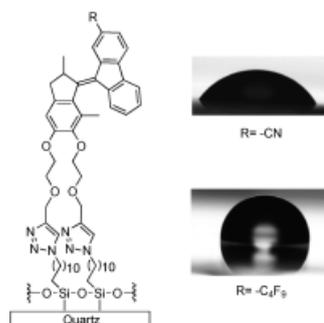


Interfaces between organic electron-donating (D) and electron-accepting (A) materials have the ability to generate charge carriers on illumination. Efficient organic solar cells require a high yield for this process, combined with a minimum of energy losses. Here, we investigate the role of the lowest energy emissive interfacial charge-transfer state (CT₁) in the charge generation process. We measure the quantum yield and the electric field dependence of charge generation on excitation of the charge-transfer (CT) state manifold via weakly allowed, low-energy optical transitions. For a wide range of photovoltaic devices based on polymer:fullerene, small-molecule:C60 and polymer:polymer blends, our study reveals that the internal quantum efficiency (IQE) is essentially independent of whether or not D, A or CT states with an energy higher than that of CT₁ are excited. The best materials systems show an IQE higher than 90% without the need for excess electronic or vibrational energy.

- Towards Dynamic Control of Wettability by Using Functionalized Altitudinal Molecular Motors on Solid Surfaces

London, G.; Chen, K.-Y.; Carroll, G. T.; Feringa, B. L. *Chem. Eur. J.* **2013**, *19*, 10690–10697.

Abstract:



We report the synthesis of altitudinal molecular motors that contain functional groups in their rotor part. In an approach to achieve dynamic control over the properties of solid surfaces, a hydrophobic perfluorobutyl chain and a relatively hydrophilic cyano group were introduced to the rotor part of the motors. Molecular motors were attached to quartz surfaces by using interfacial 1,3-dipolar cycloadditions. To test the effect of the functional groups on the rotary motion, photochemical and thermal isomerization studies of the motors were performed both in solution and when attached to the surface. We found that the substituents have no significant effect on the thermal and photochemical processes, and the functionalized motors preserved their rotary function both in solution and on a quartz surface. Preliminary results on the influence of the functional groups on surface wettability are also described.

- Self-Assembled π -Extended Condensed Benzothiophene Nanoribbons for Field-Effect Transistors

3

Pan, Z.; Liu, Y.; Fan, F.; Chen, Y.; Li, Y.; Zhan, X.; Song, Y. *Chem. Eur. J.* **2013**, *19*, 9771–9774.

Abstract:

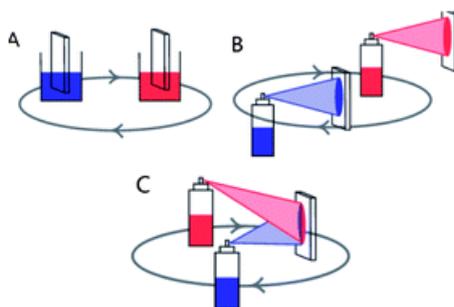


Nanostructures: A new air-stable π -extended condensed benzothiophene was prepared by starting from 4,8-dioctyl-oxybenzo[1,2-b:4,5-b']dithiophene in about 54% overall yield. Highly ordered 1D organic nanoribbons of the resultant compound were formed by molecular self-assembly. An individual nanoribbon-based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

- Just spray it – LbL assembly enters a new age

Dierendonck, M.; De Koker, S.; De Rycke, R.; De Geest, B. G. *Soft Matter* **2014**, *10*, 804-807.

Abstract:

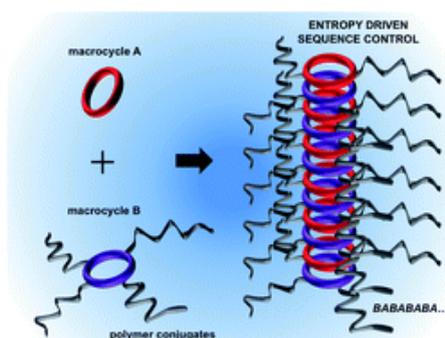


Over the past two decades the Layer-by-Layer (LbL) assembly of multilayer thin films has witnessed an explosive growth. However, this has so far not been translated into numerous industrial applications mainly owing to the time-consuming multistep assembly procedure which was originally based on dipping of a substrate into a solution. More recently the use of spray-based approaches, both for planar films as well as for the construction of polymeric particles, has emerged. Here we highlight these recent advances that have the potential to move the LbL field forward.

- Directing the self-assembly of supra-biomolecular nanotubes using entropic forces

Ruiz, L.; Keten, S. *Soft Matter* **2014**, *10*, 851-861.

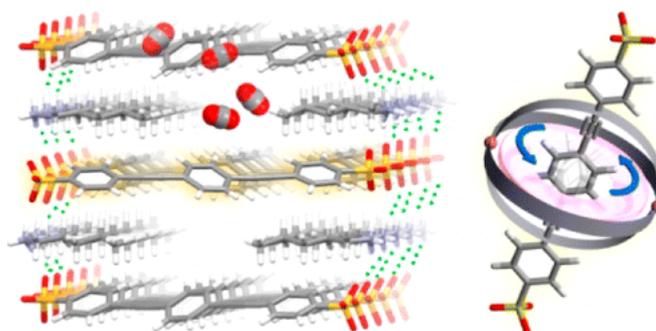
Abstract:



Peptide self-assembly, ubiquitous in biology, is one of the most promising ‘bottom-up’ approaches for the generation of synthetic supramolecular architectures. However, directing the self-assembly of functional peptides into predictable ordered structures most often requires precise tuning of weak intermolecular forces. Existing strategies are generally based on specific interactions between molecular mediators that require complex chemical synthesis pathways and elaborated design rules. Here we establish a theoretical framework that delineates a generic route towards directing the self-assembly of small peptides by simply using entropic forces generated by the polymer chains attached to the peptides. We demonstrate the viability of this concept for polymer-conjugated peptide nanotubes using coarse-grained molecular dynamics (CGMD) simulations combined with theoretical calculations. We show that conjugated polymer chains create an entropic penalty due to chain confinement upon assembly, and illustrate that the self-assembly process can be directed by merely varying the degree of polymer conjugation. Specifically, the entropic penalty, and consequently, the binding energy between peptides can be greatly varied by changing the length and the number of conjugated polymers. Extending this concept for peptides with different degrees of conjugation reveals a path towards controlling the stacking sequence of binary mixtures. Remarkably, we find that a large disparity in the conjugation degree of the two peptides results in a preference towards alternating mixed sequences that minimize the entropic penalty of confinement in the thermodynamic limit. Our study explains recent experiments on polymer–peptide conjugates and sets the stage for utilizing entropic forces to guide the stacking sequence of functional macrocycles in tubular assemblies.

- Engineering Switchable Rotors in Molecular Crystals with Open Porosity
Comotti, A.; Bracco, S.; Yamamoto, A.; Beretta, M.; Hirukawa, T.; Tohnai, N.; Miyata, M.; Sozzani, P. *J. Am. Chem. Soc.* **2014**, *136*, 618-621.

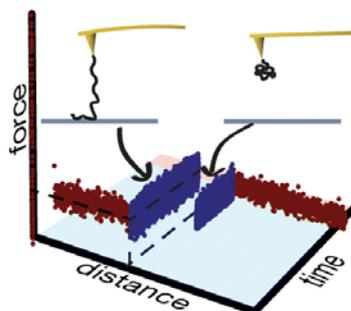
Abstract:



The first example of a porous molecular crystal containing rotors is presented. The permanently porous crystal architecture is sustained by rotor-bearing molecular rods which are connected through charge-assisted hydrogen bonds. The rotors, as fast as 108 Hz at 240 K, are exposed to the crystalline channels, which absorb CO₂ and I₂ vapors at low pressure. The rotor dynamics could be switched off and on by I₂ absorption/desorption, showing remarkable change of material dynamics by the interaction with gaseous species and suggesting the use of molecular crystals in sensing and pollutant management.

- Peptide Desorption Kinetics from Single Molecule Force Spectroscopy Studies
Krysiak, S.; Liese, S.; Netz, R. R.; Hugel, T. *J. Am. Chem. Soc.* **2014**, *136*, 688-697.

Abstract:

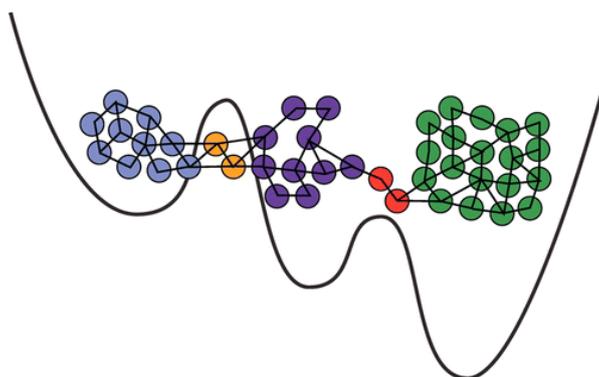


We use a combined experimental/theoretical approach to determine the intrinsic monomeric desorption rate k_0 of polytyrosine and polylysine homopeptides from flat surfaces. To this end, single polypeptide molecules are covalently attached to an AFM cantilever tip and desorbed from hydrophobic self-assembled monolayers in two complementary experimental protocols. In the constant-pulling-velocity protocol, the cantilever is moved at finite velocity away from the surface and the distance at which the constant plateau force regime ends and the polymer detaches is recorded. In the waiting-time protocol, the cantilever is held at a fixed distance above the surface and the time until the polymer detaches is recorded. The desorption plateau force is varied between 10 and 90 pN, by systematically changing the aqueous solvent quality via the addition of ethanol or salt. A simultaneous fit of the experimental data from both protocols with simple two-state kinetic polymer theory allows to unambiguously disentangle and determine the model parameters corresponding to polymer contour length L , Kuhn length a , adsorption free energy λ , and intrinsic monomeric desorption rate k_0 . Crucial to our analysis is that a statistically significant number of single-polymer desorption experiments are done with one and the same single polymer molecule for different solvent qualities. The surprisingly low value of about $k_0 \approx 10^5$ Hz points to significant cooperativity in the desorption process of single polymers.

- Chemical Kinetics and Mechanisms of Complex Systems: A Perspective on Recent Theoretical Advances

Klippenstein, S. J.; Pande, V. S.; Truhlar, D. G. *J. Am. Chem. Soc.* **2014**, *136*, 528–546.

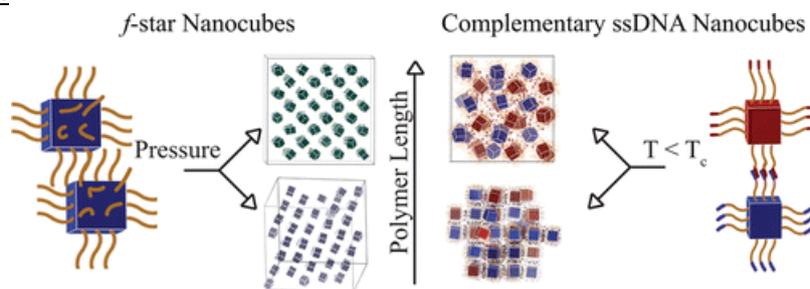
Abstract:



This Perspective presents a personal overview of the current status of the theory of chemical kinetics and mechanisms for complex processes. We attempt to assess the status of the field for reactions in the gas phase, at gas–solid interfaces, in liquid solutions, in enzymes, and for protein folding. Some unifying concepts such as potential energy surfaces, free energy, master equations, and reaction coordinates occur in more than one area. We hope this Perspective will be useful for highlighting recent advances and for identifying important areas for future research.

- Self-Assembly and Crystallization of Hairy (f-Star) and DNA-Grafted Nanocubes
Knorowski, C.; Travasset, A. *J. Am. Chem. Soc.* **2014**, *136*, 653–659.

Abstract:



Nanoparticle superlattices are key to realizing many of the materials that will solve current technological challenges. Particularly important for their optical, mechanical or catalytic properties are superlattices of anisotropic (nonspherical) nanoparticles. The key challenge is how to program anisotropic nanoparticles to self-assemble into the relevant structures. In this Article, using numerical simulations, we show that “hairy” (f-star) or DNA grafted on nanocubes provides a general framework to direct the self-assembly into phases with crystalline, liquid crystalline, rotator, or noncrystalline phases with both long-range positional and orientational order. We discuss the relevance of these phases for engineering nanomaterials or micromaterials displaying precise orientational order, realization of dry superlattices as well as for the field of programmed self-assembly of anisotropic nanoparticles in general.

- Development of Toroidal Nanostructures by Self-Assembly: Rational Designs and Applications
Kim, Y.; Li, W.; Shin, S.; Lee, M. *Acc. Chem. Res.*, **2013**, *46*, 2888–2897.

Abstract:



Toroidal nanostructures are symmetrical ring-shaped structures with a central internal pore. Interestingly, in nature, many transmembrane proteins such as β -barrels and α -helical bundles have toroidal shapes. Because of this similarity, toroidal nanostructures can provide a template for the development of transmembrane channels. However, because of the lack of guiding principles for the construction of toroids, researchers have not widely studied the self-assembly of toroidal nanostructures as compared with the work on other supramolecular architectures.

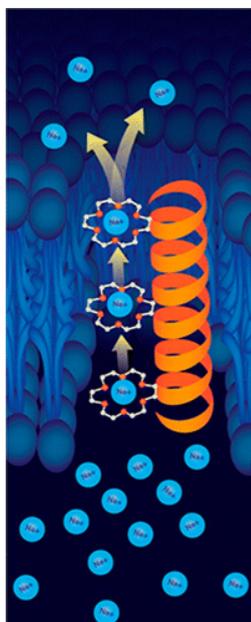
In this Account, we describe our recent efforts to construct toroidal nanostructures through the self-assembly of rationally designed building blocks. In one strategy for building these structures, we induce interfacial curvatures within the building blocks. When we laterally graft a bulky hydrophilic segment onto a *p*-oligophenyl rod or β -sheet peptides, the backbones of the self-assembled structures can bend in response to the steric effect of these large side groups, driving the *p*-

oligophenyl rod or β -sheet peptides to form nanosized toroids. In another strategy, we can build toroids from bent-shaped building blocks by stacking the macrocycles. Aromatic segments with an internal angle of 120° can associate with each other in aqueous solution to form a hexameric macrocycle. Then these macrocycles can stack on top of each other via hydrophobic and π - π interactions and form highly uniform toroidal nanostructures. We provide many examples that illustrate these guiding principles for constructing toroidal nanostructures in aqueous solution.

Efforts to create toroidal nanostructures through the self-assembly of elaborately designed molecular modules provide a fundamental approach toward the development of artificial transmembrane channels. Among the various toroids that we developed, a few nanostructures can insert into lipid membranes and allow limited transport in vesicles.

- Exploiting Peptide Nanostructures To Construct Functional Artificial Ion Channels
Otis, F.; Auger, M.; Voyer, N. *Acc. Chem. Res.* **2013**, *46*, 2934–2943.

Abstract:



Natural ion channel proteins possess remarkable properties that researchers could exploit to develop nanochemotherapeutics and diagnostic devices. Unfortunately, the poor stability, limited availability, and complexity of these structures have precluded their use in practical devices. One solution to these limitations is to develop simpler molecular systems through chemical synthesis that mimic the salient properties of artificial ion channels.

Inspired by natural channel proteins, our group has developed a family of peptide nanostructures that create channels for ions by aligning crown ethers on top of each other when they adopt an α -helical conformation. Advantages to this crown ether/peptide framework approach include the ease of synthesis, the predictability of their conformations, and the ability to fine-tune and engineer their properties.

We have synthesized these structures using solid phase methods from artificial crown ether amino acids made from L-DOPA. Circular dichroism and FTIR spectroscopy studies in different media confirmed that the nanostructures adopt the predicted α -helical conformation. Fluorescence studies verified the crown ether stacking arrangement. We confirmed the channel activity by single-channel measurements using a modified patch-clamp technique, planar lipid bilayer (PLB) assays, and various vesicle experiments. From the results, we estimate that a 6 Å distance between two

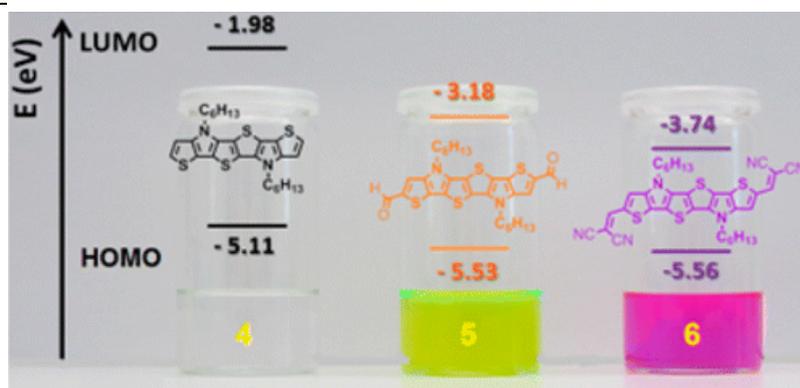
relays is ideal for sodium cation transport, but relatively efficient ion transport can still occur with an 11 Å distance between two crown ethers. Biophysical studies demonstrated that peptide channels operate as monomers in an equilibrium between adsorption at the surface and an active, transmembrane orientation.

Toward practical applications of these systems, we have prepared channel analogs that bear a biotin moiety, and we have used them as nanotransducers successfully to detect avidin. Analogs of channel peptide nanostructures showed cytotoxicity against breast and leukemia cancer cells.

Overall, we have prepared well-defined nanostructures with designed properties, demonstrated their transport abilities, and described their mechanism of action. We have also illustrated the advantages and the versatility of polypeptides for the construction of functional nanoscale artificial ion channels.

- Synthesis and Structural Analysis of Thiophene-Pyrrole-Based S,N-Heteroacenes
Wetzel, C.; Mishra, A.; Mena-Osteritz, E.; Liess, A.; Stolte, M.; Würthner, F.; Bäuerle, P. *Org. Lett.* **2014**, *16*, 362-365.

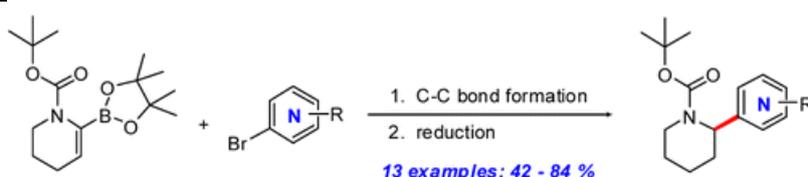
Abstract:



Fused *S,N*-heterohexacene **4** was synthesized by applying Pd-catalyzed tandem Buchwald–Hartwig coupling and further functionalized to corresponding acceptor-capped derivatives **5** and **6** showing bond length equalization in the π -conjugated backbone and intense optical transitions. Organic thin film transistors (OTFTs) based on a vacuum-deposited film of **6** exhibit p-channel charge-carrier mobilities as high as $0.021 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and current on/off ratios of 10^5 .

- Expedient Synthesis of α -Heteroaryl Piperidines Using a Pd-Catalyzed Suzuki Cross-Coupling–Reduction Sequence
Hesp, K. D.; Fernando, D. P.; Jiao, W.; Londregan, A. T. *Org. Lett.* **2014**, *16*, 413-415.

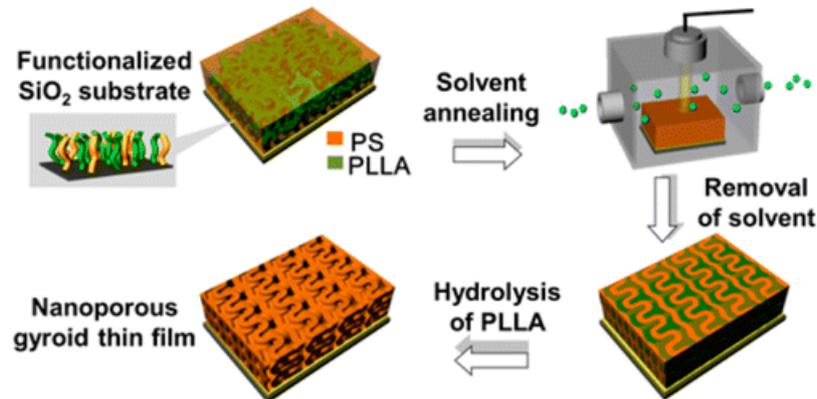
Abstract:



A method for the modular synthesis of α -heteroaryl piperidines is reported. The two-step procedure consists of an initial Pd-catalyzed Suzuki cross-coupling of the heteroaryl bromide with a boronate ester derived from *N*-Boc piperidone, followed by subsequent tetrahydropyridine reduction. Using this method, α -heteroaryl piperidine products featuring a broad range of pharmaceutically relevant azine and diazine substitutions have been prepared.

- Controlled Ordering of Block Copolymer Gyroid Thin Films by Solvent Annealing
She, M.-S.; Lo, T.-Y.; Ho, R.-M. *Macromolecules* **2014**, *47*, 175–182.

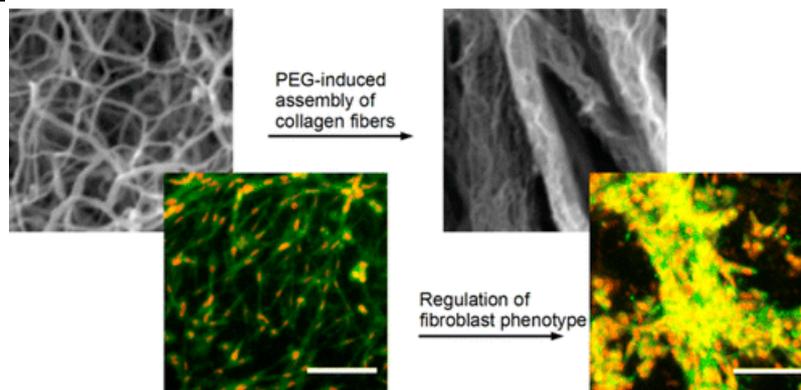
Abstract:



This work presents an approach to achieve controlled ordering of polystyrene-block-poly(l-lactide) (PS–PLLA) gyroid thin films on a neutral substrate using solvent annealing. Interesting morphological evolution from gyroid to cylinder can be found while using a partially selective solvent for the PS block to anneal the PS–PLLA thin film. To acquire a thin-film sample with thermodynamically stable gyroid morphology, a nonpreferential solvent should be used for solvent annealing to enable controlled ordering of gyroid thin film with the (211)_G plane parallel to the air surface and also the functionalized substrate. By taking advantage of degradable character of the PLLA block, nanoporous PS with well-defined texture can be fabricated by hydrolysis and used as a template for synthesis of various nanohybrids and nanoporous materials.

- Generation of Cell-Instructive Collagen Gels through Thermodynamic Control
Liang, Y.; Kong, H.; Tong, Y. W. *ACS Macro Lett.* **2013**, *2*, 1077–1081.

Abstract:



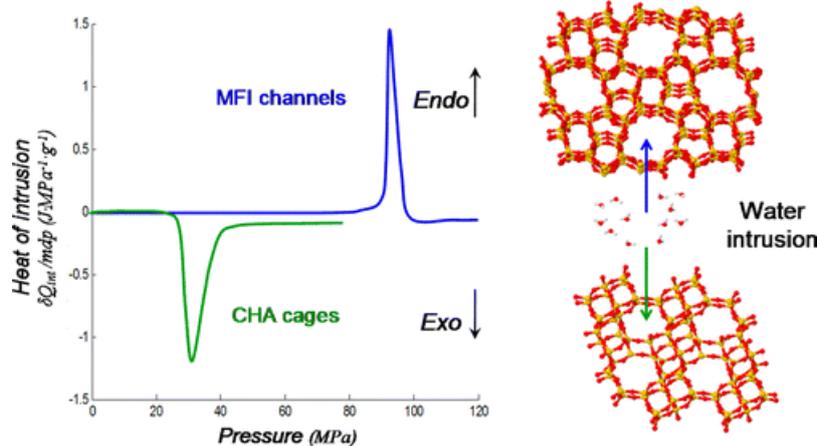
Recent studies have demonstrated the usefulness of three-dimensional hydrogel scaffolds for cell instruction. However, the control of gel architectures in cell-friendly conditions remains a challenge. Here, we report a novel method to generate unique three-dimensional collagen gel structures for the modulation of cell phenotypes. This was achieved by directing collagen self-assembly with unreactive hydrophilic polyethylene glycol (PEG) chains. Our approach allowed the fiber sizes and mechanics of three-dimensional collagen gels to be readily controlled. It also enabled the recapitulation of distinctive structures such as large perimysial collagen cables. Through different experiments, we elucidated the underlying mechanism for this PEG-mediated thermodynamic regulation of gel structure. We further used these cell-instructive three-dimensional gels to bring about pronounced

morphological changes in encapsulated fibroblasts and their activation to form contractile bundles. Overall, our platform fills a gap in the existing array of collagen scaffolds and can potentially be adapted to a variety of self-assembling systems.

- Confinement of Water in Hydrophobic Nanopores: Effect of the Geometry on the Energy of Intrusion

Karbowiak, T.; Weber, G.; Bellat, J.-P. *Langmuir* **2014**, *1*, 213–219.

Abstract:

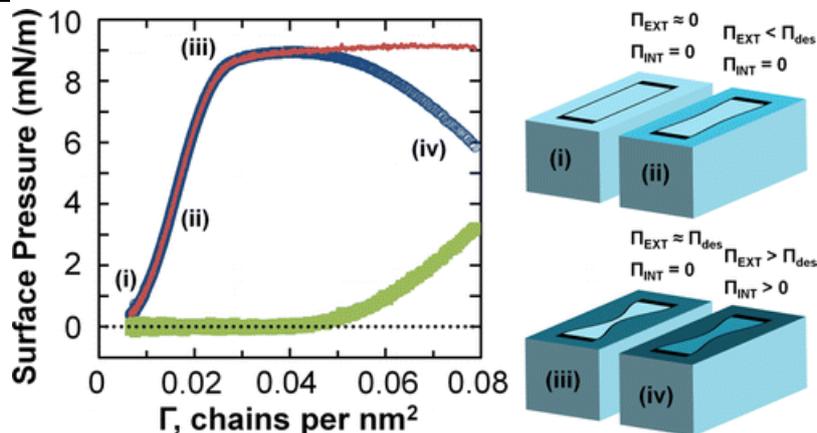


Water confinement in the hydrophobic nanopores of highly siliceous zeolite having MFI and CHA topology is investigated by high pressure manometry coupled to differential calorimetry. Surprisingly, the intrusion of water is endothermic for MFI but exothermic for CHA. This phase transition depends on the geometry of the environment in which water is confined: channels (MFI) or cavities (CHA). The energy of intrusion is mainly governed by the change in the coordination of water molecules when they are forced to enter the nanopores and to adopt a weaker, hydrogen-bonded structure. At such a nanoscale, the properties of the molecules are governed strongly by geometrical restraints. This implies that the use of classical macroscopic equations such as Laplace–Washburn will have limitations at the molecular level.

- Adsorption Energies of Poly(ethylene oxide)-Based Surfactants and Nanoparticles on an Air–Water Surface

Zell, Z. A.; Isa, L.; Ilg, P.; Leal, G. L.; Squires, T. M. *Langmuir* **2014**, *1*, 110–119.

Abstract:



The self-assembly of polymer-based surfactants and nanoparticles on fluid–fluid interfaces is central to many applications, including dispersion stabilization, creation of novel 2D materials, and surface patterning. Very often these processes involve compressing interfacial monolayers of particles or polymers to obtain a desired material microstructure. At high surface pressures, however, even highly interfacially active objects can desorb from the interface. Methods of directly measuring the energy which keeps the polymer or particles bound to the interface (adsorption/desorption energies) are therefore of high interest for these processes. Moreover, though a geometric description linking adsorption energy and wetting properties through the definition of a contact angle can be established for rigid nano- or microparticles, such a description breaks down for deformable or aggregating objects. Here, we demonstrate a technique to quantify desorption energies directly, by comparing surface pressure–density compression measurements using a Wilhelmy plate and a custom-microfabricated deflection tensiometer. We focus on poly(ethylene oxide)-based polymers and nanoparticles. For PEO-based homo- and copolymers, the adsorption energy of PEO chains scales linearly with molecular weight and can be tuned by changing the subphase composition. Moreover, the desorption surface pressure of PEO-stabilized nanoparticles corresponds to the saturation surface pressure for spontaneously adsorbed monolayers, yielding trapping energies of $\sim 10^3 k_B T$.

- White-Light-Emitting Supramolecular Gels
Praveen, V. K.; Ranjith, C.; Armaroli, N. *Angew. Chem. Int. Ed.* **2014**, *53*, 365–368.
Abstract:



Let there be light, let it be white: Recent developments in the use of chromophore-based gels as scaffolds for the assembly of white-light-emitting soft materials have been significant. The main advantage of this approach lies in the facile accommodation of selected luminescent components within the gel. Excitation-energy-transfer processes between these components ultimately generate the desired light output.

- Dative Bonds in Main-Group Compounds: A Case for Fewer Arrows!
Himmel, D.; Krossing, I.; Schnepf, A. *Angew. Chem. Int. Ed.* **2014**, *53*, 370–374.
Abstract:



or



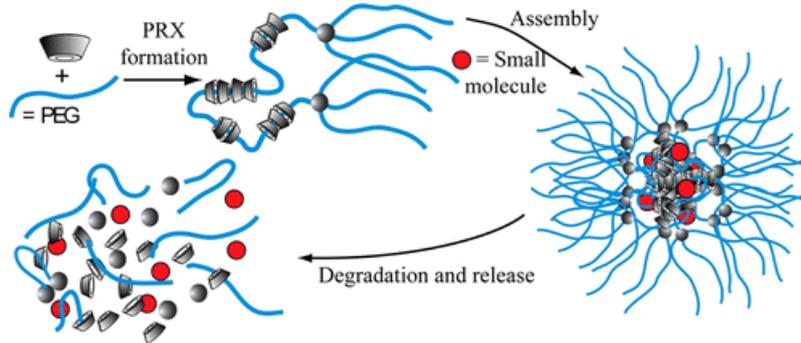
Risky business? The use of dative bonds to describe the electronic structure of main-group compounds has come into vogue in recent years. But where are the limits? When does the description as a dative bond make sense and when is this view misleading? This Essay develops the idea on the basis of current examples.

- Self-Assembled Stimuli-Responsive Polyrotaxane Core–Shell Particles

Tardy, B. L.; Dam, H. H.; Kamphuis, M. M. J.; Richardson, J. J.; Caruso, F. *Biomacromolecules* **2014**, *15*, 53–59.

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Abstract:

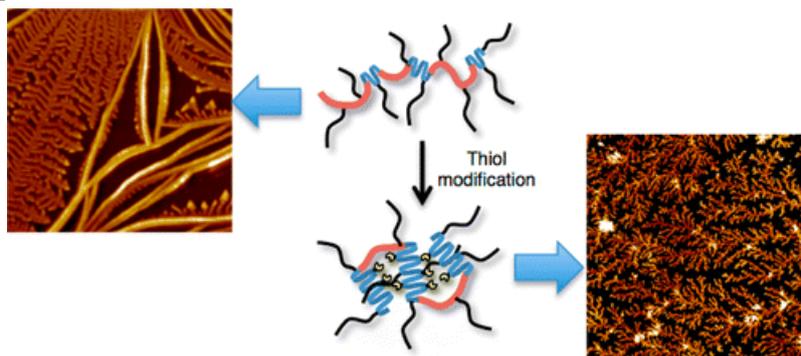


Thermodynamically assembled core–shell nanocarriers are potential candidates for drug delivery applications due to their submicrometer size and the ability to load drugs into their hydrophobic core. Herein, we describe the formation of core–shell particles that consist of noncovalent polymers, that is, polyrotaxanes (PRXs), that form an α -cyclodextrin (α CD) core surrounded by a corona of low-fouling poly(ethylene glycol) (PEG). The PRX core–shell particles are able to sequester small organic molecules, such as pyrene and calcein, releasing these small molecules during degradation. The small, cellular peptide, glutathione, was used to degrade the particles through the reductive cleavage of disulfide bonds that stabilize the individual PRX polymers. Cleavage of a single bond allows for the degradation of the supramolecular-polymer, making these PRX core–shell particles highly responsive. Furthermore, these particles demonstrate negligible cytotoxicity in mammalian cells, making them promising carriers for future drug delivery research.

- Self-Assembly of High Molecular Weight Polypeptide Copolymers Studied via Diffusion Limited Aggregation

Meier, C.; Wu, Y.; Pramanik, G.; Weil, T. *Biomacromolecules* **2014**, *15*, 219–227.

Abstract:

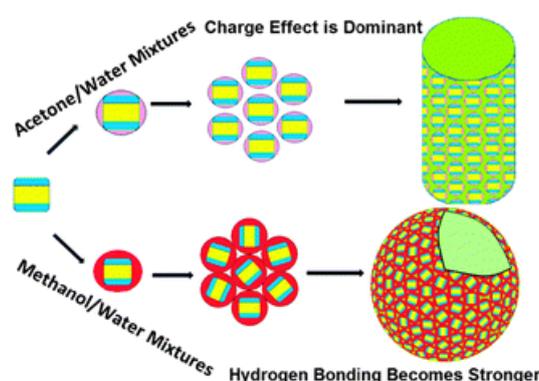


The assembly of high molecular weight polypeptides into complex architectures exhibiting structural complexity ranging from the nano- to the mesoscale is of fundamental importance for various protein-related diseases but also hold great promise for various nano- and biotechnological applications. Here, the aggregation of partially unfolded high molecular weight polypeptides into multiscale fractal structures is investigated by means of diffusion limited aggregation and atomic force microscopy. The zeta potential, the hydrodynamic radius, and the obtained fractal morphologies were correlated with the conformation of the polypeptide backbones as obtained from circular dichroism measurements. The polypeptides are modified with polyethylene oxide side chains

to stabilize the polypeptides and to normalize intermolecular interactions. The modification with the hydrophobic thioctic acid alters the folding of the polypeptide backbone, resulting in a change in solution aggregation and fractal morphology. We found that a more compact folding results in dense and highly branched structures, whereas a less compact folded polypeptide chain yields a more directional assembly. Our results provide first evidence for the role of compactness of polypeptide folding on aggregation. Furthermore, the mesoscale-structured biofilms were used to achieve a hierarchical protein assembly, which is demonstrated by deposition of Rhodamine-labeled HSA with the preassembled fractal structures. These results contribute important insights to the fundamental understanding of the aggregation of high molecular weight polypeptides in general and provide opportunities to study nanostructure-related effects on biological systems such as adhesion, proliferation, and the development of, for example, neuronal cells.

- The self-assembly of a macroion with anisotropic surface charge density distribution
Haso, F.; Fang, X.; Yin, P.; Li, D.; Ross, J. L.; Liu, T. *Chem. Commun.* **2014**, 49, 609-611.

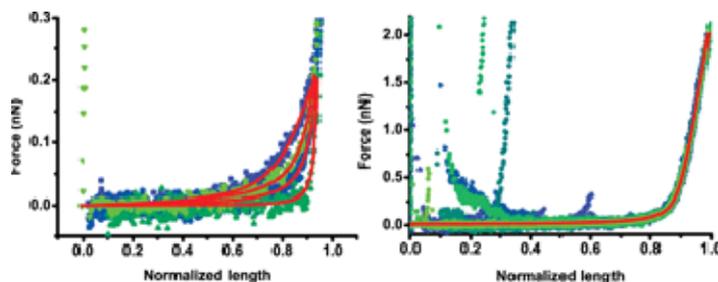
Abstract:



A macroion, having anisotropic surface charge density distribution, shows unique self-assembly behavior in polar solvents. Regular “blackberry”-like assemblies form in methanol-water mixtures due to counter-ion mediated attraction and the strong contribution of hydrogen bonding. However, rod-like assemblies form in acetone-water mixtures as the charge inhomogeneity effect overcomes the non-directional hydrogen bonding.

- Stiffness *versus* architecture of single helical polyisocyanopeptides
van Buul, A. M.; Schwartz, E.; Brocorens, P.; Koepf, M.; Beljonne, D.; Maan, J. C.; Christianen, P. C. M.; Kouwer, P. H. J.; Nolte, R. J. M.; Engelkamp, H.; Blank, K.; Rowan, A. E. *Chem. Sci.* **2013**, 4, 2357-2363.

Abstract:

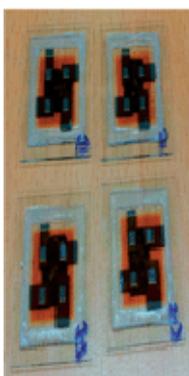


Helical structures play a vital role in nature, offering mechanical rigidity, chirality and structural definition to biological systems. Little is known about the influence of the helical architecture on the intrinsic properties of polymers. Here, we offer an insight into the nano architecture of helical

polymers by measuring helical polyisocyanopeptides with single molecule force spectroscopy. An unprecedented large heterogeneity in the stiffness of the polymers was found. The heterogeneity persisted when the stiffness of these polymers was steered by: (1) enhancing the formation of the hydrogen bonding network along the polymer, (2) *via* π - π stacking interactions of aromatic perylenes, and (3) by changing the stereochemistry of the side chain. However, the heterogeneity was lost after completely disrupting the secondary structure by the addition of trifluoroacetic acid. Molecular dynamics simulations revealed three possible structural conformations which can account for the observed heterogeneity and their corresponding energy landscape is proposed.

- High performance organic photovoltaics with zinc oxide and graphene oxide buffer layers
Yusoff, A. R. M.; Kim, H. P.; Jang, J. *Nanoscale* **2014**, *6*, 1537–1544.

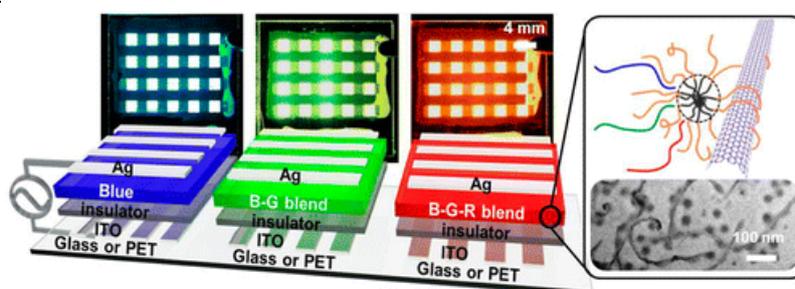
Abstract:



We report air stable inverted organic photovoltaics (OPVs) incorporating graphene oxide (GO) and solution processed zinc oxide (ZnO) as hole transport and electron transport layers, respectively. Both the hole transport layer and the electron transport layer (HTL and ETL) are of advantage in high transparency and environmental stability. The use of GO and ZnO in poly(2,7-carbazole) derivative (PCDTBT):fullerene derivative (PC₇₀BM)-based inverted OPVs leads to an improved device stability and enhanced high open circuit voltage (V_{oc}) of 0.81 V, a short-circuit current density (J_{sc}) of 14.10 mA cm⁻², and a fill factor (FF) of 54.44 along with a power conversion efficiency of 6.20%.

- Extremely Bright Full Color Alternating Current Electroluminescence of Solution-Blended Fluorescent Polymers with Self-Assembled Block Copolymer Micelles
Cho, S. H.; Jo, S. S.; Hwang, I.; Sung, J.; Seo, J.; Jung, S.-H.; Bae, I.; Choi, J. R.; Cho, H.; Lee, T.; Lee, J. K.; Lee, T.-W.; Park, C. *ACS Nano* **2013**, *7*, 10809–10817.

Abstract:



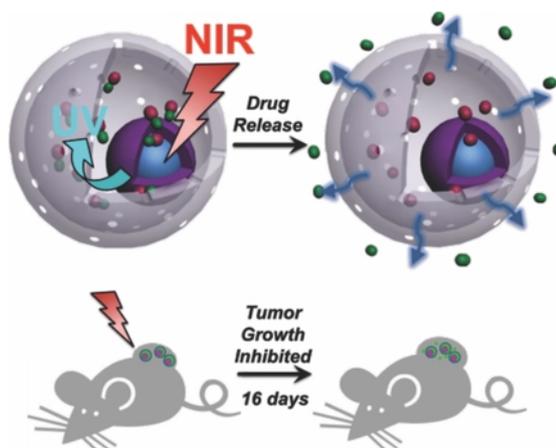
Electroluminescent (EL) devices operating at alternating current (AC) electricity have been of great interest due to not only their unique light emitting mechanism of carrier generation and recombination but also their great potential for applications in displays, sensors, and lighting. Despite

great success of AC-EL devices, most device properties are far from real implementation. In particular, the current state-of-the-art brightness of the solution-processed AC-EL devices is a few hundred candela per square meter (cd m^{-2}) and most of the works have been devoted to red and white emission. In this manuscript, we report extremely bright full color polymer AC-EL devices with brightness of approximately 2300, 6000, and 5000 cd m^{-2} for blue (B), green (G), and red (R) emission, respectively. The high brightness of blue emission was attributed to individually networked multiwalled carbon nanotubes (MWNTs) for the facile carrier injection as well as self-assembled block copolymer micelles for suppression of interchain nonradiative energy quenching. In addition, effective FRET from a solution-blended thin film of B-G and B-G-R fluorescent polymers led to very bright green and red EL under AC voltage, respectively. The solution-processed AC-EL device also worked properly with vacuum-free Ag paste on a mechanically flexible polymer substrate. Finally, we successfully demonstrated the long-term operation reliability of our AC-EL device for over 15 h.

- Near-Infrared Photoregulated Drug Release in Living Tumor Tissue via Yolk-Shell Upconversion Nanocages

Zhao, L.; Peng, J.; Huang, Q.; Li, C.; Chen, M.; Sun, Y.; Lin, Q.; Zhu, L.; Li, F. *Adv. Funct. Mater.* **2014**, *24*, 363-371.

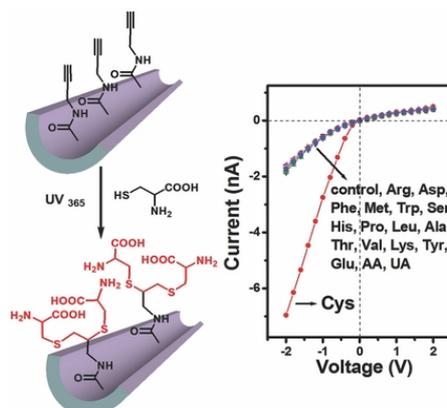
Abstract:



Phototrigger-controlled drug-release devices (PDDs) can be conveniently manipulated by light to obtain on-demand release patterns, thereby affording an improved therapeutic efficacy. However, no example of the PDDs has been demonstrated beyond the cellular level to date. By loading 7-amino-coumarin derivative caged anticancer drug chlorambucil to yolk-shell structured nanocages possessing upconversion nanophosphors (UCNPs) as moveable core and silica as mesoporous shell, a near-infrared (NIR)-regulated PDD is successfully created. In vitro experiments demonstrate that drug release from the PDD could be triggered by continuous-wave 980 nm light in a controlled pattern. The PDD could be taken up by cancer cells and release the drug to kill cancer cells upon NIR irradiation. Further in vivo studies demonstrate that the PDD can effectively respond to the NIR stimuli in living tissue. This is the first example of successful NIR-regulated drug release in living animal model. Such achievement resolves the problem of low tissue penetration depth for traditional PDDs by adopting UCNPs as an NIR light switcher, which gives impetus to practical applications.

- Fabrication of Cysteine-Responsive Biomimetic Single Nanochannels by a Thiol-yne Reaction Strategy and Their Application for Sensing in Urine Samples

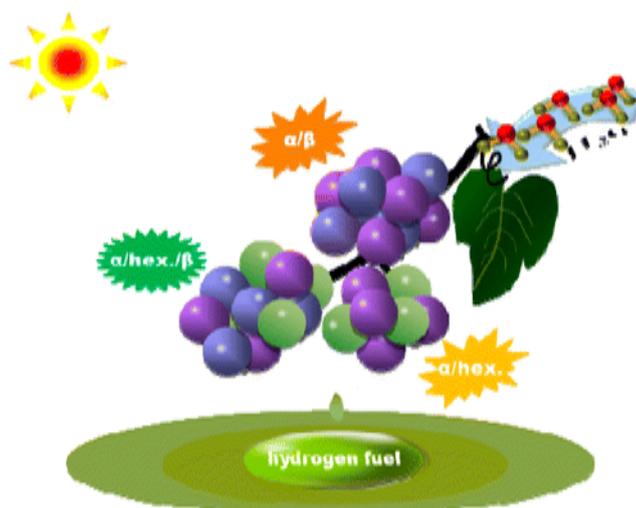
Sun, Z.; Han, C.; Song, M.; Wen, L.; Tian, D.; Li, H.; Jiang, L. *Adv. Mater.* **2014**, *26*, 455-460.

Abstract:

A photoinitiated thiol-yne click reaction strategy is used to fabricate a novel responsive biomimetic nanochannel platform. It displays a selective response for Cys by way of covalent bond formation on the channel surface. This system can be applied for Cys sensing with high specificity and non-interference performance in complex matrices and human urine samples.

- Control of Phase Coexistence in Calcium Tantalate Composite Photocatalysts for Highly Efficient Hydrogen Production

Wang, P.; Chen, P.; Kostka, A.; Marschall, R.; Wark, M. *Chem. Mater.* **2013**, *25*, 4739–4745.

Abstract:

Design and fabrication of semiconductor based composite photocatalysts with matching band structure is an important strategy to improve charge separation of photogenerated electron-hole pairs for photocatalytic hydrogen production. In our study, by aid of the simple and cost-effective molten salts method, a series of phase-controlled and composition-tuned calcium tantalate composite photocatalysts has been prepared by adjusting the initial atomic ratio of Ta/Ca precursors. We demonstrate the strong correlation between the photocatalytic activities of calcium tantalate composite photocatalysts for hydrogen evolution and respective phase compositions. Without any cocatalysts, these composites with the optimized phase composition of cubic α - CaTa_2O_6 /hexagonal $\text{Ca}_2\text{Ta}_2\text{O}_7$, cubic CaTa_2O_6 /hexagonal $\text{Ca}_2\text{Ta}_2\text{O}_7$ /orthorhombic β - CaTa_2O_6 , or cubic α - CaTa_2O_6 /orthorhombic β - CaTa_2O_6 showed very high photocatalytic H_2 production activities in the presence of methanol. It is attributed mainly to a significantly improved photoexcited charge carrier separation via the junctions and interfaces in the composites. Further by in situ photodeposition of

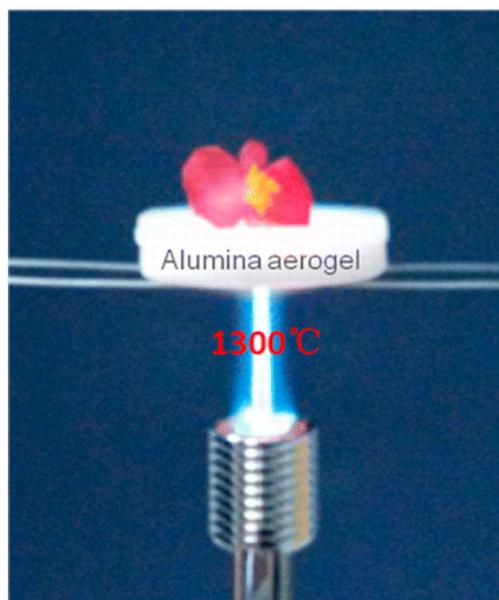
noble metal nanoparticles (Pt or Rh) as cocatalysts the photocatalytic activity of these composites was greatly promoted for H₂ production. The study on convenient fabrication of phase-coexisting composite photocatalysts with matching band structure for improving the photocatalytic hydrogen production sheds light on developing efficient composite photocatalyst as a means for conversion of solar energy to chemical energy.

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- Nanoengineering Super Heat-Resistant, Strong Alumina Aerogels

Zu, G.; Shen, J.; Zou, L.; Wang, W.; Lian, Y.; Zhang, Z.; Du, A. *Chem. Mater.* **2013**, *25*, 4757–4764.

Abstract:



Because of ultralow thermal conductivity, excellent catalytic activity, and better heat resistance than silica aerogel, alumina-based aerogel has drawn great interest as thermal insulators and catalysts. However, it is too fragile and sinters above 1000 °C (it shrinks drastically, >50%, and leaves the surface area as low as 10–70 m²/g at 1300 °C), which badly limits its high-temperature applications. Herein, super heat-resistant, strong alumina aerogels are prepared via a novel acetone-aniline in situ water formation (ISWF) method combined with novel modification techniques: supercritical fluid modification (SCFM) and hexamethyldisilazane gas phase modification. The heat resistance of alumina aerogel is enhanced up to 1300 °C via this method. The shrinkage of the optimized alumina aerogel is reduced to as low as 1 and 5% and the corresponding surface area reaches up to 152–261 and 125–136 m²/g after being heated to 1200 and 1300 °C for 2 h, respectively. The strength is significantly increased by more than 120% through SCFM. It also exhibits excellent thermal insulation properties at temperatures up to 1300 °C. This may significantly contribute to their practical ultrahigh-temperature applications in thermal insulations, catalysts, catalyst supports, etc.