Although there has been for the past 20 years great interest in the synthesis and use of metal nanoparticles, little attention has been paid to the complexity of the surface of these species. In particular, the different aspects concerning the ligands present, their location, their mode of binding, and their dynamics have been little studied. Our group has started in the early 1990s an investigation of the surface coordination chemistry of ruthenium and platinum nanoparticles but at that time with a lack of adequate techniques to fulfill our ambition. Over 10 years later, we went back to this problem and could obtain a more precise vision of the surface species.

This Account is centered on ruthenium chemistry. This metal has been the most studied in our group, first thanks to the availability of a precursor, Ru(cyclooctadiene)(cyclooctatriene) (Ru(COD)(COT)), which possesses the ability to decompose in very mild conditions without leaving residues on the resulting nanoparticles and second because of the absence of magnetic perturbations (Knight shift, paramagnetism, ferromagnetism, etc.), which has allowed the use of solution and solid state NMR. In this respect, it has been possible to evidence the presence of a high concentration of hydrides on the surface of these particles, to study their dynamics, and to show that since the polarity of the Ru−H bond is similar to that of the C−H bond, a Ru/H NP would behave as a big lipophilic entity. The second point was to characterize the coordination of ancillary ligands. This has been achieved for different ligands, in particular phosphines and carbenes, which made possible the study of the modification of NP reactivity induced by surface ligands. This led to the conclusion that the presence of surface ligands can benefit both the activity of NP catalysts and their selectivity. If it was expected that the selectivity could be modulated, the promoting effect from the presence of ligands on, for example, arene or CO hydrogenation was totally unexpected. Playing with poison atoms (Sn, Fe, etc.) or ligands (CO) may allow us to play with the reactivity of the NPs to make them more selective for selected reactions. Finally, the search for specific ligands for nanoparticles is still in its infancy, but some examples have been found as have specific reactions of nanoparticles. Obviously arene hydrogenation and CO hydrogenation were well-known in heterogeneous catalysis, but we could demonstrate that they can be carried out in very mild conditions on ligand stabilized RuNPs. On the other hand, the enantiospecific C−H activation leading to enantioselective labeling of large organic or biomolecules or the C−C bond cleavage in mild conditions were both unexpected. There is still much work to perform for reaching the degree of control on nanoparticles that is presently achieved in organometallic molecular chemistry, but this work shows that it is possible.
Comment: This account paper deals with Ru NPs but the concepts can be extended to other kind of particles. What I really enjoyed was that for once people really try to understand what is happening at the surface of a metallic NP.

**Designing Helical Molecular Capsules Based on Folded Aromatic Amide Oligomers**


The ab initio rational structure-based design of a synthetic molecular receptor for a given complex biomolecular guest remains an elusive objective, yet remarkable progress has been achieved in recent years. This Account deals with the use of folded artificial aromatic amide oligomers, also termed aromatic foldamers, inspired from biopolymer structures, for the design of helical molecular capsules that can recognize guest molecules, completely surround them, and isolate them from the solvent, thus giving rise to a sort of guest encapsulation associated with slow binding and release kinetics. The development of new amino acid, diacid, and diamine monomers, a main source of creativity in this field, progress in their assembly into ever longer oligoamide sequences, and the predictability of the folded structures due to their inherent rigidity and simple folding principles, allowed for the design and preparation of unimolecular and bimolecular capsule shapes. These capsules consist of molecular helices having a large diameter in the middle and a narrow diameter at both ends thus creating a cavity suitable for binding a guest molecule. The understanding of molecular recognition properties within these bioinspired containers has greatly progressed. Recognition of simple guests such as diols or amino-alcohols may thus be predicted, and hosts can be proposed for guests as complex as saccharides using first principle design. Taking advantage of the modular nature of oligomeric sequences, of their synthetic accessibility and of their propensity to grow into crystals suitable for X-ray crystallographic analysis, a structure-based iterative design methodology has been developed that eventually yielded exquisite guest selectivity, affinity, and diastereoselectivity. This methodology involves rational negative design steps during which changes in the foldamer capsule sequence are not intended to improve binding to the targeted guest but instead to exclude the binding of other guests while preserving key interactions with the target. Metal ions can also be introduced at the inner rim of foldamer capsules and eventually assist the binding of an organic guest. These results demonstrate the viability of an ab initio approach to abiotic receptor design based on aromatic foldamers. The dynamic of the capsules associated with their self-organized nature provides opportunities to not only tune guest binding and selectivity, but also guest capture and release kinetics as well as cavity size and shape. Controlled release thus emerges as a realistic objective. Recent progress thus opens up multiple perspectives for the development of tailored hosts, sensors, and carriers structurally and
conceptually different from earlier generations of macrocyclic-based receptors or from supramolecular containers produced by self-assembly.

**Comment:** Foldamers is one of the few domains where we try to make things even simpler than nature does. Huc’s group is one of the leading group in this domain.

### 3D Superstructures with An Orthorhombic Lattice Assembled by Colloidal PbS Quantum Dots


We report a new type of metamaterial comprising a highly ordered 3D network of 3-7 nm lead sulfide quantum dots self-assembled in an organic matrix formed by amphiphilic ligands (oleic acid molecules). The obtained 3D superstructures possess an orthorhombic lattice with the distance between the nanocrystals as large as 10-40 nm. Analysis of self-assembly and destruction of the superstructures in time performed by a SAXS technique shows that their morphology depends on the quantity of amphiphilic ligands and width of the quantum dot size and its distribution. Formation of the superstructures is discussed in terms of a model describing the lyotropic crystal formation by micelles from three-phase mixtures. The results show that the organic molecules possessing surfactant properties and capable of forming micelles with nanoparticles as a micelle core can be utilized as building blocks for the creation of novel metamaterials based on a highly ordered 3D network of semiconductors, metals or magnetic nanoparticles.

**Comment:** Self-assembly of quantum dots into 3D superstructures is cool. This work gives a clear SAXS analysis and can be a good reference for SAXS analysis.
Trithiazolyl-1,3,5-triazines Bearing Decyloxybenzene Moieties: Synthesis, Photophysical and Electrochemical Properties, and Self-assembly Behavior


We report the synthesis, photophysical properties, redox characteristics, and self-assembly behavior of disk-shaped trithiazolyl-1,3,5-triazines that bear decyloxybenzene moieties. These compounds were synthesized by a Migita-Kosugi-Stille coupling reaction of 1,3,5-trichlorotriazine with three different tributyltin(thiazoles) as the key step. The structure-property relationships, namely the effects of the incorporation of thiazole units into the triazine unit, the conjugation connectivity between the thiazole and triazine units, and the insertion of ethynylene spacers between the thiazole and decyloxybenzene moieties on the properties of the trithiazolyl-1,3,5-triazines were comprehensively investigated. Binding of the triazine core at the 5-position of the thiazole moieties effectively extended the π-conjugation and afforded high fluorescence quantum yields. The ethynylene spacers substantially lowered the LUMO level relative to the HOMO level. The prepared trithiazolyl-1,3,5-triazines self-assembled in solution, and the introduction of thiazole units at the 5-position enhanced this behavior. Detailed thermodynamic studies on the self-association behavior were conducted, and the formation of self-assembled 1D clusters is disclosed.

Comment: This work studies the π-conjugation of trithiazolyl-1,3,5-triazine derivatives. It’s a nice work.

Reversible Disassembly of Metallasupramolecular Structures Mediated by a Metastable-State Photoacid


The addition of a metastable-state photoacid to solutions containing metal–ligand assemblies renders the systems light responsive. Upon irradiation, proton transfer from the photoacid to the ligand is observed, resulting in disassembly of the metallasupramolecular structure. In the dark, the process is fully reversed. Light-induced switching was demonstrated.
for six different metal–ligand assemblies containing Pd$^{II}$, Pt$^{II}$ or Ru$^{II}$ complexes and bridging polypyridyl ligands. The methodology allows liberating guest molecules with light.

**Comment:** The authors have been able to control the disassembly of some supramolecular structures using an uncommon methodology. Indeed, they used a photoacid (PAH), activated under irradiation of violet light (~425 nm), to protonate the ligands of the assemblies. While this work remains interesting in its own right, what struck me are the opportunities offered by a photoacid in our own supramolecular systems. Indeed, it would allow us to control the pH of a mixture using light irradiation instead of adding some acids or bases (in this article the pH seems to have been modified by more than two units).

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**From Precision Polymers to Complex Materials and Systems**


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Complex chemical systems, such as living biological matter, are highly organized structures based on discrete molecules in constant dynamic interactions. These natural materials can evolve and adapt to their environment. By contrast, man-made materials exhibit simpler properties. In this Review, we highlight that most of the necessary elements for the development of more complex synthetic matter are available today. Using modern strategies, such as controlled radical polymerizations, supramolecular polymerizations or stepwise synthesis, polymers with precisely controlled molecular structures can be synthesized. Moreover, such tailored polymers can be folded or self-assembled into defined nanoscale morphologies. These self-organized macromolecular objects can be at thermal equilibrium or can be driven out of equilibrium. Recently, in the latter case, interesting dynamic materials have been developed. However, this is just a start, and more complex adaptive materials are anticipated.

**Comment:** If there is nothing to see, read some reviews.
Drug Self-delivery Systems based on Hyperbranched Polyprodrugs towards Tumor Therapy

Amphiphilic hyperbranched polyprodrugs (DOX-S-S-PEG) with drug repeat units in hydrophobic core linked by disulfide bonds were developed as drug self-delivery systems for cancer therapy. The hydroxyl groups and the amine group in doxorubicin (DOX) were linked by 3,3’-dithiodipropionic acid as hydrophobic hyperbranched cores, then amino-terminated polyethylene glycol monomethyl ether (mPEG-NH2) as hydrophilic shell was linked to hydrophobic cores to form amphiphilic and glutathione (GSH)-responsive micelle of hyperbranched polyprodrugs. The amphiphilic micelles can be disrupted under GSH (1 mg mL\(^{-1}\)) circumstance. Cell viability of A549 cells and 293T cells was evaluated by CCK-8 and Muse Annexin V & Dead Cell Kit. The disrupted polyprodrugs maintained drug activity for killing tumor cells. Meanwhile, the undisrupted polyprodrugs possessed low cytotoxicity to normal cells. The cell uptake experiments showed that the micelles of DOX-S-S-PEG were taken up by A549 cells and distributed to cell nuclei. Thus, the drug self-delivery systems with drug repeat units in hydrophobic cores linked by disulfide bonds showed significant special advantages: 1) facile one-pot synthesis; 2) completely without toxic or non-degradable polymers; 3) DOX itself functions as fluorescent labeled molecule and self-delivery carrier; 4) drug with inactive form in hyperbranched cores and low cytotoxicity to normal cells. These advantages make them excellent drug self-delivery systems for potential high efficient cancer therapy.

Comment: This amphiphilic hyperbranched polyprodrug, which can be easily synthesized, showed low cytotoxicity to normal cells and high cytotoxicity to tumor cells. How to combine DCC with tumor detection and treatment is a good direction.

3D-Printed Biomimetic Scaffold Simulating Microfibril Muscle Structure
In the human body, microfibril structures can be found in several types of tissue, such as muscles, nerves, and even tendons. However, most micropatterned fabrication methods have focused on 2D surface patterned configurations, which imitate the alignment and fusion of cardiac and skeletal muscle cells. Despite the development of these 2D methods, it has continued to be a challenge to fabricate realistic 3D microfibril structures. The goal of this study is to develop a micropatterned polycaprolactone (PCL) microfiber strut. This process uses a **microfibrillation/leaching process of poly(vinyl alcohol) (PVA) from a PVA/PCL mixture** to imitate skeletal muscle cell alignment and fusion in vitro. To attain the optimal processing conditions, a variety of parameters—including a mixture ratio, processing temperature, and pneumatic pressure—are considered. To increase biocompatibility of a microfibrous PCL bundle, the fabricated structure is supplemented with type-I collagen. The myoblasts (C2C12 cells) are used to determine the cellular responses of the fabricated structure. By analyzing cell proliferation and myogenic differentiation, it can be confirmed that the hybrid microfibrillated structure can be an important potential platform to obtain efficient regeneration of muscle cells.

**Comment**: The main driving force for the formation of the aligned fibrillated structure during 3D printing is the hydrophobic/hydrophilic interaction, which originates from the amphiphilic structure of PVA.
Hydrogen-Bonded Liquid Crystals in Confined Spaces—Toward Photonic Hybrid Materials

Spengler, M.; Dong, R.; Michal, C.; Hamad, W.; MacLachlan, M.*; Giese, M.*  

A series of hybrid materials based on chiral nematic mesoporous organosilica (CNMO) films infiltrated with liquid crystalline hydrogen-bonded assemblies is prepared and characterized with respect to the mutual manipulation of the photonic properties of the host and the liquid-crystalline behavior of the guest. Detailed differential scanning calorimetry studies reveal the impact of confinement on the mesomorphic behavior of the liquid crystalline assemblies in the pores of the CNMO films. The photonic properties of the chiral nematic mesoporous host can be controlled by changing the temperature or irradiating the films with UV light. These stimuli-induced phase transitions are accompanied by changes in the orientational order of the mesogens as revealed by $^{19}$F NMR spectroscopy. The combination of confinement and changes in the molecular orientation in a unique hybrid material based on hydrogen-bonded liquid crystals and a porous host with a chiral nematic mesostructure is an interesting concept for the design of optical sensors, reflectors, or filters.

Comment: a) There is a lower pore-size limit allowing for the self-assembly of liquid crystals into supramolecular columns. b) Solid state $^{19}$F NMR was employed to investigate the order of the guest molecules in the CNMO host. c) The irradiation with UV light on the Azo-containing guests was performed at quite high temperature (60, 88, 95°C), which might be the main reason for the fast relaxation (1s) from trans form to cis form.

CD74 is a Novel Transcription Regulator

CD74 is a cell-surface receptor for the cytokine macrophage migration inhibitory factor. Macrophage migration inhibitory factor binding to CD74 induces its intramembrane cleavage and the release of its cytosolic intracellular domain (CD74–ICD), which regulates cell survival. In the present study, we characterized the transcriptional activity of CD74–ICD in chronic lymphocytic B cells. We show that following CD74 activation, CD74–ICD interacts with the transcription factors RUNX (Runt related transcription factor) and NF-κB and binds to proximal and distal regulatory sites enriched for genes involved in apoptosis, immune response, and cell migration. This process leads to regulation of expression of these genes. Our results suggest that identifying targets of CD74 will help in understanding of essential pathways regulating B-cell survival in health and disease.

**Comment:** CD74-ICD is a small 42-amino acid peptide, with no distinctive DNA binding region. It is supposed that it exerts its function in a complex with other transcription factors. Based on bioinformatics predictions of potential coregulators, Gil-Yarom et al shed more light on its crucial role as a transcription regulator, controlling pathways involved in immune regulation and immune diseases.

**The C-Terminal Extension Landscape of Naturally Presented HLA-I Ligands**
HLA-I molecules play a central role in antigen presentation. They typically bind 9- to 12-mer peptides, and their canonical binding mode involves anchor residues at the second and last positions of their ligands. To investigate potential noncanonical binding modes, we collected in-depth and accurate HLA peptidomics datasets covering 54 HLA-I alleles and developed algorithms to analyze these data. Our results reveal frequent (442 unique peptides) and statistically significant C-terminal extensions for at least eight alleles, including the common HLA-A03:01, HLA-A31:01, and HLA-A68:01. High resolution crystal structure of HLA-A68:01 with such a ligand uncovers structural changes taking place to accommodate C-terminal extensions and helps unraveling sequence and structural properties predictive of the presence of these extensions. Scanning viral proteomes with the C-terminal extension motifs identifies many putative epitopes and we demonstrate direct recognition by human CD8+ T cells of a 10-mer epitope from cytomegalovirus predicted to follow the C-terminal extension binding mode.

Comment: Human leukocyte antigen class I (HLA-I) molecules play a central role in immune recognition by presenting peptides from the intracellular matrix to T-cells. Peptides (canonically 9-mer or 12-mers) originating from proteasomal degradation form complexes with the HLA-I molecule binding motifs. The protein-peptide complex is then transported to the cell surface where it is recognized by T cells triggering an immune response. Gfeller et al introduce a statistical approach to rigorously investigate N- and C-terminal non-canonical extensions in large datasets of naturally presented peptides and whether these ligands can be recognized by CD8 T cells.

Dynamic Peptide Libraries for the Discovery of Supramolecular Nanomaterials

Sequence-specific polymers, such as oligonucleotides and peptides, can be used as building blocks for functional supramolecular nanomaterials. The design and selection of suitable self-assembling sequences is, however, challenging because of the vast combinatorial space available. Here we report a methodology that allows the peptide sequence space to be searched for self-assembling structures. In this approach, unprotected homo- and heterodipeptides (including aromatic, aliphatic, polar and charged amino acids) are subjected to continuous enzymatic
condensation, hydrolysis and sequence exchange to create a dynamic combinatorial peptide library. The free-energy change associated with the assembly process itself gives rise to selective amplification of self-assembling candidates. By changing the environmental conditions during the selection process, different sequences and consequent nanoscale morphologies are selected.

Comment: Short peptide sequences are powerful building blocks for designing new nanomaterials, but their self-assembled structures are difficult to predict. Ulijn and colleagues present a methodology to select peptide sequences from dynamic combinatorial libraries that produce the most stable supramolecular nanostructures.

**Sequence Diversification by Divergent C-Terminal Elongation of Peptides**


Sequence diversification at the C terminus is traditionally limited by significant epimerization of the C-terminal residue during its activation toward nucleophilic attack, thus mandating repetition of the peptide synthesis for each targeted variation. Here, we accomplish divergent C-terminal elongation of a single peptide substrate with concomitant resin cleavage via displacement of an N-acyl urea moiety. Sterically hindered amino acids such as Ile and Pro are well-tolerated in this approach, which proceeds reasonable conversion and no detectable epimerization of the starting peptide’s C-terminal amino acid.

Comment: Peptide sequences are not usually modified at the C-terminal end. C-terminal activation tends to lead to the undesired epimerization and repetition of the SPPS synthesis remains the only choice. The authors present a method of backbone diversification and C-terminal peptide elongation (without epimerization) using MeNbz as a reactive moiety sensible to nucleophilic attack.

**Photoinduced Release of a Chemical Fuel for Acid-Base Operated Molecular Machines**

Biagini, C; Lanzalunga, O; Mandolini, L; Di Pietri, Flaminia; Di Stefano, S;* Chem. Eur. J. 2018, ASAP.
Back and forth motions of the acid-base operated molecular switch 1 are photo-controlled by irradiation of a solution which also contains the photolabile prefuel 4. The photo stimulated deprotection of the prefuel produces controlled amounts of acid 2 whose base-promoted decarboxylation fuels the back and forth motions of the Sauvage type [2]-catenane based molecular switch. Since switch 1 and prefuel 4 do not interact in the absence of irradiation, an excess of the latter with respect to 1 can be added to the solution from the beginning. In principle, a photo-control of the back and forth motions of any molecular machine whose operation is guided by protonation/deprotonation, could be attained by use of prefuel 4, or of any other protected acid that undergoes deprotection by irradiation with light at a proper wavelength, followed by decarboxylation under conveniently mild conditions.

Comment: I think this work could be interested for the group, especially for those are working on molecular machine

**Boosting Luminescence of Planar-Fluorophore-Tagged Metal–Organic Cages Via Weak Supramolecular Interactions**

Luo, D; Li, M; Xiao-Ping, Z; Dang, Li;* Chem. Eur. J. 2018, ASAP.

A variety of planar organic fluorophores (R=phenyl, naphthalenyl, pyrenyl) and luminescence promotors (X=Cl, Br, I) were equipped, respectively, on the alternatively arranged vertices of cubic ZnII-imidazolate cages through orthogonal subcomponent self-assembly. It was found that
supramolecular interactions, especially weak C−H⋯X interactions, play a key role in activating an efficient radiative pathway, coupled with reduced nonradiative decay rate through metal coordination, therefore significantly boosting the emission quantum yields of the system. This finding provides a strategy that utilizes molecular geometry and supramolecular interactions to modulate the emission efficiency of luminescent cage-based materials.

**Comment:** In this work the authors describe a system made by cage-based materials and they succeed in tuning the fluorescence through supramolecular interactions.

**An AIEE Fluorescent Supramolecular Cross-linked Polymer Network Based on Pillar[5]arene Host–guest Recognition: Construction and Application in Explosive Detection**


Here a novel fluorescent supramolecular cross-linked polymer network with aggregation induced enhanced emission (AIEE) properties was constructed via pillar[5]arene-based host–guest recognition. Furthermore, the supramolecular polymer network can be used for explosive detection in both solution and thin films.

**Comment:** Supramolecular polymers with AIE or AIEE effect are often reported. However, the novelty in this paper is that the solution and film can also work for the detection of nitro-compound (i.e. explosives).
Mechanochemical Post-Polymerization Modification: Solvent-Free Solid-State Synthesis of Functional Polymers


Mechanochemical postpolymerization modification is reported herein. The fast and efficient synthesis of a library of macromolecules with functional diversity and structural uniformity was realized without a solvent by means of a high speed ball-milling technique. A series of polymers prepared from 4-vinylbenzaldehyde (4-VBA) underwent solid-state Schiff base formations with a series of amines and amine derivatives. The efficient mixing and energy delivery provided by the collisions between balls not only promoted rapid imine formation but also eliminated the need for a chemical solvent, which is highly desirable for green chemical synthesis.

Comment: With the increasing importance of green chemistry, mechanochemistry has gained interest back recently. Schiff base mechanochemical formation is well-known and the authors successfully applied it for post-polymerization modification. I do believe that mechanochemistry will become more and more important in the upcoming years, especially for commodity materials, so stay tuned!

Open-to-Air RAFT Polymerization in Complex Solvents: From Whisky to Fermentation Broth


We investigate the use of in situ enzyme degassing to facilitate the open-to-air reversible addition–fragmentation chain transfer (RAFT) polymerization of hydroxyethyl acrylate (HEA) in
a wide range of complex aqueous solvents, including, beer, wine, liquor, and fermentation broth. This enzyme-assisted polymerization procedure is impressively robust, and poly(HEA) was attained with good control over molecular weight and a narrow dispersity in nearly all of the solvents tested. Kinetics experiments on HEA polymerization in whisky and spectroscopic analysis of the purified polymers suggest high end-group fidelity, as does the successful chain extension of a poly(HEA) macro chain transfer agent with narrow dispersity. These results suggest enzyme-assisted RAFT may be a powerful and underutilized tool for high-throughput screening and materials discovery and may simplify the synthesis of well-defined polymers in complex conditions.

Comment: Open-to-air RAFT polymerization is a trendy topic lately, because of the need to adapt this powerful technique in milder and air-tolerant conditions. Here, the authors use a glucose oxidase, an enzyme converting oxygen into hydrogen peroxide, to degas the system and hence allow for an open-to-air polymerization. It even worked in complex solutions (and obviously, the choice of their complex mixtures is not why I read the article in the first place) and was adaptable for several monomers.

### Three-Dimensional Helical Inorganic Thermoelectric Generators and Photodetectors for Stretchable and Wearable Electronic Devices


![Image of a three-dimensional helical inorganic thermoelectric generator](image)

Stretchable, light-weight and breathable thermoelectric generators (TEGs) are highly desired for wearable electronic devices as promising power sources. However, it remains challenging to realize high-performance stretchable TEGs where the employment of inorganic materials is inevitable. Here, we provide the first three-dimensional helical inorganic TEG which is highly stretchable (~100% strain), stable (1000 cycles of stretching), light-weight and breathable, thus indicating its great potential as a portable and wearable power supply that harvests energy from the human body. More importantly, we propose a novel, versatile and effective strategy which artfully transforms rigid electronic devices to stretchable helical ones. This ingenious and general approach for developing various functional wearable electronic devices is further exemplified by ZnO photodetectors, which are also demonstrated as highly stretchable (~600% strain), deformable and breathable. The intelligent architecture design and assembly technique reported in this work will aid in pushing wearable electronic devices a step forward.

Comment: This paper may be out of subject in our team, but I found it intriguing. Indeed, they manage to create some stretchable electronic devises through (as they like to say) an intelligent methodology. I don’t know if this technique can be applied on triarylamines but we could definitely use the three-dimensional helical structure to increase the stretchability of our gels (if they are strong enough).
A NIR-responsive Azobenzene-based Supramolecular Hydrogel Using Upconverting Nanoparticles


To circumvent the need for direct UV excitation in a supramolecular hydrogel composed of an azobenzene-modified poly(acrylic acid) copolymer and deoxycholate-β-cyclodextrin as a crosslinker, we modified this system for use with LiYF₄: Tm³⁺/Yb³⁺ upconverting nanoparticles, which emit UV light upon NIR excitation. A complete gel-sol transition was observed in 60 minutes upon 980 nm irradiation. No change was observed under similar conditions of a control sample over the same period of time.

Comment: Here, a similar concept using a photo-acid strategy as mentioned in my week 14 group literature is employed. The difference is that in this example they introduce LiYF₄:Tm³⁺/Yb³⁺ upconverting nanoparticles, leading to the sol-gel transition using near infrared light.

Template-Directed Synthesis of a Conjugated Zinc Porphyrin Nanoball

We report the template-directed synthesis of a π-conjugated 14-porphyrin nanoball. This structure consists of two intersecting nanorings containing six and 10 porphyrin units. Fluorescence upconversion spectroscopy experiments demonstrate that electronic excitation delocalizes over the whole three-dimensional π system in less than 0.3 ps if the nanoball is bound to its templates or over 2 ps if the nanoball is empty.

Comment: Fourteen porphyrin in one cycle electronic delocalized molecule?! This should make you want to read this article, but if you still resist, you will find therein a fascinating synthesis and some interesting UV-vis-NIR analysis along with DFT calculations.

Highly Selective Artificial K⁺ Channels: An Example of Selectivity-Induced Transmembrane Potential


Natural KcsA K⁺ channels conduct at high rates with an extraordinary selectivity for K⁺ cations, excluding the Na⁺ or other cations. Biomimetic artificial channels have been designed in order to mimic the ionic activity of KcsA channels, but simple artificial systems presenting high K⁺/Na⁺ selectivity are rare. Here we report an artificial ion channel of H-bonded hexyl-benzoureido-15-crown-5-ether, where K⁺ cations are highly preferred to Na⁺ cations. The K⁺-channel conductance is interpreted as arising in the formation of oligomeric highly cooperative channels, resulting in the cation-induced membrane polarization and enhanced transport rates without or under pH-active gradient. These channels are selectively responsive to the presence of K⁺ cations, even in the presence of a large excess of Na⁺. From the conceptual point of view, these channels express a synergistic adaptive behavior: the addition of the K⁺ cation drives the selection and the construction of constitutional polarized ion channels toward the selective conduction of the K⁺ cation that promotes their generation in the first place.

Comment: Interesting paper showing the relation between the structure of the channel and the selectivity of the ions. As we already developed a synthetic ionic channel with trarylalamines, can we introduce dynamic motion in the self-assembled structure with the motor or azobenzene to get a modulation of the ionic selectivity?
Molecular knots have become highly attractive to chemists because of their prospective properties in mimicking biomolecules and machines. Only a few examples of molecular knots from the billions tabulated by mathematicians have been realized and molecular knots with more than eight crossings have not been reported to date. We report here the coordination-driven [8+8] self-assembly of a higher-generation molecular knot comprising as many as sixteen crossings. Its solid-state X-ray crystal structure and multinuclear 2D NMR findings confirmed its architecture and topology. The formation of this molecular knot appears to depend on the functionalities and geometries of donor and acceptor in terms of generating appropriate angles and strong π-π interactions supported by hydrophobic effects. This study shows coordination-driven self-assembly offers a powerful potential means of synthesizing more and more complicated molecular knots and of understanding differences between the properties of knotted and unknotted structures.

Comment: Efficient characterization, but I feel like the main text isn’t auto-sufficient and needs the supporting information too much. In addition, is it my English or are there a few sentences written in a weird way? I wonder then if this article is really Angewandte-level… I’d like to know what you think!
Calculating Curly Arrows from \textit{ab initio} Wavefunctions


Despite being at the heart of chemical thought, the curly arrow notation of reaction mechanisms has been treated with suspicion—the connection with rigorous molecular quantum mechanics being unclear. The connection requires a view of the wavefunction that goes beyond molecular orbitals and rests on the most fundamental property of electrons. The antisymmetry of electronic wavefunctions requires that an $N$-electron wavefunction repeat itself in $3N$ dimensions, thus exhibiting tiles. Inspection of wavefunction tiles permits insight into structure and mechanism. Here, we demonstrate that analysis of the wavefunction tile along a reaction coordinate reveals the electron movements depicted by the curly arrow notation for several reactions. The Diels–Alder reaction is revealed to involve the separation and counter propagation of electron spins. This unprecedented method of extracting the movements of electrons during a chemical reaction is a breakthrough in connecting traditional depictions of chemical mechanism with state-of-the-art quantum chemical calculations.

Comment: The paper is not easy to read, they even have equations. The figures do not show what I would like to see for such a title! And, somewhere in the paper, they say “the 'curly arrow' beloved of students of organic reaction mechanisms”. Seriously, does any student likes the curly arrow? If something it was part of my worst (student) nightmares. But they have a point and indeed being able to “calculate” the path of a curly arrow gives validity to many of our mechanisms and the hope to, eventually, come with a good description of reactions. It also has the bonus to finally end the mockery involving mechanisms and curly arrows.

Tension Stimulated Drives Tissue Formation in Scaffold-free Systems


![Figure showing Young's modulus and Ultimate tensile strength](image-url)
Scaffold-free systems have emerged as viable approaches for engineering load-bearing tissues. However, the tensile properties of engineered tissues have remained far below the values for native tissue. Here, by using self-assembled articular cartilage as a model to examine the effects of intermittent and continuous tension stimulation on tissue formation, we show that the application of tension alone, or in combination with matrix remodelling and synthesis agents, leads to neocartilage with tensile properties approaching those of native tissue. Implantation of tension-stimulated tissues results in neotissues that are morphologically reminiscent of native cartilage. We also show that tension stimulation can be translated to a human cell source to generate anisotropic human neocartilage with enhanced tensile properties. Tension stimulation, which results in nearly sixfold improvement in tensile properties over unstimulated controls, may allow the engineering of mechanically robust biological replacements of native tissue.

Comment: What caught my attention is the use of tension as a stimulus for tissue (neo-cartilage) growth and repair. The use of tension in this way was new to me and seemed contradictory at first, but it is well explained in the article.

**Autonomous Motility of Polymer Films**


Adaptive soft materials exhibit a diverse set of behaviors including reconfiguration, actuation, and locomotion. These responses however, are typically optimized in isolation. Here, the interrelation between these behaviors is established through a state space framework, using Nylon 6 thin films in a humidity gradient as an experimental testbed. It is determined that the dynamic behaviors are a result of not only a response to but also an interaction with the applied stimulus, which can be tuned via control of the environment and film characteristics, including size,
permeability, and coefficient of hygroscopic expansion to target a desired behavior such as multimodal locomotion. Using these insights, it is demonstrated that films simultaneously harvest energy and information from the environment to autonomously move down a stimulus gradient. Improved understanding of the coupling between an adaptive material and its environment aids the development of materials that integrate closed loop autonomous sensing, actuation, and locomotion.

**Comment:** Here they explain in detail the moisture sensitive mechanical response, which can be tuned by the size and shape of the film, as well as stimulus strength. Although older studies have already described the behavioral states in more detail, this study focuses on the quantitative evaluation of the energetics behind previously described states.

**Multistate Photoswitches: Macrocyclic Dihydroazulene/Azobenzene Conjugates**


Molecules comprised of three covalently linked bi-stable switches can exist in states described by a combination of binary numbers, one for each individual switch: \( \{000\}, \{001\}, \text{etc.} \) Here we have linked three photo-/thermoswitches together in a rigid macrocyclic structure, one azobenzene (bit no 1) and two dihydroazulenes (DHAs; bits no 2 and 3) and demonstrate how electronic interactions and unfavorable strain in some states can be used to control the speed by which a certain state is reached. More specifically, upon irradiation of state \( \{000\} \), the AZB isomerizes from *trans* to *cis* and the two DHAs to vinylheptafulvenes (VHFs), generating \( \{111\} \). The thermal VHF-to-DHA back-reactions from this state also occur stepwise and can be accelerated by photo-induced AZB *cis*-to-*trans* conversion, proceeding via \( \{011\} \) to ultimately furnish \( \{000\} \). Overall, the accessibility to a specific state of one bit was found to depend on the states of its neighboring bits.
Comment: Much easier to read than expected from the first appearance. It might just have needed a nice scheme with the energy barriers of the transitions instead of energies of formation.

An Artificial Flexible Visual Memory System Based on an UV-Motivated Memristor


For the mimicry of human visual memory, a prominent challenge is how to detect and store the image information by electronic devices, which demands a multifunctional integration to sense light like eyes and to memorize image information like the brain by transforming optical signals to electrical signals that can be recognized by electronic devices. Although current image sensors can perceive simple images in real time, the image information fades away when the external image stimuli are removed. The deficiency between the state-of-the-art image sensors and visual memory system inspires the logical integration of image sensors and memory devices to realize the sensing and memory process toward light information for the bionic design of human visual memory. Hence, a facile architecture is designed to construct artificial flexible visual memory system by employing an UV-motivated memristor. The visual memory arrays can realize the detection and memory process of UV light distribution with a patterned image for a long-term retention and the stored image information can be reset by a negative voltage sweep and reprogrammed to the same or another image distribution, which proves the effective reusability. These results provide new opportunities for the mimicry of human visual memory and enable the flexible visual memory device to be applied in future wearable electronics, electronic eyes, multifunctional robotics, and auxiliary equipment for visual handicapped.

Comment: While many studies focus on mimicking the (human) visual system, very few have incorporated mechanisms to retain and memorize the images after the light stimulus has been removed. Here they show the integration of a memristor based memory device to an UV image sensor. One image pixel corresponds to one memory unit. I think it is a rather straightforward and good principle. The results are very promising for future retinal prosthesis.

Atomic Scale Imaging of Magnetic Circular Dichroism by Achromatic Electron Microscopy
In order to obtain a fundamental understanding of the interplay between charge, spin, orbital and lattice degrees of freedom in magnetic materials and to predict and control their physical properties, experimental techniques are required that are capable of accessing local magnetic information with atomic-scale spatial resolution. Here, we show that a combination of electron energy-loss magnetic chiral dichroism and chromatic-aberration-corrected transmission electron microscopy, which reduces the focal spread of in-elastically scattered electrons by orders of magnitude when compared with the use of spherical aberration correction alone, can achieve atomic-scale imaging of magnetic circular dichroism and provide element-selective orbital and spin magnetic moments atomic plane by atomic plane. This unique capability, which we demonstrate for Sr$_2$FeMoO$_6$, opens the door to local atomic-level studies of spin configurations in a multitude of materials that exhibit different types of magnetic coupling, thereby contributing to a detailed understanding of the physical origins of magnetic properties of materials at the highest spatial resolution.

Comment: I have chosen this article because I thought that an article atomic scale imaging would be very interesting. And it is, however it is a very technical article that describes a state of the art technique. Therefore, I found it very difficult to read and understand.

**One-Step Block Copolymer Synthesis versus Sequential Monomer Addition: A Fundamental Study Reveals That One Methyl Group Makes a Difference**

Block copolymers of polyisoprene and polystyrene are key materials for polymer nanostructures as well as for several commercially established thermoplastic elastomers. In a combined experimental and kinetic Monte Carlo simulation study, the direct (i.e., statistical) living anionic copolymerization of a mixture of isoprene (I) and 4-methylstyrene (4MS) in nonpolar media was investigated on a fundamental level. In situ 1H NMR spectroscopy enabled to directly monitor gradient formation during the copolymerization and to determine the nature of the gradient. In addition, a precise comparison with the established copolymerization of isoprene and styrene (I/S) was possible. Statistical copolymerization in both systems leads to tapered block copolymers due to an extremely slow crossover from isoprene to the styrenic monomer. For the system I/4MS the determination of the reactivity ratios shows highly disparate values with $r_I = 25.4$ and $r_{4MS} = 0.007$, resulting in a steep gradient of the comonomer composition. The rate constants determined from online NMR studies were used for a kinetic Monte Carlo simulation, revealing structural details, such as the distribution of the homopolymer sequences for both blocks, which are a consequence of the peculiar kinetics of the diene/styrene systems. DFT calculations were used to compare the established copolymerization of isoprene and styrene with the isoprene/4-methylstyrene system. A variety of gradient copolymers differing in molecular weight and monomer feed composition were synthesized, confirming strong microphase segregation as a consequence of the blocklike structure. The one-pot synthesis of such tapered block copolymers, avoiding high vacuum or break-seal techniques, is a key advantage for the preparation of ultrahigh molecular weight block copolymers ($M_n > 1.2 \times 10^6$ g/mol) in one synthetic step. These materials show microphase-segregated bulk structures like diblock copolymers prepared by sequential block copolymer synthesis. Because of the living nature of the tapered block copolymer structures, a vast variety of complex structures are accessible by the addition of further monomers or monomer mixtures in subsequent steps.

Comment: Beautiful paper with clear and reasonable (included in silico) experiments and wide theoretical background. The concept “One-pot block copolymer synthesis” using atypical monomer 4-methylstyrene has been proved.
Fast Healing of Polyurethane Thermosets Using Reversible Triazolinedione Chemistry and Shape-Memory


Healable and remoldable polyurethane networks having poly(ε-caprolactone) soft segments were prepared in a one-pot procedure using a thermoreversible cross-linker based on triazolinedione (TAD) chemistry. A single heating step triggers both shape-recovery and reversible TAD chemistry, which allows fast shape-memory assisted healing from large scale damage up to 1 mm. The network compositions were optimized to maximize healing efficiency. The thermomechanical properties of the materials were studied in-depth by thermal analysis, tensile measurements, and rheology. This work validates reversible TAD chemistry as a novel, highly effective chemistry for fast intrinsic healing of high-modulus thermosets without loss of structural integrity.

Comment: Nice self-healing ability and multistep PU molding.

Non-Isocyanate Polyurethane Thermoplastic Elastomer: Amide-Based Chain Extender Yields Enhanced Nanophase Separation and Properties in Polyhydroxyurethane


Non-isocyanate polyurethane thermoplastic elastomers were prepared using a novel amide-based chain extender and polyhydroxyurethane (PHU) soft segments. The amide-based chain extender was designed to significantly enhance the phase separation in the resulting thermoplastic elastomers. The enhanced nanophase separation was confirmed through advanced microscopy techniques, and the improved mechanical properties were demonstrated through dynamic mechanical analysis. This work represents a significant advancement in the development of non-isocyanate polyurethane thermoplastic elastomers, opening up new possibilities for applications requiring thermoplastic materials with enhanced performance.
Non-isocyanate polyurethane (NIPU) was synthesized via cyclic carbonate aminolysis using poly(ethylene oxide) (PEO)- and poly(tetramethylene oxide) (PTMO)-based soft segments, divinylbenzene dicyclocarbonate as hard segment, and diamine–diamide (DDA) chain extender. Characterization of the resulting segmented polyhydroxyurethanes (PHUs) reveals that the use of amide-based DDA chain extender leads to unprecedented improvements in nanophase separation and thermal and mechanical properties over segmented PHUs without DDA chain extender. With PEO-based soft segments, previously known to yield only phase-mixed PHUs, use of DDA chain extender yields nanophase-separated PHUs above a certain hard-segment content, as characterized by small-angle X-ray scattering. With PTMO-based soft segments, previously known to yield nanophase-separated PHUs with broad interphase, use of DDA chain extender produces nanophase-separated PHUs with sharp domain interphase, leading to wide, relatively temperature-independent rubbery plateau regions and much improved thermal properties with flow temperature as high as 200 °C. The PTMO-based PHUs with 19–34 wt % hard-segment content exhibit tunable mechanical properties with Young’s modulus ranging from 6.6 to 43.2 MPa and tensile strength from 2.4 to 6.7 MPa, with ~300% elongation at break. Cyclic tensile testing shows that these PHUs exhibit elastomeric recovery with attributes very similar to conventional, isocyanate-based thermoplastic polyurethane elastomers. Comment: Unique biocompatible TPU with graft structure has been designed. Material has excellent mechanics taking into account for this TPU to be amorphous. However, industrial scaling.

Comment: The first PHU with nanobeheterogeneities and good mechanical properties.

Cooperativity Principles in Self-Assembled Nanomedicine
Li, Y.; Wang, Y.; Huang, G.; Gao, J.* Chem. Rev. 2018, ASAP.

Nanomedicine is a discipline that applies nanoscience and nanotechnology principles to the prevention, diagnosis, and treatment of human diseases. Self-assembly of molecular components is becoming a common strategy in the design and syntheses of nanomaterials for biomedical applications. In both natural and synthetic self-assembled nanostructures, molecular cooperativity is emerging as an important hallmark. In many cases, interplay of many types of noncovalent interactions leads to dynamic nanosystems with emergent properties where the whole is bigger than the sum of the parts. In this review, we provide a comprehensive analysis of the cooperativity principles in multiple self-assembled nanostructures. We
discuss the molecular origin and quantitative modeling of cooperative behaviors. In selected systems, we describe the examples on how to leverage molecular cooperativity to design nanomedicine with improved diagnostic precision and therapeutic efficacy in medicine.

Comment: First I chose this review to make sure I could find it “eventually” if ever the need of citing it comes, but it is much more interesting than expected. Of course, many of the concepts are a bit blurry, but some sections, notably on cooperative signaling are worth a quick look.