• **Modular Synthesis of Cell-Permeating 2-Ketoglutarate Esters**
  Abstract:

  Cell-permeating esters of 2-ketoglutarate (2-KG) have been synthesized through a convergent sequence from two modules in two and three steps, respectively. This route provides access to a full series of mono- and disubstituted 2-KG esters, enabling us to define the effect of regioisomeric masking on metabolite release and antihypoxic activity in cell-based assays. In addition to providing insight into the biological activity of cell permeable 2-KG esters, the straightforward and modular nature of this synthetic route may prove useful for the development of next-generation 2-KG analogues for diagnostic and therapeutic applications.

• **Optimized Diazo Scaffold for Protein Esterification**
  Abstract:

  The O-alkylation of carboxylic acids with diazo compounds provides a means to esterify carboxylic acids in aqueous solution. A Hammett analysis of the reactivity of diazo compounds derived from phenylglycinamide revealed that the (p-methylphenyl)glycinamide scaffold has an especially high reaction rate and ester/alcohol product ratio and esterifies protein carboxyl groups more efficiently than any known reagent.

• **“Turn-On” Protein Fluorescence: In Situ Formation of Cyanine Dyes**
  Abstract:
Protein reengineering of cellular retinoic acid binding protein II (CRABPII) has yielded a genetically addressable system, capable of binding a profluorophoric chromophore that results in fluorescent protein/chromophore complexes. These complexes exhibit far-red emission, with high quantum efficiencies and brightness and also exhibit excellent pH stability spanning the range of 2–11. In the course of this study, it became evident that single mutations of L121E and R59W were most effective in improving the fluorescent characteristics of CRABPII mutants as well as the kinetics of complex formation. The readily crystallizable nature of these proteins was invaluable to provide clues for the observed spectroscopic behavior that results from single mutation of key residues.

- **Cy3 Photoprotection Mediated by Ni\(^{2+}\) for Extended Single-Molecule Imaging: Old Tricks for New Techniques**
  Abstract:
  The photostability of reporter fluorophores in single-molecule fluorescence imaging is of paramount importance, as it dictates the amount of relevant information that may be acquired before photobleaching occurs. Quenchers of triplet excited states are thus required to minimize blinking and sensitization of singlet oxygen. Through a combination of single-molecule studies and ensemble mechanistic studies including laser flash photolysis and time-resolved fluorescence, we demonstrate herein that Ni\(^{2+}\) provides a much desired physical route (chemically inert) to quench the triplet excited state of Cy3, the most ubiquitous green emissive dye utilized in single-molecule studies.

- **Fabrication of 2D Au Nanorings with Pt Framework**
  Abstract:
Surface plasmonics of nanomaterials has been one of the main research themes in nanoscience. Spherical and elongated nanoparticles show their corresponding unique optical features mainly depending on the physical dimensions. Here we successfully synthesized Au nanorings having Pt framework (Pt@Au nanorings) with high uniformity through wet-chemistry. The synthetic strategy consisted of serial reactions involving site-selective growth of Pt on the rim of Au nanoplates, subsequent etching of Au nanoplates, followed by regrowth of Au on the Pt rim. In this synthetic method, Au$^{3+}$ ions exhibited dual functionality as an etchant and a metal precursor. The resultant product, Pt@Au nanorings, exhibited unique localized surface plasmon resonance (LSPR) bands originating from the Au shell. The inner Pt skeleton turns out to be important to hold structural stability.

- **Bipolar Gold(III) Complexes for Solution-Processable Organic Light-Emitting Devices with a Small Efficiency Roll-Off**

Abstract:

A new class of bipolar alkynylgold(III) complexes containing triphenylamine and benzimidazole moieties has been synthesized, characterized, and applied as phosphorescent dopants in the fabrication of solution-processable organic light-emitting devices (OLEDs). The incorporation of methyl groups in the central phenyl unit has been found to rigidify the molecule to reduce nonradiative decay, yielding a high photoluminescence quantum yield of up to 75% in spin-coated thin films. In addition, the realization of highly efficient solution-processable OLEDs with an extremely small external quantum efficiency (EQE) roll-off has been demonstrated. At practical
brightness level of 1000 cd m$^{-2}$, the optimized devices exhibited a high EQE of up to 10.0% and an extremely small roll-off of less than 1%.

- **Luminescence-Driven Reversible Handedness Inversion of Self-Organized Helical Superstructures Enabled by a Novel Near-Infrared Light Nanotransducer**
  Abstract: Nanotransducer-impregnated self-organized helical superstructures are found to exhibit unprecedented reversible handedness inversion upon irradiation by the dual-wavelength near-infrared light. Upon near-infrared laser irradiation at 808 nm, the helical twist sense changes from right-handed to left-handed through an achiral liquid-crystal phase, whereas its reverse process occurs upon the near-infrared laser irradiation at 980 nm.

- **Colorimetric Logic Gates Based on Poly(2-alkyl-2-oxazoline)-Coated Gold Nanoparticles**
  Abstract: A straightforward end-capping strategy is applied to synthesize xanthate-functional poly(2-alkyl-2-oxazoline)s (PAOx) that enable gold nanoparticle functionalization by a direct “grafting to” approach with citrate-stabilized gold nanoparticles (AuNPs). Owing to the presence of remaining citrate groups, the obtained PAOx@AuNPs exhibit dual stabilization by repulsive electrostatic and steric interactions giving access to water soluble molecular AND logic gates, wherein environmental
temperature and ionic strength constitute the input signals, and the solution color the output signal. The temperature input value could be tuned by variation of the PAOx polymer composition, from 22 °C for poly(2-propyl-2-oxazoline)@AuNPs to 85 °C for poly(2-ethyl-2-oxazoline)@AuNPs. Besides, advancing the fascinating field of molecular logic gates, the present research offers a facile strategy for the synthesis of PAOx@AuNPs of interest in fields spanning nanotechnology and biomedical sciences. In addition, the functionalization of PAOx with xanthate offers straightforward access to thiol-functional PAOx of high interest in polymer science.

- **Optically isotropic liquid crystal media formulated by doping star-shaped cyclic oligosiloxane liquid crystal surfactants in twin nematic liquid crystals**

Abstract:

The formation of optically isotropic liquid crystal (LC) media has been investigated by doping the star-shaped LC molecular surfactants (SiLC) into the rod-shaped twin LC host molecules (DiLC). The experimental phase diagram was constructed on the basis of differential scanning calorimetry (DSC) and then a theoretical calculation was conducted through a combined Flory–Huggins (FH)/Maier–Saupe–McMillan (MSM)/phase field (PF) model to account for the experimental results. The phase diagram of the SiLC/DiLC mixtures revealed the broad coexistence regions such as smectic A + crystal (SmA₂ + Cr₂), liquid + crystal (L₁ + Cr₂), and liquid + nematic (L₁ + N₂) at the intermediate composition along with the narrow single phase crystal (Cr₂), smectic (SmA₁), and nematic (N₂) regions. The morphologies and structures of these coexistence regions were further confirmed by polarized optical microscopy (POM) and wide-angle X-ray diffraction (WAXD). At the 80/20 SiLC/DiLC composition, the optical anisotropy was induced under an alternating current (AC) electric field above its isotropization temperature. The formation of an optically isotropic LC medium in mixtures of the SiLC molecular surfactants and nematic LC host may allow us to develop new electro-optical devices.

- **Tunable synthesis of self-assembled cyclic peptide nanotubes and nanoparticles**

Abstract:
While tremendous efforts have been made in investigating scalable approaches for fabricating nanoparticles, less progress has been made in scalable synthesis of cyclic peptide nanoparticles and nanotubes, despite their great potential for broader biomedical applications. In this paper, tunable synthesis of self-assembled cyclic peptide nanotubes and nanoparticles using three different methods, phase equilibrium, pH-driven, and pH-sensitive methods, were proposed and investigated. The goal is scalable nanomanufacturing of cyclic peptide nanoparticles and nanotubes with different sizes in large quality by controlling multiple process parameters. Cyclo-(L-Gln-D-Ala-L-Glu-D-Ala-)$_2$ was applied to illustrate the proposed ideas. In the study, mass spectrometry and high performance liquid chromatography were employed to verify the chemical structures and purity of the cyclic peptides. Morphology and size of the synthesized nanomaterials were characterized using atomic force microscopy and dynamic light scattering. The dimensions of the self-assembled nanostructures were found to be strongly influenced by the cyclic peptide concentration, side chain modification, pH values, reaction time, stirring intensity, and sonication time. This paper proposed an overall strategy to integrate all the parameters to achieve optimal synthesis outputs. Mechanisms of the self-assembly of the cyclic peptide nanotubes and nanoparticles under variable conditions and tunable parameters were discussed. This study contributes to scalable nanomanufacturing of cyclic peptide based self-assembled nanoparticles and nanotubes for broader biomedical applications.

- **Concentration-Controlled Reversible Phase Transitions in Self-Assembled Monolayers on HOPG Surfaces**
  Abstract:

Rational control of molecular ordering on surfaces and interfaces is vital in supramolecular chemistry and nanoscience. Here, a systematic scanning tunneling microscopy (STM) study for controlling the self-assembly behavior of alkoxylated benzene (B-OCn) molecules on a HOPG surface is presented. Three different phases have been observed and, of great importance, they can transform to each other by modifying the solute concentration. Further studies, particularly in situ diluting and concentrating experiments, demonstrate that the transitions among the three phases are highly controllable and reversible, and are driven thermodynamically. In addition, it is found that concentration-controlled reversible phase transitions are general for different chain lengths of B-OCn molecules. Such controllable and reversible phase transitions may have potential applications in the building of desirable functional organic thin films and provide a new understanding in thermodynamically driven self-assembly of organic molecules on surfaces and interfaces.
Polydiacetylene (PDA) and its derivatives are promising materials for applications in a vast number of fields, from organic electronics to biosensing. PDA is obtained through polymerization of diacetylene (DA) monomers, typically using UV irradiation. DA polymerization is a 1–4 addition reaction with both initiation and growth steps with topochemical control, leading to the “blue” polymer form as primary reaction product in bulk and at interfaces. Herein, the diacetylene monomer 10,12-pentacosadiynoic acid (DA) and the amphiphilic cationic N,N'-dioctadecylthiapentacarbocyanine (OTCC) have been used to build a mixed Langmuir monolayer. The presence of OTCC imposes a monolayer supramolecular structure instead of the typical trilayer of pure DA. Surface pressure, Brewster angle microscopy, and UV–vis reflection spectroscopy measurements, as well as computer simulations, have been used to assess in detail the supramolecular structure of the DA:OTCC Langmuir monolayer. Our experimental results indicate that the DA and OTCC molecules are sequentially arranged, with the two OTCC alkyl chains acting as spacing diacetylene units. Despite this configuration is expected to prevent photopolymerization of DA, the polymerization takes place without phase segregation, thus exclusively leading to the red polydiacetylene form. We propose a simple model for the initial formation of the “blue” or “red” PDA forms as a function of the relative orientation of the DA units. The structural insights and the proposed model concerning the supramolecular structure of the “blue” and “red” forms of the PDA are aimed at the understanding of the relation between the molecular and macroscopical features of PDAs.
This study presents near-infrared (NIR) light-responsive polymer–nanostructure composite microneedles used for on-demand transdermal drug delivery. Silica-coated lanthanum hexaboride (LaB₆@SiO₂) nanostructures were incorporated into polycaprolactone microneedles, serving as an NIR absorber. When the microneedles were irradiated with NIR light, light-to-heat transduction mediated by the LaB₆@SiO₂ nanostructures caused the microneedle melting at 50 °C. This increased the mobility of the polymer chains, enabling drug release from the matrix. Drug release from the microneedles was evaluated for four laser on/off cycles. In each cycle, the samples were irradiated until the temperature reached 50 °C for 3 min (laser on); the laser was then turned off for 30 min (laser off). The results showed that light-induced phase transition in the polymer triggered drug release from the melted microneedles. A stepwise drug-release behavior was observed after multiple cycles of NIR light exposure. No notable drug leakage was found in the off state. This NIR-light-triggerable device exhibits excellent reproducibility, low off-state leakage, and noninvasive triggerability and, thus, represents an advance in transdermal delivery technology.

- **MMP9-sensitive polymers mediate environmentally-responsive bivalirudin release and thrombin inhibition**
  Abstract:

MMP9-responsive bivalirudin-HPMA copolymers were synthesized for direct, local administration in rat spinal cord contusion injury models. Polymer-conjugated bivalirudin peptides maintained activity while demonstrating enzyme-mediated release upon MMP9 exposure and prolonged release from hyaluronic acid/methylcellulose (HAMC) hydrogels compared to free bivalirudin peptide. Localized administration of bivalirudin copolymers in vivo at the site of rat spinal cord injury decreased cellular proliferation and astrogliosis, suggesting the bivalirudin copolymer and HAMC hydrogel system are a promising therapeutic intervention for reducing immediate inflammatory responses and long term scarring.

  Abstract:
Amphiphilic pillar[5]arene-containing [2]rotaxanes have been prepared and fully characterized. In the particular case of the [2]rotaxane incorporating a 1,4-diethoxypillar[5]arene subunit, the structure of the compound was confirmed by X-ray crystal structure analysis. Owing to a good hydrophilic/hydrophobic balance, stable Langmuir films have been obtained for these rotaxanes and the size of the peripheral alkyl chains on the pillar[5]arene subunit has a dramatic influence on the reversibility during compression–decompression cycles. Indeed, when these are small enough, molecular reorganization of the rotaxane by gliding motions are capable of preventing strong π–π interactions between neighboring macrocycles in the thin film.

- **Beyond Stereoselectivity, Switchable Catalysis: Some of the Last Frontier Challenges in Ring-Opening Polymerization of Cyclic Esters**
  Abstract:

Metal-based catalysts and initiators have played a pivotal role in the ring-opening polymerization (ROP) of cyclic esters, thanks to their high activity and remarkable ability to control precisely the architectures of the resulting polyesters in terms of molar mass, dispersity, microstructure, or tacticity. Today, after two decades of extensive research, the field is slowly reaching maturity. However, several challenges remain, while original concepts have emerged around new types or new applications of catalysis. This Review is not intended to comprehensively cover all of these aspects. Rather, it provides a personal overview of the very recent progress achieved in some selected, important aspects of ROP catalysis—stereocatalysis and switchable catalysis. Hence, the first part addresses the development of new metal-based catalysts for the isoselective ROP of racemic lactide towards stereoblock copolymers, and the use of syndioselective ROP metal catalysts to control the monomer sequence in copolymers. A second part covers the development of ROP catalysts—primarily metal-based catalysts, but also organocatalysts—that can be externally
regulated by the use of chemical or photo stimuli to switch them between two states with different catalytic abilities. Current challenges and opportunities are highlighted.

- **Synthesis of ultrathin polymer insulating layers by initiated chemical vapour deposition for low-power soft electronics**
  Abstract:

  Insulating layers based on oxides and nitrides provide high capacitance, low leakage, high breakdown field and resistance to electrical stresses when used in electronic devices based on rigid substrates. However, their typically high process temperatures and brittleness make it difficult to achieve similar performance in flexible or organic electronics. Here, we show that poly(1,3,5-trimethyl-1,3,5-trivinyl cyclotrisiloxane) (pV3D3) prepared via a one-step, solvent-free technique called initiated chemical vapour deposition (iCVD) is a versatile polymeric insulating layer that meets a wide range of requirements for next-generation electronic devices. Highly uniform and pure ultrathin films of pV3D3 with excellent insulating properties, a large energy gap (>8 eV), tunnelling-limited leakage characteristics and resistance to a tensile strain of up to 4% are demonstrated. The low process temperature, surface-growth character, and solvent-free nature of the iCVD process enable pV3D3 to be grown conformally on plastic substrates to yield flexible field-effect transistors as well as on a variety of channel layers, including organics, oxides, and graphene.

- **Mode matching in multiresonant plasmonic nanoantennas for enhanced second harmonic generation**
  Abstract:

  ![Mode matching in multiresonant plasmonic nanoantennas for enhanced second harmonic generation](image)
Boosting nonlinear frequency conversion in extremely confined volumes remains a challenge in nano-optics research, but can enable applications in nanomedicine, photocatalysis and background-free biosensing. To obtain brighter nonlinear nanoscale sources, approaches that enhance the electromagnetic field intensity and counter the lack of phase matching in nanoplasmonic systems are often employed. However, the high degree of symmetry in the crystalline structure of plasmonic materials (metals in particular) and in nanoantenna designs strongly quenches second harmonic generation. Here, we describe doubly-resonant single-crystalline gold nanostructures with no axial symmetry displaying spatial mode overlap at both the excitation and second harmonic wavelengths. The combination of these features allows the attainment of a nonlinear coefficient for second harmonic generation of $\sim 5 \times 10^{-10}$ W$^{-1}$, enabling a second harmonic photon yield higher than $3 \times 10^6$ photons per second. Theoretical estimations point toward the use of our nonlinear plasmonic nanoantennas as efficient platforms for label-free molecular sensing.

- **Supramolecular Polylactides by the Cooperative Interaction of the End Groups and Stereocomplexation**

  **Abstract:**

  The controlled ring-opening polymerization of L-lactide and D-lactide using 2-aminopyridine (AP), isocytosine (IC), uridine (U), and 2-ureido-4[1H]-pyrimidinone (UPy-OH) initiators with stannous(II) octanoate as catalyst leads to polylactides (AP-PLA-OH, IC-PLA-OH, U-PLA-OH, and UPy-PLA-OH), which are capable of forming strong hydrogen bonds and consequently self-assemble. By means of “$^1$H NMR titration”, the association constant ($K_a$) was determined for chosen model systems composed of polylactides with uridine and aminopyridine end groups. The coupling reaction of UPy-PLA-OH with diisocyanates was used to obtain PLLA and PDLA with UPy end groups on both sides of the chain: UPy-PLLA-UPy and UPy-PDLA-UPy. The SEC analysis of the telechelic UPy-PLA-UPy revealed the presence of a supramolecular polymer with a high-molecular-weight fraction ($M_n \approx 70,000$ g/mol) compared with the molar mass of the starting dimer (UPy-PLA-OH, $M_n \approx 7000$ g/mol), which confirms the strong complementary interactions of the end groups. Moreover, the influence of the end groups of enantiomeric PLAs on their thermal properties and morphology was investigated. Additionally, the influence of the modified PLA enantiomers on the stereocomplexation phenomenon was analyzed. It was observed that stereocomplexes prepared from PLAs with UPy or U end groups on one chain end lead to the formation of microspheres during precipitation from $N$-methylpyrrolidone into methanol. The microscopic analysis of the telechelic UPy-PLLA-UPy/UPy-PDLA-UPy stereocomplex resulting from the precipitation from chloroform into methanol revealed a fibrous morphology. The probable mechanism of formation of the hierarchical structure of this stereocomplex material, which can be related to the specific geometry of the enantiomeric chains (mainly in a parallel arrangement), was proposed.
**Thermally Cross-Linked Anion Exchange Membranes from Solvent Processable Isoprene Containing Ionomers**
Tsai, T.-H.; Ertem, S. P.; Maes, A. M.; Seifert, S.; Herring, A. M.; Coughlin, E. B.

**Abstract:**
Random copolymers of isoprene and 4-vinyl-benzyl chloride (VBCl) with varying compositions were synthesized via nitroxide-mediated polymerization. Subsequent quaternization afforded solvent processable and cross-linkable ionomers with a wide range of ion exchange capacities (IECs). Solution cast membranes were thermally cross-linked to form anion exchange membranes. Cross-linking was achieved by taking advantage of the unsaturations on the polyisoprene backbone, without added cross-linkers. A strong correlation was found between water uptake and ion conductivity of the membranes: conductivities of the membranes with IECs beyond a critical value were found to be constant related to their high water absorption. Environmentally controlled small-angle X-ray scattering experiments revealed a correlation between the average distance between ionic clusters and the ion conductivity, indicating that a well-connected network of ion clusters is necessary for efficient ion conduction and high ion conductivity.

**Manipulation of the band gap and efficiency of a minimalist push-pull molecular donor for organic solar cells**
Jiang, Y.; Cabanetos, C.; Allain, M.; Liu, P.; Roncali, J.

**Abstract:**
A small push–pull compound involving a methyl-diphenylamine donor block connected to a dicyanovinyl acceptor group through a 2,5-thienyl spacer has been synthesized (1). Comparison with a reference compound containing a triphenylamine block (2) shows that the replacement of a phenyl group by a methyl group has limited effects on the electronic properties of the molecule but induces major changes in the structure and electronic properties of the resulting material such as a $\sim$0.30
eV reduction of the optical band gap and fifty-fold increase of the hole-mobility. Results of X-ray diffraction on single crystals show that the replacement of a phenyl by a methyl group results in a change from head-to-tail to face-to-face arrangement of the dipolar molecules in the crystal. A preliminary evaluation of the potential of the new compound as a donor material in basic bilayer cells of 0.28 cm² with C₆₀ as the acceptor reveals a ca. 33% increase of the power conversion efficiency compared to the reference compound.

- Enhanced electro-optic activity from the triaryliminophenyl-based chromophores by introducing heteroatoms to the donor
  

  Abstract:

A series of chromophores T₁–T₃ based on the same thiophene π-conjugation and tricyanofuran acceptor (TCF) but with different heteroatoms in the triaryliminophenyl (TAA) donors have been synthesized and systematically investigated in this study. Density functional theory (DFT) was used to calculate the HOMO–LUMO energy gaps and first-order hyperpolarizability ($\beta$) of these chromophores. Moreover, to determine the redox properties of these chromophores, cyclic voltammetry (CV) experiments were performed. After introducing the heteroatom to the benzene ring of the TAA donor, reduced energy gaps of 1.28 and 0.84 eV were obtained for chromophores T₂ and T₃, respectively, which was much lower than for chromophore T₁ ($\Delta E = 1.46$ eV). These chromophores showed excellent thermal stability with their decomposition temperatures all above 280 °C. Compared with results obtained from the chromophore without the heteroatom (T₁), these new chromophores show better intramolecular charge-transfer (ICT) absorption. Most importantly, the high molecular hyperpolarizability ($\theta$) of these chromophores can be effectively translated into large electro-optic (EO) coefficients ($r_{33}$) in the poled polymers. The electro-optic coefficient of poled films containing 25 wt% of these new chromophores doped in amorphous polycarbonate (APC) afforded values of 16, 58 and 95 pm V⁻¹ at 1310 nm for chromophores T₁–T₃, respectively. High $r_{33}$ values indicated that introducing heteroatom to the benzene ring of the TAA donor can efficiently improve the electron-donating ability, which improves the hyperpolarizability ($\theta$). The long-chain on the benzene ring of the TAA donor, acting as the isolation group, may reduce intermolecular electrostatic interactions, thus enhancing the macroscopic EO activity. These properties, together with the good solubility, suggest the potential use of these new chromophores as advanced material devices.

- Electric-field–induced assembly and propulsion of chiral colloidal clusters
  

  Abstract:
Chiral molecules with opposite handedness exhibit distinct physical, chemical, or biological properties. They pose challenges as well as opportunities in understanding the phase behavior of soft matter, designing enantioselective catalysts, and manufacturing single-handed pharmaceuticals. Microscopic particles, arranged in a chiral configuration, could also exhibit unusual optical, electric, or magnetic responses. Here we report a simple method to assemble achiral building blocks, i.e., the asymmetric colloidal dimers, into a family of chiral clusters. Under alternating current electric fields, two to four lying dimers associate closely with a central standing dimer and form both right- and left-handed clusters on a conducting substrate. The cluster configuration is primarily determined by the induced dipolar interactions between constituent dimers. Our theoretical model reveals that in-plane dipolar repulsion between petals in the cluster favors the achiral configuration, whereas out-of-plane attraction between the central dimer and surrounding petals favors a chiral arrangement. It is the competition between these two interactions that dictates the final configuration. The theoretical chirality phase diagram is found to be in excellent agreement with experimental observations. We further demonstrate that the broken symmetry in chiral clusters induces an unbalanced electrohydrodynamic flow surrounding them. As a result, they rotate in opposite directions according to their handedness. Both the assembly and propulsion mechanisms revealed here can be potentially applied to other types of asymmetric particles. Such kinds of chiral colloids will be useful for fabricating metamaterials, making model systems for both chiral molecules and active matter, or building propellers for microscale transport.

- **Rational design of self-assembly pathways for complex multicomponent structures**
  **Abstract:**

The field of complex self-assembly is moving toward the design of multiparticle structures consisting of thousands of distinct building blocks. To exploit the potential benefits of structures with such “addressable complexity,” we need to understand the factors that optimize the yield and the kinetics of self-assembly. Here we use a simple theoretical method to explain the key features responsible for the unexpected success of DNA-brick experiments, which are currently the only
demonstration of reliable self-assembly with such a large number of components. Simulations confirm that our theory accurately predicts the narrow temperature window in which error-free assembly can occur. Even more strikingly, our theory predicts that correct assembly of the complete structure may require a time-dependent experimental protocol. Further- more, we predict that low coordination numbers result in non-classical nucleation behavior, which we find to be essential for achieving optimal nucleation kinetics under mild growth conditions. We also show that, rather surprisingly, the use of heterogeneous bond energies improves the nucleation kinetics and in fact appears to be necessary for assembling certain intricate 3D structures. This observation makes it possible to sculpt nucleation path- ways by tuning the distribution of interaction strengths. These insights not only suggest how to improve the design of structures based on DNA bricks, but also point the way toward the creation of a much wider class of chemical or colloidal structures with addressable complexity.

- **Membrane-Assisted Growth of DNA Origami Nanostructure Arrays**

  **Abstract:** Biological membranes fulfill many important tasks within living organisms. In addition to separating cellular volumes, membranes confine the space available to membrane-associated proteins to two dimensions (2D), which greatly increases their probability to interact with each other and assemble into multiprotein complexes. We here employed two DNA origami structures functionalized with cholesterol moieties as membrane anchors—a three-layered rectangular block and a Y-shaped DNA structure—to mimic membrane-assisted assembly into hierarchical superstructures on supported lipid bilayers and small unilamellar vesicles. As designed, the DNA constructs adhered to the lipid bilayers mediated by the cholesterol anchors and diffused freely in 2D with diffusion coefficients depending on their size and number of cholesterol modifications. Different sets of multimerization oligonucleotides added to bilayer-bound origami block structures induced the growth of either linear polymers or two-dimensional lattices on the membrane. Y-shaped DNA origami structures associated into triskelion homotrimers and further assembled into weakly ordered arrays of hexagons and pentagons, which resembled the geometry of clathrin-coated pits. Our results demonstrate the potential to realize artificial self-assembling systems that mimic the hierarchical formation of polyhedral lattices on cytoplasmic membranes.

- **Silicon Nanowire-Induced Maturation of Cardiomyocytes Derived from Human Induced Pluripotent Stem Cells**

  **Abstract:**
The current inability to derive mature cardiomyocytes from human pluripotent stem cells has been the limiting step for transitioning this powerful technology into clinical therapies. To address this, scaffold-based tissue engineering approaches have been utilized to mimic heart development in vitro and promote maturation of cardiomyocytes derived from human pluripotent stem cells. While scaffolds can provide 3D microenvironments, current scaffolds lack the matched physical/chemical/biological properties of native extracellular environments. On the other hand, scaffold-free, 3D cardiac spheroids (i.e., spherical-shaped microtissues) prepared by seeding cardiomyocytes into agarose microwells were shown to improve cardiac functions. However, cardiomyocytes within the spheroids could not assemble in a controlled manner and led to compromised, unsynchronized contractions. Here, we show, for the first time, that incorporation of a trace amount (i.e., \(\sim 0.004\%\) w/v) of electrically conductive silicon nanowires (e-SiNWs) in otherwise scaffold-free cardiac spheroids can form an electrically conductive network, leading to synchronized and significantly enhanced contraction (i.e., >55% increase in average contraction amplitude), resulting in significantly more advanced cellular structural and contractile maturation.

- **Robustness of synthetic circadian clocks to multiple environmental changes**
  
  **Abstract:**
  
  A molecular network that mimics circadian clocks from cyanobacteria is constructed in silico. Simulating its oscillatory behaviour under variable conditions reveals its robustness relative to networks of alternative topologies. The principles for synthetic chemical circadian networks to work properly are consequently highlighted.
• **Alignment of nanostructured tripeptide gels by directional ultrasonication**


Abstract:

We demonstrate an *in situ* ultrasonic approach to influence self-assembly across the supramolecular to micron length scales, showing enhancement of supramolecular interactions, chirality and orientation, which depends on the peptide sequence and solvent environment. This is the first successful demonstration of using oscillating pressure waves to generate anisotropic organo- and hydrogels consisting of oriented tripeptides structures.

• **PNA as a Biosupramolecular Tag for Programmable Assemblies and Reactions**


Abstract:

The programmability of oligonucleotide hybridization offers an attractive platform for the design of assemblies with emergent properties or functions. Developments in DNA nanotechnologies have transformed our thinking about the applications of nucleic acids. Progress from designed assemblies to functional outputs will continue to benefit from functionalities added to the nucleic acids that can participate in reactions or interactions beyond hybridization. In that respect, peptide nucleic acids (PNAs) are interesting because they combine the hybridization properties of DNA with the modularity of peptides. In fact, PNAs form more stable duplexes with DNA or RNA than the corresponding natural homoduplexes. The high stability achieved with shorter oligomers (an 8-mer is sufficient for a stable duplex at room temperature) typically results in very high sequence fidelity in the hybridization with negligible impact of the ionic strength of the buffer due to the lack of electrostatic repulsion between the duplex strands. The simple peptidic backbone of PNA has been shown to be tolerant of modifications with substitutions that further enhance the duplex stability.
while providing opportunities for functionalization. Moreover, the metabolic stability of PNAs facilitates their integration into systems that interface with biology. Over the past decade, there has been a growing interest in using PNAs as biosupramolecular tags to program assemblies and reactions. A series of robust templated reactions have been developed with functionalized PNA. These reactions can be used to translate DNA templates into functional polymers of unprecedented complexity, fluorescent outputs, or bioactive small molecules. Furthermore, cellular nucleic acids (mRNA or miRNA) have been harnessed to promote assemblies and reactions in live cells. The tolerance of PNA synthesis also lends itself to the encoding of small molecules that can be further assembled on the basis of their nucleic acid sequences. It is now well-established that hybridization-based assemblies displaying two or more ligands can interact synergistically with a target biomolecule. These assemblies have now been shown to be functional in vivo. Similarly, PNA-tagged macromolecules have been used to prepare bioactive assemblies and three-dimensional nanostructures. Several technologies based on DNA-templated synthesis of sequence-defined polymers or DNA-templated display of ligands have been shown to be compatible with reiterative cycles of selection/amplification starting with large libraries of DNA templates, bringing the power of in vitro evolution to synthetic molecules and offering the possibility of exploring uncharted molecular diversity space with unprecedented scope and speed.

- **Specific light-up bioprobes based on AIEgen conjugates**
  Abstract:

Driven by the high demand for sensitive and specific tools for optical sensing and imaging, bioprobes with various working mechanisms and advanced functionalities are flourishing at an incredible speed. Conventional fluorescent probes suffer from the notorious effect of aggregation-caused quenching that imposes limitation on their labelling efficiency or concentration to achieve desired sensitivity. The recently emerged fluorogens with an aggregation-induced emission (AIE) feature offer a timely remedy to tackle the challenge. Utilizing the unique properties of AIE fluorogens (AIEgens), specific light-up probes have been constructed through functionalization with recognition elements, showing advantages such as low background interference, a high signal to noise ratio and superior photostability with activatable therapeutic effects. In this tutorial review, we summarize the recent progress in the development of specific AIEgen-based light-up bioprobes. Through illustration of their operation mechanisms and application examples, we hope to provide guidelines for the design of more advanced AIE sensing and imaging platforms with high selectivity, great sensitivity and wide adaptability to a broad range of biomedical applications. Programmability of oligonucleotide hybridization offers an attractive platform for the design of assemblies with emergent properties or functions.
• **Orthogonal Insertion of Lanthanide and Transition-Metal Atoms in Metal–Organic Networks on Surfaces**


**Abstract:**

Surface-confined d–f bimetallic 2D coordination nanosystems have been achieved by using a three-step procedure that exploits orthogonal coordination interactions of CN-functionalized free-base porphyrin linkers with rare-earth and transition-metal centers. By systematic STM investigations the assembly process was established and the resulting nanoarchitectures characterized at the molecular level.

• **Total Synthesis of Ellagitannins through Regioselective Sequential Functionalization of Unprotected Glucose**


**Abstract:**

Short and sweet: Very short total syntheses of ellagitannins were achieved through sequential and regioselective functionalization of the hydroxy groups of unprotected glucose.