December 7th, 2023
Big Auditorium 0.013, Department of Chemistry
Conference program

Chair: Prof. Stefan Salentinig

14:00 - 14:05: Welcome from Prof. Andreas Kilbinger, Frimat director

Session 1: Bioactive Materials and Interfaces

14:05 - 14:20:	Jules Valentin	"Antimicrobial Cationic Coating for Rapid Self-Disinfecting Surfaces"
14:20 - 14:35:	Saquib Farooq	"Synthesis and Aggregation Studies of Macrocycles and Helices with Hydrophobic Inner Surfaces"
14:35 - 14:50:	Aleksandra Adamczyk	"Orienting Single Molecules in DNA Origami Constructs"
14:50 - 15:05:	Akhil Pratap Singh	"Intramolecular Hydrogen Bonding: A Key Factor in RNA Binding to Ordered Phosphatidylcholines Lipid Bilayer"
15:05 - 15:20:	Matteo Frigerio	"The effect of pH on enzyme catalyzed lipolysis at the oil/ water interface"
15:20 - 15:45:		Coffee Break

Session 2: Separation Materials

15:45 - 16:00:	Timur Ashirov	"From 0D to 3D for CO2 Separation: Fully Conjugated Porous Organic Polymers Prepared via Diels-Alder Polymerization Reaction"
16:00 - 16:15:	Patrick Fritz	"Tetraoxa[8]circulene – Based Porous Polymers for Lithium Ion Capture and Battery Recycling"

Session 3: Optically Active Materials

16:15 - 16:30:	Diana Potes Vecini	"Hematite (α-Fe2O3) NanoCubes: A Facile and Eco-friendly Synthesis"
16:30 - 16:45:	Jansie Smart	"Order and Disorder in Opals"
16:45 - 17:00:	Antoine Scalabre	"Two-Level Ordering in Nano-Rattles for Optical Properties"
17:00 - 17:15:	Marta Oggioni	"Mechanochromic Luminescent Polymers Made Easy"
17:15 - 17:30:	A. A. Boopathi	"Tuning Helical Supramolecular Polymers with Photo-Switchable Cationic Pyridine-Pyrene (PyPy) for OLEDs"

17:30 - 19:00: **Extended Poster Session and Apero**

Antimicrobial Cationic Coating for Rapid Self-Disinfecting Surfaces

J. Valentin[1], S. Watts[1], M. Gontsarik[1], A. Lassenberger[1], A. Wolfensberger[2], S. Brugger[2], M. Zabara[3],
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[3] *Livinguard AG, Cham, Switzerland.*

The prevention of microbial infections is a global challenge. Efficient antimicrobial coatings that rapidly kill microorganisms upon contact can help minimize their transmission. This work demonstrates the scalable synthesis and characterization of self-disinfecting nanofilms for the post-modification of hospital-relevant surfaces. Photoinitiated bulk polymerization of an air-dried [2-(methacryloyloxy)ethyl] trimethylammonium chloride (METAC) film on cotton (gowns), nitrile rubber (protective gloves), and glass surfaces (tables, screens) is used for their supercharging. A 6 nm thick coating dominated by cationic quarternary amine groups was shown by a combination of spectroscopic imaging ellipsometry and X-ray photoelectron spectroscopy. Surface chemistry analysis with XPS showed the covalent attachment of the coating to the surface. Further, all the coated surfaces demonstrated a significant increase in surface charge after coating. Antimicrobial *in vitro* evaluation of the coated surfaces demonstrated >3 log reductions of *Staphylococcus aureus* and *Escherichia coli* populations within 5 min of contact. The antibacterial activity is attributed to the strong surface charge leading to bacterial membrane disruption via the strong electrostatic interaction with the surface. The coating's range of compatible materials and its rapid bactericidal activity can combat the surface transmission of bacteria and may help to contain the spread of infectious diseases. Its synthesis in environmental conditions is promising for integration into industrial processes.

Synthesis and Aggregation Studies of Macrocycles and Helices with Hydrophobic inner Surfaces

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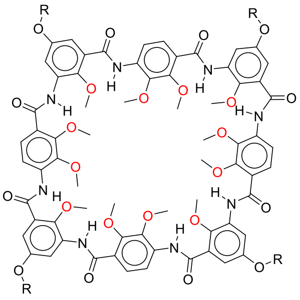
Keywords: Macrocycles, Helical polymers, and aggregation

Macrocycles and foldamers with substantial tubular cavities are intriguing and have captured significant attention. Foldamers and macrocycles with non-collapsible hydrophilic cavities have demonstrated exceptional properties in areas such as cation recognition and highly conducting membranes.[1] Conversely, helical foldamers and macrocycles that are rich in hydrophobic interior surfaces have shown exceptional performance in water permeation experiments.[2,3] However, the synthesis of these hydrophobic-surfaced macrocycles remains a significant challenge, with only a few existing reports.[4] Herein, we report the synthesis of helices **1a** and macrocycle **1** with an internal diameter of 0.9 nm and a hydrophobic interior surface. Additionally, we also obtained macrocycles **2** and **3**. These macrocycles were structurally characterized by single-crystal X-ray structures. The aggregation of the macrocycles both in solution and the solid state were investigated.



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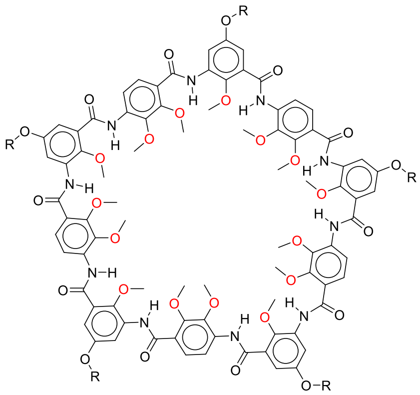

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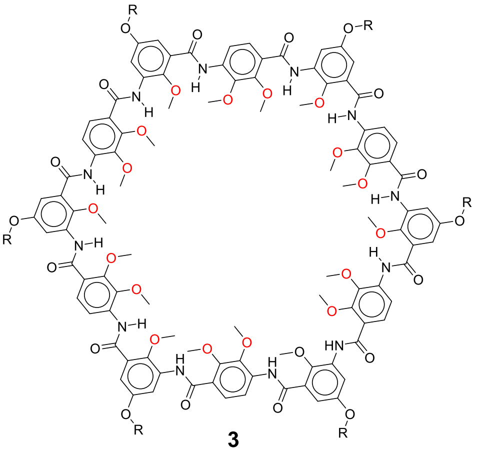

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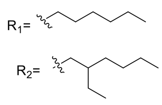
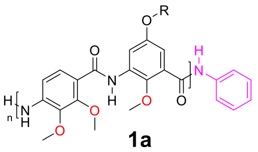
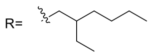




1a

n = 5,10,20,and 30



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Orienting single molecules in DNA origami constructs

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Over the last decade, DNA nanotechnology has been increasingly used to self-assemble functional nanostructures. One of the main advantages of this approach is that different species including colloidal nanoparticles and single photon emitters such as fluorophores can be positioned with nm precision and stoichiometric control [1]. This has been exploited for a growing number of nanophotonic applications [2]. While the relative distance between the hybrid species has been controlled up to the nanometer range, no control over the relative orientation has been exerted.

We present a method to both position and orient single photon emitters within DNA origami constructs. In particular, we exploit the ability of DNA origami to exert forces in order to “stretch” covalently incorporated dyes and deterministically align them with the orientation of double-stranded DNA helix they are located at (Fig 1.). We study the dye´s three dimensional orientation and wobbling using three independent techniques: polarization-resolved excitation measurement, point-spread function (PSF) analysis [3] and the four-polarization image splitting method [4] combined with a super-resolution (nanoscopy) measurement using the DNA-PAINT technique [5] to retrieve the orientation of the DNA origami “host” structure.

Our results show that by simply removing a number of nucleotides adjacent to both ends of the doubly-linked fluorophore, the dye transitions from a non-predictable orientation given by a combination of external factors to an orientation aligned with the predesign direction of the host ds-DNA helix. We believe this work shows a simple way to deterministically orient dyes which constitute the last degree of freedom required to manipulate the interaction of single photon emitters and fully control the coupling to other species.

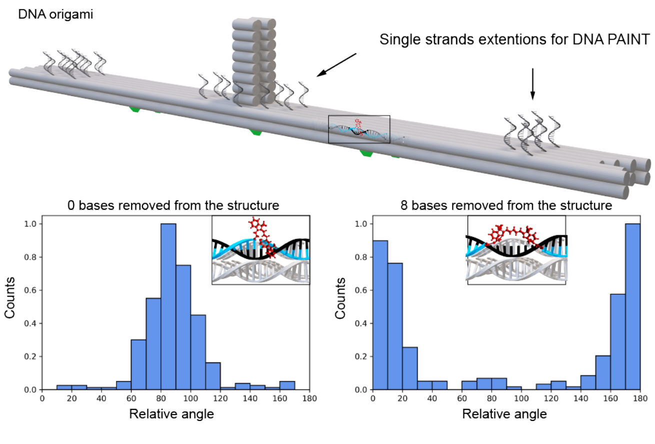

Fig. 1: Different orientation of a fluorescent dye in respect to DNA origami ‘host’ structure obtained for the structures with a different number of removed adjacent nucleotides.

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Intramolecular hydrogen bonding: A key factor in RNA binding to ordered phosphatidylcholines lipid bilayer

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Introduction

RNA therapeutics have made significant progress in gene therapy for treating a wide range of diseases [1]. However, RNA requires robust delivery systems that overcome several major hurdles, such as loss of RNA activity [2] to work more efficiently inside the target cells. Although lipid-RNA conjugates have shown promise as delivery carriers [3], it is obscure how lipids interact with various lipid bilayer phases as well as RNA-based therapeutics, such as messenger RNA (mRNA), small interfering RNA (siRNA) *etc.* [4]. Exploring the structural based RNA interactions with lipids are therefore of paramount importance as such direct interactions influence RNA activity [5,6].

Results

In this work, we carried out molecular dynamics (MD) simulations to extensively investigate RNA-lipid membrane interactions, which can affect RNA activity by changing the RNA structure or chemical microenvironment. We focus on understanding the RNA–lipid binding that depends on the primary sequence, secondary structure, and length of RNA as well as the nature of membrane (ordered *vs* liquid phase). Our MD findings demonstrate that short RNAs rich in guanine have more potent RNA-lipid interactions than other types, particularly for gel membrane. Furthermore, results also show that double standard structures promote lipid binding. Interestingly, our observation aligns with experimental studies [5,6]. Overall, simulation results reveal that intramolecular hydrogen bonding plays a key role in RNA binding to ordered phospholipid bilayer, explaining experimental observations. This work not only complements the experimental findings but also provides a wealth of detailed information at the molecular-to-atomic level, which is certain to help for accelerating the research on RNA-lipid assemblies for task specific application such as design a lipid based Nano carrier for mRNA or siRNA delivery.

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Frimat Conference 2023

The effect of pH on enzyme catalyzed lipolysis at the oil/water interface

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ABSTRACT

Triglycerides are a vital source of nutrients and energy. However, they are not adsorbed intact in the digestive tract. Lipases and pH operate at the oil-water interface and hydrolyze them into more hydrophilic and amphiphilic products, including fatty acids and monoglycerides. Their effect on the structure of the oil-water interface, which is key for digestion kinetics and nutrient transfer, is not yet fully understood. They may generate new oil-water interfaces that assure sufficient progress of digestion.

This contribution reports on the interfacial modification during pH- and enzyme-triggered hydrolysis of triolein in the presence of water. Spinning drop tensiometry, imaging ellipsometry, and microfocus small angle X-ray scattering (SAXS) demonstrate the formation of nanostructured interfacial layers between oil and water. The simultaneous analysis of colloidal structure formation in the oil and water phases with SAXS and dynamic light scattering showed the spontaneous formation of highly monodisperse water-in-oil emulsions inside the triolein phase, containing lipase. Techniques such as Karl Fischer titration and Bradford's assay confirm the water transfer into the triolein. Importantly, acid-base titration shows the lipase retains its ability to break down lipids once in the oil phase.

The findings offer valuable insights into pH and lipase-catalyzed triglyceride hydrolysis. We've explored various pH and ionic strength conditions to understand this process better. Hydrolysis time and pH were found to have symbiotic effects, gradually tuning the oil-based environment to more hydrophilic structures with high internal surface area. This knowledge contributes to the fundamental colloidal understanding of the lipid digestion process that is vital for survival and nutrient supply. The colloidal structure formation is linked to its function as carrier for lipases and nutrients.

From 0D to 3D for CO_2 separation: Fully Conjugated Porous Organic Polymers Prepared via Diels-Alder Polymerization Reaction

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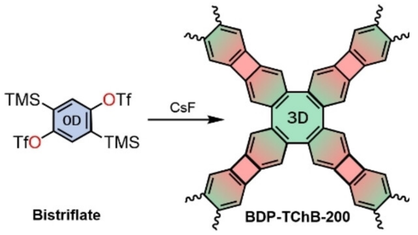
Anthropogenic emissions have significantly increased the atmospheric carbon dioxide (CO_2) level, which has now exceeded 418 ppm, resulting in global warming, climate change and ocean acidification. To decrease CO_2 emissions from large point sources, amine-scrubbing using aqueous solutions of alkyl amines has been conventionally applied. While this approach offers high selectivity and low cost, the low uptake capacity, high energy penalty for regeneration, and the degradation and corrosive nature of amines present important challenges. Porous materials have emerged as potential alternatives owing to their high surface areas and tailor-made properties for high CO_2 affinity. Porous organic polymers (POPs) are a promising class of porous materials owing their high porosity, structural tunability, excellent chemical and thermal stability. One of the important criteria is the abundance of micropores (<2 nm) and ultramicropores (<0.7 nm) which are essential factor to increase CO_2 affinity owing to the interaction of CO_2 with multiple binding sites. Therefore, synthetic strategies to develop POPs with desired pore size that is specific for CO_2 is a daunting task. Herein, we show the base-catalyzed direct synthesis of a fully conjugated 3D POPs, named benzyne-derived polymers (BDPs), containing biphenylene and tetraphenylene moieties starting from a simple bisbenzyne precursor, which undergoes [2+2] and [2+2+2+2] cycloaddition reactions to form BDPs primarily composed of biphenylene and tetraphenylene moieties. The resulting polymers exhibited ultramicroporous structures with surface areas up to 544 $m^2\ g^{-1}$ and very high CO_2/N_2 selectivities.



BET Surface area: 544 $m^2 \cdot g^{-1}$
IAST CO_2/N_2 selectivity: 65.4

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Tetraoxa[8]circulene – Based Porous Polymers for Lithium Ion Capture and Battery Recycling

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Tetraoxa[8]circulenes (TOCs) are a subclass of hetero[X]circulenes that have seen considerable interest from the computational community due to their aromatic motifs and from experimentalists due to their electronic properties. [1] Despite that, only a few small-molecule TOCs have been reported in the literature, while extended structures such as polymers or framework materials were missing completely.

In 2022, we reported the first extended polymeric TOC (pTOCs) based on a Lewis acid-mediated cyclization procedure.[2] The obtained polymers featured tunable porosity and could be post-synthetically doped to tune their semiconducting properties. Based on these findings, we developed new protocols for synthesizing pTOCs and obtained a system with crown ether-like pores capable of selectively capturing Li-ions from complex mixtures (Na^+, Ca^{2+}, Mg^{2+}, …). Considering the prominence of battery-powered devices and vehicles as well as the availability and cost of raw materials we explored the material's potential for the recycling of Li from used energy storage devices. Due to the high chemical stability of the material and its high selectivity toward lithium, we were able to capture lithium from a wide range of battery chemistries ranging from Li-ion over lithium-sulfur to lithium metal.

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Hematite (α-Fe_2O_3) nanoCubes: a facile and eco-friendly synthesis

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The self-assembly of nano- and microparticles into 2D and 3D architectures has gained attention due to the properties of the obtained structures, which rely on their chemical composition, morphology, size, and size distribution. Iron oxide particles are particularly relevant because of their optical, catalytic, and magnetic properties. For this reason, a wide variety of methods have been developed for their synthesis. However, controlling their size and shape is still an ongoing challenge. From this standpoint, hematite is particularly interesting because different sol-gel methods have been developed to prepare them in various shapes, such as spindles, peanuts, and cubes. These methods suffer, unfortunately, from reproducibility issues and need long synthesis protocols. Based on room-temperature ionic liquids (ILs), a sustainable two-step approach was developed to synthesize cubic hematite particles with well-controlled size and shape, as showcased in the SEM image below. ILs are opening a new way to obtain structure-shaped inorganic nanomaterials under more efficient, safer, and environmentally friendly conditions. The synthetic protocol for fabricating cubic hematite requires $FeCl_3$ as an iron precursor and an IL as a stabilizer and structure-controlling agent. In this work, different ILs, all based on ammonium and imidazolium chlorides, have been tested, to study the influence of the aliphatic chain length on the morphology of hematite cubes. The effects of temperature and reaction time were also studied to understand better the various variables' impact on the formation mechanism. The SEM images show that well-defined and uniform hematite cubes have been grown using different ammonium chloride-based ionic liquids, in contrast to the poorer results obtained with imidazolium chloride.

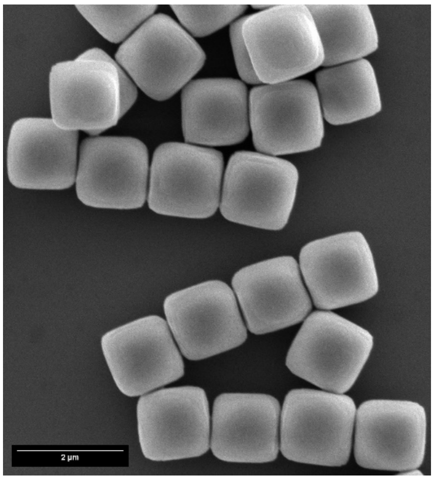

Figure 1: SEM Image of hematite cubes synthesized with Decyl-trimethyl ammonium chloride.

Order and Disorder in Opals

Jansie Smart[1]*, Alessandro Parisotto*[2]*, Kata Dorbic*[1]*, Phillippa Knight*[3] *and Marco Lattuada*[1]

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[2] *Adolf Merkel Institute, University of Fribourg, Switzerland*
[3] *Cambridge University, United Kingdom*

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Some animals make use for structural colours to interact with the environment around them. Structural colour comes from the interaction of light with the structures in a material so it doesn't fade like normal pigments. These colours can be mimicked by arranging monodisperse colloids in crystals by making use of self-assembly. When the size of the colloids are on the order of visible light (400-700 nm) structural colours can be seen. The amount of order and disorder in the crystalline structure allows structural colours to have different properties. Highly ordered photonic crystals show structural colours with an angular dependence, when a low degree of disorder is introduced the structural colours begin to have a much lower angle dependence

We are introducing disorder into self-assembled colloidal crystals through non-spherical dimpled particle templates, by trying to control the disorder by the size of the dimple in the particle itself. The final particle arrangements within the self-assembled structures and the visible light reflection spectra (in real and in reciprocal space) are used.

The synthesis of the dimpled particles results in drastic changes of the surface properties of the particles, changing from hydrophobic polymeric particles to hydrophilic carbon based particles. These changes impact the self-assembly behaviour in the system, as the hydrophobicity of the particles play a role in the way particles self-assemble in evaporation deposition. This required modifications to the particle synthesis and a particle surface preparation with the assistance of surfactants, to enable the particles to be stable enough to form ordered crystalline arrangements.

Keywords: Colloidal crystals, disorder, dimpled colloidal particles, scatterogram

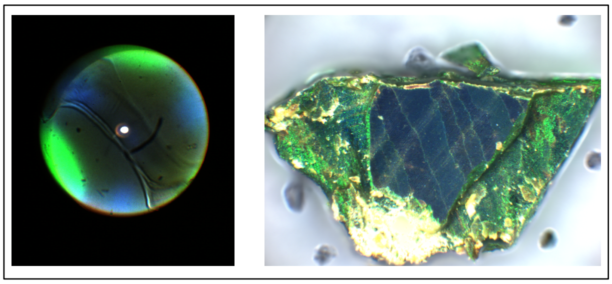

Figure1. *Left: a scatterogram of these assembled dimpled particles and Right: an optical image of the assembled particles.*

References

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Two-level ordering in nano-rattles for optical properties

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Yolk-shell nano-particles (also named nano-rattles), are in the center of many studies thanks to their interesting properties in multiple fields ranging from medicine to physics.[1] These properties come from both, the non-homogeneous composition of the nano-rattles, and also from the particular environment around the core, as it behaves like a nano-reactor. Synthesizing such nano-objects is challenging,[2] but we decided to take it one step further by organizing them in different ways and levels for optical effects.

In a first part we focused on obtaining a controllable and reversible way of aggregating the nano-particles, using silica spheres as model. The second part focused on the development of anisotropic and magnetic nano-particles and on how to use these as starting point for the synthesis of the desired nano-rattles. Having such a high control over the organization of nano-materials might allow to control opalescent properties of the aggregates.

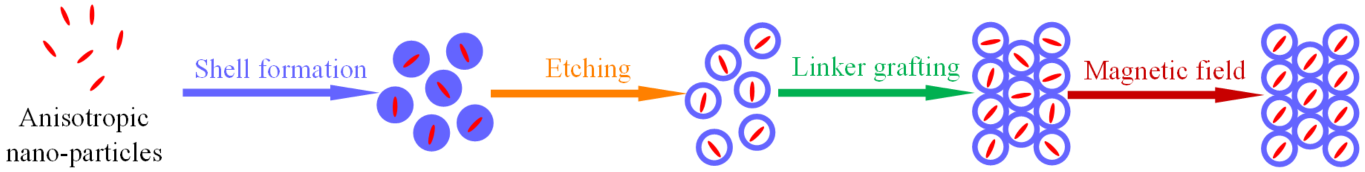

Figure 1. Schematic representation of the different synthesis and organization steps

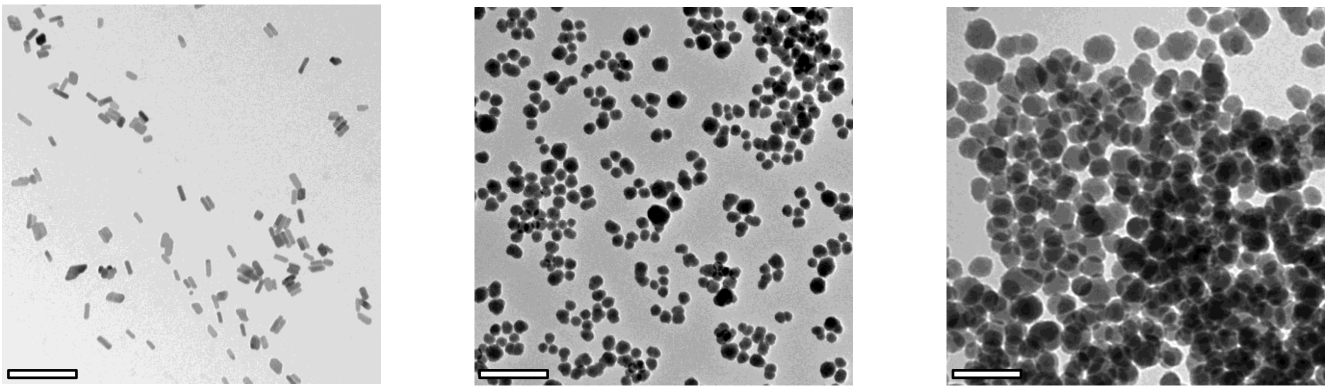

Figure 2. TEM pictures of synthesized $NaGdF_4$ nanorods (left) and of functionalized silica beads before (middle) and after (right) irradiation at 380nm (scales: 200nm)

References

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Mechanochromic luminescent polymers made easy

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A mechanochromic material can show an optical response, *i.e.*, a change in its absorption/emission spectrum, when subjected to mechanical deformation. Mechanochromism in polymeric materials allows monitoring of the emergence of stresses and strains as a consequence of deformation by visible colour changes or absorbance/fluorescence measurements. [1] A mechanochromic polymer can be achieved by covalently attaching specific chromophores to its backbone or by simple blending of a mechanochromic dye with the polymer matrix. The latter approach was introduced by Löwe and Weder [2] and is conceptually the easiest. The authors originally blended an excimer-forming dye, oligo(*p*-phenylene vinylene) (cyano-OPV), with polyethylene, rendering it mechanochromic. Excimer-forming motifs emit light at different wavelengths when close in space (for example, when aggregated in a polymer matrix), where they can form supramolecular dimers termed excimers, and when far apart (if these aggregates disassemble due to deformation), in their monomeric form. [3] Recently, Calvino et al. [4] expanded the excimer-forming dye concept by tethering cyano-OPV to the ends of a short poly(ethylene-*co*-butylene) (PEB) chain. This was shown to be more effective than its small-molecule counterpart in rendering semicrystalline as well as amorphous polymers mechanochromic. While effective, this cyano-OPV-functionalised PEB is accessed via a rather laborious synthesis. This work aims to demonstrate that similar mechanochromism can be achieved by tethering another excimer-forming moiety, pyrene, to telechelic PEB (**Py-PEB**) in a one-step synthesis. **Py-PEB** was accessed by the esterification of hydroxy-terminated PEB with 1-pyrenebutyric acid. Small quantities (0.1-1 wt%) of the dye were necessary to impart both semicrystalline poly(ε-caprolactone) and an amorphous poly(urethane) matrix with mechanochromism. This was demonstrated via simultaneous recording of fluorescence spectra and tensile testing of polymeric films. These showed an immediate decrease in the excimeric fluorescence of pyrene with respect to its monomeric response as the stretching of the samples increased, signalling the breaking of the excimers and the stretching of the **Py-PEB** chains.

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Tuning Helical Supramolecular Polymers with Photo-Switchable Cationic Pyridine-Pyrene (PyPy) for OLEDs

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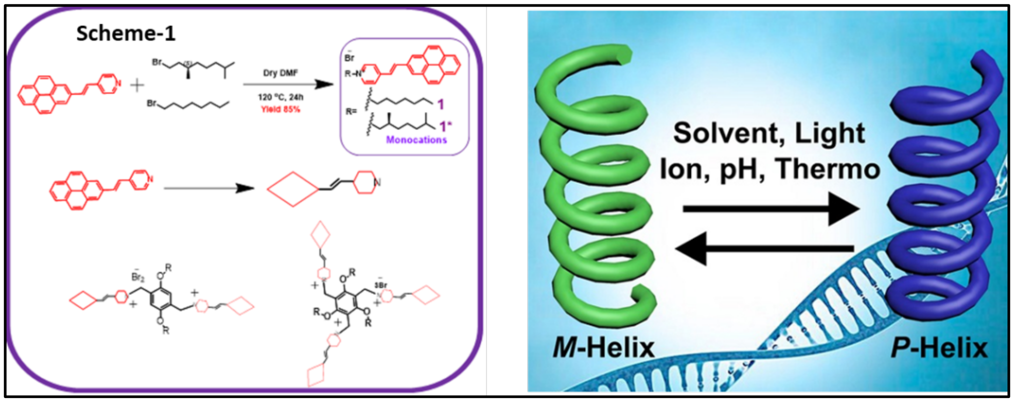
Abstract

Chiral organic supramolecular polymer dyes capable of circularly polarized luminescence (CPL) offer opportunities to reduce operating costs and maximize energy efficiency in organic light emitting devises (OLEDs) by increasing the overall amount of light passed through polarised device filters. The linear light is equally made up of right- and left-handed circularly polarised light, traditional OLEDs can only use 50% of the light emitted by the active layer and are thus fundamentally limited in energy output efficiency. To regulate the traditional chiral organic CPL, supramolecular chemistry is used to influence the arrangements of the molecules through noncovalent forces,[1] in these work we design an organic dyes pyridine-pyrene (PyPy) to explore the photoswitches topologies. Herein, we present the photochemistry of PyPy, which can control by a macromolecular environment. Through the decoration of a pyridine moiety with a conjugated aromatic pyrene containing a double bond accessible to [2 +2] photocycloaddition. Their Inherent helical supramolecular polymerization makes them especially attractive as functional materials with the capability of manipulating and responding to polarized light. We approached by developing mono, di- and trication PyPy (quaternization with chiral and achiral aliphatic chains), as a result of which comparative helical supramolecular polymer interactions study of mono, di- and trication PyPy polar molecules in different polar and non-polar solvents. In addition to establishing fundamental structure, light-Induced photochemistry, chiroptoelectronic properties,[2] and CPL under aggregation[3] for optimize the circularly polarized LEDs.



Keywords: circularly polarized luminescence (CPL), organic light emitting devises (OLEDs), and helical supramolecular polymers.

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