano-finger.

- Trifluoromethylation of arenes and heteroarenes by means of photoredox catalysis
  Nagib, D. A.; MacMillan, D. W. C. *Nature* **2011,** *480*, 224-228.
  Abstract:



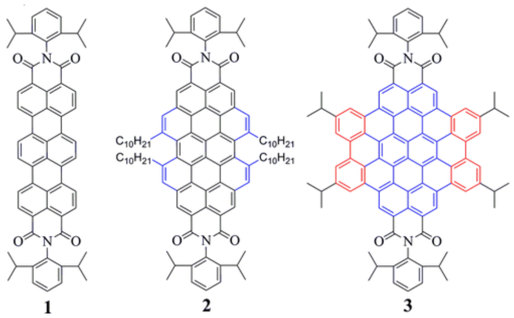
Modern drug discovery relies on the continual development of synthetic methodology to address the many challenges associated with the design of new pharmaceutical agents1. One such challenge arises from the enzymatic metabolism of drugs in vivo by cytochrome P450 oxidases, which use single-electron oxidative mechanisms to rapidly modify small molecules to facilitate their excretion2. A commonly used synthetic strategy to protect against in vivo metabolism involves the incorporation of electron-withdrawing functionality, such as the trifluoromethyl (CF3) group, into drug candidates3. The CF3 group enjoys a privileged role in the realm of medicinal chemistry because its incorporation into small molecules often enhances efficacy by promoting electrostatic interactions with targets, improving cellular membrane permeability, and increasing robustness towards oxidative metabolism of the drug4, 5, 6. Although common pharmacophores often bear CF3 motifs in an aromatic system, access to such analogues typically requires the incorporation of the CF3 group, or a surrogate moiety, at the start of a multi-step synthetic sequence. Here we report a mild, operationally simple strategy for the direct trifluoromethylation of unactivated arenes and heteroarenes through a radical-mediated mechanism using commercial photocatalysts and a household light bulb. We demonstrate the broad utility of this transformation through addition of CF3 to a number of heteroaromatic and aromatic systems. The benefit to medicinal chemistry and applicability to late-stage drug development is also shown through examples of the direct trifluoromethylation of widely prescribed pharmaceutical agents.

- Single-molecule protein arrays enabled by scanning probe block copolymer lithography.
  Chai, J.; Wong, L. S.; Giam, L.; Mirkin, C. A., *Proc. Nat. Acad. Sci. USA* **2011,** *108*, 19521-19525.
  Abstract:



The ability to control the placement of individual protein molecules on surfaces could enable advances in a wide range of areas, from the development of nanoscale biomolecular devices to fundamental studies in cell biology. Such control, however, remains a challenge in nanobiotechnology due to the limitations of current lithographic techniques. Herein we report an approach that combines scanning probe block copolymer lithography with site-selective immobilization strategies to create arrays of proteins down to the single-molecule level with arbitrary pattern control. Scanning probe block copolymer lithography was used to synthesize individual sub-10-nm single crystal gold nanoparticles that can act as scaffolds for the adsorption of functionalized alkylthiol monolayers, which facilitate the immobilization of specific proteins. The number of protein molecules that adsorb onto the nanoparticles is dependent upon particle size; when the particle size approaches the dimensions of a protein molecule, each particle can support a single protein. This was demonstrated with both gold nanoparticle and quantum dot labeling coupled with transmission electron microscopy imaging experiments. The immobilized proteins remain bioactive, as evidenced by enzymatic assays and antigen-antibody binding experiments. Importantly, this approach to generate single-biomolecule arrays is, in principle, applicable to many parallelized cantilever and cantilever-free scanning probe molecular printing methods.

- Core-Extended Terrylene Diimide on the Bay Region: Synthesis and Optical and Electrochemical Properties
  Bai, Q.; Gao, B.; Ai, Q.; Wu, Y.; Ba, X. *Org. Lett.* **2011**, *13*, 6484–6487.
  Abstract:



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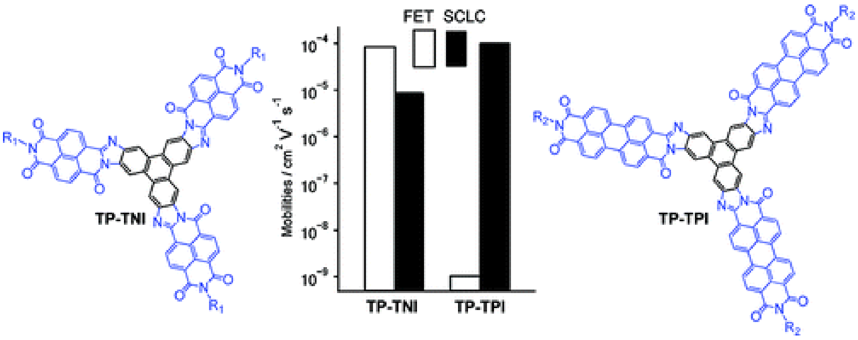
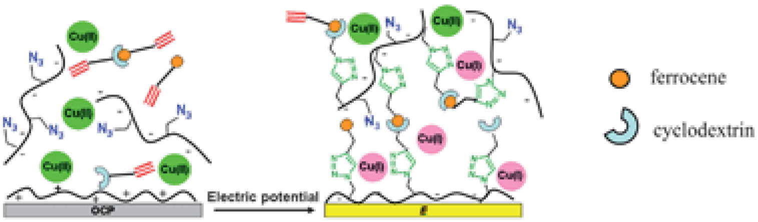
Two novel core-extended terrylene diimides on the bay region (CETDIs) were synthesized via annulation of the four additional ethylene units or benzene units on the bay region of the terrylene diimide core. The optical and electrochemical properties of the two compounds were investigated. These CETDIs exhibited broad absorption spectra with high extinction coefficients, which span a wide range in the ultraviolet and visible spectrum from 300 to 700 nm. Furthermore, the redox process of the CETDIs increased from two waves to four waves, and the lowest unoccupied molecular orbital (LUMO) levels were enhanced from −4.00 to −3.59 eV.

- Charge Transport Anisotropy in *n*-Type Disk-Shaped Triphenylene-Tris(aroyleneimidazole)s
  Zhang, Y.; , Hanifi, D.; , Alvarez, S.; Antonio, F.; Pun, A.; Klivansky, L. M.; Hexemer, A.; Ma, B.; Liu, Y. *Org. Lett.* **2011**, *13*, 6528–6531.
  Abstract:



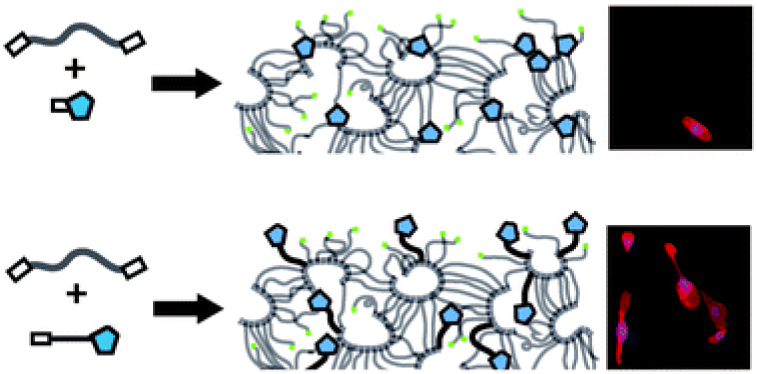
Two novel n-type disk-shaped molecules containing a triphenylene core and three fused naphthaleneimide imidazole or peryleneimide imidazole “arms” are synthesized and characterized. The n-type charge carrier mobilities of these molecules are evaluated by both field effect transistors and space-charge limited-current measurements, which exhibit drastically different mobility anisotropy. A strong correlation between film morphology and the charge transport behavior is established by X-ray scattering and atomic force microscopic analyses.

- One-pot morphogen driven self-constructing films based on non-covalent host–guest interactions
  Rydzek, G.; Parat, A.; Polavarapu, P.; Baehr, C.; Voegel, J.-C.; Hemmerlé, J.; Senger, B.; Frisch, B.; Schaaf, P.; Jierry, L.; Boulmedais, F. *Soft Matter* **2012**, *8*, 446-453.
  Abstract:



The construction of films with complex architectures through one-pot reactions taking place exclusively on a surface remains a challenge. Recently, to address this problem, we introduced a concept based on morphogen-driven film buildup. We used Cu(I) as morphogen and the Huisgens click-reaction between azide and alkyne groups on polymers as film building blocks. Here, we extend this concept to films whose integrity is based exclusively on non-covalent host–guest interactions that are reversible allowing much broader tunability of the film properties. We trigger electrochemically the self-construction of films based on clickable host (cyclodextrin) and guests (ferrocene or adamantane) both functionalized by alkyne functions and poly(acrylic acid) bearing azide groups. Under voltammetry cycles, where Cu(I) is formed *in situ* from Cu(II), the film builds up by the non-reversible covalent grafting of the host and guest molecules to poly(acrylic acid) chains through triazole formation and by the subsequent formation of reversible host–guest interactions which entirely support the film cohesion. This process leads to the continuous self-construction of a nanometre size film whose thickness increases with the application time of the electrochemical stimulus. The growth rate of the film can be tuned by changing in the buildup solution either the relative ratio in concentration of host and guest or through the competition between clickable and non-clickable guest molecules. The effect of different stimuli leading to the dissolution of the film is also reported.

- Hydrogels with well-defined peptide-hydrogel spacing and concentration: impact on epithelial cell behavior
  Wilson, M. J.; Liliensiek, S. J.; Murphy, C. J.; Murphy, W. L.; Nealey, P. F. *Soft Matter* **2012**, *8*, 390-398.
  Abstract:



The spacing of peptides away from a hydrogel matrix dramatically impacts their availability and subsequent interactions with cells. Peptides were synthesized with monodisperse poly(ethylene glycol) spacers of different lengths that separate the peptide from the monomeric functionality which reacts during hydrogel polymerization. Specifically, bioactive RGD ligands were conjugated to PEG_5, PEG_{11} or PEG_{27} spacers *via* solid phase techniques and then functionalized with an acryloyl end group. These acryloyl-PEGx-RGD conjugates were then copolymerized with PEGDA to form an inert hydrogel network decorated with RGD ligands for cell interactions. As the PEG spacer length increases, the RGD concentration required to support cell attachment and spreading decreases. The competitive detachment of hTCEpi cells in the presence of soluble linear RGD also shows non-linear dependence on the PEG spacer length, as more cells remained attached and spread on gels functionalized with longer PEG-RGD conjugates in comparison to the shorter PEG-RGD conjugates. The strategy and synthetic techniques developed here allow for reproducible control over peptide-hydrogel spacing and peptide concentration, and may be extended for incorporation of multiple peptides and to other hydrogel platforms.