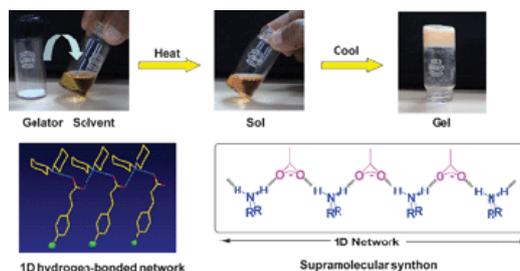


- Supramolecular gelling agents: can they be designed?  
Dastidar, P. *Chem. Soc. Rev.* **2008**, 37, 2699 - 2715.

Abstract:

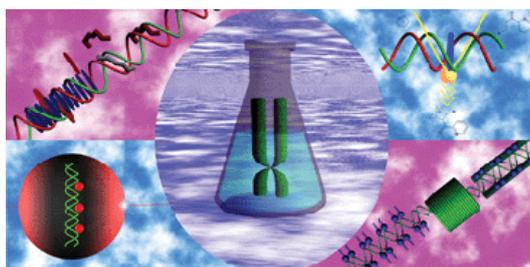


The last two decades have witnessed an upsurge of research activities in the area of supramolecular gelators, especially low molecular mass organic gelators (LMOGs), not only for academic interests but also for their potential applications in materials science. However, most of the gelators are serendipitously obtained; their rational design and synthesis is still a major challenge. Wide structural diversities of the molecules known to act as LMOGs and a dearth of molecular level understanding of gelation mechanisms make it difficult to pin-point a particular strategy to achieve rational design of gelators. Nevertheless, some efforts are being made to achieve this goal. Once a gelling agent is serendipitously obtained, new gelling agents with novel properties may be prepared by modifying the parent gelator molecule following a *molecular engineering* rationale; however, such approach is limited to the same class of gelling agent generated from the parent gelating scaffold. A *crystal engineering* approach wherein the single-crystal structure of a molecule is correlated with its gelling/nongelling behaviour (*structure–property correlation*) allows molecular level understandings of the self-assembly of the gelator and nongelator molecules and therefore, provides new insights into the design aspects of supramolecular gelling agents. This *tutorial review* aims at highlighting some of the developments covering both *molecular* and *crystal engineering* approaches in designing LMOGs.

- Applied Chemistry of Natural DNA

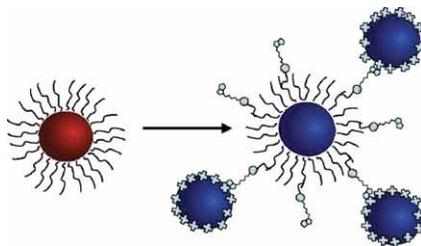
Liu, X.-D.; Diao, H.-Y.; Nishi, N. *Chem. Soc. Rev.* **2008**, 37, 2745 - 2757.

Abstract:



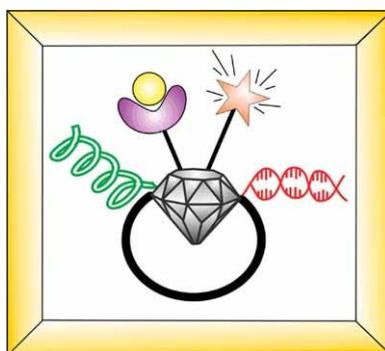
Recently, natural DNA has emerged as an appealing biomacromolecule for functional materials. It is abundant and renewable, and possesses the well known double helix structure that promises many unique properties difficult to find in other polymers. Natural DNA has been applied in electronic, optical and biomaterials, as a catalyst for enantioselective reactions, and as a material for cleaning the environment. Most of the applications are based on combining DNA with other chemicals or nanoparticles by electrostatic binding, intercalation or groove binding. In this *critical review* article, recent developments in utilizing natural DNA are reviewed by focusing on three basic properties of DNA: the electrostatic property as a polyelectrolyte, selective affinity for small molecules, and biocompatibility (128 references).

- Enzyme-Responsive Nanoparticle Systems  
Ghadiali, J. E.; Stevens, M. M. *Adv. Mater.* **2008**, *20*, 4359-4363.  
Abstract:



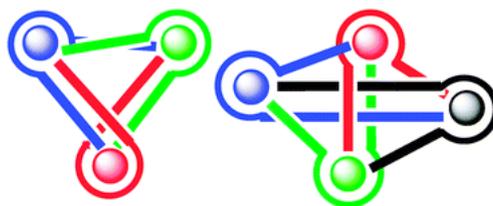
Inorganic nanoparticles and their accompanying diverse physical properties are now virtually in routine use as imaging tools in cell-biology. In addition to serving as excellent contrast agents, their size- and environment-dependent optical and magnetic properties can be harnessed to create enzyme biosensor devices of extremely high sensitivity, whilst circumventing the numerous technical limitations associated with traditional enzyme assays. In this Research News article we discuss recent advances in field of enzyme-responsive nanoparticle systems, where the activity of an enzyme elicits a specific response in the nanoparticle assembly to produce a signal relating to enzyme activity, focusing on three important systems: DNA-structured nanoparticles, protein kinases and proteases.

- Diamond Nanoparticles: Jewels for Chemistry and Physics  
Krueger, A. *Adv. Mater.* **2008**, *20*, 2445-2449.  
Abstract:



Nanodiamond materials have become broadly available. Their synthesis is usually carried out by explosion or shock wave methods. They exhibit a unique surface structure and can be functionalized in various ways. This opens a broad range of applications in composites, biological systems, electronics, and surface technology.

- Direct synthesis and structural characterisation of tri- and tetra-nuclear silver metallaknotanes by self-assembly approach  
Bourlier, J., Jouaiti, A., Kyritsakas-Gruber, N., Allouche, L., Planeix, J.-M., Hosseini, M.W.; *Chem. Commun.* **2008**, 6191 – 6193.  
Abstract :

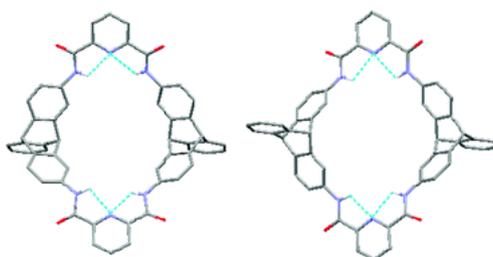


The combination of ligands based on two quinoline units acting as primary coordinating sites connected by tetra- or penta-ethyleneoxy fragments behaving as secondary interaction sites leads spontaneously in a one-pot reaction to the formation of tri- and terta-nuclear metalla-organic knots in the presence of silver cation.

- Triptycene-based tetralactam macrocycles: synthesis, structure and complexation with squaraine

Xue, M.; Chen, C.-F. *Chem. Commun.* **2008**, 6128 – 6130.

Abstract :

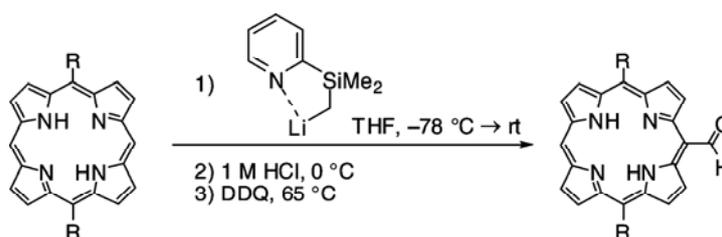


Two novel triptycene-based tetralactam macrocycles as a pair of diastereomers were synthesized, and showed highly efficient complexation with squaraine, which could subsequently protect the squaraine dye from polar solvents.

- One-Pot Synthesis of meso-Formylporphyrins by SNAr Reaction of 5,15-Disubstituted Porphyrins with (2-Pyridyldimethylsilyl)methyl lithium

Takanami T.; Wakita A.; Sawaizumi A.; Iso K.; Onodera H.; Suda K. *Org. Lett.* **2008**, *10*, 685-687

Abstract :

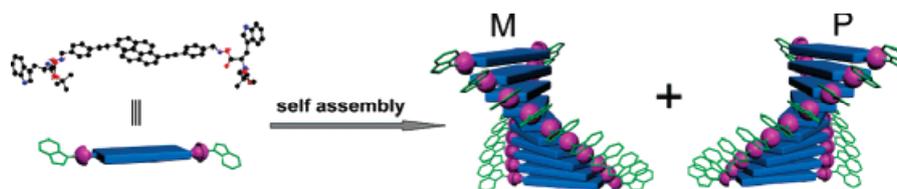


A simple, one-pot procedure that converts 5,15-substituted porphyrins into the corresponding meso-formylated porphyrins has been developed. The method, based on a new synthetic concept for functionalized porphyrins utilizing the (2-pyridyldimethylsilyl)methyl group as a latent formyl functionality, affords the desired product in good yield and is especially appropriate for the direct formylation of free base porphyrins, which has never been achieved by known methods.

- Supramolecular Helix of an Amphiphilic Pyrene Derivative Induced by Chiral Tryptophan through Electrostatic Interactions

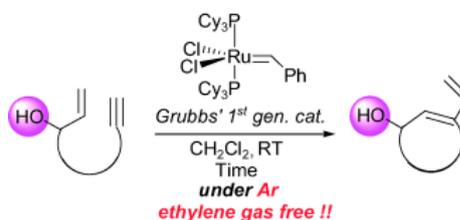
Xiao J.; Xu J.; Cui S.; Liu H.; Wang S.; Li Y. *Org. Lett.*, **2008**, *10*, 645-648

Abstract :



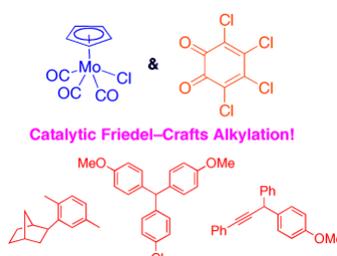
An amphiphilic pyrene derivative (PyDNH3) bearing positively charged ammonium cations has been synthesized and characterized. Self-assembly of PyDNH3 in the presence of chiral tryptophan derivatives was investigated in ethanol/water by optical and chiroptical spectra, indicating the formation of helical aggregates. Scanning electron microscope (SEM) images showed the formation of ring-shape structures.

- Acceleration Effect of an Allylic Hydroxy Group on Ring-Closing Enyne Metathesis of Terminal Alkynes: Scope, Application, and Mechanistic Insights  
Imahori, T.; Ojima, H.; Yoshimura, Y.; Takahata, H. *Chem. Eur. J.* **2008**, *14*, 10762 – 10771.  
Abstract :



An interesting acceleration effect of an allylic hydroxy group on ring-closing enyne metathesis has been found. Ring-closing enyne metathesis of terminal alkynes possessing an allylic hydroxy group proceeded smoothly without the ethylene atmosphere generally necessary to promote the reaction. The synthesis of (+)-isofagomine with the aid of this efficient reaction has been demonstrated. Mechanistic studies of the acceleration effect were also carried out. Results of NMR studies suggested that the reaction proceeded via an "ene-then-yne" pathway. Kinetic studies indicated switching of the rate-determining step as a consequence of the presence of an allylic hydroxy group. These results suggest acceleration of the reentry step of Ru-carbene species by the allylic hydroxy group.

- Versatile Friedel-Crafts-Type Alkylation of Benzene Derivatives Using a Molybdenum Complex/*ortho*-Chloranil Catalytic System  
Yamamoto, Y.; Itonaga, K. *Chem. Eur. J.* **2008**, *14*, 10705-10715.  
Abstract :



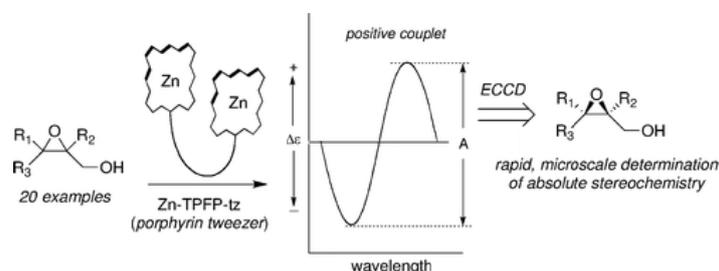
A variety of molybdenum complexes catalyze Friedel-Crafts-type alkylation reactions of benzene derivatives with alkenes and alcohols in the presence of an organic oxidant, *o*-chloranil. The utilization of [Mo(CO)<sub>6</sub>] and two equivalents of *o*-chloranil catalytically furnished the hydroarylation product of norbornene with *p*-xylene at 80 °C, whereas [Cr(CO)<sub>6</sub>] and [W(CO)<sub>6</sub>] failed to catalyze the same reaction, thus indicating the importance of the molybdenum source. The best results were

obtained when a molybdenum(II) complex  $[\text{CpMoCl}(\text{CO})_3]$  (Cp=cyclopentadienyl) was used as a precatalyst. The hydroarylation reactions also took place with styrenes, cyclohexenes, and 1-hexene as olefin substrates. The electrophilic-substitution mechanism was proposed on the basis of the *ortho/para* selectivities and the Markovnikov selectivities observed for the hydroarylation products. Our hypothesis was further corroborated by the fact that in the presence of the  $[\text{CpMoCl}(\text{CO})_3]/o$ -chloranil catalytic system, secondary, benzylic, or allylic alcohols participated in the alkylation of benzenes with similar selectivities.

- Prompt Determination of Absolute Configuration for Epoxy Alcohols via Exciton Chirality Protocol

Li, X.; Borhan, B. *J. Am. Chem. Soc.* **2008**, *130*, 16126–16127.

Abstract:

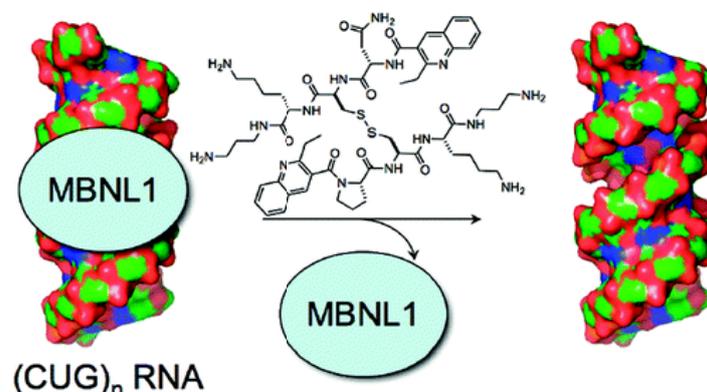


A microscale protocol for determination of absolute configurations of 2,3-epoxy alcohols is described. 2,3-Disubstituted (*cis* and *trans*), 2,2-disubstituted, 2,2,3-trisubstituted, and 2,3,3-trisubstituted epoxy alcohols rendered prominent ECCD signals upon complexing with a Lewis acidic porphyrin tweezer and consequently provide straightforward assignment of chirality for epoxy alcohols. This method proved to be rapid, simple, sensitive, and reliable for the class of molecules listed above.

- Dynamic Combinatorial Selection of Molecules Capable of Inhibiting the (CUG) Repeat RNA–MBNL1 Interaction In Vitro: Discovery of Lead Compounds Targeting Myotonic Dystrophy (DM1)

Gareiss, P. C.; Sobczak, K.; McNaughton, B. R.; Palde, P. B.; Thornton, C. A.; Miller, B. L. *J. Am. Chem. Soc.* **2008**, *130*, 16254–16261.

Abstract:



Myotonic dystrophy type 1 (DM1), the most common form of muscular dystrophy in adults, is an RNA-mediated disease. Dramatically expanded (CUG) repeats accumulate in nuclei and sequester RNA-binding proteins such as the splicing regulator MBNL1. We have employed resin-bound dynamic combinatorial chemistry (RBDCC) to identify the first examples of compounds able to inhibit MBNL1

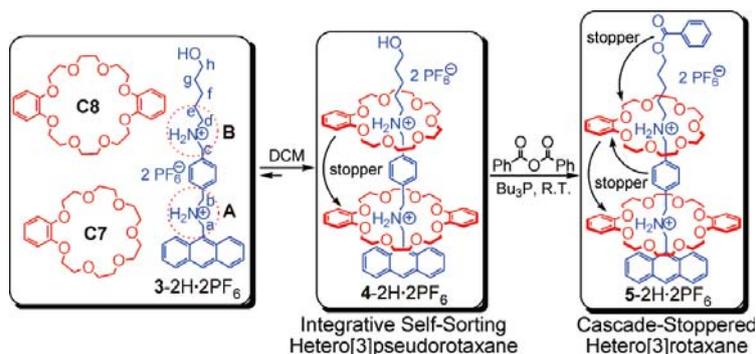
binding to (CUG) repeat RNA. Screening an RBDCL with a theoretical diversity of 11 325 members yielded several molecules with significant selectivity for binding to (CUG) repeat RNA over other sequences. These compounds were also able to inhibit the interaction of GGG-(CUG)<sub>109</sub>-GGG RNA with MBNL1 in vitro, with  $K_i$  values in the low micromolar range.

6

- Self-Sorting Organization of Two Heteroditopic Monomers to Supramolecular Alternating Copolymers

Wang, F.; Han, C.; He, C.; Zhou, Q.; Zhang, J.; Wang, C.; Li, N.; Huang, F. *J. Am. Chem. Soc.* **2008**, *130*, 11254–11255.

Abstract:

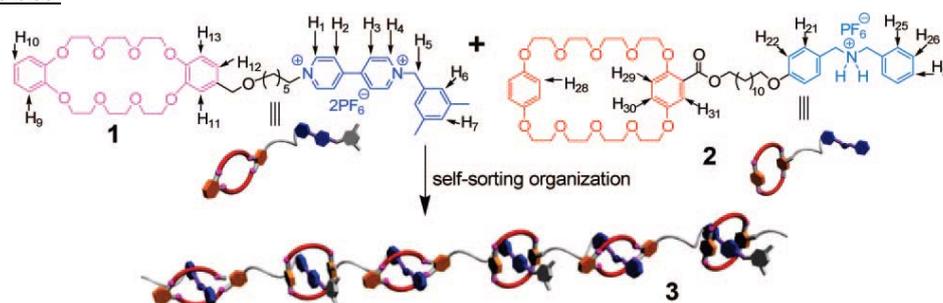


Self-sorting organization of two AB-type heteroditopic monomers led to the formation of linear supramolecular alternating copolymers driven by host–guest noncovalent interactions based on the bis(*p*-phenylene)-34-crown-10/paraquat derivative and dibenzo-24-crown-8/dibenzylammonium salt recognition motifs as confirmed by <sup>1</sup>H NMR, cyclic voltammetry, dynamic light scattering, viscosity measurements, and scanning electron microscopy.

- Integrative Self-Sorting: Construction of a Cascade-Stoppered Hetero[3]rotaxane

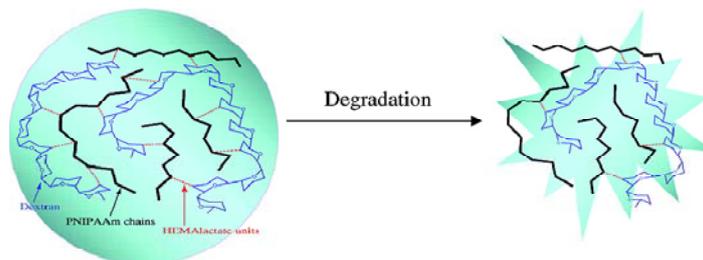
Jiang, W.; Winkler, H. D. F.; Schalley, C. A. *J. Am. Chem. Soc.* **2008**, *130*, 13852–13853.

Abstract:



In this Communication, a competing self-sorting system containing benzo-21-crown-7, dibenzo-24-crown-8 and two secondary ammonium salts is constructed, which is then modified to achieve a hetero[3]pseudorotaxane with a specific sequence of wheels. With these two systems, we successfully demonstrate the concept of integrative self-sorting, and their relation. Furthermore, based on this self-sorting scheme, a hetero[3]rotaxane with an efficient stopper cascade has been synthesized.

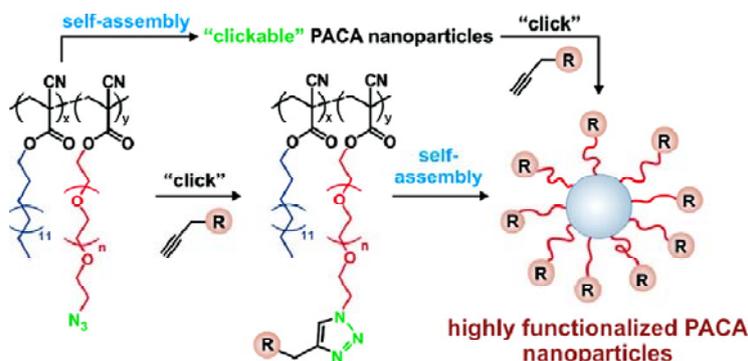
- Novel Nanogels with Both Thermoresponsive and Hydrolytically Degradable Properties
- Huang, X.; Misra, G. P.; Vaish, A.; Flanagan, J. M.; Sutermeister, B.; Lowe, T. L. *Macromolecules* **2008**, *41*, 8339-8345.

Abstract :

A series of novel nanogels with both thermoresponsive and hydrolytically degradable properties were synthesized by emulsion polymerization of *N*-isopropylacrylamide (NIPAAm) and dextran-lactate-2-hydroxyethyl methacrylate (DEXlactateHEMA), a hydrolytically degradable and cross-linkable dextran derivative, without using low molar mass surfactants. Various lengths of degradable oligolactate units and different precursor feeding ratios between NIPAAm and DEXlactateHEMA were used to synthesize the nanogels. FTIR measurements confirmed the chemical compositions and hydrolytic degradation of the synthesized nanogels. Dynamic light scattering measurements of the hydrodynamic radii of the nanogels in phosphate buffer saline (PBS, pH 7.4) against temperature and angle revealed that the nanogels were thermoresponsive with a lower critical solution temperature (LCST) of  $\sim 32^{\circ}\text{C}$ . The size and morphology changes of the nanogels with degradation were investigated by using transmission electron microscopy, atomic force microscopy, and static light scattering techniques. AFM image analysis and Holtzer plots revealed that the nanogels became more rigid with degradation in water solutions.

- Synthesis of Highly Functionalized Poly(alkyl cyanoacrylate) Nanoparticles by Means of Click Chemistry

Nicolas, J.; Bensaid, F. *Macromolecules* **2008**, *41*, 8418-8428.

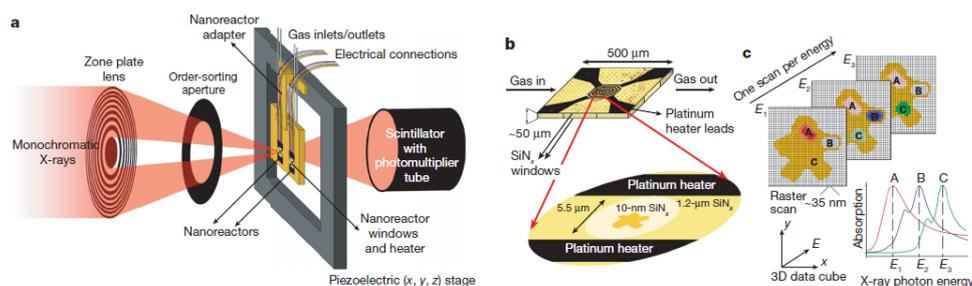
Abstract :

A general methodology was proposed to prepare highly functionalized poly(alkyl cyanoacrylate) nanoparticles by means of Huisgen 1,3-dipolar cyclo-addition, the so-called click chemistry. To achieve this goal, different protocols were investigated to obtain azidopoly(ethylene glycol) cyanoacetate of variable molar mass, followed by a Knoevenagel condensation-Michael addition reaction with hexadecyl cyanoacetate to produce a poly[(hexadecyl cyanoacrylate)-co-azidopoly(ethylene glycol) cyanoacrylate] (P(HDCA-co-N3PEGCA)) copolymer, displaying azide functionalities at the extremity of the PEG chains. As a proof of concept, model alkynes were quantitatively coupled either to the P(HDCA-co-N3PEGCA) copolymers in homogeneous medium followed by self-assembly in aqueous solution or directly at the surface of the preformed P(HDCA-co-N3PEGCA) nanoparticles in aqueous dispersed medium, both yielding highly functionalized nanoparticles. This versatile approach, using alkyl cyanoacrylate derivatives, opened the door to

ligand-functionalized and biodegradable nanoparticles with “stealth” properties for biomedical applications.

- Nanoscale chemical imaging of a working catalyst by scanning transmission X-ray microscopy de Smit, E.; Swart, I.; Creemer, J. F.; Hoveling, G. H.; Gilles, M. K.; Tyliszczak, T.; Kooyman, P. J.; Zandbergen, H. W.; Morin, C.; Weckhuysen, B. M.; de Groot, F. M. F. *Nature* **2008**, *456*, 222-225.

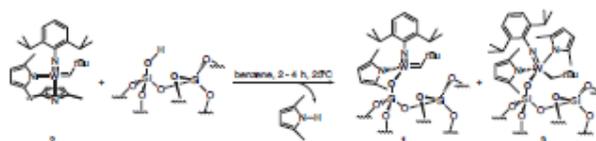
Abstract :



The modern chemical industry uses heterogeneous catalysts in almost every production process. They commonly consist of nanometre-size active components (typically metals or metal oxides) dispersed on a high-surface-area solid support, with performance depending on the catalysts' nanometre-size features and on interactions involving the active components, the support and the reactant and product molecules. To gain insight into the mechanisms of heterogeneous catalysts, which could guide the design of improved or novel catalysts, it is thus necessary to have a detailed characterization of the physicochemical composition of heterogeneous catalysts in their working state at the nanometre scale. Scanning probe microscopy methods have been used to study inorganic catalyst phases at subnanometre resolution, but detailed leads chemical information of the materials in their working state is often difficult to obtain. By contrast, optical microspectroscopic approaches offer much flexibility for *in situ* chemical characterization; however, this comes at the expense of limited spatial resolution. A recent development promising high spatial resolution and chemical characterization capabilities is scanning transmission X-ray microscopy, which has been used in a proof-of-principle study to characterize a solid catalyst. Here we show that when adapting a nanoreactor specially designed for high-resolution electron microscopy, scanning transmission X-ray microscopy can be used at atmospheric pressure and up to 350 °C to monitor *in situ* phase changes in a complex iron-based Fisher–Tropsch catalyst and the nature and location of carbon species produced. We expect that our system, which is capable of operating up to 500 °C, will open new opportunities for nanometre-resolution imaging of a range of important chemical processes taking place on solids in gaseous or liquid environments.

- Direct observation of reaction intermediates for a well defined heterogeneous alkene metathesis catalyst  
Blanc, F.; Berthoud, R.; Copéret, C.; Lesage, A.; Emsley, L.; Singh, R.; Krickmann, T.; Schrock, R. R. *Proc. Nat. Acad. Sci.* **2008**, *105*, 12123-12127.

Abstract:

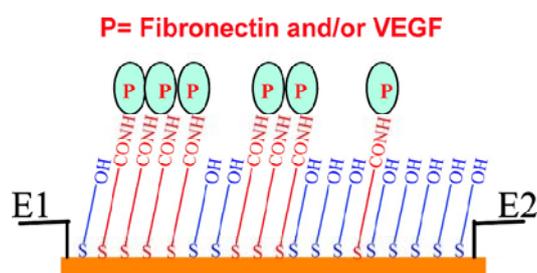


Grafting of  $[W(\equiv NAr)(=CHtBu)(2,5-Me_2NC_4H_2)_2]$  on a silica partially dehydroxylated at  $700^\circ C$  ( $SiO_2(700)$ ) generates the corresponding monosiloxy complex  $[(\equiv SiO)W(\equiv NAr)(=CHtBu)(2,5-Me_2NC_4H_2)_2]$  as the major species ( $\approx 90\%$ ) along with  $[(\equiv SiO)W(\equiv NAr)(CH_2tBu)(2,5-Me_2NC_4H_2)_2]$ , according to mass balance analysis, IR, and NMR studies. This heterogeneous catalyst displays good activity and stability in the metathesis of propene. Very importantly, solid state NMR spectroscopy allows observation of the propagating alkylidene as well as stable metallacyclobutane intermediates. These species have the same reactivity as the initial surface complex  $[(\equiv SiO)W(\equiv NAr)(=CHtBu)(2,5-Me_2NC_4H_2)_2]$ , which shows that they are the key intermediates of alkene metathesis.

- Endothelial Cell Migration on Surface-Density Gradients of Fibronectin, VEGF, or Both Proteins

Liu, L.; Ratner, B. D.; Sage, E. H.; Jiang, S. *Langmuir* **2007**, *23*, 11168-11173.

Abstract:

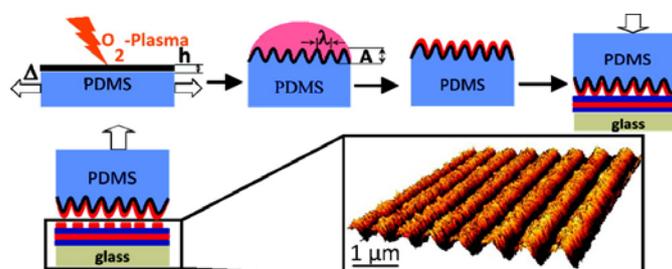


Cell migration is essential to many physiological processes, including angiogenesis, which is critical to the success of implanted biomaterials and tissue-engineered constructs. Gradients play an important role in cell migration. Previous work on cell migration has been mostly executed either in the concentration gradients of stimuli (e.g., VEGF) in bulk or hydrogels or on the surface-density gradients of ECM proteins (e.g., fibronectin) or small ligands (e.g., RGD). Little work has been done to investigate how cell migration responds to the surface-density gradients of growth factors. No work has been done to study how the surface gradients of both adhesive proteins and growth factors influence cell migration. In this work, we studied the effect of the surface-density gradients of fibronectin (FN), VEGF, or both proteins on endothelial cell migration. Gradients with different slopes were prepared to study how the gradient slope affects cell migration. The gradients were generated by first forming a counter-propagating C15COOH/C11OH self assembled monolayer (SAM) gradient using a surface electrochemistry approach, followed by activating the  $-COOH$  moieties and covalently immobilizing proteins onto the surface. Fourier transform infrared spectra and X-ray photoelectron spectroscopy were used to characterize the SAM and protein gradients, respectively. A free cell migration assay using bovine aortic endothelial cells was performed on various gradient surfaces or on surfaces with uniform protein density. Results showed that cells on the surface-density gradients of FN, VEGF, or both proteins moved faster along the gradient direction than on the respective uniform control surface after 24-h cell culture. It is also shown that for each protein or protein combination, the directional cell displacement was not statistically different between two gradients with different slopes. Results show that the directional cell migration was increased by

about 2-fold on the VEGF gradient as compared to the FN gradient and was further increased by another 2-fold on the combined gradients of both proteins as compared to the VEGF gradient alone. This is the first work to create surface-density gradients of VEGF and the first study to generate a combined surface gradient of growth factor and ECM protein to investigate their effect on cell migration on surfaces. This work broadens our understanding of the directional movement of endothelial cells. Our findings provide useful information for directing cell migration into tissue-engineered constructs and can be potentially used for those applications where cell migration is critical, such as angiogenesis.

- A Lithography-Free Pathway for Chemical Microstructuring of Macromolecules from Aqueous Solution Based on Wrinkling  
Pretzl, M.; Schweikart, A.; Hanske, C.; Chiche, A.; Zettl, U.; Horn, A.; Böker, A.; Fery, A. *Langmuir* **2008**, *24*, 12748-12753.

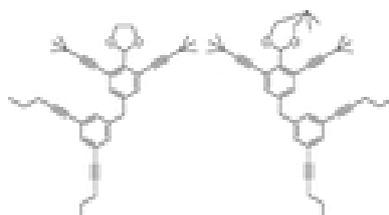
Abstract:



We report on a novel lithography-free method for obtaining chemical submicron patterns of macromolecules on flat substrates. The approach is an advancement of the well-known microcontact printing scheme: While for classical microcontact printing lithographically produced masters are needed, we show that controlled wrinkling can serve as an alternative pathway to producing such masters. These can even show submicron periodicities. We expect upscaling to larger areas to be considerably simpler than that for existing techniques, as wrinkling results in a macroscopic deformation process that is not limited in terms of substrate size. Using this approach, we demonstrate successful printing of aqueous solutions of polyelectrolytes and proteins. We study the effectiveness of the stamping process and its limits in terms of periodicities and heights of the stamps' topographical features. We find that critical wavelengths are well below 355 nm and critical amplitudes are below 40 nm and clarify the failure mechanism in this regime. This will permit further optimization of the approach in the future.

- Synthesis of Anthropomorphic Molecules: The NanoPutians  
Chanteau, S. H.; Tour, J. M. *J. Org. Chem.* **2003**, *68*, 8750-8766.

Abstract:

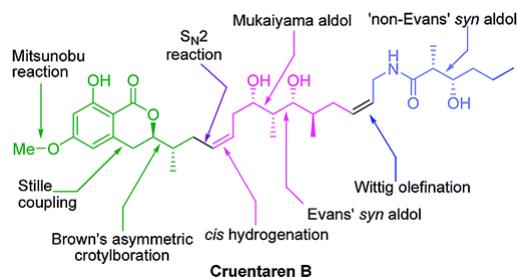


Described here are the synthetic details en route to an array of 2-nm-tall anthropomorphic molecules in monomeric, dimeric, and polymeric form. These anthropomorphic figures are called, as a class, NanoPutians. Using tools of chemical synthesis, the ultimate in designed miniaturization can be attained while preparing the most widely recognized structures: those that resemble humans.

- Total Synthesis of Cruentaren B

Chakraborty, T. K.; Chattopadhyay, A. K. *J. Org. Chem.* **2008**, *73*, 3578–3581.

Abstract:

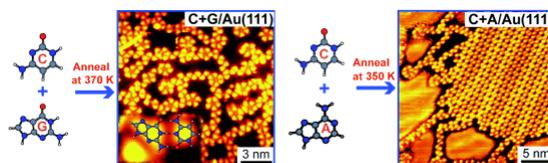


A convergent total synthesis of the cytotoxic natural product cruentaren B is completed in 26 steps (longest linear sequence) with an overall yield of 7.1%. For the construction of the C<sub>1</sub>–C<sub>11</sub> benzolactone fragment of the molecule, the key steps used were *O*-methylation, using a Mitsunobu reaction, a Stille coupling method to construct the C<sub>7</sub>–C<sub>8</sub> bond, and a Brown's asymmetric crotylboration reaction for the direct enantioselective installation of the two chiral centers present in this fragment. For diastereoselective installation of the chiral centers in the C<sub>12</sub>–C<sub>20</sub> polyketide fragment, an Evans *syn* aldol reaction on a chiral aldehyde, derived from methyl (*R*)-3-hydroxyl-2-methylpropionate, and subsequently a Mukaiyama aldol reaction were employed. For the construction of the C<sub>21</sub>–C<sub>28</sub> tail, a “non-Evans” *syn* aldol reaction was used. The three fragments were coupled by an S<sub>N</sub>2 reaction and a Wittig olefination reaction followed by standard functional group manipulations to furnish the target molecule.

- Specificity of Watson-Crick Base Pairing on a Solid Surface Studied at the Atomic Scale

Otero, R.; Xu, W.; Lukas, M.; Kelly, R. E. A.; Lægsgaard, E.; Stensgaard, I.; Kjems, J.; Kantorovich, L. N.; Besenbacher, F. *Angew. Chem. Int. Ed.* **2008**, *47*, 9673-9676.

Abstract :

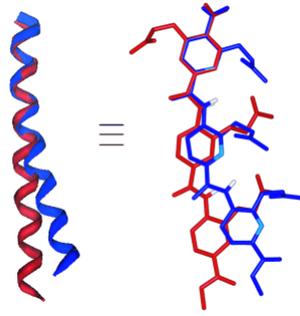


**Surface Watson-Crick base pairing** makes binary mixtures of the complementary nucleobases guanine (G) and cytosine (C) on Au(111) thermally stable up to the desorption temperature of the bases, whereas binary mixtures of the noncomplementary adenine (A) and cytosine segregate on heating (see STM images with DFT structures).

- Controlling Curvature in a Family of Oligoamide  $\alpha$ -Helix Mimetics

Saraogi, I.; Incarvito, C. D. ; Hamilton, A. D. *Angew. Chem. Int. Ed.* **2008**, *47*, 9691-9694.

Abstract :



**Catching up with the curve!** The natural curvature found in a majority of  $\alpha$ -helices has been mimicked in small synthetic oligoamide scaffolds. Differences in hydrogen-bonding patterns in these scaffolds lead to mimetics with varying degrees of curvature in the backbone. This adds another parameter to the structural and functional mimicry of  $\alpha$ -helices.