Interplay of Light and Self-Assembly in Functional Soft Materials

From Photo-Controlled to Photonic Structures

Mikko Poutanen
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Photo-responsive molecules in combination with self-assembled structures have been widely used in devising soft functional materials. Especially photoisomerizable azobenzene molecules incorporated into supramolecular structures or liquid crystalline systems, which enable the control of order and amplifying the molecular photo-response to a macroscopic scale, have triggered great interest. On the other hand, larger-scale self-assemblies based on, e.g., block copolymer or colloidal structures may significantly modify light propagation in the self-assembled materials, leading to photonic properties and structural colors. The main focus of this thesis lies in this intriguing interplay between light and self-assembly shown by these photo-controlled and photonic systems.

**Publication I** studies the effect of self-assembly on the photoresponse and isomerization kinetics of azobenzenes in hydrogen-bonded polymeric complexes. These complexes of hydroxylazobenzene derivatives are used to demonstrate a drastic increase in the thermal *cis*-trans isomerization rate upon a transition from a disordered low-azobenzene-content state to a high-concentration state with lamellar smectic-like order. Comparison between disordered and ordered high-concentration states shows that the former exhibits significantly slower kinetics, pinpointing the importance of cooperativity created by the molecular order and alignment.

In **Publication II** the amorphous hydrogen-bonded complexes of hydroxylazobenzenes are used to demonstrate how thermal isomerization kinetics of azobenzenes can be exploited in optical sensing of hydrogen-bonding gas vapors, especially relative humidity. The thermal isomerization of different complexes is shown to exhibit exponential changes with huge dynamic range, high reproducibility and tunability in the presence of water and ethanol. The use as a sensor is further demonstrated. Using isomerization kinetics for sensing is potentially opening new avenues for using azobenzene molecules and their supramolecular complexes in practical applications.

**Publication III** investigates halogen-bonded supramolecular liquid crystals containing azobenzene moieties. These complexes of stilbazole and fluorinated azobenzene derivatives are shown to systematically form liquid crystals held together by the highly directional halogen bonding. The photoisomerization-induced LC-isotropic transition is studied in detail, and the *cis*-isomer content required for the transition is determined.

In **Publication IV** a generic method is developed for using the self-assembly of block copolymer micelles with a quaternizable block to create photonic fluids and 3D photonic crystals. For this, reaching micelles with narrow size distributions and highly swollen coronae is critical. The observed crystallization demonstrates that these qualities are reached. The micelles spontaneously assemble in up to millimeter-sized crystal lattices. In addition, the photonic crystals result in extremely narrow reflection peaks ranging over the visible region, have high tunability through changes in concentration and salinity, and form reversibly.
Tekijä
Mikko Poutanen

Väitöskirjan nimi
Valon ja itsesarjestyminen vuorovuoroavikutus pehmeissä toiminnallisissa materiaaleissa

Julkaisija
Perustieteiden korkeakoulu

Yksikkö
Teknillisen fysiikan laitos

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Esseeväitöskirja

Tiivistelmä

Julkaisussa I tutkitaan itsesarjestyminen vaikutusta atsobentseenin isomerisaatiokinetiikkaan vetsisitoutuvissa polymeerikompleksisissa. Termin isomerisaation näyttää kiihtyvän hydrosiatsobenseenimokkeissa konsentraation kasvaessa. Pienellä konsentraatiolla näytteet ovat epäjarjestyneitä, kun taas suuren konsentraation näytteet järjestävät lamellaaariin smektisiin rakenteisiin. Vertailu suureen konsentraation vastaavaan epäjarjestyneeseen kompleksiin osoittaa erityisesti molekyylien järjestyksestä ja suuntautumisesta syntyvän keskinäisen vuorovaiheuksen olevan tärkeää isomerisaatiokinetiikan kannalta.


Avainsanat
itsesarjestyminen, valoon reagoiva, atsobentseeni, lohkopolymeri, miselli, fotonikide

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urn
The research presented in this thesis has been carried out in the Molecular Materials group at the Department of Applied Physics at Aalto University School of Science. My journey in the group started as a summer student in 2010 and continued as a doctoral candidate in autumn 2013. Ever since I got involved in the world of soft nanomaterials, I have been astonished and intrigued by the variety of complex phenomena and how those are utilized and molded into something new. I still am.

I want to express my deepest gratitude to my supervisor Prof. Olli Ikkala for the overwhelming enthusiasm towards science, support and never-ending ideas, but most of all, for creating the excellent environment for doing science and grow as scientists – as well as people. I was also privileged to work under the instruction of Prof. Arri Priimägi. After founding his own research group Smart Photonic Materials at Tampere University of Technology, I was welcome to be part in that even though often from a distance. Thank you for the guidance and support, and importantly, the ideas and optimism when things did not go as planned. Thank you also for the non-work-related discussions we had during my visits to Tampere.

I want to thank all my coauthors for the efforts that you did for the manuscripts. Especially, I want to thank André Gröschel as without him the paper on the photonic crystals would not exist. I want to thank him also for his example in academic endeavors and the numerous discussions we had about science. Special thanks also to Marco Saccone and Francisco Fernandez-Palacio for the work we did together with the halogen-bonded liquid crystals. Furthermore, I thank Zafar Ahmed, Lauri Rautkari, Tina Gröschel, Giulia Guidetti, Silvia Vignolini, Oleg Borisov, Giancarlo Terraneo, Giuseppe Resnati and Pierangelo Metrangolo for their contributions.

Prof. Stefan Hecht and Prof. Svetlana Santer I thank for the preliminary examination of the manuscript. I want to also express my most sincere thanks to Prof. Albert Schenning for accepting the invitation to act as the opponent in the upcoming dissertation.

Thank you for all the former and current members of Molecular Materials, Soft Matter and Wetting, and Active Matter for creating the excellent working
environment. Especially thanks to Jukka Hassinen, Matti Toivonen, Lahja Martikainen, Ville Liljeström, Teemu Myllymäki and Tomy Cherian for all the work and non-work related discussions we had throughout the years.

Finally, I want to thank my family and friends. Thank you mom and dad for always encouraging me in my curiosity. You always pushed me forward and supported me in my academic endeavours. It wasn't always easy, but you supported me in those moments when I needed it the most. Thank you Heikki for all the time and discussions we've shared throughout life, and keeping my feet on the ground when I needed it. Riikka, I am ever so grateful for sharing my life with such a warmhearted person as you. Thank you for your endless support, and sharing all the ups and downs with me.

Espoo, August 26, 2018,

Mikko Poutanen
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List of Publications

This thesis consists of an overview and of the following publications which are referred to in the text by their Roman numerals.


III Fernandez-Palacio, Francisco*; Poutanen, Mikko*; Saccone, Marco; Siiskonen, Antti; Terraneo, Giancarlo; Resnati, Giuseppe; Ikkala, Olli; Metrangolo, Pierangelo; Priimagi, Arri. Efficient Light-Induced Phase Transitions in Halogen-Bonded Liquid Crystals. Chemistry of Materials, 28, 8314-8321, 2016. * These authors contributed equally.

IV Poutanen, Mikko; Guidetti, Giulia; Gröschel, Tina, I.; Borisov, Oleg V.; Vignolini, Silvia; Ikkala, Olli; Gröschel, Andre H.. Block Copolymer Micelles for Photonic Fluids and Crystals. ACS Nano, 12, 3149-3158, 2018.
List of Publications
Author’s Contribution

Publication I: “Structurally Controlled Dynamics in Azobenzene-Based Supramolecular Self-Assemblies in Solid State”

The author had the main role in planning, prepared the molecules and complexes, performed all the experiments and wrote the first draft of the manuscript. The manuscript was finalized together with coauthors.

Publication II: “Thermal Isomerization of Hydroxyazobenzenes as a Platform for Vapor Sensing”

The author conceived the idea, planned the research, prepared all of the samples, performed all the experiments except for the dynamical vapor sorption measurement and wrote the first draft of the manuscript. The manuscript was finalized together with coauthors.

Publication III: “ Efficient Light-Induced Phase Transitions in Halogen-Bonded Liquid Crystals”

The author planned and conducted the experiments for the analysis of the photochemical response, analyzed the results and wrote the corresponding parts of the manuscript. F. Fernandez-Palacio prepared the complexes.

Publication IV: “Block Copolymer Micelles for Photonic Fluids and Crystals”

The author planned the characterization of the crystallization and optical properties and performed the related experiments except for measurement of single
crystal reflection spectra, performed by G. Guidetti, and fluorescence confocal microscopy, which was performed by André Gröschel. The author compiled all the results and had a major role in writing the manuscript.
# List of symbols and abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>2PAP</td>
<td>4-[(4-ethylphenyl)azo]phenol</td>
</tr>
<tr>
<td>8PAP</td>
<td>4-[(4-octylphenyl)azo]phenol</td>
</tr>
<tr>
<td>BCP</td>
<td>Block copolymer</td>
</tr>
<tr>
<td>Cryo-TEM</td>
<td>Cryo-Transmission electron microscopy</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic light scattering</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>FCC</td>
<td>Face-centered cubic</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>HB</td>
<td>Hydrogen bonding</td>
</tr>
<tr>
<td>LC</td>
<td>Liquid crystal</td>
</tr>
<tr>
<td>LCE</td>
<td>Liquid crystalline elastomer</td>
</tr>
<tr>
<td>MPF</td>
<td>Micellar photonic fluid</td>
</tr>
<tr>
<td>MPC</td>
<td>Micellar photonic crystal</td>
</tr>
<tr>
<td>nPAP</td>
<td>4-[(4-alkylphenyl)azo]phenol (alkyl = ethyl or octyl)</td>
</tr>
<tr>
<td>P4VP</td>
<td>Poly(4-vinyl pyridine)</td>
</tr>
<tr>
<td>P2VP</td>
<td>Poly(2-vinyl pyridine)</td>
</tr>
<tr>
<td>POM</td>
<td>Polarized optical microscopy</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PSS</td>
<td>Photo stationary state</td>
</tr>
<tr>
<td>RH</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>SAXS</td>
<td>Small-angle X-ray scattering</td>
</tr>
<tr>
<td>SV</td>
<td>Polystyrene-b-poly(2-vinylpyridine) block copolymer</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet radiation ($\lambda &lt;$ 400 nm)</td>
</tr>
<tr>
<td>X</td>
<td>A halogen atom (F, Br, I)</td>
</tr>
<tr>
<td>XB</td>
<td>Halogen bonding</td>
</tr>
<tr>
<td>A</td>
<td>Absorbance</td>
</tr>
<tr>
<td>$a$</td>
<td>Lattice constant of the unit cell</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Stretching exponent in stretched exponential function</td>
</tr>
<tr>
<td>$c$</td>
<td>Concentration</td>
</tr>
<tr>
<td>$d_{hkl}$</td>
<td>Interplanar distance according to Miller's indices $h$, $k$, $l$.</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>Molecular absorption coefficient</td>
</tr>
<tr>
<td>$E_a$</td>
<td>Activation energy</td>
</tr>
<tr>
<td>$f_{cis}$</td>
<td>cis-fraction</td>
</tr>
<tr>
<td>$I$</td>
<td>Light intensity</td>
</tr>
<tr>
<td>$I_s$</td>
<td>Ionic strength of the solution</td>
</tr>
<tr>
<td>$k$</td>
<td>Thermal isomerization rate constant</td>
</tr>
<tr>
<td>$\kappa^{-1}$</td>
<td>Debye screening length</td>
</tr>
<tr>
<td>$m_{core}$</td>
<td>Mass of the micelle core</td>
</tr>
<tr>
<td>$m_{corona}$</td>
<td>Mass of the micelle corona</td>
</tr>
<tr>
<td>$N_A$</td>
<td>Avogadro’s constant</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength of light</td>
</tr>
<tr>
<td>$\lambda_{RH}$</td>
<td>Constant related to the $RH$ dependence of thermal isomerization kinetics</td>
</tr>
<tr>
<td>$M_w$</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Quantum yield of isomerization</td>
</tr>
<tr>
<td>$\varphi$</td>
<td>Volume fraction</td>
</tr>
<tr>
<td>$p_{H_2O}$</td>
<td>Vapor pressure of water</td>
</tr>
<tr>
<td>$p_{sat}$</td>
<td>Saturation vapor pressure of water</td>
</tr>
<tr>
<td>$q$</td>
<td>Scattering vector</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
</tr>
<tr>
<td>$R$</td>
<td>Gas constant</td>
</tr>
<tr>
<td>$R_{core}$</td>
<td>Radius of the micelle core</td>
</tr>
<tr>
<td>$R_h$</td>
<td>Hydrodynamic radius</td>
</tr>
<tr>
<td>$R_{micelle}$</td>
<td>Radius of the micelle</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>$x$</td>
<td>Nominal complexation degree</td>
</tr>
</tbody>
</table>
1. Introduction

Throughout history, a constant challenge for technological development has been to create ever-more delicate and better-functioning materials and structures. The resulting technological advances have progressed hand-in-hand with our understanding on the underlying chemical and physical principles governing the materials properties. Understanding these principles is the key to develop structure-property-function relationships leading to highly functional static, responsive and dynamic materials. From these principles and relationships, many have been learned from natural materials showing highly hierarchical structures spanning from nano- to macro-scale.\textsuperscript{1–3} Natural materials have also shown the possibilities of responsive optical materials,\textsuperscript{4} which allow for highly tunable, more complex and sophisticated functionalities for different emerging applications. Understanding the possibilities of responsive and highly hierarchical structures has created the demand to control materials properties at multiple length scales, amplify responses from molecular changes and in general utilize materials to their full potential. This has lead to taking advantage of the nano-scale structures and effects.

The control of nanomaterials, having at least one dimension within size range of 1-100 nm, requires non-conventional approaches owing to the small sizes. The lower end of the size range even overlaps with that of molecules. To give scale for a single nanometer, the diameter of a human hair is around 20 µm, i.e. 20 000 nm. The ability to control nanomaterials has been achieved through numerous technological inventions that allow for precise control and probing of their properties at extremely high resolution.\textsuperscript{5} In creating nanostructures, there are two different approaches: bottom-up and top-down. The top-down approach is the traditional approach where the structures are carved from an existing material, whereas the bottom-up approach creates the structures by assembling smaller particles into ordered entities.

In nanomaterial science, the bottom-up approach is referred to as self-assembly,\textsuperscript{6} where the strict control of the particle-particle interactions through design leads to spontaneous formation of order, possibly even over multiple length scales. As an example, in liquid crystals the orientational order of the nanometer sized molecules can extend up to millimeters, i.e. over $10^6$ molecules stack sponta-
neously side-by-side. The self-assemblies of supramolecular complexes, liquid crystals, block copolymers, and colloids offer a widely utilized toolkit that can be applied in a large range of functional materials.

The dynamic nature of non-covalent supramolecular interactions leads to non-linear responses to environmental stimuli as often observed in soft matter. In combination with self-assembled order, the materials lead to highly responsive functional structures.\textsuperscript{7–10} The phase transitions observed in self-assembled materials amplify the responses. The responses to for example chemical, physical or mechanical stimuli introduce new dynamic functionalities to the static materials, and have been under extensive research owing to the large range of potential applications in nanomaterials.

An especially interesting trigger for responsive materials is light. Light is all around us and its interactions with materials are responsible for intriguing phenomena in our environment. As electromagnetic radiation light interacts with molecules through absorption caused by molecular resonances, or with structures having dimensions in similar size range as the wavelength of light. For visible light, the wavelength ranges from 400 to 700 nm. One of the most captivating phenomenon induced by light is our vision, which is caused by the light-induced change in the structure of opsins proteins, i.e., the isomerization of their retinal chromophore. This tiny change in the molecular conformation triggers a sophisticated cascade creating the visual impulses in our brains. These light-induced changes in the conformation of photochromic molecules combined with a suitable amplifying mechanism are the basis of creating photo-responsive materials.

This thesis focuses on the interplay of light and self-assembling functional materials. Self-assemblies are used both to create light-responsive materials, but also to create photonic structures, \textit{i.e.} control light propagation with self-assemblies. Throughout the thesis, self-assembled materials on different length scales, ranging from supramolecular complexes to colloids, are used to create the studied materials. The photo-responsive materials are created by using azobenzenes as the photochromic molecules. The photo-responses, and especially the kinetics of isomerization, are studied in self-assembling systems. On the other hand, the possibilities to extend the applications of block copolymer micelles to photonic crystals are studied.

\subsection{1.1 Outline of the thesis}

The thesis starts by giving an introduction and literature review to the main topics of the thesis: different self-assemblies and photo-controllable systems. The self-assembly section introduces the basics of all self-assemblies used in this work ranging from supramolecular complexation and liquid crystallinity to block copolymer and colloidal self-assemblies. The section on photo-controllable materials concentrates on azobenzene molecules, their isomerization mechanism
and applying them to control self-assemblies. The literature review is followed by the results section, which gives an overview of the main results of the publications, and the compiling part ends this thesis with brief conclusions, view of scientific significance and outlook based on the results.

Figure 1.1 shows how the different publications are connected to the different levels of self-assembling structures and how they divide into creating photo-responsive and photonic structures. **Publication I** investigates the thermal isomerization of an interesting subgroup of azobenzenes—hydroxyazobenzenes—and their isomerization behavior in hydrogen-bonded polymeric complexes forming lamellar self-assemblies. Their applicability to form gas sensors based on thermal isomerization kinetics is studied in **Publication II**. In **Publication III**, halogen-bonded photo-responsive supramolecular liquid crystals are studied, and here, the discussion concentrates on the results of the photochemical studies of the manuscript. **Publication IV** demonstrates the use of block copolymer micelles to create 3D photonic colloidal crystals. The related discussion concentrates on the strict requirements for the assembling micelles as well as the formation and photonic properties of the formed colloidal crystals.

**Figure 1.1.** Schematic presentation on how the publications use self-assemblies at different length scales. Publications I-III utilize azobenzene molecules combined with supramolecular self-assemblies to create photo-responsive functional materials and Publication IV creates tunable photonic crystal through self-assembly of block copolymer micelles, which assemble through colloidal crystallization.
Introduction
2. **Self-assembly**

### 2.1 **Self-assembly as a tool for functional nanomaterials**

In material science, nanomaterials raise significant interest owing to the deviation from bulk properties of the macroscopic materials when the particle or domain size is reduced to nanometers. This deviation occurs, for example, through increased interface-to-volume ratio and emerging quantum mechanical effects. A drastic and well-known example is the plasmonic resonances of metal nanoparticles, which gives rise to their size-dependent absorption of light. Controlling and preparing nanomaterials with one or more dimensions in the range 1–100 nm requires non-traditional approaches, i.e., the normal top-down manufacturing becomes tedious. For static materials, the current lithographic methods such as photolithography or even electron/ion beam lithography allow high precision for example for electronic circuit manufacturing. However, such methods are not viable for creating materials with larger area or quantities, and there other approaches are needed.

The alternative approach to creating and controlling nanostructures is to take advantage of molecular and nanoscale interactions, like molecular recognition through hydrogen bonding or electrostatic interactions. This is the bottom-up approach through self-assembly of small building blocks. By definition, self-assembly is the spontaneous, autonomous and reversible organization of molecular units into ordered structures through non-covalent interactions. Self-assemblies have been widely studied for example for liquid crystal assemblies, soft lithography, fabrication of biomaterials, biomedical applications, and photonic crystals.

Self-assemblies are governed by thermodynamics, and thermodynamics indicate that systems evolve towards their minimum free-energy state. Therefore, self-assembly is based on the minimization of Gibbs free-energy, \( G \),

\[
G = H - TS, \tag{2.1}
\]
where $T$ is temperature, $H$ enthalpy and $S$ entropy. Strictly speaking, the minimization of Gibbs free energy is applicable only to an isothermal and isobaric process, which is the most common case in self-assembling systems. Following the definition of Gibbs free energy, the creation of order can occur either through a decrease of enthalpy or by the maximization of entropy. The changes in enthalpy arise from the strengthening of interactions between the self-assembling parts, whereas entropy is related to the number of possible micro-states of the system. An example of entropy driven self-assembly is the parallel packing of hard-rods predicted by Onsager.\textsuperscript{18} In this ideal system, only excluded volume effects are considered and above a limiting concentration, all the rods orient parallel to each other. In such oriented structure, the increase in translational entropy related to the movement of the rods overcomes the loss of entropy arising from the orientation of the rods. In practice, both enthalpy and entropy are changing. An illustrative example is the micelle formation of amphiphilic surfactants consisting of hydrophilic and hydrophobic parts. The entropy of the surfactant molecules decreases in the packing of the molecules during the micellization process. Still, owing to the enthalpy change, the free energy of the system is decreased upon enclosing the hydrophobic alkyl tails of the surfactant molecules inside the micelles.\textsuperscript{19} The enthalpy decrease comprises that of the surfactant and water molecules. Also the entropy of water molecules plays a role, and enthalpic and entropic contributions of water create the hydrophobic effect driving the micellization.\textsuperscript{20,21} Overall, creating self-assembling structures is balancing between the two components.

Self-assembly can be utilized at multiple length scales starting from the molecular level.\textsuperscript{14,21} At the molecular level, self-assembly is the arrangement of molecules into defined structures. It can be driven by inter- or intramolecular non-covalent interactions. For example, intermolecular complexes driven by hydrogen, halogen and ionic bonding can form. Usually, such supramolecular complexes form between molecules with complementary functionalities, but the same moiety can also have both bond-donating and bond-accepting functionalities. The next level of self-assembly is the arrangement of molecules or supramolecular complexes. A good example of this is liquid crystallinity, where molecules are collectively arranged on a macroscopic level with long range orientational order.\textsuperscript{22} Another level to self-assembly is brought by the polymeric materials, especially block copolymers.\textsuperscript{23,24} Through the different properties of the polymer blocks, the block copolymers can assemble into a variety of structures either in bulk or solution. The size range is usually tens of nanometers and in solution block copolymer self-assemblies create colloidal particles. Beyond this, colloids can be self-assembled into larger complexes via colloidal self-assembly.

Self-assemblies are possible in systems where the constituting particles are mobile, i.e., have enough energy to overcome local energy barriers. Without movement, the system is kinetically trapped in local energy minima and will never reach the thermodynamic equilibrium. The challenge of creating complex
self-assemblies is that the order is encoded in the molecular constituents as geometric structures and supramolecular interactions. To be robust, the interactions should be strong, but reaching the global energy minimum requires dynamic nature of the components. Therefore, in practice, the self-assemblies are often guided by gradual changes in environmental conditions towards the global thermodynamic minimum. In solution, this can occur via gradual solvent exchange, decrease in ionic strength or simply by lowering the temperature. Still, encoding such interactions over multiple length scales requires specific knowledge of the interactions at all the different length scales.

As non-covalent, supramolecular, systems the self-assemblies of soft matter are often dynamic and offer a good basis for responsive material systems. Through a change in the environmental conditions or through a structural change within the material, the system can exhibit a strong non-linear response, like a phase transition, leading to a responsive material. A simple example are liquid crystals, where the order is destroyed through the increase in temperature and reformed again upon cooling. Also functional molecular moieties are embedded into the assemblies to achieve responses to external stimuli, and anisotropic components are utilized to allow a larger range of structures.

Overall, with the current understanding, a large range of self-assemblies can be created and ever-more complex self-assembling systems are demonstrated. However, a constant challenge is the dispersity of the assembling structures and the eventual defects from the size dispersity. A good example is self-assembly of block copolymers, where a number of polymer chains aggregate together to form micelles. It is difficult to create low polydispersity micelles as during the formation of the micelles, the difference between having slightly different amount of polymer chains is energetically small. The same concerns, for example, defects or domain boundaries in self-assembled materials. These effects can be detrimental in some applications.

2.2 Supramolecular complexation

Supramolecular complexation is the formation of an intermolecular complex through molecular-level reversible non-covalent interactions. Such interactions include van der Waals forces, hydrogen bonding (HB), halogen bonding (XB), and ionic bonds. Biological systems are an excellent example of the possibilities of supramolecular complexation. In biological systems, supramolecular complexation governs for example the base-pairing of DNA, the specificity of enzymatic reactions and much more. As a non-specific interaction, van der Waals interactions are not favored in self-assembling systems, but all the others have their own benefits. These and the polymer complexes formed thereof are more explicitly described in the following sections. Also other types of complexes like metal coordination complexes and inclusion complexes of cyclic molecules such as cucurbituril or cyclodextrin exist. In the inclusion complexes non-
specific interactions such as van der Waals interactions in combination with the
geometric fit and hydrophobic effects arising from the interactions and entropy
of water molecules form stable supramolecular complexes.29,30

2.2.1 Hydrogen bonding

Hydrogen bond (HB) is an attractive electrostatic interaction between the posi-
tive partial charge of a hydrogen atom covalently bonded into an electronegative
atom and a lone electron pair or another heteroatom with negative charge
(Figure 2.1a).25,31 The hydrogen atom with the partial positive charge acts as
hydrogen bond donor, that is, donates positive charge and a lone electron pair of
an electronegative atom acts as the hydrogen bond acceptor. Hydrogen bond is
directional and relatively strong. In crystals, the hydrogen bond enthalpies span
from 0.2 to 40 kcal/mol depending on the hydrogen bond forming species.32 Even
though hydrogen bonding is considered relatively strong, in comparison to the
average thermal energy of a molecule, 0.89 kcal/mol, the interaction strength
is often of similar magnitude. This indicates that the formation of a hydrogen
bond is reversible and the bonding is dynamic.

In supramolecular complexes used in self-assembly, the bonding is controlled
by choosing the correct hydrogen bond donors and acceptors for the molecular
entities. This way the desired bonding can be achieved. An example of a
complexation formed by a single hydrogen bond is the hydrogen bonding formed
by a pyridine and a phenol (Figure 2.1b). Such hydrogen bond is strong due
to the delocalization of electrons from the oxygen in the phenol-group by the
benzene ring, leading to the strong positive charge of the hydrogen of the phenol,
and on the other hand, the electronegativity of the nitrogen in the pyridine
group, which attracts the electrons from the aromatic ring.32 Especially with
single hydrogen bonding moieties, other hydrogen bond forming molecules, like
water, compete with the desired hydrogen bonding.

Figure 2.1. a) Schematic presentation of hydrogen bonding. b) Examples of hydrogen-bond-
forming complexes: (1) water–water, (2) phenol–pyridine, (3) adenine–thymine and
(4) ureidopyrimidinone–ureidopyrimidinone.
Hydrogen-bonded complex can be formed by a single hydrogen bond as with phenol and pyridine, but also through multiple simultaneous hydrogen bonds. As an example, the DNA base pair of adenine and thymine complex forms through two hydrogen bonds (Figure 2.1b). Also three and four hydrogen bonds are possible, and they further increase the energy of the complexation. For example, hydrogen bonding of ureidopyrimidinones has been used to create supramolecular polymers where the polymer chains are held together by hydrogen bonds instead of the normal covalent bonding.33,34

2.2.2 Halogen bonding

Halogen bonding, often abbreviated as XB, is a non-covalent interaction which was defined in 2013 by IUPAC.35

A halogen bond occurs when there is evidence of a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity.

Early reports of interactions that could be characterized as halogen bonding date back to the beginning of the 19th century. They were described in more detail in the 1970s through X-ray crystallography,36 but the interest re-emerged in the 1990s with the development of supramolecular chemistry. In supramolecular chemistry, halogen bond has been among the least exploited non-covalent interactions, but recently there has been tremendous interest.37–40 As an example, it has been shown to be ubiquitous in biological systems,41,42 where its significance has been recognized only recently.

As stated by the definition, the formation of a halogen bond occurs between a halogen atom (XB donor) and a nucleophilic region (XB acceptor), generally a lone electron pair (Figure 2.2a). The electron distribution of a halogen atom (X) covalently bound to an electron-rich molecular entity is anisotropic. The anisotropy relates to the depletion of the outer lobe of the p-orbital of the halogen atom involved in the covalent bonding. This leads to a so called σ-hole as introduced by Politzer et.al.43 The σ-hole has positive electrostatic potential, which creates an attractive interaction with nucleophilic entities. As examples (Figure 2.2b), halogenated perfluoroalkanes, molecular halogens and halobenzenes function as XB donors, and on the other hand, chloride ion, ammonia and pyridine function as XB acceptors. The σ-hole formation occurs with all halogen atoms, but the heavier halogens (I, Br) form stronger halogen bonds.

The strength of halogen bonding depends strongly on the forming moieties, and the interaction energies range from 2.4 kcal/mol up to 36 kcal/mol.44 As an example, the positive region of iodobenzene is stronger than bromobenzene (Figure 2.2d-e), which leads to stronger halogen bonding. The positive charge is further increased by introducing electrophilic atoms/groups (F) to the benzene...
The high directionality is one of the most useful properties of halogen bonding. The bond angles are very often close to 180°, with respect to the covalent R-X bond. This is extremely useful for rational material design. The directionality arises from the focused electrophilic region surrounded by the negatively charged ring in the halogen atom. The XB is more directional than the HB, where the more hemispherical nature of the positive charge decreases the directionality. As an interaction between an electrophilic and a nucleophilic region, halogen bonding is very similar to hydrogen bonding. As shown in Figure 2.2, for example the nucleophilic region in pyridine can function as both XB and HB acceptor. In some cases, this causes a competition between the two interactions, and in such cases, it is the relative strength and environmental interactions that determine, which interaction dominates. As an example, the polarity of the solvent can switch the dominating interaction in crystallization of mixtures of 1,4-diodotetrafluorobenzene and hydroquinones with 1,2-bis(4-pyridyl)ethane. In this case, XB is dominating in polar solvents because of the more hydrophobic nature, whereas HB is dominating in more non-polar solvents. Besides competing, halogen bonding has been shown to coexist with hydrogen bonding. In such cases, the halogen atom acts as a hydrogen bond acceptor. The electrophilic and nucleophilic regions in the halogen atom are close to orthogonal, which leads to halogen and hydrogen bonding to coexist as orthogonal.
2.2.3 Ionic complexes

Besides hydrogen and halogen bonding, ionic complexes can be utilized in various self-assembling structures.\(^{47,48}\) The ionic complexes are based on the electrostatic interaction of cationic and anionic molecules or larger building blocks (tectonic units). These building blocks can be for example polyelectrolytes, charged surfactants, multivalent counter-ions or inorganic clusters, and charged mesogenic structures like disks or rods. Such building blocks are readily available without extensive chemical synthesis, and the variability of the components allows a large range of structures to be created. As charged compounds, the building blocks have a hydrophilic nature, and therefore, the complexation occurs often in water solutions or dispersions. The complexation occurs often upon plain mixing and can result in 1:1 complexes owing to the charge neutralization taking place in complexation.

Coulombic forces are long-ranging when compared with other supramolecular interactions. The drawback is that the charge–charge interactions are also non-selective. However, non-selective assemblies are utilized widely, and in these, the electrostatic interactions function mainly to glue the oppositely charged structures. In more sophisticated self-assemblies the electrostatic interactions are combined with secondary supramolecular interactions, which guide the assemblies through inducing cooperative effects. In bulk structures, these ionic complexes can form nanostructures for example through microphase separation of hydrophobic alkyl tails.

2.2.4 Polymeric complexes

Supramolecular complexation can be also applied to polymers\(^9,49–51\) as long as the needed functional groups can be embedded into the polymer chain. As an example, the lone electron pair of the pyridine in poly(4-vinyl pyridine) (P4VP) acts as good hydrogen bond acceptor. This has been widely utilized for complexation through carboxylic acid groups and phenols.\(^{52–54}\) The pyridine group functions also as halogen bond acceptor, and therefore, P4VP has been utilized with different halogen bonding moieties.\(^{55}\)

Supramolecular complexation of small molecules with polymeric matrices functions as a facile toolbox for modification of the polymer. The modification is often done through simply dissolving both components in the same solvent, mixing desired ratios and removing the solvent. Ionically bonded systems often precipitate upon mixing due to charge neutralization even as 1:1 molar complexes. From the assembly point-of-view, the complexing of the small molecules to the polymer backbone can lead to elongation of the polymer due to high packing frustrations.\(^{53}\) This creates supramolecular polymer brushes. On the other hand, if the small molecule has a tendency to arrange or phase separate for example due to mesogenic moiety or long alkyl chain, microstructure and order formation can occur. This tendency to form order is utilized in creating
supramolecular liquid crystalline polymers. Supramolecular liquid crystals have been extensively studied for example by Kato et al.\(^{50,51}\)

To create functional materials and take advantage of the polymeric complexes, active small molecules, especially photoactive molecules, have been complexed into the material.\(^{56,57}\) In these complexes, the supramolecular hydrogen and halogen bonded complexes have been shown to allow efficient photopatterning.\(^{55,58–60}\)

### 2.3 Liquid crystallinity

Liquid crystalline (LC) phase is a peculiar form of matter which flows like a liquid but still exhibits order alike crystalline material.\(^{22}\) Liquid-crystalline states are characterized by a long-range orientational order and possibly a partial positional order. Liquid crystals are widely applied in different technological applications owing mostly to the optical properties arising from the orientational order combined with the controllability with electric fields. For a few decades since the 1990s, liquid crystal displays (LCDs) have dominated the display technologies, and only the recent emergence of alternative OLED-based technologies are challenging the status of LCDs. Owing to this and other fields of applications, the fundamental properties of LCs have been extensively studied.\(^{22,61}\)

Liquid crystalline states are self-assembled states of material, and as such, governed by the molecular constituting units. Fundamentally, there are two main classes of liquid crystals: *thermotropic* and *lyotropic*. The first class, thermotropic LCs have a stable mesophase, that is, LC phase in a certain temperature range. Thermotropic LCs are formed purely from the mesogenic molecules without the presence of solvent, and the mesogenic molecules are usually either rod-like (calamitic) or planar (discotic). Lyotropic LCs, on the other hand, form when the constituting units are dissolved or dispersed in a solvent at high concentrations. The lyotropic LCs have a stable mesophase in a certain concentration range. The units can be amphiphilic molecules, rigid polymers, or high aspect ratio rods, like cellulose nanocrystals. In this work, thermotropic liquid crystals are used.

The different liquid crystalline phases are classified based on their molecular order. The common liquid crystalline phases are: smectic, nematic, and columnar (Figure 2.3). Rod-like molecules form smectic and nematic LC phases. Often these molecules form of rigid aromatic center and an alkyl chain at either one or both ends. 4-Cyano-4’-pentylbiphenyl (5CB) is an example of such a molecule. In the nematic phase, the molecules have only an orientational order, whereas in smectic phases the molecules have also positional order. Due to having higher order, smectic phases occur below the temperature range of the nematic phase. The phases are commonly characterized by the polarized optical microscopy (POM), where some of the different LC phases can be recognized from the Schlieren textures. Examples of the nematic and smectic phases are
Figure 2.3. Schematic presentation of liquid crystalline phases: a) nematic, b) smectic, c) cholesteric (chiral nematic), d) discotic and e) blue phases. Polarized optical micrographs of f) nematic phase and g) smectic phase.

shown in Figure 2.3. The detailed characterization is often done with X-ray diffraction. Columnar phases are formed by planar, disk- or bowl-like, molecules which stack into cylinders. These LC phases have subphases, and as an example smectic phases are divided based on the order (tilting and possible packing) of the molecules within the layers and columnar phases based on the arrangement of the cylinders.

Liquid crystal phases, which have a chiral twist, can also have photonic properties. These are the cholesteric (chiral nematic) (Figure 2.3c) and blue phases (Figure 2.3e). In cholesteric phases, the orientation of the molecules rotates gradually with a pitch often in the scale of visible light. The rotation can be either left or right handed depending on the chiral dopant inducing the twist. Due to the rotation, cholesteric phases can reflect the corresponding circularly polarized light. The reflected wavelength varies with the pitch. Blue phases can occur between the chiral nematic and isotropic phases. In blue phases, the molecules have a double chiral twist and the molecules align to cylinder-like arrangements, which pack in various ways to form the subclasses. The blue phases are observed rarely and have narrow temperature ranges except in polymer stabilized systems. The chiral phases are of interest especially because the optical response can be tuned with various stimuli and function even as sensors.

An interesting group of LCs are supramolecular liquid crystals. They are formed of non-mesogenic molecules, which are capable of forming supramolecular complexes. A well-established example is the LC formation through hy-
drogen bonding between aromatic carboxyl acids. Various supramolecular LCs including low-molecular-weight rod-like and disk-like, polymers with side-chain, main-chain and host-guest structures have been reported.\textsuperscript{50} In combination with phase segregation, the formed supramolecular liquid crystals introduce additional functionalities for sensing, transportation of electrons and ions, and templating.\textsuperscript{68,69}

### 2.4 Block copolymer self-assembly

Block copolymers (BCP), which comprise two or more covalently linked polymer segments offer a versatile platform for self-assembled structures.\textsuperscript{24,70,71} Because of differences in interaction energies and solubilities, the blocks tend to microphase separate, thus forming different mesophases. These structures are formed both in bulk and solution. In bulk, the variability in the chemical nature of the monomers, lengths of the polymer blocks, microstructures of the polymers \textit{etc.} allow to rationally design the self-assembling structures. In solution, also interfacial energies and solvent interactions affect the structures. The structures in solution are formed through selective aggregation of specific blocks, whereas in bulk, the self-assemblies are driven mostly by enthalpic microphase separation. In bulk, the self-assembling principles of diblock copolymers are rather well-known, and they traditionally form spherical, cylindrical, gyroid (bicontinuous) and lamellar structures. Introducing a third block increases the number of possible structures,\textsuperscript{72} and introducing functional monomers or supramolecular complexation\textsuperscript{73} of functional units, can allow to further control the self-assemblies. The challenges in bulk self-assemblies are often related to the slow kinetics of the polymer chains, or local free-energy minima during the assemblies, which lead to defects and variations in the structures.

**Figure 2.4.** Schematic presentation of A-b-B block copolymer self-assembly in solution through selective aggregation of both blocks. Small fraction of the aggregated block leads to spherical micelles, and the increase in the fraction leads sequentially to cylinders and polymersomes.
In solution, block copolymer micelles are prepared by controlled aggregation of a specific block from a dissolved state of the block copolymer (Figure 2.4). In practice, this is usually done by solvent-exchange from a cosolvent of two different blocks to a selective solvent to the corona block. With diblock copolymers, the formed structures are governed mostly by the relative fractions of the two blocks, $f_{AB}$, but also by interfacial energies and solvent interactions. Usually, a short aggregating block leads to micellar structures (Figure 2.4), and progressively increasing $f_{AB}$ leads first to cylindrical micelles and then to lamellar structures (vesicles/polymersomes). In the BCP micellar particles, the corona usually remains soluble, which provides a stabilizing layer for the particles. Increasing the complexity of the starting polymer allows to also form more complex structures, like micelles with structured cores.\textsuperscript{74}

A rapid formation of the micelles leads often to disperse particle sizes because of the kinetic entrapment of the polymers in non-equilibrium states. Therefore, slow solvent exchange, for example through dialysis, is often preferred. In structures with increasing complexity, reaching the global thermodynamic minimum is increasingly challenging. The works by Gröschel \textit{et al.} demonstrate that guiding the self-assemblies by step-wise preparation process through dynamic intermediate assemblies can lead to highly monodisperse and rationally controlled structures.\textsuperscript{74–76} In practice, the assembly of intermediates is achieved through a sequential solvent exchange of increasingly selective solvents. This gives an important route for improving the monodispersity of the particles.

After the BCP self-assembly process, the selective chemical modification of the blocks is a route to fix the structures by covalent cross-linking or to introduce a further functionality to the polymer assembly. As an example, bulk self-assemblies have been cross-linked to allow redispersing to create janus particles\textsuperscript{73} or lamellar bulk self-assemblies of PS-$b$-P4VP have been quaternized in the works led by E. L. Thomas \textit{et al.} to create solvent swollen photonic structures. Also other photonic structures have been created from block copolymers in the bulk phases.\textsuperscript{53,80–83} In creating photonic structures from block copolymers, methods to increase the elongation of the polymer chains are widely utilized either through solvent swelling or using polymer brushes.

For the purpose of describing the micelles used in Publication IV, the structure of spherical micelles with a polyelectrolyte corona is covered briefly through a simple mathematical model. The structure and formation of especially spherical BCP micelles have been investigated thoroughly,\textsuperscript{70,84,85} and also more extensive models exist.

In the simplified model for a micelle consisting of a solid core with radius $R_{\text{core}}$ and a charged polyelectrolyte corona in a salt-free solution, the density of the polymer in the corona, $\rho_{\text{corona}}(r)$, can be assumed to scale as $\rho \sim (r/R_{\text{core}})^{-2}$.\textsuperscript{70} This assumes uniform stretching of the polymer chains, which can imply also straight chains. For the polyelectrolyte micelles, the density of the corona decreases faster than in non-charged micelles, which implies longer extension of the corona. In the model, the total mass of the corona is required to follow the
**Figure 2.5.** An example of the density profile of a polyelectrolyte micelle. The used values are similar to the micelles (SV1) in Publication IV. The radius of the core is 10 nm and the radius of the micelle is 80 nm, i.e., \( r/R_{\text{core}} = 8 \).

The mass ratio of the different blocks in the polymer \( f = m_{\text{core}}/m_{\text{corona}} \). The mass of the micelle core is given by \( m_{\text{core}} = \frac{4}{3} \rho_{\text{core}} \pi R_{\text{core}}^3 \), where the radius of the core can be approximated for example from transmission electron microscope images. The mass of the corona is calculated as follows:

\[
m_{\text{corona}} = 4\pi \int_{R_{\text{core}}}^{R_{\text{micelle}}} \rho_{\text{corona}}(r)r^2 dr,
\]

where \( R_{\text{micelle}} \) has to be approximated from experimental results. Considering the scaling relation of the corona, this simplifies to:

\[
m_{\text{corona}} = 4\pi \rho_{\text{int}} R_{\text{core}}^2 (R_{\text{micelle}} - R_{\text{core}}),
\]

where \( \rho_{\text{int}} \) is the density of the polymer at the core-corona interface. The fraction at the interface is given by

\[
\rho_{\text{int}} = \frac{R_{\text{core}} \rho_{\text{core}}}{3f(R_{\text{micelle}} - R_{\text{core}})}.
\]

Overall, the density profile of the micelles is then described by

\[
\rho(r) = \begin{cases} 
\rho_{\text{core}} & \text{if } r < R_{\text{core}} \\
\rho_{\text{int}} \left( \frac{r}{R_{\text{core}}} \right)^{-2} & \text{if } R_{\text{core}} < r < R_{\text{micelle}} \\
0 & \text{if } r > R_{\text{micelle}}.
\end{cases}
\]

16
The model illustrates that for a highly charged polyelectrolyte micelle in salt-free water-solution, the corona is highly extended and the polymer density at the periphery of the corona is extremely low. Figure 2.5 shows an example of such a profile approximated for the micelles used in Publication IV. The core diameter is 10 nm and the approximated micelle radius is 80 nm. With these micelles, the proportionality of the corona density to \((r/R_{\text{core}})^{-2}\) indicates that the density of the corona drops to below 10%, with respect to the density at the interface, at somewhat over 30 nm. This implies that further away from the core, the corona is mostly water.

### 2.5 Colloidal self-assembly

By definition colloids are mixtures, where particles with a diameter in the range of 1-1000 nm are dispersed in a continuous phase. An example of a colloid would be the above described block copolymer micelles dispersed into a continuous liquid phase. Colloidal self-assemblies,\(^{86-88}\) i.e., assemblies of colloidal particles into ordered structures, are again a step into larger scale self-assemblies compared to molecular complexes or BCP self-assemblies. As they can have dimensions in the range of half of the wavelength of visible light, colloidal self-assemblies are often utilized in creating photonic structures.\(^{17,89}\)

The main types of colloidal self-assemblies (Figure 2.6) are the crystallization and order formation through: (1) attractive interactions, (2) entropic (no interactions) and (3) repulsion. Via the strict control of attractive interactions for example spherical\(^{90}\) and rod-like\(^{91}\) biological virus-particles have been self-assembled with gold nanoparticles. Colloidal crystals formed through attractive interactions can form despite changes in particle concentrations. On the other hand, the second-class of crystallization, occurs only above a certain concentration threshold, i.e. it is a lyotropic crystallization. These hard colloids in charge screened conditions have been used as a model system for example for studying crystal nucleation and glass transition.\(^{92,93}\) For hard colloids, there are no attractive or repulsive interactions in addition to volume exclusion, and therefore, the crystallization occurs through entropy. The crystallization occurs only above volume fraction of \(\varphi > 0.545\) and is limited by the glass transition occurring at \(\varphi = 0.58\). The crystalline phase has a face-centered-cubic (FCC) lattice, which is also observed in the natural opals (see Figure 2.7). The system also separates to form crystalline and amorphous areas depending on the volume fractions. The third type of crystallization is most commonly observed with charged colloids in salt-free water dispersions when the Debye screening length is large and the electrostatic interaction effective at long separation.\(^{94,95}\) The radius of the particles plus the effective length scale of the repulsive interaction define an effective volume fraction, and when the effective volume fraction is high enough, crystallization can be observed. Depending on the effective volume fraction and interaction potential, the particles have been shown to have FCC
lattices, but also body-centered-cubic lattices.\textsuperscript{94} Importantly, both type 2 and 3 crystallizations occur only at high concentrations, and therefore, break upon dilution, and mechanically solid crystals cannot be achieved.

Considering attractive and repulsive colloidal crystallizations, there the self-assembly is mostly governed by the inter-particle interactions of the colloids.\textsuperscript{96} For colloids, van der Waals and electrostatic interactions are the dominating ones. Especially for the electrostatic interactions, the solvent has a dominating role and the self-assemblies can be controlled by adjusting the properties of the solvent. In case of charged colloids in water, either having charged groups on the surface or having a polyelectrolyte corona, the electrostatic interactions between the colloids dominate the behavior as a long range interaction. The effective length scale of electrostatic interactions is highly dependent on the salinity of the solution. A characteristic length scale of the interaction is given by the Debye screening length

\[ \kappa^{-1} = \sqrt{\frac{\epsilon_r \epsilon_0 k_B T}{2 N_A e^2 I_s}}, \]  

where \( \epsilon_r \) and \( \epsilon_0 \) are the relative permittivity and that of vacuum, \( k_B \) is the Boltzmann constant, \( T \) temperature, \( N_A \) Avogadro’s constant, \( e \) elementary charge and \( I \) is the ionic strength of the solution. The ionic strength is given by

\[ I_s = \frac{1}{2} \sum_{i=1}^{n} c_i z_i^2, \]

where \( c_i \) and \( z_i \) are the concentration and valence of the ion \( i \). Beyond this length scale, the Coulombic interactions are screened by the ions present in the solution.

An obvious requirement for the crystallization of colloids is having monodisperse particles, and if two or more particles are used that the particle sizes are compatible with the intended crystal phase. With polydisperse particles, the crystallization is prevented and a random packing/aggregation is formed, except for special cases.\textsuperscript{97} The incompatible particles will lead to defects in the lattices. Many different routes have been developed for creating monodisperse organic and inorganic spheres and polymeric hydrogels.\textsuperscript{17} Block copolymer micelles have
been also shown to form lyotropic crystalline assemblies with lattice spacings of tens of nanometers.\textsuperscript{98}

As self-assembled structures, most colloidal crystals are fragile, which is why different post-modifications have been introduced. The crystal structures can be fixed for example by mineralization of silica,\textsuperscript{99} or through formation of a covalently linked gel. In these cases, the colloidal crystal can functions as a sacrificial template, which can be removed for example by a dissolution step. The resulting structure is called an inverse opal. Generally, the robustness of the structures achieved through post-modifications brings further options for the use of colloidal self-assemblies.

When colloidal crystals have dimensions in the range of 200-1000 nm, the colloidal crystals can function as photonic crystals. In these structures, the periodicity of refractive index creates photonic band gaps, which reflect visible light. Structural colors exhibited by such photonic structures are observed widely in natural material.\textsuperscript{100,101} Opals (Figure 2.7a) are an example of such a structure formed in nature, which has been widely replicated synthetically. Natural opals are crystals of spherical silica particles with a face-centered-cubic (FCC) lattice (Figure 2.7b) formed through colloidal crystallization. Various approaches to create photonic structures have been devised using colloidal crystals.\textsuperscript{17,89,102} Also responsive photonic crystals have been developed.\textsuperscript{8}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{opals.png}
\caption{a) Natural opals as an example of colloidal crystallization leading to photonic structures. b) The face-centered cubic lattice of opals.}
\end{figure}
Self-assembly
3. Introduction to azobenzene-containing materials

3.1 Photochromic molecules

Light is ubiquitous, and many processes around us rely on reactions of molecules to light. As an example, our vision is based on the reaction of opsin molecules to light, which triggers isomerization of the molecule leading to a complex cascade of reactions resulting in the visual impulse in our eyes. Such molecules, which exhibit a reversible transformation upon light irradiation, are called photochromic molecules. The most often used photochromic molecules include azobenzenes, stilbenes, diarylethenes and spiropyrans (Figure 3.1), but also many others exist.\textsuperscript{103} The photochromic reactions can arise from \textit{trans-cis} isomerization of a double bond, like in azobenzenes and stilbenes (see Figure 3.1), and also in the opsin molecules, but also from ring-opening/closing reactions as in diarylethenes and spiropyrans. Overall, photochromic molecules have been used to demonstrate a wide range of light-responsive materials.\textsuperscript{103–106} The different photochromic molecules each have their advantages and disadvantages, making them suitable for different applications.

Azobenzene and stilbene are both mesogenic, rod-like, molecules, which exhibit a large shape-change upon isomerization.\textsuperscript{107} The \textit{trans}-isomers can be isomerized with UV light and also the reverse \textit{cis-trans} isomerization can be induced with light. However, it occurs also thermally, i.e., the \textit{cis}-isomer is metastable. Stilbene has more stable \textit{cis}-isomer and previously, stilbene has been a popular model to study the isomerization process.\textsuperscript{103} However, it has a significant drawback: the isomerization yields also in cyclization, which after oxidation is non-reversible.\textsuperscript{103} Azobenzene derivatives do not have this problem, and the isomerization process is fully reversible, which is why azobenzene molecules have overwhelmed stilbene derivatives in devising light-responsive materials.

Azobenzenes have been long used in photoalignment,\textsuperscript{108,109} light-driven surface patterning,\textsuperscript{110} non-linear optics,\textsuperscript{57,105} and in combination with liquid crystals to create for example tunable photonic materials\textsuperscript{10,64,111,112} or with liquid crystal elastomers to create photo-mechanical materials.\textsuperscript{113–115} In addition to
these, azobenzenes have been used to modify biological systems\textsuperscript{\textcopyright{116}} and develop optochemical genetics.\textsuperscript{\textcopyright{117}} The wide applicability has lead to development of azobenzene synthesis to allow a large range of tunability by different substituting groups.\textsuperscript{\textcopyright{118,119}} Azobenzenes are the molecules of choice in this thesis and they are covered in detail in the next sections.

Diarylethenes and spiropyrans are based on ring-opening/closing (Figure 3.1), and the reactions are fully reversible. The significant advantage of diarylethenes is that the photocyclization process can be thermally stable.\textsuperscript{\textcopyright{106,120,121}} As also the other molecules, diarylethenes and their photo-response and absorption spectra can be highly tuned with covalent substitutions. However, the use of diarylethenes in responsive materials with other than optical response (based on absorption change) is limited by the small geometric shape change. Still, the developed applications take advantage of this change, and actually owing to the small geometric change, they are shown to function in fully crystalline actuators.\textsuperscript{\textcopyright{122,123}} Spiropyrans, on the other hand, are not thermally stable, but exhibit strong spectral and geometric changes. The charge induced in the ring-opening affects significantly the behavior of the formed merocyanine. In responsive materials, spiropyrans are multi-responsive, and in addition to light, they can respond to temperature, metal ions, redox potential and mechanical stress.\textsuperscript{\textcopyright{124,125}}

### 3.2 Photoisomerization of azobenzene

Azobenzenes, one of the most employed photochromic molecules and the ones used in this thesis, consist of two phenyl rings connected by an azo linkage (–N=N–). They exhibit efficient trans-cis and cis-trans photoisomerization
Figure 3.2. a) Isomerization and geometry change of azobenzene molecules. b) Simplified picture of the isomerization process. c) Example spectra of azobenzene showing the $\pi - \pi^*$ and $n - \pi^*$ absorption peaks. Absorption spectra are from Publication III. Adapted with permission from Publication III. Copyright ©2016 American Chemical Society.

(Figure 3.2a), but the cis–trans isomerization occurs also thermally. The photoisomerization occurs by photoexcitation of the ground state to higher energy level $S_1$ or $S_2$ states (Figure 3.2b). The $n - \pi^*$ and $\pi - \pi^*$ transitions excite the molecules to $S_1$ and $S_2$ states, respectively. The excited states relax to a common energy state with around 90° dihedral angle of the C-N=N-C moiety, which is followed by the isomerization process with specific quantum yields to cis– and trans-isomers. The trans–cis quantum yields for example in hexane are 0.11 and 0.25 for the excitations through $\pi - \pi^*$ and $n - \pi^*$ transitions. It is also important to note that the absorption is anisotropic and only light polarized along the molecular axis leads to absorption and therefore isomerization. Overall, the photoisomerization process is complex and there are multiple overlapping mechanisms. For a more detailed description, the reader is guided to the good review by Bandara et al.

The absorption spectra of the isomers have characteristic features arising from the different absorption bands (Figure 3.2). The usual absorption spectra of a trans-isomer is dominated by a peak arising from the $\pi - \pi^*$ transition, which for non-substituted azobenzene is around 320 nm. Figure 3.2c uses the spectra from molecules in Publication III (see Figure 4.6 on page 39) as an example, and in these molecules, the peak is shifted to 360 nm. Additionally the $n - \pi^*$ peak can be visible at higher wavelengths, but for trans-isomers this is significantly weaker than the $\pi - \pi^*$ absorption. For the cis-isomer, the $\pi - \pi^*$ transition is weaker and at lower wavelengths (for non-substituted AB at 250–270 nm), but the $n - \pi^*$ transitions are stronger and located at around 450 nm. These lead to the characteristic changes (Figure 3.2c) upon illumination.

The rate equation for the change of cis-isomer content, $c_{cis}$, in the isomerization process

$$\text{trans} \xrightarrow{hv} \text{cis}, \quad (3.1)$$
can be written as

\[
\frac{dc_{\text{cis}}}{dt} = 1000 I_0 \frac{1 - 10^{-A'}}{A'} \left( c_{\text{trans}}' \phi_{\text{trans}}' c_{\text{trans}} - c_{\text{cis}}' \phi_{\text{cis}}' c_{\text{cis}} \right) - k c_{\text{cis}},
\]

(3.2)

where the primed values denote that they are for the illumination wavelength. \(^{126}\) 

\(I_0\) denotes illumination intensity, \(A\) absorbance, \(\epsilon\) corresponding molar absorptivities, \(\phi\) corresponding quantum yields, and \(k\) is thermal isomerization rate constant. As an equilibrium between the two isomers, the total concentration is constant, \(c_{\text{tot}} = c_{\text{trans}} + c_{\text{cis}}\). Without further analysis of the equation it is clear that an equilibrium, a photostationary state (PSS), is reached and this depends on molar absorption coefficients, quantum yields, illumination wavelength, illumination intensity and thermal isomerization coefficient. The spectra of the cis-isomer cannot be directly measured, but the wavelength dependence of the PSS states in the absence of thermal isomerization can be used to determine the absorption spectra of the cis-isomer with the so called Fischer’s method. \(^{127}\) The spectra can be further used to determine the cis- and trans-fractions in the sample. The use of the absorption spectra to determine the fractions is described in more detail in Section 4.2.3, where also the presence of thermal isomerization is considered.

The trans- and cis-isomers have distinctively different geometric, electronic and optical properties, which are utilized to create the functionalities in photo-responsive materials. The trans-isomer has a planar rod-like geometry, whereas the cis-isomer adopts a kinked shape with a tilt in the angles of the phenyl rings (Figure 3.2a). As an example, the rod-like mesogenic trans-isomer is compatible with calamitic LCs, whereas the cis-isomer creates packing frustrations in the LC phases. For unsubstituted azobenzene, the kinked shape leads also to a dipole moment of 3.1 D in the cis-isomer, whereas the dipole moment of the trans-isomer is 0 D leading to changed solubility and interfacial properties.

A useful aspect of azobenzene molecules is their variability through different chemical substitutions of the aromatic rings. Traditionally, the molecules have been categorized into three classes: 1) azobenzene, 2) aminoazobenzene and 3) pseudostilbene-type molecules. \(^{128}\) The categorization is based on the relative energies of \(\pi - \pi^*\) and \(n - \pi^*\) transitions, and owing to the substitutions, the molecules have differences in the intrinsic isomerization mechanisms and thermal isomerization rate. In azobenzene type, regardless of the substitution, such as alkyl chains, the behavior is similar to non-substituted azobenzene with separated transitions. Aminoazobenzene type molecules have electron donating amino or hydroxy substitutions, which shift the \(\pi - \pi^*\) transition to higher wavelength causing a partial overlap with \(n - \pi^*\) transition. Pseudostilbene-type molecules are push-pull azobenzenes having electron withdrawing and electron donating groups, and in these the transitions overlap. Because of the overlap, selective isomerization is not possible.

The recent synthesis developments have been aimed at more stable cis-isomer and to for example allow visible light activated molecules. \(^{129–131}\) The group of Andrew Woolley has developed significant advances especially in the devel-
opment of visible light activated azobenzenes. For the visible light actuation, the normally overlapping $n - \pi^*$ transitions have been separated by inducing distortions to the trans-isomer or influencing the energy levels of the molecular orbitals by for example ortho-substitutions. The separation allows to selectively address the trans-isomers also with visible light through the $n - \pi^*$ transition. Also combined ortho-fluorination and –amination have been shown to yield in visible light switchable azobenzenes. The visible light activation is especially important for biological applications.

Also in improving the stability of the cis-isomer, ortho-fluorination has proven to be successful. The ortho-tetrafluorooazobenzenes developed in the works led by David Bléger and Stefan Hecht have received considerable interest recently. In ortho-fluorinated azobenzene, the $\sigma$-electron withdrawing property of the fluorines has been attributed to the increased stability of the cis-isomer. The cis-lifetime of ortho-fluorinated azobenzene is ca. 700 days, which is significantly longer than for non-substituted azobenzene and the isomer can in most applications be considered as stable.

### 3.3 Thermal isomerization

An important property of azobenzenes is that the cis-isomer is generally not stable. The metastability of the cis-isomer shows as the spontaneous thermal cis-trans-isomerization process. As a spontaneous process reversing the effect induced by illumination, it is essential to consider the effects of thermal isomerization for the applications, especially ones based on the presence of cis-isomer.

![Thermal isomerization mechanisms of azobenzenes: inversion and rotation.](image)

Mechanistically, there are two classically considered mechanisms for thermal isomerization: rotation and inversion (Figure 3.3). The different mechanisms and their relative contributions have been long under investigation, and they vary depending on the molecular substitution. In non-substituted azobenzene,
the inversion is the dominating thermal isomerization mechanism, and it has thermal cis-lifetime in the range of tens of hours. In aminoazobenzenes, the electron donating substituents somewhat lower the energy barrier for thermal isomerization, leading to shorter lifetimes, but in addition, in this class the solvent polarity, substituent position and inter- and intramolecular hydrogen bonds can have a strong effect. Depending on the conditions, either rotation or inversion dominates. In push-pull azobenzenes the rotational mechanism is considered to dominate and they show extremely short lifetimes in the range from milliseconds to seconds. Also push-pull azobenzenes can show large effects with varying solvent polarity. Hydroxyazobenzenes, included in the aminoazobenzene class, are somewhat a special group of azobenzenes. In these, the azo-hydrazone tautomerization occurring upon formation of inter- or intramolecular hydrogen bonds has a significant role.\textsuperscript{135–137} Hydroxyazobenzenes are used in Publications I and II (Section 4.1) and are covered in more detail in that discussion.

The thermal isomerization is a spontaneous process, and usually follows first-order kinetics, which means that all cis-isomers in the sample have a similar probability to isomerize to trans-isomers. Mathematically, the first-order kinetics of thermal isomerization for cis-isomer concentration, \( c_{\text{cis}} \), are described as

\[
c_{\text{cis}}(t) = c_{\text{cis},0} \cdot e^{-kt}, \tag{3.3}
\]

where \( c_{\text{cis},0} \) is the concentration of cis-isomers at \( t = 0 \), \( t \) is time, and \( k \) is the thermal isomerization constant. The first-order kinetics are generally observed in non-glassy systems where the azobenzenes do not show any cooperative effects. It has been shown that in glassy states, the isomerization deviates from the first-order kinetics. In these cases, double or triple exponential or Kohlrausch-Williams-Watts functions have been used. The KWW-function, also known as stretched exponential function, is defined as follows:

\[
c_{\text{cis}}(t) = c_{\text{cis},0} \cdot e^{-(kt)^\beta}, \tag{3.4}
\]

where \( \beta \) is the stretching exponent. The function is equal to first-order kinetics when \( \beta = 1 \). With double or triple exponential functions, the difficulty is to find a physical meaning for the relaxation times. Therefore, instead of assuming a limited number of relaxation times, KWW-function assumes a continuous distribution of the relaxation times. The KWW-function has been experimentally determined, but it has been shown to describe for example relaxations in glassy materials\textsuperscript{138} and decays of luminescence in time-resolved experiments.\textsuperscript{139} Also cooperative effects have been shown to lead to non-first-order kinetics. In nanofibers of oligomers with azobenzene molecules in the backbones, it has been shown that the isomerization speed can depend on the cis-isomer fraction.\textsuperscript{140}

### 3.4 Photocontrol of self-assemblies

Light offers an excellent trigger for creating responsive materials. It can be accurately controlled both spatially and temporally. The additional properties such
Introduction to azobenzene-containing materials

The isomerization of the photochromic molecules, especially azobenzenes, have been widely used to control both self-assembling and other systems. Even though the selection of potential applications is large, the applications of azobenzene in responsive systems can be roughly divided into two different categories (Figure 3.4) based on what creates the photoresponse: (i) presence of the cis-isomer and (ii) cyclic isomerization.

In the first category, the response is given by the presence of the cis-isomer due to its molecular properties differing from the trans-isomer (Figure 3.4a). The response is reversed by cis–trans-isomerization either by light or thermally. The molecular differences as such are generally not enough to create other than optical responses (change in absorption), and therefore, the response often requires amplification. For this reason, phase transitions or supramolecular complexing induced by the presence of the cis-isomer are used to magnify the responses. As was mentioned in section 2.1, self-assembling structures are often dynamic and sensitive to small changes, which makes them optimal for amplification of the responses with phase transitions for example. A good...
example is the applications where azobenzene molecules are used to induce isothermal order-disorder transitions in liquid crystals. These transitions exploit the incompatibility between the geometric shape of the cis-isomer and liquid crystal phases. Also solubility changes arising from changes in intermolecular bonding and increased dipole moment have been demonstrated. For example, particles can be aggregated with these changes, but also swelling/contraction of hydrogels and interfacial properties of azo-surfactants can be affected. Due to the induced phase transitions, the responses of this category are mainly on-off-type.

In the second category, the response arising from the illumination does not require the presence of the cis-isomer. These applications include for example photoalignment and photopatterning. In these applications the response is created by the isomerization when it is repeated enough due to light intensity gradients or polarization effects. Push-pull azobenzenes, such as Disperse Red 1, are often utilized in these applications. As an example, in photoalignment the azobenzene-containing material is illuminated with a polarized light. Due to the polarization dependence of the molecular absorptivities, the molecules oriented along the polarization axis are excited whereas the molecules orthogonal to the polarization are not excited. As the excitation and isomerization lead to reorganization of the molecules, the molecules are effectively aligned orthogonal to the polarization. Besides orienting the molecules, when the azobenzene moieties are part of a self-assembled structures, the whole structure can be oriented. For example, block copolymer structures have been oriented on a larger scale using photoalignment.

### 3.5 Selected applications

The following discussion gives a few examples of applications where azobenzene and photochromic molecules have been used. The range of applications is wide and only a few interesting approaches demonstrating the range of applications are described.

A topic that has raised strong interest recently is photoactuation based on liquid crystalline elastomers (LCEs), which can exhibit an order-disorder transition upon exposure to light. The photo-response in the liquid crystal elastomers is achieved by embedding azobenzene molecules into a matrix of liquid crystalline monomers, which are then polymerized in the liquid crystalline state. Upon exposure by UV, the kinked shape of the created cis-isomers creates an isothermal order-disorder transition. The order-disorder transition of the oriented liquid crystal then induces mechanical deformation in the material. The material contracts along the orientation of the rod-like liquid crystal molecules and expands in the other two directions. The same effect can be created also photothermally in LCE films. The approach can be widely tuned by altering the orientation and anisotropy of the LCE films. LCEs have been applied to create...
for example surfaces with altering surface topographies upon exposure with light, an artificial flytrap and a self-regulating iris. The relaxation of the response occurs generally on the same timescale as thermal isomerization, making it a crucial factor for the applicability of the azobenzene moieties for these films. In the LCE films, it has been shown that a fluorinated azobenzene can be used to create shape persistent polymer networks. Another invention has been to use azobenzene-containing surface function-alizations in gold nanoparticles. The gold nanoparticles are dispersed in a hydrophobic solvent (toluene) and upon illumination with light the created more hydrophilic cis-isomers trigger aggregation of the nanoparticles. The same approach has been widened to create self-erasing inks, promote chemical reactions by creating reversible nanoflasks, and even turned around so that non-photoresponsive nanoparticles can be aggregated with light. Overall, the illumination changes the solution behavior of the particles, either by altering the particles or the solvent properties. Here again, a transition in solubility is used to amplify the polarity change of the azobenzene molecules. The transition is again directly linked to the cis-isomer fraction and the transition is reversed upon thermal isomerization.

Another class of applications brought up here are the sensor applications, giving background for the results of Publication II. As said earlier, in many of the applications, as in all of the above mentioned, the response of the isomerization is amplified by using phase transitions leading to an on-off-type response. For a sensor, the optimal response is linear, and phase transitions are not useful as such. For other photochromic molecules, examples of quantitative sensors exist. For example, time response of diarylethene reactions have been used for amine detection. However, sensor applications other than sensing light based on isomerization of azobenzene are limited. For azobenzenes, light-activated selective complexing, like entrapment of specific ions, has been demonstrated and also used for sensing, but isomerization kinetics have not been used for sensing.
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4. Results

4.1 Thermal isomerization of hydroxyazobenzenes – structural effects and sensing

An essential feature, and in some cases, the biggest drawback of azobenzenes is their thermal cis-trans isomerization. For many applications, the lifetime of tens of hours, i.e., lifetime of non-substituted azobenzenes, is enough, as on short time scales, the system is practically stable. However, there are plenty of applications, which require either longer or shorter lifetimes. Overall, understanding the mechanisms affecting thermal isomerization are important. Publication I aims at giving insight in the effect of molecular order on thermal isomerization in case of hydroxyazobenzenes. Similar hydroxyazobenzene-polymer complexes and their thermal isomerization are then exploited as a novel platform for gas sensing in Publication II.

4.1.1 Structural effects on the lifetime of cis-isomer in supramolecular complexes (Publication I)

Supramolecular polymer-hydroxyazobenzene complexes (Figure 4.1) were prepared by mixing from poly(4-vinyl pyridine) (P4VP, $M_w = 50$ kDa/mol) and 4-[(4-ethylphenyl)-azo]phenol (2PAP) or 4-[(4-octylphenyl)azo]phenol (8PAP). The complexes were prepared at different molar ratios of PAP molecules and P4VP monomeric units. Here, azo/pyridine molar ratios are denoted as nominal complexation degrees, $x$. The structural properties of similar P4VP-nPAP complexes at $x = 1$ have been studied before.\textsuperscript{56} There the alkyl chain length was determined to dictate the structure formation and properties of the observed lamellar packing. The complexes are formed through hydrogen bonding, which can be confirmed by studying Fourier transform infrared (FTIR) spectra of the complexes (Figure 4.1b). In the spectra the peak at 993 cm$^{-1}$ corresponding to the non-bound pyridine groups decreases and the corresponding peak of the hydrogen-bonded pyridine group at 1008 cm$^{-1}$ increases. In the samples, the
Results

peak at 1008 cm\(^{-1}\) is partially overlapped by a peak from the nPAP molecules.

**Figure 4.1.** a) Complexes of the 2PAP and 8PAP molecules, b) their infrared spectra and c) small-angle X-ray scattering data. d) Schematic representation of the disordered structure at low-concentrations and the lamellar and bottle-brush structures and their POM images at higher concentration for 8PAP and 2PAP, respectively. Adapted with permission from Publication I. Copyright ©2016 American Chemical Society.

Structural analysis by small-angle X-ray scattering (SAXS) shows a distinct difference between the two complexes (Figure 4.1c) arising from the different alkyl chain lengths. Upon increase of the complexation degree, \(x\), the 2PAP complexes remain amorphous, even though at \(x > 0.25\) the structures start showing a broad correlation peak at \(q = 0.23\) Å\(^{-1}\) indicating a characteristic length scale with dimension of 2.3 nm in the material. The hydrogen bonding shown by FTIR, and therefore, supramolecular grafting, indicates a bottle-brush type of structure at high concentrations. Such structures have been demonstrated previously with other hydrogen-bonded P4VP complexes.\(^{154}\) On the other hand, the 8PAP complexes show clear formation of a smectic-type liquid crystalline phase at high \(x\). For \(x = 1.0\), SAXS data shows a narrow reflection at \(q^* = 0.165\) Å\(^{-1}\) and its small second-order reflection \(2q^*\) indicating a lamellar order with a periodicity of 3.8 nm. The lamellar, smectic-like, order is seen also in the polarized optical microscope (POM) image, which shows a birefringent LC-type of texture. All 2PAP complexes, and the low-concentration 8PAP complexes lack the birefringence indicating an amorphous structure. The difference between the two molecules arises from the longer hydrophobic alkyl chain of the 8PAP molecule, which increases the tendency for the alkyl chains to pack tightly side-by-side, and therefore, form an LC structure. In the absence of the polymer, 8PAP molecules do not show such a liquid crystalline phase.
Results

From the material perspective, the two complexes behave similarly except for the structural difference. The glass transition temperature ($T_g$) is expected to affect the isomerization and were therefore characterized (Figure 4.2a). The $T_g$’s, describing the temperature at which the polymer chains are able to relax within the experimental time-frame, were characterized with differential scanning calorimetry (DSC). In the non-relaxed states below the glass transition temperature, also the thermal relaxation of the azobenzenes is likely hindered. The complexes show similar $T_g$’s (4.2a) and besides the structural differences are therefore considered to be comparable.

![Diagram showing $T_g$ and $k$ vs. degree of complexation](image)

**Figure 4.2.** a) Glass transition temperature and b) the thermal isomerization rate coefficient as a function of nominal complexation degree. Adapted with permission from Publication I. Copyright ©2016 American Chemical Society.

Upon UV-illumination, all the show photostationary states with high cis-fractions as indicated by the strong decrease in the absorbance of the trans-isomer peak around 360 nm. With increasing the complexation degree, absorption maximum of the trans-isomer shows a blue-shift from 362 nm to 354 nm, indicative of stronger chromophore-chromophore interactions. The increased interactions arising from the tight packing induced by the separation of the alkyl chains and formation of lamellar order are expected to play a role in the isomerization behavior.

Thermal isomerization between the different complexes shows notable differences (Figure 4.2b). The thermal relaxation curves were fitted with a stretched exponential function, also known as Kohlraus-Williams-Watts-function, which is known to explain e.g. glassy relaxations. For the 2PAP complexes the isomerization coefficient, $k$ (see Equation 3.4 for definition), increases from $3.1 \times 10^{-5}$ s$^{-1}$ ($x=0.01$) to $3.4 \times 10^{-3}$ s$^{-1}$ ($x=1.00$). However, even though being similar from material perspective, the behavior of the 8PAP complexes differs from that of the 2PAP samples. At low complexation degree the samples behave similarly, and 8PAP complex ($x=0.01$) shows isomerization coefficient of $2.1 \times 10^{-5}$ s$^{-1}$. At low concentrations the nPAP molecules are as individual molecules in the polymer matrix and no differences are expected, and therefore the similarity confirms
that the molecules are comparable. At higher molar ratios \( x \geq 0.25 \), on the other hand, the 8PAP complexes show shorter lifetimes, i.e., higher thermal isomerization coefficients. At \( x = 1.00 \), the 8PAP complexes show isomerization coefficient of 0.12 s\(^{-1}\), which is 5700 times higher than at \( x = 0.01 \). Even though large differences in the thermal isomerization coefficients have been reported for hydroxyazobenzenes, such a difference has not been reported before in the solid state, especially considering that the polymer matrix remains constant.

The 2PAP and 8PAP molecules start deviating from each other at \( x = 0.25 \), which is the same concentration at which SAXS starts showing indications of structure formation. For hydroxyazobenzenes, the hydrogen-bond-assisted tautomerization is known to create significant differences in the lifetimes.\(^{107,137}\) They have been studied especially in works led by Dolores Velasco.\(^{136,156,157}\)

In the current materials, when measured under nitrogen atmosphere, the only hydrogen-bond donors in the complexes are the phenol-groups of the nPAP molecules. Therefore, all the effects from the tautomerization must occur due to cooperative effects between the nPAP molecules. The differences at the high complexation degree unequivocally show that the smectic-like assembly promotes cooperative effects between the 8PAP molecules most likely due to the stringent proximity of the molecules arising from the supramolecular self-assembly. This increases the tautomerization by promoting the chromophore–chromophore hydrogen bonding.

The results demonstrate the importance of considering the subtle effects of the microenvironments induced by structural self-assemblies on the thermal isomerization kinetics. The effects are significant in the case of 4-hydroxyazobenzenes, but similar effects are expected with other azobenzene molecules showing solvent polarity dependences (aminoazobenzenes and push-pull azobenzenes).\(^{107,158}\) The effects on thermal lifetime are important in most self-assembled systems, where there are cooperative effects between the molecules. The other aspect of the results is that we have demonstrated a system where we can modularly tune the lifetime of the cis-isomer with the chromophore concentration. Such modular tunability can be exploited for example in the sensing application depicted in the following section.

### 4.1.2 Gas sensing through thermal isomerization (Publication II)

Even though azobenzenes have been used in a wide range of applications, sensing is one of the fields where the isomerization of azobenzenes has been used less. Light-activated reactions have been demonstrated, but the direct use of isomerization kinetics for sensing has not been reported. As mentioned in Sections 3.4 and 3.5, to magnify the response from the molecular change, azobenzene molecules are used to induce phase transitions, and for sensing, such approach is not viable. Sensing requires a continuously changing parameter that can be easily measured, and for azobenzenes the isomerization process is the simplest of such a response. For a non-substituted azobenzene, environmental changes
do not induce significant changes. However, hydroxyazobenzenes can show up to five orders of magnitude difference in the thermal isomerization speed in different solvents.\textsuperscript{107} This environmental dependence can be used for sensing, and here it is demonstrated for sensing relative humidity and ethanol vapors.

In this work, the amorphous complexes of poly(4-vinyl pyridine) and 4-(4-ethylphenyl)azo]phenol, used also in Publication I, are used to demonstrate a robust platform for vapor sensing (Figure 4.3). The only difference is the small molecular weight of the polymer ($M_w = 1.1$ kDa). Having small, oligomeric P4VP chains still lowers the glass transition temperature of complexes and the materials are non-glassy also at dry conditions. The active layer of the gas sensor is the thin (ca. 1 µm) film of the complexes spin coated onto glass or quartz substrates. The film is of good optical quality owing to the supramolecular complexes formed through the hydrogen-bonding between P4VP and 2PAP, and furthermore, the films have a high azobenzene content of up to 80 w-%. This allows to use thin films and have easily measurable absorbance values. The films have a normal absorption spectrum of azobenzenes, with the $\pi-\pi^*$ absorption peak at ca. 362 nm. The films were illuminated with 365 nm UV-LED equipped with a 10 nm band-pass filter, and as it overlaps with the absorbance peak it isomerizes the molecules efficiently. The spectral changes are reproducible at constant environmental conditions (Figure 4.3e). The samples do not show photoaligning, which upon illumination with non-polarized light would be seen as a decrease in the absorption upon continued illumination.

Relative humidity, $RH$, is by definition the ratio of water vapor pressure, $p_{H_2O}$ in the air with saturation vapor pressure of water, $p_{sat}$:

$$RH = \frac{p_{H_2O}}{p_{sat}(T)}$$

An important aspect with $RH$ is that the saturation pressure varies as a function of temperature, and therefore, they are usually measured simultaneously. Relative humidity is measured most commonly with capacitive-type sensors. In the sensor, water is adsorbed from the environment to a hydrophilic layer in the sensor, where it induces a capacitance change, which is measured electronically. The major advantage is that the capacitance change is not strongly dependent on temperature. A large range of different sensors with electric and optical signals have been built,\textsuperscript{159–161} and most sensors rely on the same principle that adsorbed water vapor induces a change in the material. Water vapor adsorption is used also in this work to induce a change. The complexes used are slightly hydrophilic mostly owing to molecular groups being able to function as hydrogen bond acceptors. Based on water vapor adsorption measurements, the material adsorbs approximately 3.0 w-% of water at 90% RH (Figure 4.3f).

In the studied complexes, the dependence of the thermal isomerization on $RH$ is significant and the time constants show an exponential, $\propto e^{k_{RH}RH}$, dependence on RH (Figure 4.4a-b). From 0 to 100% RH the change in the used P4VP-2PAP 1:1 complexes can be extrapolated to be three orders of magnitude.
With this sample, the isomerization constant changes from 0.01 to 3.73 s\(^{-1}\) when going from 2.6% RH to 82.7% RH. The extrapolated values mean that the lifetimes change from hundreds of seconds to even below one second.

As thermal isomerization is a spontaneously occurring process it shows also a temperature dependence, which can be described simply by the Arrhenius-equation

\[ k = k_0 \cdot e^{-E_a/(R \cdot T)}, \]  

where \(k_0\) is reaction-related constant, \(E_a\) is the (apparent) activation energy, \(T\) is temperature and \(R\) is the gas constant. \(E_a\) is described as apparent activation energy as for a complex reaction it does not necessarily describe the real activation energy of the reaction. Arrhenius equation leads to a straight line on a logarithmic plot when x-axis is plotted as 1/T (Figure 4.4c). For the nominally equimolar P4VP-2PAP complex \(E_a\) is 146 ± 7 kJ/mol.

Strangely, the dependence of the thermal isomerization constant on \(RH\) and temperature are decoupled and change independent of each other. This is seen as the same coefficients \(\lambda_{RH}\) (parallel lines in Figure 4.4b). Therefore, based on the experimental data, the time constant can be described as

\[ k(T, RH) = k_0 e^{-E_a/(R \cdot T)} \cdot e^{\lambda_{RH} \cdot RH}. \]
In the description, it is good to note the definition of relative humidity (Equation 4.1), which states that relative humidity with a constant water vapor pressure is also a function of temperature.

The mechanism for the $RH$ dependence is the hydrogen-bond-assisted tautomerization of the hydroxyazobenzenes. As was shown in Figure 4.3f, the adsorbed water vapor content increases with $RH$, which is consistent with the decrease of the lifetime when the number of water molecules, and thus the hydrogen-bonding-induced tautomerization increases. Overall, the tautomerization leads to an intrinsic change in the isomerization pathway by easing the rotational pathway for cis-trans isomerization. Unfortunately, the exact dependence for the link between the adsorbed water content and isomerization coefficient is not known. Also the mechanism and understanding the decoupling of the Arrhenius-behavior and $RH$ dependence require further studies.

The thermal isomerization is shown to work as a sensor (Figure 4.5). The lifetime changes continuously and swiftly upon an $RH$ transient and when the temperature of the measurement is known, the data shown in Figure 4.4 can be used to translate the lifetimes into $RH$ values (Figure 4.5b). By altering the azobenzene molecules, it was also shown that the response can be tuned, and a change of almost 5 orders of magnitude were observed for P4VP-2PAP 9:1, i.e., in a sample with less chromophores. Considering the results from Publication I, it is not surprising that the response is larger with a lower concentration sample. In these samples, the speed-up of the isomerization due to chromophore-chromophore hydrogen bonding is negligible and the adsorbed
water molecules have a larger effect. The significance of tautomerization was also demonstrated by showing that the dependence disappears by changing the 4-hydroxy functionalization to a 4-methoxy group. Similar, strong response is shown to be achieved also with ethanol vapors (Figure 4.5d).

Figure 4.5. a) Response of the absorbance change upon cycled UV-illumination upon an RH transient from humid to dry condition and back. b) The extracted isomerization rate coefficients. c) Demonstration of the tunability of the system by using different complexes. d) The response of P4VP-2PAP 1:1 complex to ethanol vapors. Adapted with permission from Publication II. Copyright ©2018 American Chemical Society.

The demonstrated RH dependence allows especially high changes in the signal, high reproducibility and tunability, and the approach can be used as a robust platform for vapor sensing. The significant advantages are that the sensor can be miniaturized to function in an optical fiber, it measures an intrinsic parameter (not dependent on geometry) and can be further developed to function with multiple wavelengths. The development of the approach needs to still address the temperature dependence and lifetime of the azobenzene layer. For the temperature dependence, combining multiple chromophores in a same sample, should allow to distinguish both RH and temperature with a single sensor.

To conclude, the developed sensor is a new approach to utilize the isomerization of azobenzenes and is expected to open new avenues also for creating combinations for light-responsive and environment-responsive systems. Such highly responsive systems that couple multiple responses are a prerequisite for creating more complex dynamic materials.
4.2 Supramolecular liquid crystals and photoinduced phase transitions (Publication III)

Publication III studies a new family of light-responsive halogen-bonded supramolecular liquid crystals. Here the discussion is divided between the formation of the liquid crystalline phases, their photochemical response and the detailed analysis of the cis-fraction needed for the full LC-to-isotropic transition.

4.2.1 Halogen bonded supramolecular liquid crystals

An important area of the contemporary nanosciences is to create order and complexity through self-assembly of simple building blocks. From this viewpoint, supramolecular LCs are pertinent as they offer possibilities to develop and increase the tunability and modularity of conventional LC systems. They can also easily bring forth and allow embedding new functionalities not possible in single-component LCs. In supramolecular LCs, specific and directional non-covalent interactions are used to combine two non-mesogenic molecules. As was introduced in Section 2.2.2, halogen bonding (XB) is highly directional, which makes it an excellent interaction to drive the formation of LCs.

The studied LCs are formed by dimeric complexes of stilbazoles and alkoxy-azobenzenes containing an iodo-tetrafluoroarene ring (Figure 4.6). In total, 15 complexes with varying alkyl chain lengths were prepared. The complexes are denoted as $1-n \cdot 2-m$, where $n$ and $m$ are the alkyl chain lengths. The fluorine atoms have many functions in the complexes. They increase significantly the strength of the halogen bonding (see section 2.2.2 and Figure 2.2), but also affect the photochemical behavior by stabilizing the cis-isomer and inducing arene-perfluoroarene quadrupolar interactions between the complexes. Fluorination has been also shown to be effective in tailoring the anisotropy of the LCs. In the complexes, the halogen bond is formed between iodine and pyridine functionalities. Crystallographic data from single crystals confirms this halogen bonding and also its directionality in these complexes. The characterized three complexes $1-8 \cdot 2-2$, $1-10 \cdot 2-1$ and $1-12 \cdot 2-1$ have $C-I \cdot \cdots N$ bond angles of 178.6°, 174.3° and 174.5°, respectively. In the complexes, based on the bond lengths of around 2.77-2.82 Å, the strength of the halogen bond was approximated to be 6.5 kcal/mol. Comparing to the average thermal kinetic energy of a molecule at

![Figure 4.6. Halogen-bonded complexes of stilbazoles and azobenzenes. Adapted with permission from Publication III. Copyright ©2018 American Chemical Society.](image-url)
room temperature, 0.89 kcal/mol, the interaction is significantly stronger and sufficiently strong to allow the formation of mesogenic, calamitic complex.

**Figure 4.7.** The liquid crystalline phase transition temperatures of the halogen bonded LCs. *Adapted with permission from Publication III. Copyright ©2018 American Chemical Society.*

Liquid crystal phases were analyzed with differential scanning calorimetry and polarized optical microscope equipped with a heating stage. The phase transition temperatures are depicted in Figure 4.7. All of the complexes showed enantiotropic LC phases except for 1-12•2-12, which was monotropic. The sample has the longest alkyl chains in both ends and the monotropic phases could be expected because of the long alkyl chain lengths. The samples with long alkyl chains show smectic A and nematic phases and the others only nematic. The crystal-to-smectic/nematic transition occurs between 80-100°C. In many of the complexes the nematic phase extends over a broad range, up to 30°C. From the comparison, destabilization of the nematic phase can be observed as the nematic-isotropic transition temperature decreases upon increase of the alkyl chain lengths. The behavior of the LC phases in the complexes is similar to that of other stilbazole complexes.\(^{163}\)

The systematic formation of LC phases with broad nematic phases in this new group of supramolecular LCs strengthens the status of halogen bonding as an optimal interaction for supramolecular LCs. However, in the complexes the LC phase temperature range could be lower. Using mixtures of complexes naturally lowers the tendency to crystallize, and the melting point was shown to be lowered by 10°C in the used example. Still, further lowering the LC temperature range to room temperature, while maintaining the photo-responsive property of azobenzenes, is a target for future work. The modularity of the supramolecular
approach is optimal for this kind of tuning.

4.2.2 Order-disorder transitions in supramolecular halogen bonded liquid crystals

Azobenzene molecules render the complexes photo-responsive allowing to control the order by creating photo-induced order-disorder transitions. Such transitions are the basis of many applications of photoresponsive LCs, and are utilized for example in photo-responsive LCEs. Detailed studies on the transition have been conducted in azobenzene-doped LCs.\textsuperscript{10,164–166} Unfortunately, rather often the detailed characterization of the conditions leading to the order-disorder transition are skipped. In supramolecular LCs, the studies have concentrated on the overall response. Here, we studied the transition in more detail and also characterized the \textit{cis}-fraction needed for the full LC-to-isotropic transition for the first time in supramolecular LCs. The \textit{cis}-fraction characterization is described in the next section.

The light-induced LC-isotropic transition is characterized with POM, birefringence measurement and extinction measurements at 400 nm and 700 nm (Figure 4.8e). The extinction measurement at 700 nm shows the scattering upon transition. The transition is exemplified by the complex 1-10\textbullet2-8, measured at 110°C in a planar 2 µm LC cell. In the isothermal order-disorder transition upon illumination with UV-light (395 nm) the order rapidly disappears, showing as loss of birefringence. The loss of birefringence is seen in the light intensity measured through crossed polarizers at ±45° and also in POM. Continued UV-illumination is seen as a decrease in extinction at 400 nm arising from isomerization of the azobenzene. Upon ceasing the illumination, the extinction shows the thermal isomerization continuing until a low enough \textit{cis}-fraction is achieved. Only then

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4_8.png}
\caption{a-d) POM images of the photoinduced nematic-to-isotropic phase transition and e) extinction, absorption and birefringence measurements of a transition at similar conditions. Adapted with permission from Publication III. Copyright ©2016 American Chemical Society.}
\end{figure}
the reverse isotropic-to-LC transition occurs. The absorbance value, i.e. *cis*-fraction at the transition was shown to be constant regardless of the illumination time or wavelength, which pinpoints that the *cis*-fraction limits the transition. This simultaneously indicates the importance of thermal isomerization speed in the complexes as without visible light illumination, it dictates the reverse transition. Considering the measurement conditions, the fluorination in the used azobenzene molecules leads to a rather long half-life of *ca.* 51 s. At room temperature a lifetime of *ca.* 12 days was measured in dilute DMF solution at room temperature.

An interesting observation was that the isotropic-to-nematic transition shows an intermediate phase separation into isotropic and nematic domains. The separation is better visible in the slower reverse transition, but the scattering peak observed also in nematic-to-isotropic transition hints that the separation occurs in both cases. Similar photochemical phase separation has been observed previously in azobenzene-doped LCs.\textsuperscript{167,168} The separation is expected to lead to trans-rich LC and *cis*-rich isotropic phases. This also suggests that the *cis*-fraction in the pure LC phase is even lower than the limiting absorbance value suggests. This is supported by the resemblance of the time dependence of birefringence increase to that of thermal isomerization, as in the beginning of the transition, birefringence mostly depicts the area of the LC domains. Overall, the phase separation process seems to give the limit to reaching full nematic-to-isotropic transition. The result suggests also that preventing the phase separation would possibly allow to induce order-disorder transitions at even lower *cis*-fractions. Overall, the relevance of the phase separation process warrants further studies as it is relevant for optimizing the photo-responsive LCs for applications.

The rich variety of the photoinduced processes observed in the azobenzene-containing materials was further demonstrated by the complexes showing a crystal-to-isotropic phase transition. This phase transition occurred at illumination power of 40 mW/cm\textsuperscript{2} at 85°C, so 10°C below the melting point and 30°C below the clearing point. The high intensity was needed to induce the transition, but the liquid phase was confirmed to cease at very low light intensities, which only maintain the *cis*-isomer fraction in the samples, confirming the relevance of the *cis*-fraction also in this case. Such photo-liquification has been also previously reported\textsuperscript{169,170} and studied for applications such as control of porosity in crystalline materials.\textsuperscript{171}

### 4.2.3 *Cis*-fraction and order-disorder transition

To understand a photoinduced order-disorder transition, it is essential to know how the isomerization relates to the phase transition. Unfortunately, this is rather often discarded due to not always being straightforward. It is complicated by the anisotropic nature of the liquid crystals, which makes analyzing the absorption spectra of the azobenzene in the LCs rather difficult. To simplify the
Results

approach, instead of studying the cis-fractions in the LC phase, the isotropic-to-nematic transition is studied. For this, first the spectra of the cis-isomer is needed. In the measurement temperatures, also the thermal isomerization needs to be considered. With the known absorption spectra, the absorbance values at the transition allow to calculate the cis-fraction when the LC phase emerges. As was explained above, in this case, the complete order-disorder transition is limited by the phase separation rather than the direct cis-fraction in the LC phase.

Considering an isotropic sample containing azobenzene, the system is always either in the fully-relaxed state, i.e., trans-state, or a mixture of the two isomers. A complete transition to cis-state is practically impossible, and therefore, the spectra of the cis-isomer cannot be directly measured. By assuming the absorbance of the cis-isomer to be zero at a specific wavelength range, a lower limit estimate can be given even without information of the cis-spectra. A solution for this problem was developed by Fischer et al., and the methodology for applying to samples with significant thermal isomerization by Rau et al. The following gives a shortened explanation of the method as applied to trans-cis isomerization.

First, the photostationary state spectra in the absence of thermal isomerization is determined. In the photostationary state, the absorption spectra is constant, that is, there is no change in cis-isomer concentration. Starting from equation 3.2 on page 24 and by assuming that the total concentration of the isomers is constant and that absorbance is given by the sum of the two isomer, i.e., $A = \epsilon_{\text{trans}}c_{\text{trans}} + \epsilon_{\text{cis}}c_{\text{cis}}$ the following equation can be derived

$$\frac{1}{A_{\text{PSS}} - A_{\text{trans}}} = \frac{\epsilon_{\text{trans}}\phi_{\text{trans}} + \epsilon_{\text{cis}}\phi_{\text{cis}}}{(\epsilon_{\text{cis}} - \epsilon_{\text{trans}})A'_{\text{trans}}\phi'_{\text{trans}}}$$

$$+ \frac{k}{1000(\epsilon_{\text{cis}} - \epsilon_{\text{trans}})A'_{\text{trans}}\phi'_{\text{trans}}} \left(\frac{A'_{\text{PSS}}}{1 - 10^{-A'_{\text{PSS}}}}\right) \frac{1}{I_0}.$$  \hspace{1cm} (4.4)

In the equation $A_{\text{PSS}}$ refers to the absorbance at the photostationary state and $A_{\text{trans}}$ to the absorbance of all trans-state. $\epsilon$ denotes the molar absorptivities, $\phi$ quantum yields and $k$ thermal isomerization coefficient and $I_0$ the illumination intensity. For the derivation, refer to the paper by Rau et al. It is important to note that the first part of the right-hand side is not dependent on $k$, and either if $k$ approaches 0 or $I_0$ approaches infinity, the second part vanishes. Based on the equation, plotting $(A_{\text{PSS}} - A_{\text{trans}})^{-1}$ as a function of $X = A'_{\text{PSS}}/ \left[1000(1 - 10^{-A'_{\text{PSS}}}) \cdot I_0^{-1}\right]$ leads to a straight line (Figure 4.9). The intercept of this line with y-axis corresponds to the photostationary state at infinite illumination intensity or better said, in the absence of thermal isomerization. The PSS states determined by extrapolation to infinite intensity can then be used for the Fischer’s method. The resulting data for the complex 1-10•2-8 as measured at 120°C is shown in Figure 4.9. For this temperature above the clearing point of the LCs we can directly measure also the all-trans absorption spectra.
Secondly, the absorption spectra of the cis-isomer is determined by Fischer’s method. The analysis starts from the assumption that the ratio of the isomer concentrations is determined by the ratios of quantum yields and molar absorptivities at a specific illumination wavelength:

\[
\left(\frac{[\text{trans}]}{[\text{cis}]\lambda}\right) = \left(\frac{\phi_{\text{cis}}}{\phi_{\text{trans}}\lambda}\right) \left(\frac{\epsilon_{\text{cis}}}{\epsilon_{\text{trans}}\lambda}\right) = \left(\frac{\phi_{\text{cis}}}{\phi_{\text{trans}}\lambda}\right) \left(\frac{A_{\text{cis}}}{A_{\text{trans}}\lambda}\right)
\] (4.5)

Then considering two of such PSSs at two arbitrary wavelengths, again assuming that only two isomers are present and by assuming that the ratio of the quantum yields is constant, it is possible to calculate the cis-isomer spectra. For the derivation, the reader is guided to the paper by Fischer or to the book by Sekkat. For the complex 1-10•2-8, the calculated spectrum is shown in Figure 4.10. Note that the wavelength range is limited to 400 nm because of the high absorbance below that even in the 2 µm cell.

Lastly, we need to consider the behavior of the sample in the measurement temperature. Because the sample is in an LC state, the measurement of the absorption of the trans-isomer is not possible. We experienced slight changes in absorption upon change of temperature, mostly due to the changes in the LC cell, and therefore, determine the trans-absorption separately by exponential fitting to the thermal relaxation data. An example is shown in Figure 4.10b.
As the absorption spectra is given by the absorbance of the two isomers, the \( f_{\text{cis}} \)-fraction, at the phase transition \( (T = 210\, \text{s}) \) is determined from

\[
A = f_{\text{cis}}A_{\text{cis}} + (1 - f_{\text{cis}})A_{\text{trans}}
\]  

(4.6)

The analysis for the sample 1-10•2-8 reveals that the \( f_{\text{cis}} \)-fraction from the azobenzene isomers is \( 7.6 \pm 0.4\% \) at \( 110^\circ\text{C} \). From the small value, we can conclude that the kinked shape of the \( f_{\text{cis}} \)-isomer also disrupts the LC phase effectively as it does in azobenzene-doped LCs. Considering the 1:1 ratio of the complexes, the overall fraction of the \( f_{\text{cis}} \)-isomers at the onset of the isotropic-nematic transition is even <4\%. The onset value corresponds to the \( f_{\text{cis}} \)-isomer fraction needed for the complete nematic-to-isotropic transition. The value was analyzed for the first time in supramolecular azobenzene-containing LCs. In the future, the analysis should be extended to cover the whole LC range of these complexes. Analyzing the \( f_{\text{cis}} \)-fractions systematically at the transitions would allow to optimize the used complexes for most effective disruption of the LC phase.
4.3 Assembly of block copolymer micelles into photonic lattices (Publication IV)

Light interacts with materials mainly through adsorption by molecules and interacting with refractive index variations as dictated by it being electromagnetic waves. The adsorption through excitations mostly creates the colors around us and in photochromic molecules leads to molecular changes, which were utilized in the previous sections. Here we exploit the interference of light with structures in the range of half of the wavelength of light and thus create photonic effects and structural colors. Photonic structures and structural colors are abundant in nature and such structures have been self-assembled before. Photonic crystals have been prepared from block copolymers and through colloidal crystallization, and applied to for example sensing. We utilize here, for the first time, self-assembled block copolymer micelles to create 3D photonic crystals.

4.3.1 Assembly to low dispersity micelles with superstretched corona

As discussed in Section 2.5, amphiphilic block copolymers can self-assemble into a variety of structures in solution and bulk through selective and controlled aggregation of one of the blocks. These structures are controlled largely by the properties of the block copolymers, and solvent interactions. Usually, a small aggregating block relative to the corona block leads to spherical micelles. These, the simplest of the assembled structures, are used in this work. The aim to assemble them to photonic crystals places stringent requirements for narrow sizedispersity and large size, not usually met by BCP micelles. The BCPs used in this work are polystyrene-\textit{b}-poly(2-vinylpyridine) (PS-\textit{b}-P2VP or SV) to function as building blocks for crystallization, it is critical that the micelles have a narrow dispersity. This can be achieved by strict control of the micellization. An important step towards controlled micellar assemblies has been to guide the structures formed in the micellization towards their thermodynamical equilibrium states by using a process with an intermediate step, which allows the micelles to equilibrate. Gröschel \textit{et. al.} showed that sequential solvent exchange through dialysis leads to excellent control of micelle properties.

For photonic properties, besides being narrowly dispersed, the micelles should be able to provide the lattice spacing for the photonic crystal. Generally, block copolymer micelles have dimensions of a few tens of nanometers, which is much less than the required lattice spacing ($\approx 150$ nm). Such micelles, have been shown to crystallize in lyotropic conditions. To increase the lattice spacing, there are alternative approaches: 1) using high molecular weight block copolymers or 2) assembling micelles from polymers containing a charged polyelectrolyte corona, or 3) inducing charges into the corona after micellization. The first approach leads easily to synthetic difficulties to achieve the needed
molecular weights and additionally, the controlled assembly is more difficult due to slower equilibration kinetics arising from the high molecular weight. In addition, this limits the range of core/corona ratios, as with small core block sizes, unimers can be expected. In the second approach, solubilities become an issue when assembling micelles directly from a block copolymer containing a polyelectrolyte block. This leads to difficulties in achieving narrowly dispersed micelles. The third approach, i.e., inducing charges after micellization through quaternization, is used in the Publication IV. This approach offers a large range of existing block copolymers with varying block compositions, requirement being a quaternizable corona, and block weights, which can be used for the approach. Also, in combination with sequential solvent exchanges, the micellization of non-charged polymers can generate low dispersity micelles.

The overall procedure for preparing micelles with superstretched coronae is presented in Figure 4.11. The polymer, here PS-b-P2VP, is dissolved in a cosolvent for both blocks, dimethylacetamide (DMAc). This is followed by solvent exchange to isopropanol, a slightly selective solvent towards P2VP, during which the micelles form. Macroscopically, the micellization is seen as a slight bluish haze arising from the Rayleigh scattering of the micelles. Being only slightly selective, the micelles with swollen cores are able to equilibrate to nearly monodisperse micelles. The second solvent exchange to methanol (MeOH), a highly selective solvent towards P2VP, decreases the swelling of the core and fixes the micelles. While in methanol, the P2VP corona is quaternized by addition of methyl iodide (MeI) and heating to 60°C. This induces charges to the corona, leading to high repulsion between the polymer chains, driving the stretching of the corona. Final solvent exchange to water further increases the stretching of the corona as the dissociation of the counterions is stronger in water than in MeOH.
The core radii is very well defined, for example, polymer PS-b-P2VP with molecular weights of 17.5 kg/mol and 55.5 kg/mol, respectively, form micelles with average core radii of 9.5 nm (Figure 4.11). The standard deviation (STD) of the micelle radii determined from the Cryo-TEM images is 0.9 nm, i.e., below 10%. Also for other polymers, similar relative STD values were observed. The size of the corona was approximated with dynamic light scattering (DLS), which indicates a highly swollen corona, with a hydrodynamic diameter, $R_h$, of 81 nm. Considering a sphere with a radius of 81 nm and a core of 9.5 nm, the volume fraction of the core is only 0.16%. For a density profile of such a micelle, refer to Section 2.4.

### 4.3.2 Crystallite formation of the micelles

Being very well defined, the micelles offer a good basis for creating colloidal crystal lattices, and with the suitable dimensions, the lattices have photonic properties. For the colloidal self-assembly, described in section 2.5, the crystallization can occur through multiple mechanisms. Most importantly, colloidal crystals can form based on attractive interactions, entropic contributions or repulsive interactions. The micelles created by the process described above are highly charged colloids, and therefore their assembly is dominated by electrostatic repulsion with possible minor entropic contributions. The electrostatic repulsion driven crystallization arises from minimization of the electrostatic energy in a crystalline lattice, where the average distance between the particles is maximized. Compared to traditional hard colloidal spheres with a surface charge, the micelles are soft particles with a highly responsive corona, which makes them more complicated to analyze.

In the experiments, the micelles were observed to crystallize within a specific concentration range. After preparation, the system starts from a gel-like state (Figure 4.12a), which upon dilution first starts showing a hue (Figure 4.12b). The state with the hue arises from the average separation between the micelles and these states are denoted as micellar photonic fluids (MPF). The hue of the MPF red-shifts upon further dilution. Beyond a specific concentration under quiescent conditions, the solution starts exhibiting crystallites (Figure 4.12c). These crystallites are denoted as micellar photonic crystals (MPC). The gel-like state prior to dilution indicates significant kinetic hindrance in the diffusion of the micelles. These kinetic hindrances are relieved upon dilution of the system, which likely allows the micelles to adapt and minimize the electrostatic repulsion, and therefore crystallize. For the tested samples, the volume fraction approximated from the hydrodynamic radii at the high concentration limit was close to 58%. This indicates that the limit is close to the overlap concentration. Based on the volume fractions, one should also note that the micelle coronae are not in close contact in the crystals, which is significant for example when considering the possibilities to fixate the micelles to the crystalline lattice.

The low concentration limit arises from the strength of electrostatic repulsion...
between the micelles, which needs to overcome the thermal energy of the micelles. The electrostatic repulsion is naturally governed by the distance between the micelles. At this point, one should note from dimensionality considerations that upon dilution, the distance between the micelles increases as a function of concentration as $\sim c^{-1/3}$. As the repulsion decreases with an increase in the distance of the micelles, a limit is reached upon which the electrostatic repulsion is too weak for crystallization to occur. In the absence of salt in the solution, the upper limit for the crystallization was observed to be dependent on the length of the micelle corona as estimated from the hydrodynamic radii by comparison of two different micelles (see Figure 4.15). The crystallization was also shown to be tunable with addition of salt, which induces contraction of the corona. This allows to crystallize all the samples beyond the high concentration limit by relieving the kinetic hindrances caused by the corona.

Owing to the photonic properties, the crystallite formation is visible to eye. The crystallites were shown to also phase separate to amorphous and crystalline phases with time (Figure 4.13b). The colors shown by the crystallites are angle dependent and the crystallites are single colored (Figure 4.13c-d). They were imaged also directly with confocal fluorescence microscopy from micelles with cores stained with a fluorescent dye. An image is shown in Figure 4.13 and it shows the crystal lattice of the micelles. When imaged macroscopically, the micelles were shown to reversibly form crystallites with dimensions up to millimeters. The micelles were also shown to allow freeze-drying while retaining their capability to form MPCs. The micelles can exhibit clear single domain
4.3.3 Photonic properties

The created micellar solutions exhibit two kinds of photonic structures: micellar photonic fluids (MPF) and micellar photonic crystals (MPC). The MPF state is an amorphous phase, in which the micelles have an average spacing corresponding to the photonic period, but lacks the crystalline order. Such photonic structures have been prepared also from other colloids.\(^{175}\) The phase was depicted schematically and illustrated by a photograph in Figure 4.12. In the MPF, the color remains even upon stirring the solution and the periodicity is also dependent on the concentration of the solution. The average spacing in MPF scales as \(\sim c^{-1/3}\) similar to the distance between the micelles. The second photonic structures, i.e., the photonic crystals, on the other hand have a well defined lattice with reflections arising from the different families of lattice planes.

For a photonic crystal, the periodicities, which produce photonic effects can be estimated with the Bragg’s law:

\[
    d_{hkl} = \frac{\lambda_{\text{air}}}{2n_{H_2O}(\lambda) \cdot \sin \theta}, \tag{4.7}
\]

where \(d_{hkl}\) is the spacing of the lattice planes, \(\lambda_{\text{air}}\) is the wavelength of the light in air, \(n_{H_2O}\) is the wavelength dependent refractive index and \(\theta\) is the angle of incidence with respect to the lattice plane. From the simple Bragg’s law, one can note that the reflected wavelength is angle dependent, which is also visible in the crystallites as shown in Figure 4.13. The indices \(h, k\) and \(l\) refer to the Miller’s indices, which are used in crystallography to note the different crystalline planes. The notation \{hkl\} refers to the whole family of lattice planes which arise from the symmetry operations meaning that \(\{100\}\) notation includes...
all six planes: (100), (010), (001), (-100), (0-10), (00-1). From the indices and the unit cell size, \( a \), of the crystalline lattice, one can calculate the spacings of the different crystalline planes as

\[
d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}.
\]

(4.8)

Using the Bragg’s law for crystallites requires considering the structure factor, which results in selection rules. For a face-centered-cubic (FCC) lattice, to show a reflection, all the indices \((hkl)\) need to be either odd or even. This indicates that the highest wavelength peak is from the family of planes \(\{111\}\) and is followed by \(\{200\}, \{220\}, \{113\}, \{222\}\) etc.

In the reflection measurements of the crystallites, the reflections show clear peaks, corresponding to the distinct colors observed also in the crystallites, which can be matched exactly to an FCC lattice. Figure 4.14 shows an example spectra, and gives the peak assignments to the corresponding families of lattice planes. The unit cell size in the example lattice corresponds to 402 nm.

The reflection spectra were measured systematically for micelles created from two different polymers: SV1 (PS\(_{168-b}\)-P2VP\(_{528}\), \(M_n = 73\) kg/mol) and SV2 (PS\(_{217-b}\)-P2VP\(_{719}\), \(M_n = 98\) kg/mol). They have core radii of 9.5 nm and 9.9 nm and hydrodynamic radii of 81 nm and 110 nm, respectively. The results show that the crystallites are able to cover the whole visible range (Figure 4.15a-c). The crystal samples with good order have especially sharp peaks with FWHM values around 3 nm, but FWHM values down to 1.1 nm were observed. The reflection spectra were also simulated by using a refractive index profile of the micelles by assuming \(\propto (R/R_{\text{core}})^{-2}\) density profile for the corona (see Section 2.4). The simulation results match the extremely sharp peaks in large size crystallites. The larger the crystals, the smaller the FWHM values. The 3 nm peak widths resulted from \(\gtrsim 36\ \mu\text{m}\) peaks. The sharp peaks arise from the small core size of the micelles and good order in the crystallites. The calculated unit cell
sizes from the measured spectra from SV1 and SV2 are shown in Figure 4.15d. Clearly, the lattice size shows a $\sim c^{-1/3}$ relationship. The reflection spectra were also simulated for a series of different lattice sizes, and the results match the measured reflection spectra with sharp peaks located in the expected positions (Figure 4.15e). Also the decrease of reflection intensity upon increased lattice size was experimentally observed.

Overall, the micellar photonic crystals, owing to the small cores with a highly diluted corona create peculiar optical properties with the extremely sharp reflection peaks that can be matched with the simulation results. More importantly, the results demonstrate that the approach of creating narrowly dispersed micelles with sequential solvent exchange followed by quaternization of the corona is a generic way for creating tunable colloidal photonic crystals.
Figure 4.15. a) A series of crystallites with a decreasing concentration showing that the crystallites can span the whole visible wavelength range. b) Measured reflectance spectra from SV1 polymer micelles at different concentrations and c) the same for SV2 micelles. d) The development of the unit cell size as a function of concentration. Note that in the inset, the micelle cores (black dots) have been drawn to scale with the lattice sizes (small 336 nm and larger 568 nm). e) Simulated reflectivity spectra. Adapted with permission from Publication IV. Copyright ©2018 American Chemical Society.
Results
5. Conclusions and outlook

This thesis highlights how the combination of light and self-assembled structures can be used to create azobenzene-based photo-responsive materials and 3D photonic crystals based on block copolymer micelles. Overall, the used self-assembled structures span the range from molecular complexes to colloidal self-assemblies. The discussion highlighted the different underlying mechanisms on how they can be utilized in designing photo-responsive and photonic materials.

In the bigger picture, supramolecular self-assemblies of azobenzenes are studied for various photoresponsive materials, where the response arises from the presence of the cis-isomer. In these applications, it is in fact the cis-trans thermal isomerization that often dictates the behavior and applicability of the materials. Therefore, Publication I studies the effects of the self-assembled structure on the isomerization kinetics of hydrogen-bonded hydroxyazobenzene-polymer complexes. The results pinpoint to cooperativity and intrinsic mechanistic changes in the thermal isomerization through intermolecular hydrogen bonding between the hydroxyazobenzenes. Confinement of the molecules created by the self-assembled lamellar smectic-like structure increases the tendency to form the chromophore–chromophore bonds, leading to a significant difference between the lamellar and disordered structures. This result is of importance especially in supramolecular photo-responsive materials, where such a difference in thermal isomerization behavior can be significant for the applicability of the self-assembled materials.

The mechanistic changes of isomerization, creating high sensitivity to environmental changes of the hydroxyazobenzenes, were utilized to develop a new type of vapor sensor for hydrogen-bonding-gases based on the isomerization kinetics of azobenzenes in Publication II. This demonstrates how exploiting the underlying mechanism of isomerization can lead to a new class of applications. The demonstrated approach is simple, robust and highly tunable and is expected to open new undiscovered possibilities for using azobenzenes to sensing or creating multi-responsive smart materials capable of adapting the photo-response to environmental changes.

With liquid crystals, the order-disorder transitions induced by isomerization of azobenzenes are utilized in many applications. Even though widely applied, in
the case of supramolecular liquid crystals, the connection of the phase transition to the \textit{cis}-isomer fraction in the material has not been investigated. Publication III demonstrates a new class of photo-responsive supramolecular stilbazole–azobenzene LCs which are based on the highly directional halogen bonding. The photo-response was studied in detail, revealing a phase separation process and order-disorder transitions. In these complexes, the \textit{cis}-fraction needed for full LC-to-isotropic transition was found to be $<4\%$ of the mesogenic molecules. Such information is useful especially for assessing the efficiency of the isomerizing molecules to disrupt the LC phase.

On the structural side, ever-more complex self-assembling structures are demonstrated. Perhaps the most significant challenge in larger scale self-assemblies, i.e., assemblies of block copolymers and colloidal particles, is the size dispersity of the building blocks. In ordered lattices, the variations of the building blocks will evidently induce defects in complex structures. To some extent the ordered structures can withstand variations, but the variations often decrease the quality of the structures. In Publication IV a method is created for preparing such highly monodisperse block copolymer micelles, which can be further applied to create 3D photonic crystals. This was achieved by guiding the micelles to their equilibrium structures through sequential solvent exchange process. Furthermore, the developed route for the micelles also addresses the challenge of increasing the size of BCP micelles to the photonic length scale through quaternization of the micelles after their formation. This created a generic route to form micellar photonic fluids and micellar photonic crystals. The fluids have a tunable hue arising from average distance between the micelles, the crystals, on the other hand, produce extremely narrow reflection peaks. A stunning property of the micellar crystals is that micelles with 10 nm core radius can be crystallized in lattices with up to 560 nm lattice constants.

The next level of self-assembling materials is to move from static to multi-responsive, adaptive and dynamic self-assemblies.\textsuperscript{176} This is a tremendous challenge and requires understanding the fundamental principles on many levels. Bringing forth multi-responsivity, adaptivity and energy feeds increases the complexity and especially the requirements for design of the subtle supramolecular interactions. This calls for joint efforts to enhance the understanding of the underlying interplay of the different mechanisms across the length scales.
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