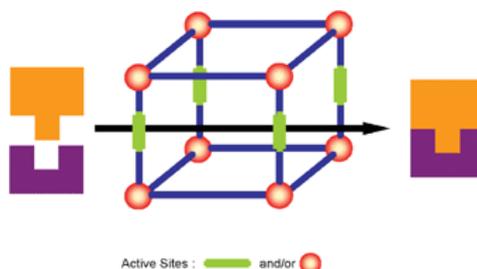


- Metal–organic framework materials as catalysts

Lee, J. Y.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. *Chem. Soc. Rev.* **2009**, *38*, 1450 – 1459.

Abstract:

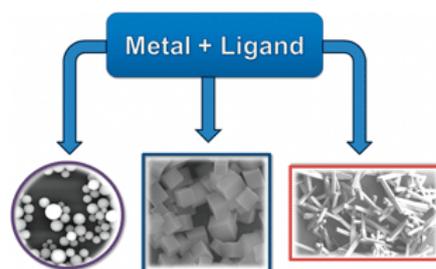


A *critical review* of the emerging field of MOF-based catalysis is presented. Discussed are examples of: (a) opportunistic catalysis with metal nodes, (b) designed catalysis with framework nodes, (c) catalysis by homogeneous catalysts incorporated as framework struts, (d) catalysis by MOF-encapsulated molecular species, (e) catalysis by metal-free organic struts or cavity modifiers, and (f) catalysis by MOF-encapsulated clusters (66 references).

- Infinite coordination polymer nano- and microparticle structures

Spokoiny, A. M.; Kim, D.; Sumrein, A.; Mirkin, C. A. *Chem. Soc. Rev.* **2009**, *38*, 1218 – 1227.

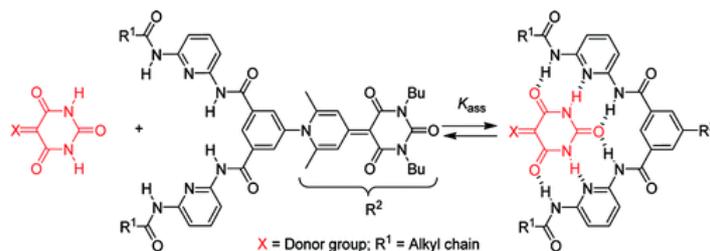
Abstract:



Infinite coordination polymer particles (ICPs) represent an area of growing interest in chemistry and materials science due to their unique and highly tailorable properties. These structures can be conveniently synthesized in high yields from the appropriate metal salts and bifunctional ligand precursors. Unlike conventional metal–organic framework materials (MOFs), these ICPs exhibit a higher level of structural tailorability, including size- and morphology-dependent properties, and therefore, the promise of a wider scope of utility. A variety of methods now exist for making numerous compositions, with modest control over particle size and shape. These structures can exhibit microporosity, tunable fluorescence, magnetic susceptibility, and unusual catalytic activity and selectivity. Perhaps most importantly, many of these ICP structures can be depolymerized (sometimes reversibly) much faster and under milder conditions than MOFs, which makes them attractive for a variety of biomedical applications. Thus far, several types of ICPs have been explored as contrast agents for magnetic resonance imaging and drug delivery systems. The groundwork for this emerging field of ICPs has been laid only in the past few years, yet significant advances have already been made. Indeed, this *tutorial review* introduces the reader to the field of ICPs, providing a guide to the work done so far, with an emphasis on synthesis, applications and future prospects.

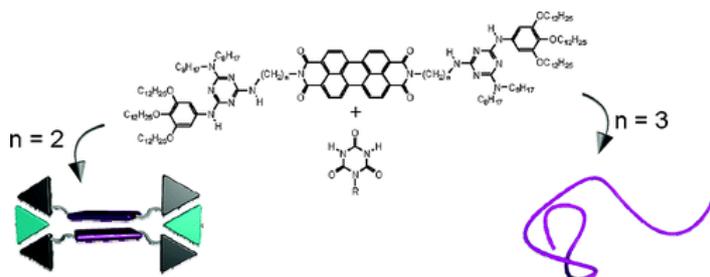
- Synthesis, Optical Properties, and LFER Analysis of Solvent-Dependent Binding Constants of Hamilton-Receptor-Connected Merocyanine Chromophores

Schmidt, J.; Schmidt, R.; Würthner, F. *J. Org. Chem.* **2008**, *73*, 6355–6362.

Abstract:

A merocyanine dye equipped with a Hamilton-receptor unit has been synthesized that enables strong noncovalent binding of other merocyanine dyes bearing barbituric acid acceptor groups by six hydrogen bonds. NMR and UV/vis titration experiments in toluene, chloroform, dichloromethane, dioxane, and THF provide evidence for the formation of 1:1 complexes even in the dipolar solvents. An enhanced binding strength is observed for the more dipolar merocyanine dyes in the head-to-tail assembly structure with binding constants up to  $>10^8 \text{ M}^{-1}$  in toluene. In the present bimolecular complexes two merocyanine chromophores are assembled in a head-to-tail fashion that affords increased dipole moments as demanded for efficient electric field induced poling processes in nonlinear optical and photorefractive polymeric hosts. The solvent dependency of the binding constants for various barbituric acid dye–Hamilton receptor complexes as well as a perylene imide–melamine complex reveals linear free energy relationships (LFER) that allow for an estimation of binding constants larger than  $10^{12} \text{ M}^{-1}$  for Hamilton receptor organized head-to-tail merocyanine bimolecular complexes in aliphatic solvents. It is suggested that such LFER are valuable tools for the estimation of binding constants in solvents where experimental binding constants cannot be determined because of solubility or spectroscopic problems.

- Formation of Supramolecular Polymers and Discrete Dimers of Perylene Bisimide Dyes Based on Melamine–Cyanurates Hydrogen-Bonding Interactions  
Seki, T.; Yagai, S.; Karatsu, T.; Kitamura, A. *J. Org. Chem.* **2008**, *73*, 3328–3335.

Abstract:

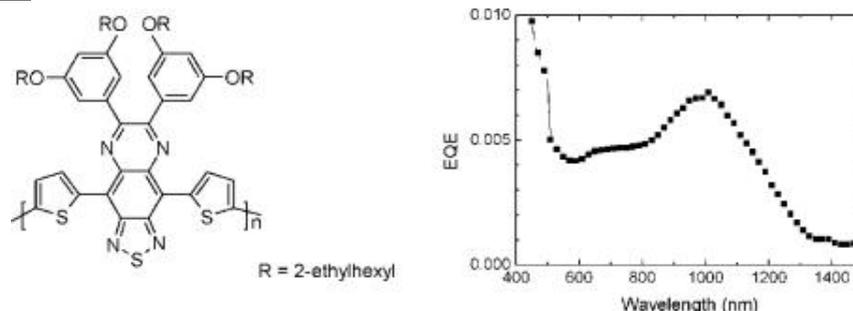
Melamine-linked perylene bisimide dyes (MPBIs) bearing an ethylene or trimethylene group as linker moieties were synthesized, and their self-aggregation and coaggregation with cyanurates through complementary triple hydrogen bonds have been investigated. UV/vis studies revealed that both the MPBIs self-assemble in nonpolar organic solvent through  $\pi$ – $\pi$  stacking interaction between perylene cores, giving self-aggregates with nearly identical thermal stabilities. Upon addition of 1 equiv of cyanurate components, however, the stabilities of the resulting aggregates were dramatically changed between the two systems, suggesting the formation of different types of hydrogen-bonded supramolecular species. Dynamic light scattering and atomic force microscopic studies revealed that the system featuring ethylene linker moieties generates a discrete dimer of MPBI supported by two cyanurate molecules, whereas the system featuring trimethylene linker moieties affords extended supramolecular polymers hierarchically organizing into nanoscopic fibers. These results demonstrate

that it is possible to obtain distinct supramolecular species by just changing the number of carbon atoms at the linker moieties of MPBI components. The present strategy for the fabrication of discrete or polymeric supramolecular assemblies should be applicable to other functional  $\pi$ -conjugated molecules.

- Photovoltaic Performance of an Ultrasmall Band Gap Polymer

Zoombelt, A. P.; Fonrodona, M.; Wienk, M. M.; Sieval, A. B.; Hummelen, J. C.; Janssen, R. A. J. *Org. Lett.* **2009**, *11*, 903-906.

Abstract:

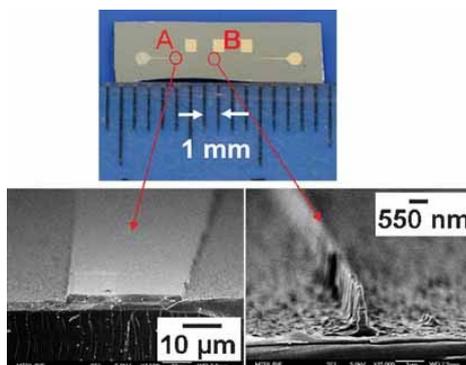


A conjugated polymer (PBTTQ) that consists of alternating electron-rich bithiophene and electron-deficient thiadiazoloquinoxaline units was synthesized via Yamamoto polymerization with  $\text{Ni}(\text{cod})_2$  and provides a band gap of 0.94 eV. This represents one of the smallest band gaps obtained for a soluble conjugated polymer. When applied in a bulk heterojunction solar cell together with [84]PCBM as the electron acceptor, the polymer affords a response up to 1.3  $\mu\text{m}$ .

- Simultaneous Fabrication of Very High Aspect Ratio Positive Nano- to Milliscale Structures

Chen, L. Q.; Chan-Park, M. B.; Zhang, Q.; Chen, P.; Li, C. M.; Li, S. *Small* **2009**, *5*, 1043 – 1050.

Abstract:



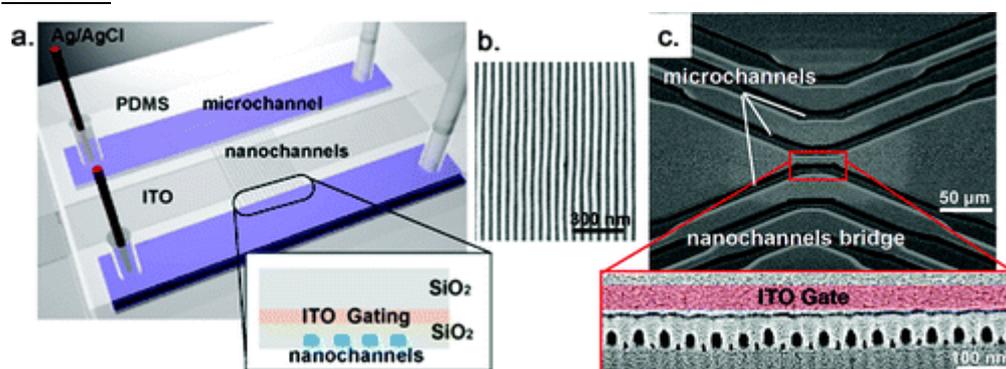
A simple and inexpensive technique for the simultaneous fabrication of positive (i.e., protruding), very high aspect (>10) ratio nanostructures together with micro- or millistructures is developed. The method involves using residual patterns of thin-film over-etching (RPTO) to produce sub-micro-/nanoscale features. The residual thin-film nanopattern is used as an etching mask for Si deep reactive ion etching. The etched Si structures are further reduced in size by Si thermal oxidation to produce amorphous  $\text{SiO}_2$ , which is subsequently etched away by HF. Two arrays of positive Si nanowalls are demonstrated with this combined RPTO- $\text{SiO}_2$ -HF technique. One array has a feature size of 150 nm and an aspect ratio of 26.7 and another has a feature size of 50 nm and an aspect ratio of 15. No other parallel reduction technique can achieve such a very high aspect ratio for 50-nm-wide nanowalls. As a demonstration of the technique to simultaneously achieve nano- and

milliscale features, a simple Si nanofluidic master mold with positive features with dimensions varying continuously from 1 mm to 200 nm and a highest aspect ratio of 6.75 is fabricated; the narrow 200-nm section is 4.5 mm long. This Si master mold is then used as a mold for UV embossing. The embossed open channels are then closed by a cover with glue bonding. A high aspect ratio is necessary to produce unblocked closed channels after the cover bonding process of the nanofluidic chip. The combined method of RPTO, Si thermal oxidation, and HF etching can be used to make complex nanofluidic systems and nano-/micro-/millistructures for diverse applications.

- Fast Nonlinear Ion Transport via Field-Induced Hydrodynamic Slip in Sub-20-nm Hydrophilic Nanofluidic Transistors

Vermesh, U.; Choi, J. S.; Vermesh, O.; Fan, R.; Nagarah, J.; Heath, J. R. *Nano Lett.* **2009**, *9*, 1315–1319.

Abstract:

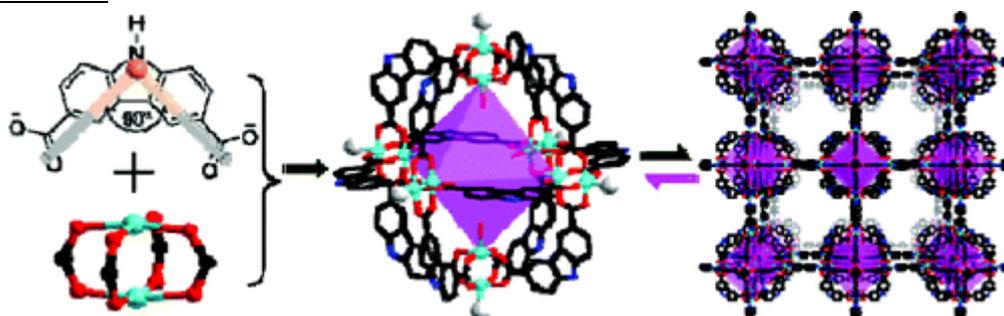


Electrolyte transport through an array of 20 nm wide, 20 μm long SiO<sub>2</sub> nanofluidic transistors is described. At sufficiently low ionic strength, the Debye screening length exceeds the channel width, and ion transport is limited by the negatively charged channel surfaces. At source–drain biases >5 V, the current exhibits a sharp, nonlinear increase, with a 20–50-fold conductance enhancement. This behavior is attributed to a breakdown of the zero-slip condition. Implications for energy conversion devices are discussed.

- Interconversion between Molecular Polyhedra and Metal–Organic Frameworks

Li, J.; Timmons, D. J.; Zhou, H. C. *J. Am. Chem. Soc.* **2009**, *131*, 6368–6369.

Abstract:

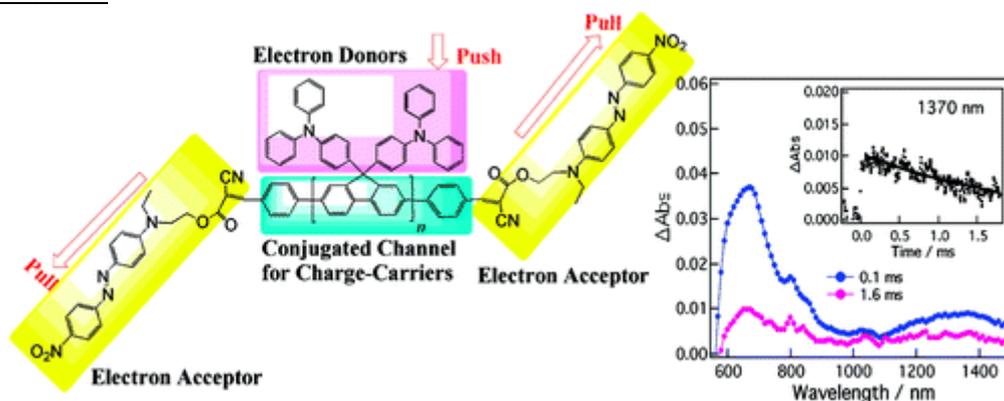


The construction of a metal–organic framework (MOF) with a pcu-a topology using a preassembled soluble molecular octahedron has been realized experimentally. The resulting MOF can also be reversibly converted to the molecular octahedron. All such conversions are based on axial-ligand substitution reactions on the molecular octahedron.

- Long-Lived Charge-Separated Configuration of a Push–Pull Archetype of Disperse Red 1 End-Capped Poly[9,9-Bis(4-diphenylaminophenyl)fluorene]

El-Khouly, M. E.; Chen, Y.; Zhuang, X.; Fukuzumi, S. *J. Am. Chem. Soc.* **2009**, *131*, 6370–6371.

Abstract:

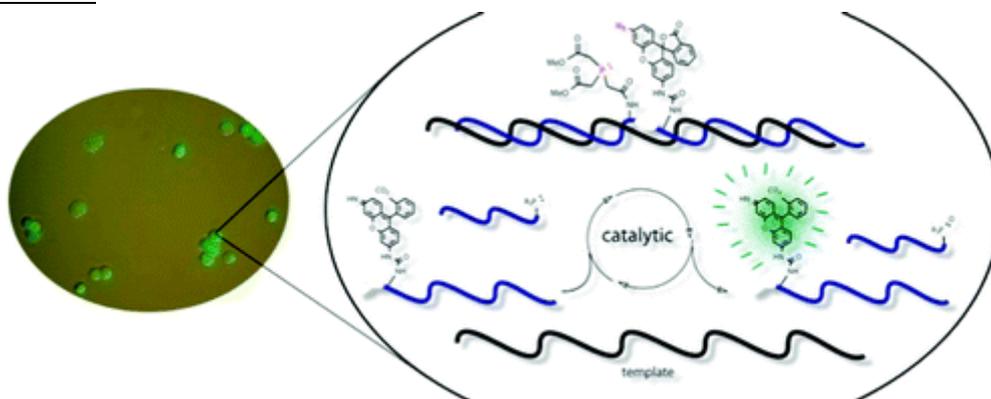


The photoinduced electron-transfer process in Disperse Red 1 end-capped poly[9,9-bis(4-diphenylaminophenyl)-2,7-fluorene], a promising material for electronic and optoelectronic devices, is reported here. The charge-separated configuration was found to be long-lived, with a lifetime of up to 2.2 ms in the polar benzonitrile, as inferred from time-resolved absorption measurements.

- Imaging of mRNA in Live Cells Using Nucleic Acid-Templated Reduction of Azidorhodamine Probes

Pianowski, Z.; Gorska, K.; Oswald, L.; Merten, C. A.; Winssinger, N. *J. Am. Chem. Soc.* **2009**, *131*, 6492–6497.

Abstract:

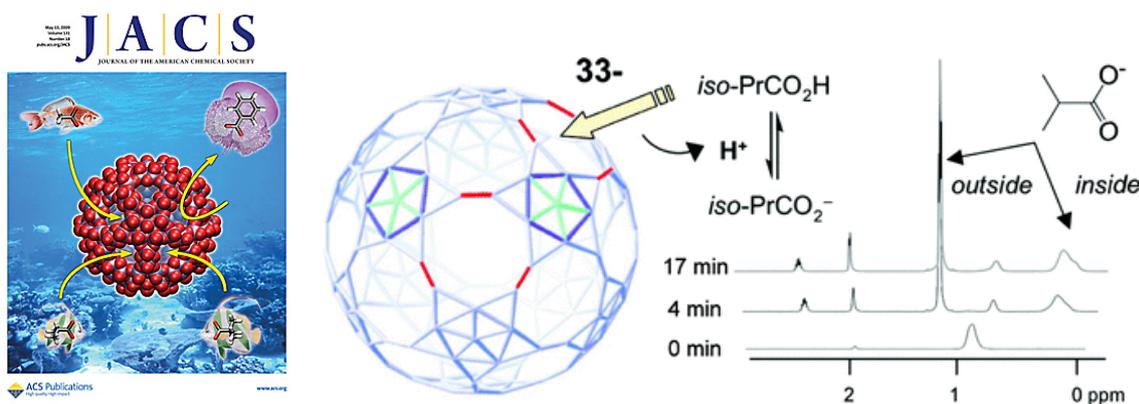


Nucleic acid-templated reactions leading to a fluorescent product represent an attractive strategy for the detection and imaging of cellular nucleic acids. Herein we report the use of a Staudinger reaction to promote the reduction of profluorescent azidorhodamine. The use of two cell-permeable GPNA probes, one labeled with the profluorescent azidorhodamine and the other with trialkylphosphine, enabled the detection of the mRNA encoding O-6-methylguanine-DNA methyltransferase in intact cells.

- Flexible Pores of a Metal Oxide-Based Capsule Permit Entry of Comparatively Larger Organic Guests

Ziv, A.; Grego, A.; Kopilevich, S.; Zeiri, L.; Miro, P.; Bo, C.; Müller, A.; Weinstock, I. A. *J. Am. Chem. Soc.* **2009**, *131*, 6380–6382.

Abstract:

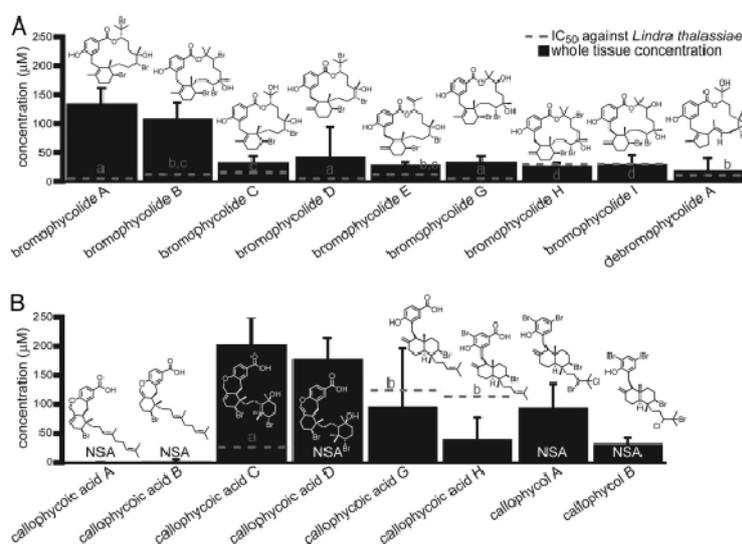


In zeolites and other rigid solid-state oxides, substrates whose sizes exceed the pore dimensions of the material are rigorously excluded. Now, using a porous 3 nm diameter capsule-like oxomolybdate complex  $[\{\text{Mo}^{\text{VI}}_6\text{O}_{21}(\text{H}_2\text{O})_6\}_{12}\{\{\text{Mo}^{\text{V}}_2\text{O}_4\}_{30}(\text{OAc})_{21}(\text{H}_2\text{O})_{18}\}]^{33-}$  as a water-soluble analogue of solid-state oxides (e.g., as a soluble analogue of 3 Å molecular sieves), we show that carboxylates (RCO<sub>2</sub><sup>-</sup>) can negotiate passage through flexible Mo<sub>9</sub>O<sub>9</sub> pores in the surface of the capsule and that the rates follow the general trend R = 1° ≫ 2° > 3° ≫ phenyl (no reaction). Surprisingly, the branched alkanes (R = *iso*-Pr and *tert*-Bu) enter the capsule even though they are larger than the crystallographic dimensions of the Mo<sub>9</sub>O<sub>9</sub> pores. Four independent lines of spectroscopic and kinetic evidence demonstrate that these organic guests enter the interior of the capsule through its Mo<sub>9</sub>O<sub>9</sub> apertures and that no irreversible changes in the metal oxide framework are involved. This unexpected phenomenon likely reflects the greater flexibility of molecular versus solid-state structures and represents a sharp departure from traditional models for diffusion through porous solid-state (rigid) oxides.

- Desorption electrospray ionization mass spectrometry reveals surface-mediated antifungal chemical defense of a tropical seaweed

Lane, A. L.; Nyadong, L.; Galhena, A. S.; Shearer, T. L.; Stout, E. P.; Parry, R. M.; Kwasnik, M.; Wang, M. D.; Hay, M. E.; Fernandez, F. M.; Kubanek, J. *Proc. Nat. Acad. Sci.* **2009**, *106*, 7314–7319.

Abstract:



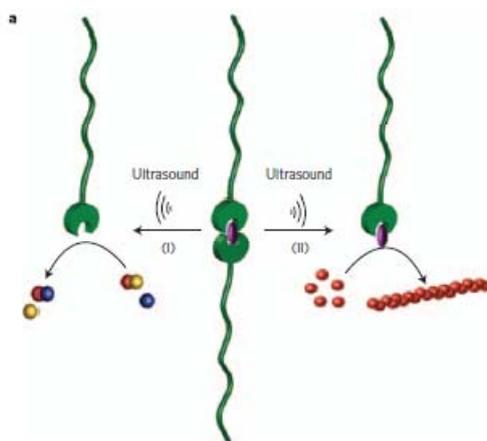
Organism surfaces represent signaling sites for attraction of allies and defense against enemies. However, our understanding of these signals has been impeded by methodological limitations that

have precluded direct fine-scale evaluation of compounds on native surfaces. Here, we asked whether natural products from the red macroalga *Callophycus serratus* act in surface-mediated defense against pathogenic microbes. Bromophycolides and callophycoic acids from algal extracts inhibited growth of *Lindra thalassiae*, a marine fungal pathogen, and represent the largest group of algal antifungal chemical defenses reported to date. Desorption electrospray ionization mass spectrometry (DESI-MS) imaging revealed that surface-associated bromophycolides were found exclusively in association with distinct surface patches at concentrations sufficient for fungal inhibition; DESI-MS also indicated the presence of bromophycolides within internal algal tissue. This is among the first examples of natural product imaging on biological surfaces, suggesting the importance of secondary metabolites in localized ecological interactions, and illustrating the potential of DESI-MS in understanding chemically-mediated biological processes.

- Activating catalysts with mechanical force

Piermattei, A.; Karthikeyan, S.; Sijbesma, R. P. *Nature Chem.* **2009**, *1*, 133-137

Abstract:

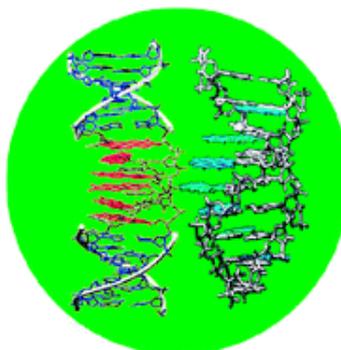


Homogeneously catalysed reactions can be 'switched on' by activating latent catalysts. Usually, activation is brought about by heat or an external chemical agent. However, activation of homogeneous catalysts with a mechanical trigger has not been demonstrated. Here, we introduce a general method to activate latent catalysts by mechanically breaking bonds between a metal and one of its ligands. We have found that silver(I) complexes of polymer-functionalized N-heterocyclic carbenes, which are latent organocatalysts, catalyse a transesterification reaction when exposed to ultrasound in solution. Furthermore, ultrasonic activation of a ruthenium biscarbene complex with appended polymer chains results in catalysis of olefin metathesis reactions. In each case, the catalytic activity results from ligand dissociation, brought about by transfer of mechanical forces from the polymeric substituents to the coordination bond. Mechanochemical catalyst activation has potential applications in transduction and amplification of mechanical signals, and mechanically initiated polymerizations hold promise as a novel repair mechanism in self-healing materials.

- DNA as a supramolecular framework for the helical arrangements of chromophores: towards photoactive DNA-based nanomaterials.

Varghese, R.; Wagenknecht, H. A. *Chem. Commun.* **2009**, 2615 – 2624.

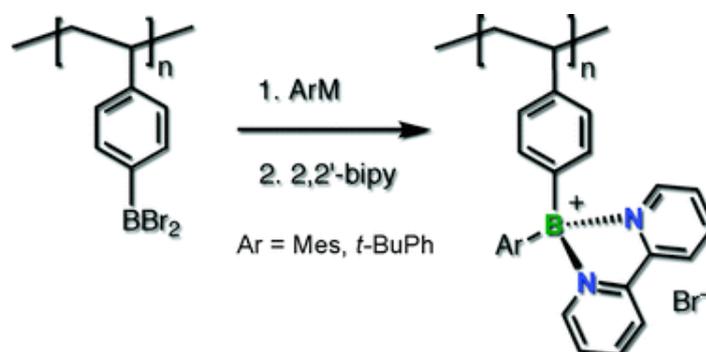
Abstract:



Nucleic acids have been emerging as supramolecular structural scaffolds for the helical organization of chromophores in the creation of functional nanomaterials mainly because of their unique structural features and synthetic accessibility. A large number of chromophores have been successfully incorporated into DNA or RNA as C-nucleosides, as base surrogates or as modified sugars using solid phase phosphoramidite chemistry. Moreover, multiple incorporations yield the helical organization of the chromophores inside or outside the DNA or RNA double helix depending upon the conjugation of the chromophores. Significant photophysical interactions are observed in the chromophore stacks resulting in unique optical properties that are significantly different from the monomer properties. In this feature article, multichromophore labelled nucleic acids are reviewed with special emphasis on the self-assembly induced modulation of the optical properties.

- Organoboronium-functionalized polystyrenes as a new class of polycations.  
Cui, C.; Jäkle, F. *Chem. Commun.* **2009**, 2744 – 2746.

Abstract:



The facile preparation of organoboronium polymers via spontaneous reaction of bromoborylated polystyrene with 2,2'-bipyridine is reported; these novel polycations represent an interesting alternative to commonly used ammonium-based polycations.

- Contribution of Electrochemistry to Organometallic Catalysis  
Jutand, A. *Chem. Rev.* **2008**, *108*, 2300-2347.

Abstract:

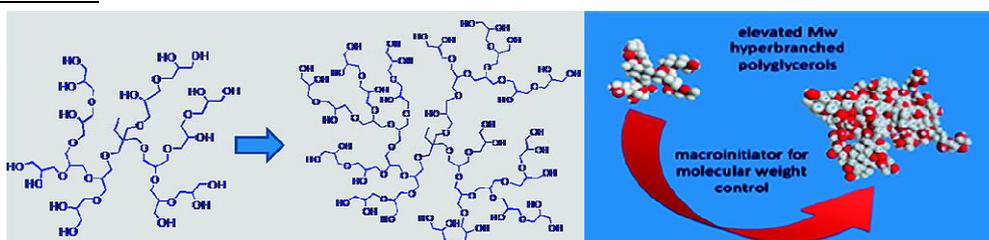


biological recognition element (biochemical receptor) which is retained in direct spatial contact with a...transduction element". Thus an ion selective electrode would not ordinarily be a biosensor even though it measures a biologically relevant species, although there are "designer" proteins now available for such purposes. In the 1970s, Adams and co-workers demonstrated the utility of direct electrochemistry for the measurement of catecholamines in the central nervous system (CNS). These analytes are very similar in structure and therefore have very similar electrochemistry, an issue that has been partly resolved. The deficiencies in selectivity have to be balanced against significantly faster response time compared to multilayered enzyme devices.

- Hyperbranched Polyglycerols with Elevated Molecular Weights: A Facile Two-Step Synthesis Protocol Based on Polyglycerol Macroinitiators.

Wilms, D.; Wurm, F.; Nieberle, J.; Böhm, P.; Kemmer-Jonas, U.; Frey, H. *Macromolecules* **2009**, *42*, 3230-3236.

Abstract:

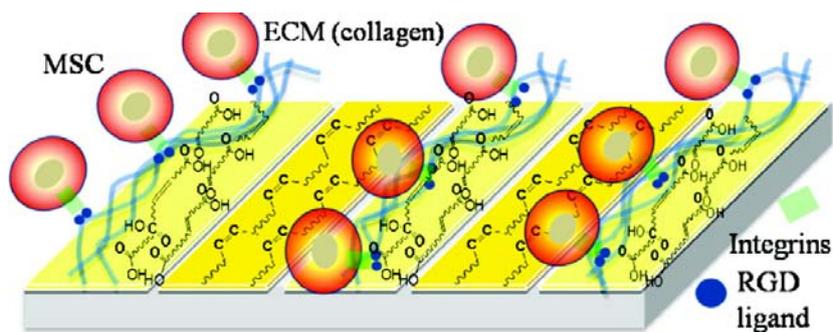


Hyperbranched polyglycerol (PG) is established as one of the few hyperbranched polymers that offer the possibility to control molecular weight up to  $M_n$  ) 6000 g/mol. This work introduces a facile 2-step strategy that relies on the use of a low molecular weight PG ( $M_n$  ) 500 and 1000 g/mol) as a macroinitiator for the slow addition of glycidol, permitting to overcome previous limitations concerning molecular weights and molecular weight control. A systematic investigation of the effect of the degree of deprotonation on the control of the polymerization reaction has been carried out. A series of hyperbranched PGs with molecular weights up to  $M_n$  ) 24000 g/mol has been obtained under fully controlled conditions. The polydispersities of the samples prepared were in the range of 1.3 to 1.8. In summary, we present the first example of a synthetic strategy for a hyperbranched polymer that is now accessible over a broad range of molecular weights (300-24000 g/mol) without the ubiquitous problem of large polydispersities or the necessity for solid supports. In addition, the samples permitted a systematic study of the degree of branching DB of the hyperbranched PGs of elevated molecular weight. Values of DB ) 0.60 to 0.63 were obtained, approximating the theoretical limit of 0.66 for slow monomer addition.

- A Fluorescent Polymer for Patterning of Mesenchymal Stem Cells.

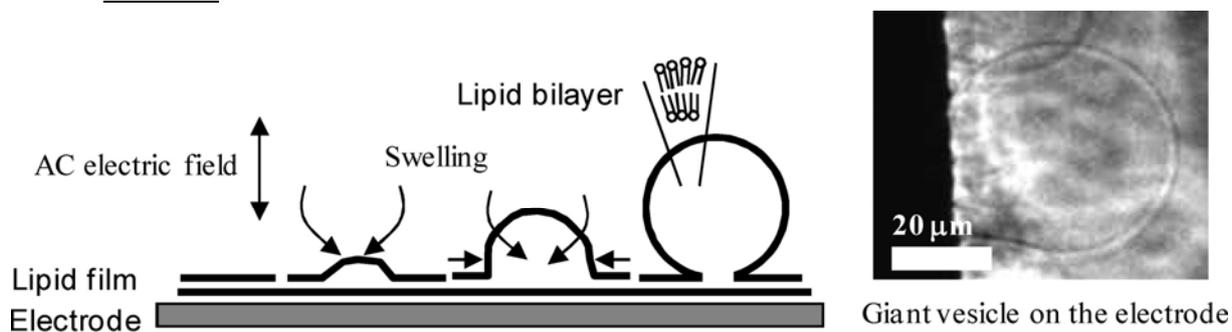
You, J.; Heo, J. S.; Lee, J.; Kim, H.-S.; Kim, H. O.; Kim, E. *Macromolecules* **2009**, *42*, 3326-3332.

Abstract :



UV exposure of a fluorescent polymer, diphenylamino-s-triazine bridged *p*-phenylene vinylene polymer (DTOPV), resulted in fluorescence quenching and a change in surface wettability via photo-oxidation. Patterned polymer films were prepared simply by exposing the polymer film to UV source through a photomask under air. The UV-exposed region was highly biocompatible and provided selective mesenchymal stem cells (MSCs) attachment on it. This allowed cell alignment and patterning along the line patterns of linear, curved, and even various letter shapes. The proliferation rate of MSCs cultured on UV exposed surface (DTOPV+UV) was higher than that of the unexposed surface, and the cells were increased to 10-fold after 6 days. The attachment of MSCs was highly selective to the UV-exposed pattern in the presence of collagen and gelatin, which induced cell patterning and attachment through hydrophilic interaction with the UV exposed area. Taking advantage of the emission from the DTOPV pattern, the cell location and pattern images were easily detected through a microscope with or without an excitation probe beam. These studies provide an exciting opportunity for novel cell patterning by a simple photopatterning process using a highly fluorescent DTOPV.

- Kinetic Study on Giant Vesicle Formation with Electroformation Method  
Shimanouchi, T.; Umakoshi, H.; Kuboi, R. *Langmuir* **2009**, *25*, 4835-4840.  
Abstract :



### Kinetic on Electroformation of Giant Vesicle

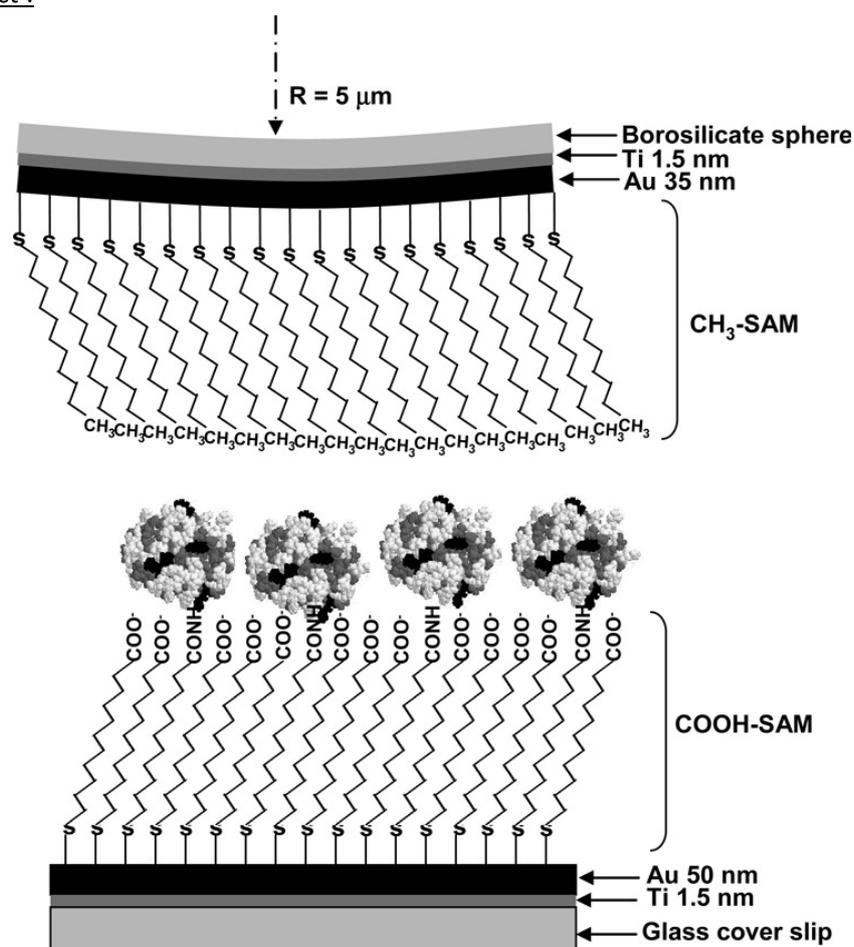
Giant vesicles (GVs) composed of zwitterionic phospholipids were prepared by the electroformation method. The growth behavior of GV was quantitatively analyzed as a first-order kinetics of the radius of GV to obtain the apparent growth rate constant  $k_{Gr}$ . On the basis of the dependence of the  $k_{Gr}$  value on the preparation temperature and the lipid composition of GV, the membrane fluidity of vesicle membranes was found to be dominant in the growth behavior of GV. The comparison of the  $k_{Gr}$  values with the membrane fluidity for GV suggested the validity of the model that the swelling of the lipid membrane could induce the growth of GV.

- Stability of Tethered Proteins

Anand, G.; Sharma, S.; Kumar, S. K.; Belfort, G. *Langmuir* **2009**, *25*, 4998-5005.

Abstract :

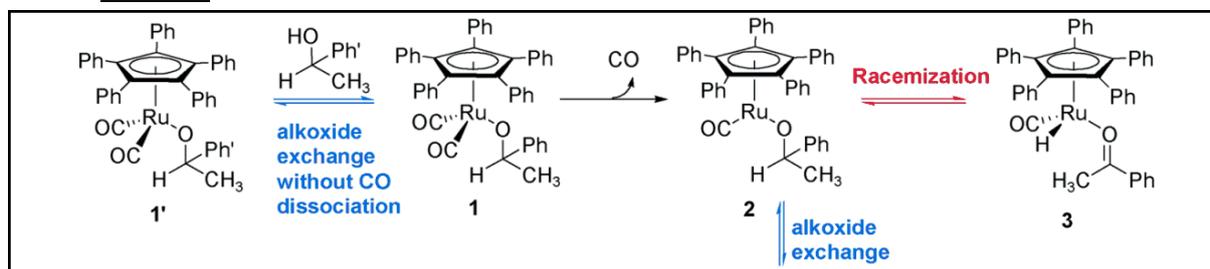
12



The stability of tethered globular proteins under denaturing conditions was interrogated with a hydrophobic surface, since conventional structural methods like circular dichroism (CD) and fluorescence or infrared spectroscopy could not be used because of the presence of an opaque solid substrate and extremely low surface concentrations. For free protein in solution, CD spectra gave well-known unfolding denaturing curves for lysozyme (LYS) and ribonuclease A (RNase A). The unfolding process for covalently tethered LYS and RNase A was followed, with multimolecular force spectroscopy (using an atomic force microscope in force-mode), via the adhesion energy between a functionalized self-assembled monolayer ( $\text{CH}_3\text{-SAM}$ ) probe and the protein molecules covalently bound to a carboxylic SAM on a gold-coated glass coverslip. The adhesion energy passed through a maximum for the tethered proteins during excursions with temperature or chemical denaturants. The initial rise in adhesion energy on increasing the temperature or GuHCl concentration was due to increasing exposure of the unfolded hydrophobic core of the proteins to the  $\text{CH}_3\text{-SAM}$  tip, while the decrease in adhesion energy at high temperature or large concentrations of denaturant is attributed to interprotein association with nearest neighbors. Attempts to recover their folded state upon cooling (or reducing GuHCl concentration) were unsuccessful. Also, dilution of surface-tethered LYS reduced the aggregation with nearest neighbors about 6-fold. These results are in qualitative agreement with Monte Carlo simulations on a simple two-letter lattice protein model, especially for low concentrations of grafted proteins.

- Racemization of Alcohols Catalyzed by  $[\text{RuCl}(\text{CO})_2(\eta^5\text{-pentaphenylcyclopentadienyl})]$  - Mechanistic Insights from Theoretical Modeling  
Nyh len, J.; Privalov, T.; B ckvall, J.-E. *Chem. Eur. J.* **2009**, *15*, 5220-5229.

Abstract:

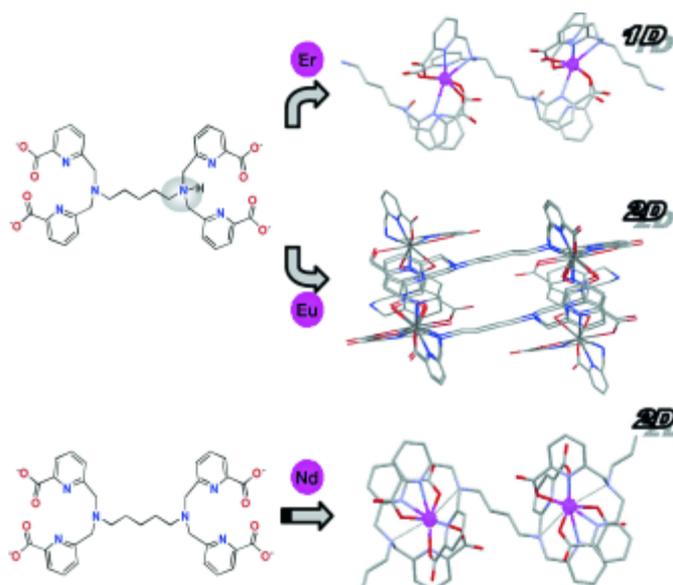


**Which mechanism?** Dissociation of a CO ligand from alkoxide complex **1** to give intermediate **2** seems to be a viable pathway for racemization according to DFT calculations. The highest Gibbs free energy barrier is 22.6 kcal mol<sup>-1</sup> for this pathway. Very fast alkoxide exchange can occur in **2** with essentially no barrier. The calculations indicate an alternative low-energy pathway for alkoxide exchange between **1** and **1'** without CO dissociation with a barrier of only 13 kcal mol<sup>-1</sup>.

Two possible pathways of inner-sphere racemization of *sec*-alcohols by using the  $[\text{RuCl}(\text{CO})_2(\eta^5\text{-pentaphenylcyclopentadienyl})]$  catalyst (**1**) have been thoroughly investigated by means of density function calculations. To be able to racemize alcohols, catalyst **1** needs to have a free coordination site on the metal. This can be achieved either by a  $\eta^5 \rightarrow \eta^3$  ring slippage or by dissociation of a carbon monoxide (CO) ligand. The  $\eta^5 \rightarrow \eta^3$  ring-slip pathway was found to have a high potential energy barrier, 42 kcal mol<sup>-1</sup>, which can be explained by steric congestion in the transition state. On the other hand, CO dissociation to give a 16-electron complex has a barrier of only 22.6 kcal mol<sup>-1</sup>. We have computationally discovered a mechanism involving CO participation that does not require  $\eta^5 \rightarrow \eta^3$  ring slippage. The key features of this mechanism are 1) CO-assisted exchange of chloride for alkoxide, 2) alcohol-alkoxide exchange, and 3) generation of an active 16-electron complex through CO dissociation with subsequent  $\beta$ -hydride elimination as the racemization step. We have found a low-energy pathway for reaction of **1** with potassium *tert*-butoxide and a pathway for fast alkoxide exchange with interaction between the incoming/leaving alcohol and one of the two CO ligands. We predict that dissociation of a Ru-bound CO ligand does not occur in these exchange reactions. Dissociation of one of the two Ru-bound CO ligands has been found necessary only at a later stage of the reaction. Though this barrier is still quite high, our results indicate that it is not necessary to cross the CO dissociation barrier for the racemization of each new alcohol. Thus, the dissociation of a CO ligand is interpreted as a rate-limiting reaction step in order to create a catalytically active 16-electron complex.

- Lanthanide-Based Coordination Polymers Assembled by a Flexible Multidentate Linker: Design, Structure, Photophysical Properties, and Dynamic Solid-State Behavior  
Marchal, C.; Filinchuk, Y.; Chen, X.-Y.; Imbert, D.; Mazzanti, M. *Chem. Eur. J.* **2009**, *15*, 5273-5288.

Abstract:



**Flexible director:** A flexible multidentate linker containing picolinate chromophores directs the selective formation of luminescent 1D lanthanide-based polymers. Partial protonation significantly decreases the preorganization of the linker, thus leading to supramolecular 1D and 2D isomers (see scheme). The lanthanide-containing 1D polymers undergo reversible structural modification in the hydration/dehydration process, which is also associated with significant differences in the luminescence emission.

Four picolinate building blocks were implemented into the multidentate linker  $N,N',N''$ -tetrakis[(6-carboxypyridin-2-yl)methyl]butylenediamine ( $H_4$ tpabn) with a linear flexible spacer to promote the assembly of lanthanide-based 1D coordination polymers. The role of the linker in directing the geometry of the final assembly is evidenced by the different results obtained in the presence of  $Htpabn^{3-}$  and  $tpabn^{4-}$  ions. The  $tpabn^{4-}$  ion leads to the desired 1D polymer  $\{[Nd(tpabn)]H_3O \cdot 6 H_2O\}_\infty$  (**12**). The  $Htpabn^{3-}$  ion leads to the assembly of  $Tb^{III}$  and  $Er^{III}$  ions into 1D zigzag chains of the general formula  $\{[M(Htpabn)] \cdot x H_2O\}_\infty$  ( $M=Tb$ ,  $x=14$  (**1**);  $M=Tb$ ,  $x=8$  (**11**);  $M=Er$ ,  $x=14$  (**2**);  $M=Er$ ,  $x=5.5$  (**4**)), a 2D network is formed by the  $Eu^{III}$  ion (i.e.,  $\{[Eu(Htpabn)] \cdot 10 H_2O\}_\infty$  (**7**)), and both supramolecular isomers (1D and 2D) are obtained by the  $Tb^{III}$  ion. The high flexibility of the polymeric chains results in a dynamic behavior with a solvent-induced reversible structural transition. The  $Tb^{III}$ - and  $Eu^{III}$ -containing polymers display high-luminescence quantum yields (38 and 18 %, respectively). A sizeable near-IR luminescence emission is observed for the  $Er^{III}$ - and  $Nd^{III}$ -containing polymers when lattice water molecules are removed.