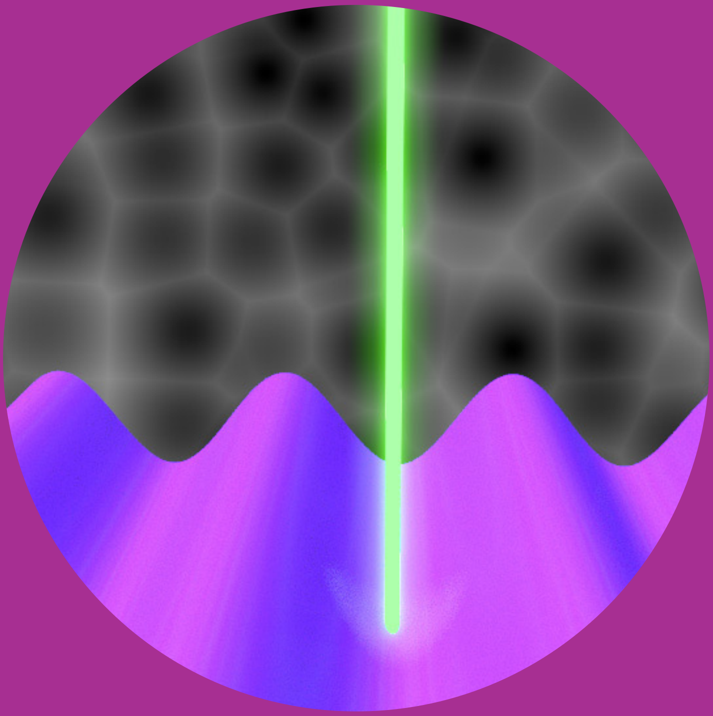
Department of Applied Physics

Design of efficient photoresponsive azobenzene materials through supramolecular functionalization

Jaana Vapaavuori



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Design of efficient photoresponsive azobenzene materials through supramolecular functionalization

Jaana Vapaavuori

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Abstract

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Abstract

Azobenzene molecules are known to change their geometry upon photon absorption. The photoisomerization process, taking place at the nanometer scale, can give rise to remarkable photoinduced macroscopic motions into the material system. The most pronounced examples of such effects are photoinduced bending of free-standing films and the formation of micron-scale surface patterns due to photoinduced mass transport. Due to their anisotropic shape, azobenzenes also contain directional information and are polarization sensitive. The phenomena arising from the photoisomerization reaction have applications not only in optics and photonics, but also in the interfaces between light and surface science, information storage, imaging, biology, energy storage and actuation. Despite the extensive research, many fundamental questions concerning the coupling between the molecular-scale reactions and the photoresponse of the material at larger scales still remain a conundrum.

This thesis seeks for guidelines for designing efficient photoresponsive materials through exploiting the toolkit of supramolecular chemistry. Supramolecular functionalization provides a powerful tool for precisely controlling the composition of the material system, which is imperative when exploring the structure–performance relationships that govern the material's light-responsive behavior. By selecting the constituent compounds in a systematic and controlled manner, we study the effect of the structural and physical parameters of the azobenzene units on their packing density, which again profoundly influences their optical performance. More specifically, the role of (i) chromophore-chromophore intermolecular interactions, (ii) flexible spacer groups, (iii) the polarity of the azobenzene units, and (iv) the architecture of the host material on *photoalignment* and *photoinduced surface patterning* are discussed. In addition to contributing to fundamental understanding of light-matter interactions in azobenzene-containing materials, our findings highlight more generally the potential of supramolecular material design in optics and photonics, and we believe that this interface will bring about applications far beyond the scope now seen.

Keywords azobenzene, photoisomerization, photoinduced birefringence, photoinduced surface patterning, supramolecular functionalization

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Tiivistelmä

Tekijä
Jaana Vapaavuori

Väitöskirjan nimi
Tutkimuksia supramolekyyläristen atsobentseenimateriaalien valovasteesta

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Tiivistelmä

Atsobentseenipohjaiset molekyylit voivat muuttaa muotoaan fotonin absorboitumisen seurauksena. Nämä nanomittakaavassa tapahtuvat valoisomerisaatioreaktiot voivat johtaa makroskooppisiin valoherätteisiin ilmiöihin, esimerkiksi kokonaisen polymeerikalvon taipumiseen tai mikrometriskaalan pintakuvioiden muodostumiseen valon vaikutuksesta. Sauvamaisen muotonsa ansiosta atsobentseenimolekyylejä voidaan myös suunnata hyödyntäen valon polarisaatiota. Näille ilmiöille on jo löytynyt käyttökohteita niin optiikan, pintatieteiden kuin biologiankin alalta. Erityisen mielenkiintoista on mahdollisuus tuottaa valovoimalla liikkuvia koneita, sillä atsobentseenimolekyylit pystyvät muuttamaan absorboimansa valoenergian suoraan liikkeeksi: mikrotasolla atsobentseenimolekyylejä voidaan käyttää muun muassa optisina kytkiminä, kun taas makrotasolla voidaan rakentaa valolla liikkuvia keinolihaksia ja moottoreita.

Huolimatta laajasta tutkimustiedosta, monet valon aikaansaamat materiaalin liikkeeseen liittyvät peruskysymykset ovat vielä vastaamatta. Tässä työssä tutkitaan, miten pienillä ja hallituilla materiaalisysteemin ominaisuuksien muutoksilla voidaan ohjata materiaalin käyttäytymistä ja valovastetta haluttuun suuntaan. Työ hyödyntää supramolekyyläristä kemiaa atsobentseenimateriaalien valmistuksessa ja korostaa entisestään tämän lähestymistavan etuja.

Väitöskirja antaa uutta tietoa siitä, miten yksittäisten atsobentseenimolekyylien fysikaaliset ja kemialliset ominaisuudet vaikuttavat supramolekyyläristen kompleksien valovasteeseen. Työssä pureudutaan muun muassa atsobentseenien välisiin vuorovaikutuksiin, pehmentävien hiilivetyketjujen merkitykseen, atsobentseeniyksikköjen polaarisuuteen ja atsobentseenit vastaanottavan isäntämolekyylin arkkitehtuurin vaikutukseen. Työ lisää ymmärrystä valoherätteisistä atsobentseenimateriaaleista ja edesauttaa uusien valoliikkeeseen perustuvien sovellusten suunnittelua.

Avainsanat atsobentseeni, fotoisomerisaatio, valoherätteinen kahtaistaittavuus, valoherätteinen pintakuviointi, supramolekyyläriset sidokset

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To all who were not given the privilege of 21 years of state-paid education

Preface

Now that I have spent over four years wandering around through the corridors of three different laboratories, I have started to feel prepared and ready to begin as a PhD student. Since I have not felt this mature before, I assume that some sort of growth as a scientist has taken place during these years owing to these inspiring and sometimes challenging environments.

I am grateful to professor Matti Kaivola for offering me the possibility to work in the Group of Optics and Photonics, for all the flexibility, and especially for all the debates on the society and university politics that often made me to open my eyes. I am sincerely indebted and thankful to the supervision of Dr. Arri Priimägi. Throughout these years, he has been available for support and encouragement in uncountable ways, the most notable perhaps being his confidence in my abilities to do science as a young, naive, and sometimes too stubborn beginner grad student. Professor Christopher Barrett is thanked for accepting me as a Research Graduate Trainee in McGill University; this unique adventure also widened my horizons a lot. Furthermore, funding from the National Graduate School in Materials Physics is greatly acknowledged.

It feels bizarre to write the forewords to "my" thesis, since all the publications have been joint research efforts. In addition to the three that I already mentioned in the previous paragraph, I acknowledge all the other co-authors of the publications, as well as all the fellow students I have been working with, although we would not have any common publications. I want to thank M. Sc. Ville Valtavirta for numerous discussions, concerning both science and the ways of doing it. I no longer consider self-loathing as a constructive attitude towards studying physics, and a great deal of that insight is thanks to him. B. Sc. Juho Hautala is thanked for teaching me the basics of ticking off other people, and soon-to-be B. Sc.

Ismo Heikkinen is thanked for always reflecting the memory of sunlight to the dark laser laboratory we work in. In addition, I want to thank the group of Molecular Materials for offering me a retreat, when the world around was too wintry, bleak, and arid for me. Special thanks go to Dr. Susanna Junnila and M. Sc. Juuso Korhonen for sharing their small office with me. I feel extremely lucky to have worked with you - always willing to help me with my computer problems and supporting me with my not-so-scientific projects related to the "how to make the (academic) world a better place".

I owe my sincere gratitude to Alexis Goulet-Hanssens, Thomas Singleton, Zahid Mahimwalla, and Miloslav Sailer, who helped me to get into the research life at McGill University. Moreover, I would like to thank Pascale Boulet and Yannic Rochon for the French Immersion and showing the warm-hearted side of the *Québecois*.

Also the balancing elements of life outside materials science have been of uttermost importance in completion of this thesis. I express my deepest gratitude to all of my friends for their understanding and wiping away my tears, when necessary. Especially Maija Vaara, Kristian Nybo, Milka Kylliäinen and Anna Backholm are thanked for their compassion and never-ending patience of listening my work-related stories. Dance group Koherenssi, Hippifyysikot ry., and Prometheus-leirin tuki ry. have been essential for me to put my scientific setbacks into real-life context.

There are no right words to thank the people back at home for their unconditional support. During this hectic spring, it has been of great help to me to find filled fridges both at my home and at my childhood home. Although I have felt happy in this neo-nomadic lifestyle of ever-changing sceneries, it is with you I will always feel at home.

Espoo, April 24, 2013,

Jaana Vapaavuori

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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.

I A. Priimagi, J. Vapaavuori, F. Rodriguez, C. Faul, M. Heino, O. Ikkala, M. Kauranen and M. Kaivola. Hydrogen-Bonded Polymer–Azobenzene Complexes: Enhanced Photoinduced Birefringence with High Temporal Stability through Interplay of Intermolecular Interactions. *Chemistry of Materials*, 20, 6358 – 6363, 2008.

II J. Vapaavuori, V. Valtavirta, T. Alasaarela, J.-I. Mamiya, A. Priimagi, A Shishido and M. Kaivola. Efficient surface structuring and photoalignment of supramolecular polymer–azobenzene complexes through rational chromophore design. *Journal of Materials Chemistry*, 21, 15437 – 15441, 2011.

III J. Vapaavuori, A. Priimagi and M. Kaivola. Photoinduced surface-relief gratings in films of supramolecular polymer–bisazobenzene complexes. *Journal of Materials Chemistry*, 20, 5260 – 5264, 2010.

IV J. Vapaavuori, Z. Mahimwalla, R. Chromik, M. Kaivola, A. Priimagi and C. Barrett. Nanoindentation study of light-induced softening of supramolecular and covalently functionalized azo polymers. *Journal of Materials Chemistry C*, 1, 2806 — 2810, 2013.

V J. Vapaavuori, A. Priimagi, A. Soininen, J. Ruokolainen, M. Kaivola, O. Ikkala, E. Kasëmi and N. Canilho. Photoinduced surface patterning of azobenzene-containing supramolecular dendrons, dendrimers and dendronized polymers. *submitted to Optical Materials Express*, 2013.

Author's Contribution

Publication I: "Hydrogen-Bonded Polymer–Azobenzene Complexes: Enhanced Photoinduced Birefringence with High Temporal Stability through Interplay of Intermolecular Interactions"

The author carried out the sample preparation and optical characterization of the materials under the instruction and supervision of A. Priimagi, following his original idea. The author participated in analyzing the results and writing the publication.

Publication II: "Efficient surface structuring and photoalignment of supramolecular polymer–azobenzene complexes through rational chromophore design"

This work was planned by the author, V. Valtavirta and A. Priimagi. The sample preparation as well as the photoalignment studies were partly done by V. Valtavirta, instructed by the author. The surface-relief grating studies and analysis was done by the author. The author participated in the analysis of all the results and also wrote a major part of the publication.

Publication III: "Photoinduced surface-relief gratings in films of supramolecular polymer–bisazobenzene complexes"

This work was initiated by A. Priimagi and the author. The author carried out the sample preparation and the optical measurements. The author wrote a major part of the publication.

Publication IV: "Nanoindentation study of light-induced softening of supramolecular and covalently functionalized azo polymers"

This work was done in collaboration with the research groups of professors C. Barrett and R. Chromik in McGill University, and the original idea was from Z. Mahimwalla. The author prepared the supramolecular samples, and performed the nanoindentation studies together with Z. Mahimwalla. The author participated in the analysis of the results and also wrote a major part of the publication.

Publication V: "Photoinduced surface patterning of azobenzene-containing supramolecular dendrons, dendrimers and dendronized polymers"

This work followed the original idea of R. Mezzenga, O. Ikkala and A. Priimagi. All the optical and thermal measurements, as well as the data analysis were done by the author. The author wrote the first version of the manuscript and contributed significantly to the writing process thereafter.

1. Introduction

What kind of challenges can be addressed with the help of photoresponsive materials?

Producing energy efficiently and environmentally friendly is one of the grand challenges of our age. Nature, being a fundamental source of inspiration for scientists, provides solutions evolved over eons. For instance, a small organism belonging to the *Archaea*, called *Halobacterium salinarum* applies a protein, which undergoes geometrical changes upon photon absorption, to directly use the energy of the absorbed light to pump the protons across the cell membranes [1]. For the scientific community, a specialized solution to the energy problem (as well as to many other problems) of mankind is yet to be found. However, photoisomerizable azobenzene-based materials studied in this thesis may take us one step closer to a prospective solution, since they enable purely photo-driven actuation, and thus use light as fuel to produce motion.

Indeed, azobenzene-based light-powered engines [2–4] and artificial muscles have already been demonstrated [5,6]. The photomechanics and simple robotics already arisen from the azobenzene research have also been reviewed recently [7,8]. These fascinating applications emerge from the conformational changes that the azobenzene units undergo upon photon absorption. Photoisomerization is clean, reversible, and highly sensitive to the polarization of the incident irradiation. These properties distinguish photoisomerizable materials from the more conventional light-responsive media, such as photoresists and photocurable polymers, which are typically isotropic and not able to carry any directional information [9]. Also, their response to light cannot be reversed.

Even if known to be driven by photoisomerization, the detailed connection between the molecular-level properties and the observed photoinduced motions occurring in azobenzene systems is still far from being completely understood. Greatly inspired by the seminal work of the research groups of Natansohn and Rochon on the photoresponsive behavior of amorphous, covalently-functionalized azobenzene-containing polymers [10, 11], this dissertation searches for guidelines for the design of efficient photoresponsive materials by adopting the toolkit of supramolecular chemistry. By using spontaneously forming non-covalent bonds between azobenzenes and host molecules, we can easily control many material parameters, and hence study the fundamental structure-function relationships that govern the photoinduced movements in azobenzene-containing materials. We focus on two types of photomotions arising from the photoisomerization reaction, namely photoinduced birefringence and photoinduced surface-relief grating formation. These phenomena are treated in more detail in Chapter 2. The principles of supramolecular binding strategies as well as the most relevant studies on state-of-the-art supramolecular azobenzene-containing complexes are the topics of Chapter 3. This thesis employs as simple model systems as possible to systematically vary the structural and physical parameters of the photoresponsive complexes. The framing of the questions relevant to this work, alongside with a short summary of the results of the publications comprising this thesis, are presented in Chapter 4. Finally, conclusions and future prospects are given in Chapter 5.

In general, this research highlights the beauty of light as a means to control some macroscopic properties of materials. We underline the ease of applying supramolecular strategies for gaining fundamental understanding on the design of materials for photoinduced birefringence and surface-relief grating formation. Although our studies are fundamental by their nature, the design of more efficient photoresponsive materials or optical devices may benefit from the results. Since new building blocks for future supramolecular complexes are constantly developed, only human imagination will limit their use in creating novel multifunctional materials.

2. Azobenzene-based photoinduced movements

All the studies in this thesis are based on the simple and clean photoisomerization reaction of azobenzene derivatives, described in more detail in Section 2.1. The light-induced configurational change renders azobenzenes good candidates for various photoresponsive applications. In the seminal review by Natansohn and Rochon, the photoinduced movements in polymeric materials were divided into three classes according to the scale at which they appear: at the molecular level, at the domain level, and at the micrometer (macroscopic) level [10]. However, the motions at different scales are closely interrelated, and a clear division between them is too simplified when aiming at understanding the effects of single parameters on the photoresponsive phenomena [8].

Considering bulk materials, the photoisomerization of azobenzene will always result in expansion or contraction of the material, as discussed in Section 2.2. Two special types of photoinduced motions have been studied in this thesis. Photoalignment of azobenzenes upon exposure with linearly polarized light is briefly reviewed in Section 2.3, and photoinduced surface patterning by applying a polarization/intensity interference pattern of light on an azopolymer film is further elaborated in Section 2.4.

2.1 Photoisomerization of azobenzene derivatives

Azobenzenes, recognized by their nitrogen-nitrogen double bond, undergo clean and reversible conformational changes upon photon absorption, which is schematically shown in Fig. 2.1. This reaction, called photoisomerization, leads to large alterations in the physical and chemical properties of the molecules: For instance, for the parent azobenzene molecule, in which R_1 and R_2 correspond to hydrogen atoms, the distance between the *para*-positions decreases by 44% [12,13] and the dipole moment increases

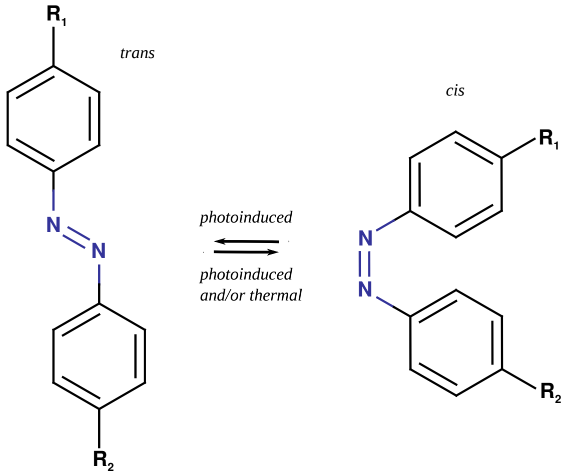

Figure 2.1. The *trans* and the *cis* isomers of a general 4,4'-substituted azobenzene molecule.

from 0 D to 3.0 D upon *trans-cis* isomerization [14].

Photon absorption can drive either the *trans*-to-*cis* or *cis*-to-*trans* reaction, depending on the energy of the photon, but since the *trans* isomer is more stable [15], the latter reaction occurs also thermally. The energy barrier to raise the molecules to the photoexcited state is 200 kJ/mol [16] making the *trans* isomer dominant at ambient conditions. The main factor governing the photoisomerization reaction is the energy (the wavelength) of the absorbed photon. Two kinds of transitions, namely $\pi \rightarrow \pi^*$ resulting from the excitation of a delocalized π-electron of the N-N double bond and $n \rightarrow \pi^*$ caused by the excitation of an electron localized on one of the nitrogen atoms, are observed in the UV-Visible region. For the *trans* isomer, the $n \rightarrow \pi^*$ transition is forbidden due to symmetry reasons, so in the ambient conditions the *trans* $\pi \rightarrow \pi^*$ transition band dominates the UV-Visible absorption spectra of azobenzene molecules.

The wavelength of the UV-Visible absorption maximum can be tuned by substituting the azobenzene using functional units with different electron-donating or -accepting properties; therefore, azobenzenes absorbing anywhere from UV to green exist. Based on the spectroscopic differences, azobenzene derivatives were divided into three different classes by Rau [17]: (i) azobenzene-type molecules, whose electronic structure is close to that of the parent azobenzene, (ii) aminoazobenzenes, which typically contain an electron-donating group, and (iii) pseudostilbene-type molecules, which have a donor-acceptor electronic structure. Due to the differences in their electronic structures, the molecules exhibit characteristic colors of yellow, orange, and red, respectively, and their absorption maxima fall to near-UV (azobenzenes), around 400 nm (aminoazobenzenes), and > 450 nm (pseudostilbenes) [17, 18].

For azobenzenes, two energetically-allowed isomerization mechanisms exist: out-of-plane rotation and in-plane inversion around the nitrogen-nitrogen double bond. Although the exact mechanism depends on the material and the environment, the inversion, requiring much less sweeping volume, is preferred [19–21]. Quantum yield describes the isomerization probability under specific excitation conditions, and it can be measured spectroscopically. The applicability of the measured quantum yields is limited, however, as this quantity depends on many external parameters, such as the irradiation wavelength, solvent polarity, temperature, and viscosity of the solvent [22].

There is an orders-of-magnitude difference in the timescales of the photoinduced and thermally-driven isomerizations. The former occurs in picoseconds [23, 24] and the latter on the order of hours, minutes or seconds for azobenzenes, aminoazobenzenes and pseudostilbenes, respectively [18]. Slower than the photoisomerization reaction, the thermal isomerization will determine the stability of the *cis*-isomer and the applicability of the chromophores. It is noteworthy, though, that moving from a solution to bulk state will affect the timescales of both the photodriven and the thermal isomerization reactions: Photoisomerization is substantially slower in bulk than in solution [25]. The thermal *cis*-to-*trans* reaction maintains its timescale and first-order character, although strained environments can add anomalously fast components to the thermal relaxation [25, 26].

Upon illumination, an azobenzene-containing sample will reach a steady state between the photoinduced and thermally-driven reactions, and in addition to the nature of the chromophore, this state depends on many external factors. The spectrum of the molecule and the thermal *cis*-lifetime provide useful insight into the molecule's applicability: Bistability, required in many photoswitching applications, is best met in azobenzene-type molecules with clearly separated *trans* and *cis* absorption bands and long *cis*-lifetime. On the other hand, pseudostilbenes are optimal for applications in which efficient *trans*-*cis*-*trans* cycling is needed.

2.2 Photocontraction and photoexpansion

When azobenzenes are bound to solid matrices, the actuation of the molecules upon photoisomerization may have a significant impact on the total volume of the material: both contraction and expansion of azopolymers upon irradiation have been observed. Barrett and colleagues have thoroughly studied this fundamental phenomenon by neutron reflectometry and ellipsometry [27–29]. They have shown that under similar irradiation conditions, an azobenzene-containing polymer may smoothly undergo a crossover from photoexpansion to photocontraction simply by changing the temperature. They attribute the tendency of the material to expand to the internal pressure created by the isomerizing molecules and to contract to the denser packing of the dipolar molecules, which is enabled by the mobility of the molecules in the material.

The above-mentioned studies were done in amorphous side-chain azopolymers, but more pronounced photomechanical changes can be induced by employing liquid-crystalline materials. The intrinsic anisotropic order of such materials can be harnessed to give rise, for instance, to unidirectional or polarization-controllable bending of free-standing polymer films [30, 31]. This fascinating feature originates from the photocontraction taking place on the surface facing the light source, while the surface on the dark side is left intact, as depicted in Fig. 2.2. In amorphous polymer blends, anisotropic photomechanical response can be induced by uniaxial strecthing of the polymer film [32]. Even if the effect is typically weaker than in liquid-crystalline polymers, bending angles of up to 90° have been demonstrated [33].

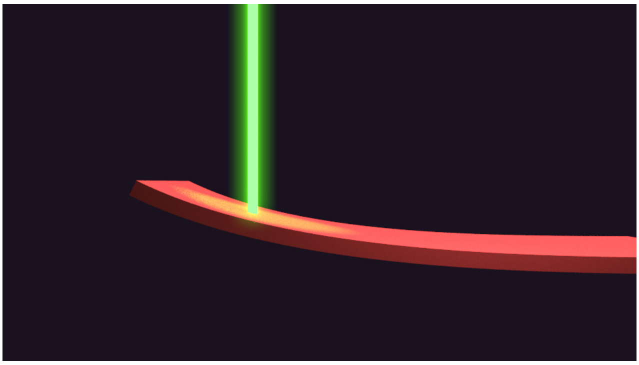

Figure 2.2. Schematic picture of the photoinduced bending of a free-standing azo-containing polymer film upon irradiation.

In addition to photoinduced bending, the photomechanical effect has potential applications for example as photodriven cantilevers and micropumps [34, 35]. Photoinduced volume changes have also been proposed as new types of UV sensors, based on the refractive-index change upon photoexpansion [36]. All these studies may lead to applications in robotics and micromechanics that are further explored in the excellent review of Mahimwalla and co-workers [8].

2.3 Photoalignment and photoinduced birefringence

According to the review of Natansohn and Rochon [10], the anisotropic distribution of the azobenzene molecules upon light irradiation was first time observed in 1952, when an azobenzene-containing viscous solution became dichroic when irradiating it with polarized light [37]. Only few further contributions appeared before the renaissance of the field in 1984, when Todorov and co-workers showed that polarization gratings can be recorded into a polymer doped with 0.06 wt-% of methyl orange, a common azobenzene dye [38].

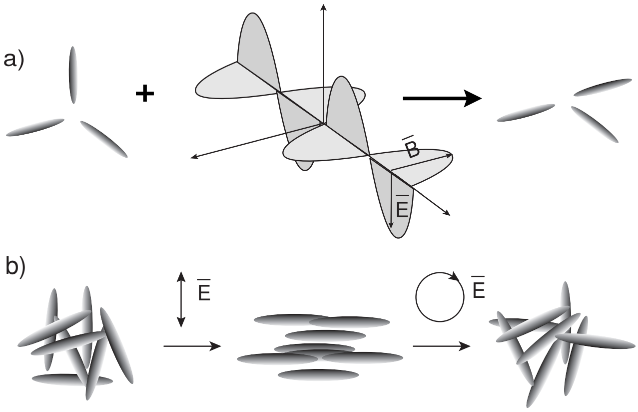

Figure 2.3. a) The tendency of an azobenzene molecule to orient under illumination by linearly polarized light. b) The alignment and the re-randomization of azobenzene molecules by linearly and circularly polarized light, respectively.

The general mechanism of photo-orientation is illustrated in Fig. 2.3a. The $\pi \rightarrow \pi^*$ transition dipole moment of the azobenzens typically coincides with the molecular plane, in good approximation along an axis connecting the midpoints of the two benzene rings [39]. Therefore, the molecules perpendicular to the polarization plane of the incident light are inert to the incoming irradiation. If an amorphous azobenzene-containing polymer film is irradiated with linearly polarized light, successive photoisomerizations statistically orient the molecules perpendicular to the polarization plane, and the resulting anisotropy can be quantified by measuring the polarized absorption spectra or birefringence of the film. The induced orientation can be further changed by switching the polarization direction of the incident light and the alignment can be re-randomized in plane with unpolarized or circularly polarized light, as shown in Fig. 2.3b.

Although the first demonstration of the photoinduced anisotropy in polymeric materials was done in azobenzene-doped polymers, it was soon understood that in order to reduce the aggregation problems when increasing the dye concentration, it was beneficial to synthesize covalently-functionalized polymers, in which the azobenzene units are attached to the polymer backbone as side chains. Eich and co-workers were the first to report holographic gratings in azobenzene-containing LC polymers through illumination with linearly-polarized light [40], and afterwards Natansohn and co-workers have contributed extensively to the understanding of the effects of the material parameters on the photo-orientation process [10, 11]. Until today, majority of these fundamental studies concerning the photoresponsive behavior of the materials have been performed using covalently-bonded polymers. Only recently, supramolecular polymer-azobenzene complexes have been reported to offer a serious alternative to covalently-bonded polymers, as discussed further in Chapter 3.

Generally, when the chromophores orient independently from each other (which is the case in amorphous azobenzene-containing polymers when the concentration is sufficiently low), a linear increase of the photoinduced birefringence as a function of increasing chromophore concentration is postulated [41]. Indeed, this linear behavior was measured for Disperse Red 1 methacrylate monomer (DR1m) copolymerized with a non-polar azobenzene co-monomer [42] and with styrene [43]. However, in the case of DR1m copolymerized with methyl methacrylate, a non-specified chromophore-chromophore interaction caused a deviation from the linear increase of photoinduced birefringence as a function of chromophore concentration [41]. One of the key findings was that this interaction takes place between the photoactive units within a polymer chain, not between the chains [41].

For studying the effect of the azobenzene character (see Section 2.1 for Rau's classification) on the photoinduced birefringence, three different homopolymers bearing azobenzene-, aminoazobenzene-, and pseudo-stilbene-type chromophores as side chains were prepared. The most efficient photoresponse was seen in the pseudo-stilbene-type side-chain polymer. Due to its large dipole moment, the same wavelength can be used to drive both the *trans-cis* and the *cis-trans* isomerizations [44]. Nevertheless, the authors admit that birefringence level comparable to that of the pseudo-stilbene type polymer can also be obtained using aminoazobenzene-type polymers even if the response time is somewhat slower, so the dipole moment hardly is the only determining factor [45].

Reversible optical storage, liquid-crystal alignment, and waveguiding are perhaps the most frequently mentioned applications for the photo-orientation process [9, 46, 47]. Indeed, stable holographic images can be recorded in azopolymers [48], and waveguides can be remotely written and erased by laser light [49]. Diffraction gratings can also be created by using 2D interference patterns of laser beams, but especially in amorphous materials surface-relief grating (SRG) formation dominates the diffracted signal. Considering holographic storage or polarization separation applications, formation of SRGs is a drawback, hence block-copolymers or cross-linked polymers have been used to suppress macroscopic material motions [50, 51]. SRGs, however, are intriguing for other purposes as will be discussed in the next Section.

2.4 Photoinduced surface-relief grating formation

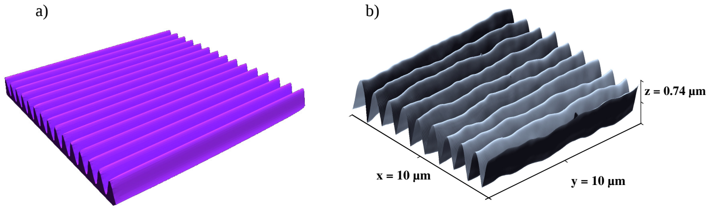

Figure 2.4. a) Schematic picture of a sinusoidal surface-relief grating and b) an atomic-force micrograph of an actual grating inscribed on a thin polymer film.

One of the most fascinating consequences of the photoisomerization reaction is polymeric mass transport on a micron scale, which is three orders of magnitude larger than the size of the photoisomerizing units [8, 52]. The SRG formation was first time observed in 1995 [53, 54]: When an azobenzene-containing polymer film was irradiated with a polarization/intensity interference pattern of light, the polymer surface deforms and adopts the form of a replica of the incident interference pattern. Fig. 2.4a illustrates a sinusoidal model surface relief, and Fig. 2.4b visualizes the atomic-force microscopy (AFM) image on an actual SRG. Soon after the discovery of SRGs, they had already been applied to diffracting elements in waveguide coupling [55] and as spectral filters [56]. Later on, these surface undulations have found use in alignment of liquid crystals [57–59] and colloidal spheres [60]. In recent years, such single-step photoinduced surface patterns have inspired unconventional and innovative applications in replica molding [61, 62], in photochemical imaging [63, 64], and in nanofabrication [65–67].

Different experimental setups can be used to produce the interference pattern needed to fabricate sinusoidal gratings. The setup used in this thesis, Lloyd's mirror interferometer, is schematically depicted in Fig. 2.5a. As shown in this figure, the second beam required to obtain the two-beam interference pattern is produced by reflecting half of the incident beam from a mirror placed at a certain angle, which determines the periodicity of the interference pattern. The formation of the surface pattern then occurs on the sample film, which is placed perpendicular to the mirror. Figure 2.5b illustrates the mass-transport of the amorphous azo-containing polymers, which typically occurs from illuminated areas towards the dark fringes of the interference pattern. This process can be detected *in situ* by guiding a non-isomerizing laser beam through the area of the interference pattern and by recording the diffraction of the probe beam from the emerging grating structures, as shown in 2.5c. Information on the mass transport process can also be gathered *ex situ* by different techniques of nanomicroscopy, such as atomic force microscopy (AFM).

The polarization of the writing beam has a strong impact on the SRG formation efficiency [68–72]. Although there are material-dependent parameters involved, as a rule of thumb, polarization combinations having an electric field gradient in the direction of the grating vector, such as p-p and RCP-LCP configurations, seem to produce larger-amplitude gratings than for instance the s-s configuration [52]. We note, however, that liquid-crystalline azo-polymers, for instance the ones reported by Seki and colleagues [73], may behave very differently from amorphous azo-polymers, which this thesis predominantly deals with. This highlights the fact that the macroscopic motions of azo-polymers are extremely complicated and driven by several distinct processes, the relative contribution of which de-

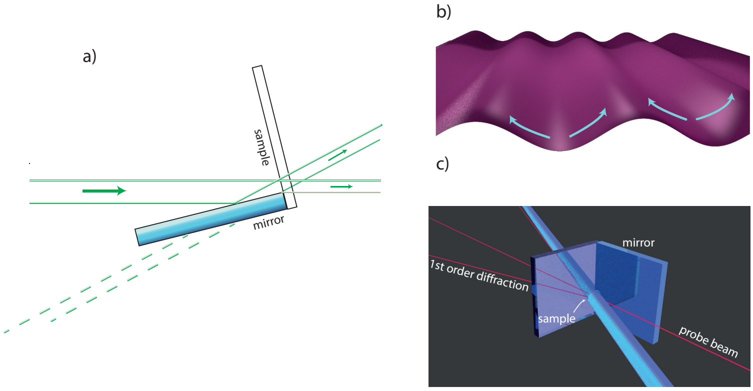

Figure 2.5. a) A schematic picture of the Lloyd's mirror setup for producing SRGs, b) the formation of a sinusoidal interference pattern and c) probing the SRG by observing the 1st order diffraction efficiency of the red probe beam.

pends on the details of the material system.

The efforts to understand the SRG formation have focused either on explaining the nature of the force moving the material [74–76], or on modeling the viscoelastic flow of the polymeric material during the formation of the surface pattern [77–80]. Very recently, Ambrosio and co-workers modeled the SRG formation in amorphous materials by a purely phenomenological model [81]. Their model explains correctly the experimentally observed phase shift of π between the resulting surface pattern and the incident interference pattern [71], and it addresses both the contribution of the total intensity and that of the electric field gradient of the interference pattern. However, the model is not yet linked to any underlying microscopic mechanism, leaving the SRG formation still unexplained.

The SRG formation efficiency has been shown to depend strongly on the molecular mass of the migrating units. For the p-p type configuration, Priimagi and co-workers showed experimentally that decreasing the molar mass of the migrating unit contributes positively to the grating modulation depth [82]. In addition, very recently, Sobolewska and co-workers showed that also the s-s configuration, typically producing only weak SRGs, can produce efficient SRGs, if the molar mass of the polymer is small enough [83].

From the perspective of fluid mechanics, it is tempting to experimentally probe the changes of the mechanical properties of the polymers under light illumination, since, in general, all the models describing the viscoelastic flow assume that the viscosity of the polymeric material is reduced from its bulk value to close to the value of the molten polymer under the light illumination [67, 79, 80]. However, it has been shown that the temperature rise of the polymer due to light intensities typically used in the grating inscription is only on the order of few kelvins [84], and also that heating of the sample above the glass transition temperature can erase the formed SRG in most of the amorphous azopolymer systems [52]. The most comprehensive study to date has been carried out by Karageorgiev and co-workers, who determined the absolute values for photoinduced changes in the elastic modulus and viscosity of the widely used covalently-functionalized pDR1M polymer using AFM-based load-penetration curves [85]. They clearly distinguished between light- and heat-induced processes showing that the changes in the elastic modulus are much more subtle than when heating the polymer above its glass transition, thus confirming that no light-induced heating is needed for the SRG process to take place in temperatures far below the glass transition.

To sum up, the origin of the SRG inscription still remains a conundrum, and as Ambrosio and co-workers suggest, it is likely that a well-selected combination of several microscopic mechanisms is needed to cover all the observed phenomena [81]. It is also noteworthy that the photo-orientation of the azobenzene molecules perpendicular to the polarization plane of the incident light still takes place and is likely to affect the SRG formation process, as suggested by Saphiannikova *et al.* [79] and experimentally observed by Zhang *et al.* [86, 87]. To make things even more complicated, also volume-density gratings within the bulk of the material have been reported, and the final diffraction grating is always a superposition of several gratings with different time dynamics and relative phases [88–90].

3. Supramolecular azobenzene complexes

3.1 Supramolecular chemistry as a tool for modern materials science

Design and fabrication of functional materials has been one of the main aims of synthetic chemistry for more than hundred years. Nevertheless, only relatively recently in 1978, the field of supramolecular chemistry was introduced by Jean-Marie Lehn, based on the research findings of the late 1960s and the early 1970s [91]. He later compiled the emerging knowledge of how to surpass the problems of synthetic chemistry by using spontaneously forming supramolecular bonds into his famous book *Supramolecular chemistry: Concepts and perspectives* [92]. According to Lehn, supramolecular chemistry is *"chemistry of molecular assemblies and intermolecular bond"* [91] and nowadays more generally *"chemistry beyond molecules"* [93]. From the very beginning, supramolecular chemists were inspired by the amazing ability of nature to produce complex and multifunctional structures by simple self-assembly of small molecules. Until today, the power of supramolecular chemistry has been shown, e.g., in the fields of molecular self-assembly, molecular recognition, template-directed synthesis, mechanically interlocked molecular architectures, biomimetics, and molecular machinery [93].

The simplest principle of supramolecular chemistry is to bring together two molecules with complementary binding sites, which are located within the molecules in such a way that the particular interaction between these sites is possible [93]. The variety of feasible noncovalent interactions as well as their strengths is huge: The strongest ionic bonds reach the strength of covalent bonds, 350 kJ/mol [94]; the weakest van der Waals forces are in the range of 0-5 kJ/mol. The most typical inter-

Table 3.1. Nature and the strengths of the most commonly-used supramolecular interactions [93,95].

Nature of interaction	Interaction strength (kJ/mol)
ion-ion	100-350
ion-dipole	50-200
halogen bonding	10-200
dipole-dipole	5-50
hydrogen bonding	4-120
cation-π	5-80
π-π stacking	0-50
van der Waals	0-5

molecular interactions employed by supramolecular chemists to date are listed in Table 3.1.

One of the requirements, and a benefit, of supramolecular chemistry is that the strength of the formed bonds is strong enough to surpass the energy of thermal randomization but, at the same time, weak enough so that the first contacts are not immediately trapped. Hence, the final structure will be self-optimized with the help of the dynamic and reversible character of the bonds [94]. Another important difference between covalent and supramolecular bonds lies in their thermodynamics: supramolecular bonds typically lack activation energy of formation. Indeed, they should be considered as equilibrium reactions, where the balance can be changed by delicate changes in the environmental conditions. For example, if the temperature is increased, the balance shifts towards breaking of the supramolecular bonds [93].

The materials studied in this dissertation are mainly based on hydrogen bonding, with the exception of one case study exploring the realm of ionic interactions. The definiton of hydrogen bonding was revised in 2011 [96], but it follows the pragmatic definition of Pimental and McMellan: *"A hydrogen bond exists between the functional group, A-H, and an atom or a group of atoms, B, in the same or different molecules, when (a) there is evidence of bond formation and (b) there is evidence that this new bond linking A-H and B specifically involves the hydrogen atom already bonded to A"* [97]. In practice, this requires that A in the covalent bond A-H withdraws electrons, leaving the proton partially unshielded (acting as hydrogen-bond donor) and that B (hydrogen-bond acceptor) has a lone-pair or polarizable π-electrons [98]. Phenol-pyridine hydrogen bonding, which the materials of this thesis are based on, falls into a class of moderate hydrogen bonds, having a bond-energy of 16-60 kJ/mol and a bond angle typically falling in the range of 130°-180° due to the fact that bent bonds are entropy-favored [98].

3.2 Supramolecular polymer-azobenzene complexes: a short review

Supramolecular strategies are employed in many light-driven machines [7]. At the molecular level, supramolecularly attached guest molecules can be twisted using azobenzene-containing host [99]. On a larger scale, supramolecular interactions can have an important role in controlling artificial muscles [6]. In Chapter 2, we discussed the photoinduced movements in conventional covalently-bonded side-chain azopolymers. This Section is devoted to treating the same photo-driven phenomena in supramolecular azobenzene-based complexes. In this context, the emerging interest in adopting supramolecular strategies can be traced back to three relative advantages compared to conventional covalently-bonded side chain polymers [100]. First, supramolecular strategies can prevent or decrease the aggregation tendency of the azobenzene molecules, thus enhancing the optical performance of the materials [101, 102]. A second advantage concerns the ease of preparation of these materials, which makes them more cost-effective in terms of potential device applications. A final advantage is that the dynamic character of these bonds allows selective detachment of the chromophores when desired [103, 104].

In the framework of supramolecular azobenzene complexes, azobenzene guests have been anchored to many different architectures of polymeric hosts, such as linear random copolymers [103, 105, 106], linear block copolymers [107, 108], crosslinked polymers [109–111], hyperbranched polymers [112] and dendrimers [112]. Additionally, low-molecular-weight azobenzene-based supramolecular materials have been introduced [94, 113].

The studies constituting this thesis mainly utilize linear homopolymers as hosts for azobenzenes, since keeping the architecture of the host material fixed and simple enables a comparison of any other fundamental properties. Therefore, we limit our focus to supramolecularly-functionalized linear homopolymers. Linear homopolymers can bind to azobenzene guests through different interactions, such as hydrogen bonding [82, 114–118], ionic bonding [86, 87, 119, 120, 120, 121], and halogen bonding [122].

Among the first studies on supramolecular control of photoresponsive polymers, in 2005, Priimagi and co-workers showed that the aggregation of well-known Disperse Red 1 (DR1) molecules can be reduced by non-covalent interactions between DR1 and the polymer backbone [114]. This interaction translates directly into a relatively more efficient photo-orientation of such supramolecular polymer-azobenzene complexes as compared to the photo-orientation of doped polymers [118]. Contemporarily, the development of ionically bonded polymer-azobenzene complexes was advanced by Xiao and colleagues. They reported that 1:1 ionic bonding between the methyl orange dye and ethylated poly(4-vinyl pyridine) (P4VP) results in a birefringence of ca. 0.07 with excellent temporal stability [123], and a year later, Zhang and co-workers achieved even higher birefringence values with very similar systems, the only difference being the use of methylated P4VP instead of the ethylated one [124]. Both Xiao and Zhang reported that the complexes formed a liquid crystalline smectic A mesophase. The excellent stability of the photoinduced anisotropic chromophore alignment was linked to the mutual tendency of the LC domain to self-align. Later on, Zhang and co-workers have studied extensively the effects brought about by flexible tails [87] and spacers [86] in stoichiometric ionic polymer-azobenzene complexes. In the former article, they concluded that long alkyl tails tend to decrease the temporal stability of photoinduced birefringence, and in the latter one they showed that the flexible spacer, placed between the photoactive unit and the polymer backbone, plays likewise an important role in the relaxation of the photoalignment. They concluded that the formation of LC structure is a key factor when aiming at high temporal stability of the birefringence: Out of all the complexes studied, the most rigid one, methyl orange complexed with methylated P4VP, resulted in the highest and the most stable birefringence.

According to the excellent contributions mentioned in the previous paragraph, it is not clear to what extent the LC order is preserved in the studied thin films, but the tendency to form LC mesophases can still be considered as a measure of the chromophore-chromophore interaction strength [86,87]. Although these examinations give decent guidelines for designing ionically-bonded polymer-azobenzene complexes for photoalignment purposes, the authors admit that the knowledge on the structure-function relationships is far from complete. When comparing these studies to the studies conducted in hydrogen-bonded systems, it is important to note the fundamental difference between the binding mechanism of these two strategies: Ionic systems favor the co-operative zipper-like binding of the guest units to polymers, whereas binding in hydrogen bonding is assumed to occur randomly [94]. In 2010, Wu and co-workers studied the photoinduced birefringence in a covalently-bonded side-chain azopolymer bearing azopyridine units [100] that were non-covalently coupled to an azobenzene (see molecule **2** in Fig. 4.1) to yield supramolecular bisazobenzene complexes [100]. At an equimolar degree of complexation, photoinduced birefringence was 0.1, and it increased slightly after ceasing the irradiation. This was attributed to the interactions between the side chains resulting in the formation of tiny wormlike birefringent texture, which could not be directly assigned to any well-known LC structure.

Photoinduced surface-relief formation in supramolecular homopolymer-azobenzene complexes was first reported by Gao and co-workers in 2007, who showed that pyridine-carboxyl hydrogen bonding is strong enough to transport the actuation of the azobenzene to the polymer backbone [116]. Zettsu and colleagues, in turn, demonstrated unambiguously that the supramolecular link between the photoactive units and the passive polymer matrix is essential for the formation of surface-relief structures in liquid-crystalline polymer-azobenzene complexes [103]. Contemporarily with this contribution, efficient SRG formation was also reported in ionically bonded polyelectrolyte-azobenzene complexes and sol-gel materials [109, 110].

In 2009, Priimagi and co-workers showed that the modulation depth of the formed gratings can be easily tuned by varying the degree of complexation, and that the modulation depth depends strongly on the molar weight of the polymer backbone [82]. Zhang and co-workers also reported on SRG formation in their complexes, finding an interesting relationship: the higher the photoinduced birefringence value, the more efficient the SRG formation [87]. Before generalizing their conclusions to our systems, it is important to note that completely different mechanisms might dominate the SRG formation in LC polymers compared to the amorphous ones. This is particularly evident in terms of the work of Seki and colleagues, who have shown that in soft LC polymers, it is essential to drive the azobenzenes to a *cis*-rich state instead of the efficient *trans-cis-trans* cycling of azobenzenes [73, 125, 126].

Very recently, Priimagi and co-workers have also shown that halogen-bonded polymer-azobenzene complexes seem to outperform the corresponding hydrogen-bonded analogues in SRG formation efficiency. This is attributed to the higher directionality of the halogen bonds compared to hydrogen bonds [122]. Halogen bonding also allows controlling the polymer-chromophore interaction strength through simple halogen-atom mutation, providing a unique tool for gaining fundamental understanding on the SRG formation process.

The purpose of this short review is to show that it is possible to fabricate efficient photoresponsive materials through ionic, hydrogen or halogen bonding between the host polymers and the azobenzenes units. Also, use of co-polymers of varying repeating units paves may lead to design of multifunctional stimuli-responsive materials [121]. One step at a time, we believe that the complexity of these materials will be greatly increased.

4. Material aspects affecting photoinduced birefringence and photoinduced surface-relief grating formation

This dissertation aims to explore some of the fundamental design principles of efficient light-responsive supramolecular materials. The main part of this thesis consists of a comparative study of hydrogen-bonded polymer-azobenzene complexes, described in detail in publications I-IV. In Section 4.1, we present the materials selected for these studies and attempt to elaborate the relevant physical and chemical parameters that govern their optical response. Section 4.2 features the material properties of thin films of these complexes, and after drawing some conclusions on the packing of the molecules based on the UV-Vis absorption spectra, we summarize the optical response of the materials in Section 4.3. Section 4.4 is devoted to a case study of SRG formation in ionically-bonded complexes of azobenzenes and dendritic molecules.

4.1 Overview of the studied materials

The polymer used as a backbone for preparing the polymer-azobenzene complexes in publications I-IV is poly(4-vinylpyridine) (P4VP), depicted in Fig. 4.1a. The pyridine group of P4VP acts as a hydrogen-bond acceptor due to its free electron pair. We used the well-known phenol-pyridine hydrogen-bonding [127,128], the existence of which we confirmed by infrared-spectroscopic measurements in each case.

We chose to work with five different azobenzene derivatives containg the phenol group, which acts as a hydrogen-bond donor (Fig. 4.1b). The key principle was to minimize the number of other functional groups within these molecules in order to ensure well-defined hydrogen bonding and to keep the different interactions occuring in the material systems as simple as possible. The chromophores used are 4-nitro-4'-hydroxyazobenzene (**1**), 4-cyano-4'-hydroxyazobenzene (**2**), 4-

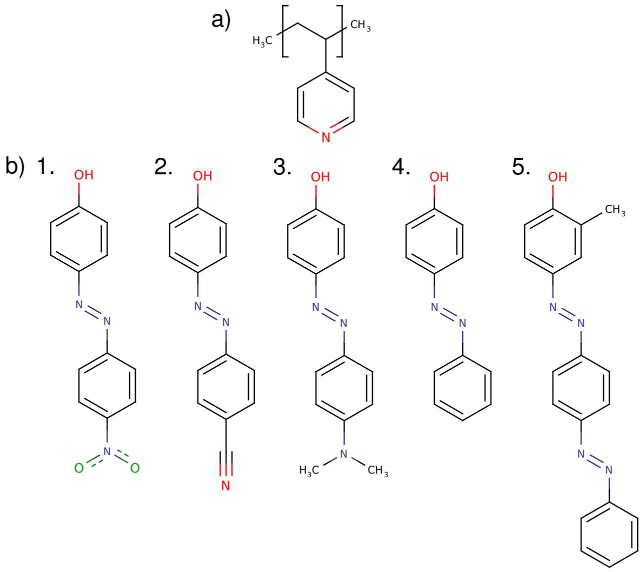

Figure 4.1. The structures of a) poly(4-vinylpyridine) (P4VP) and b) the azobenzene derivatives studied in publications I-IV.

dimethylamino-4’-hydroxyazobenzene (**3**), 4-hydroxyazobenzene (**4**) and Disperse Yellow 7 (**5**). From here on, they are referred to as chromophores **1**-**5**.

To understand the nature of the supramolecular complexes, it is imperative to first explore the properties of the studied chromophores as such. To begin with, none of the chromophores **1**-**5** contains flexible alkyl segments, making them rigid by their nature. In contrast, the bulkiness of the molecules in question varies. The cyano-substituted and the unsubstituted hydroxyazobenzenes, **2**, **4** and **5**, are rigid and rod-like. The nitro group of **1** forms a resonance structure with the benzene ring, the molecule exhibits planar configuration due to a partial double-bond character of this bond [129]. Also, the dimethylamino group in **3** is fairly planar [130], but **3** still supplements the comparison being slighly bulkier than **1**.

In addition to the conformation, two other important physical factors of these chromophores are the electrostatic dipole moment (polarity) and the transition dipole moment. Although both quantities originate from the internal charge distribution of the molecules, care must be taken in order to distinguish between them. The electrostatic dipole moment is largely responsible for the interactions between two similar molecules, whereas the transition moment determines the response of the molecule to an electromagnetic wave of given polarization.

The transition moments, μ_{ij}, can be determined by measuring the absorption spectra of the molecules in question in a dilute solution, and by calculating

$$|\mu_{ij}| = \frac{3\epsilon_0 \hbar c n}{l C \pi N_A} \int_{\Delta\nu} \frac{A(\nu)}{\nu} d\nu, \tag{4.1}$$

where n is the average refractive index of the solution, l is the path length over which the absorption occurs, C is the concentration of the absorbents in the solution, $A(\nu)$ is the absorbance of the solution, N_A is the Avogadro constant and $\Delta\nu$ is the frequency range over which the transition occurs [131]. For the dyes **1**-**4** the transition moments are comparable: 5.9 D, 5.4 D, 6.1 D and 4.5 D, respectively. Within the scope of this thesis, we have not calculated explicit values for the electrostatic dipole moments of the chromophores, but some qualitative observations based on their substitution pattern can still be made. The phenol group, common to all the molecules under investigation, is a weak electron donor [132]. As **1** and **2** contain electron-accepting nitro and cyano groups, respectively, they form a donor-acceptor structure with a relatively high ground state dipole moment. The dimethylamino group of **3**, on the other hand, is a relatively strong electron donor [132], hence we anticipate the ground-state dipole moment of **3** to be somewhat lower than for **1** and **2**. As opposed to **1**–**3**, the hydroxyazobenzenes **4** and **5** do not contain additional functional groups, indicating that their ground-state dipole moment is very low.

The intensive *trans-cis-trans* cycling, which is needed for efficient photoalignment and photoinduced mass-transport in amorphous polymers [10], is influenced by the rate constants for the photoisomerization reactions as well as the rate constant for the thermal *cis-trans* relaxation. Although the photoisomerization quantum yield in a viscous polymeric environment is much lower than in solution, the cycling between *trans* and *cis* conformations can still be efficient as long as the excitation wavelength is chosen to drive the photoisomerization to both directions.

4.2 Optical properties of the polymer-azobenzene complexes: spectral studies and packing considerations

Intermolecular interactions and molecular packing of the azobenzene units play a major role in the optical response of the material system they are incorporated into. Such interactions may alterate the UV-Vis absorption spectrum; hence we start the exploration of the optical properties of our materials by studying the spectra. In theory, through phenol-pyridine hydrogen bonding, every repeat unit of P4VP can be occupied by a chromophore. If the interactions between the chromophores are weak, the optical response of the material should increase linearly as a function of chromophore concentration [41, 133]. However, close proximity of the molecules may enable interactions between their excitonic states, which in turn alter their electronic properties. The aggregation is reported to diminish the optical response emerging from photoisomerization [114, 118, 132]. In contrast, publications I and II of this thesis, alongside with Ref. [134] argue that the chromophore-chromophore interactions can also bring about unexpected benefits. This section is thus devoted to such chromophore-chromophore interactions and their relation to the liquid-crystalline (LC) state of the material.

To evaluate the strength of the chromophore-chromophore interactions, simple estimates on the average distance, r, between the chromophores can be made by taking the cubic root of the volume occupied by one chromophore (inverse of the chromophore number density) in the material

$$r = \sqrt[3]{\rho_n^{-1}} = \sqrt[3]{\frac{V_{total}}{N_{dye}}}r = \sqrt[3]{\frac{\rho M_{dye}}{N_A f}}, \tag{4.2}$$

where ρ is the density of the matrial, ρ_n is the number density of chromophores in the material, M_{dye} is the molar mass of the chromophore, N_A is the Avogadro constant and f is the mass fraction of the chromophores in the polymer matrix. By assuming that addition of the chromophores does not change the density of the material from the density of pure P4VP (1.1 g/cm^3), we obtain an estimate for r as a function of the degree of complexation (the number of chromophores per one polymer repeat unit), as depicted in Fig. 4.2.

If two or more light absorbing chromophores are in the close proximity of each other, the exciton produced by the excitation of an electron upon absorption in one of the chromophores can transfer to the other chromophores by three different mechanisms, namely Dexter's mechanism of energy transfer [135], Forster's resonance energy transfer (FRET) [136, 137], and excitonic splitting that was proposed by Kasha and coworkers [138]. The distance dependencies of the above-mentioned mechanisms are e^{-2r}, r^{-6}, and r^{-3}, respectively. Based on the calculations of Scholes and Ghiggino, the chromophore-chromophore distance estimated for our case makes the Dexter's mechanism an implausible explanation [139]. FRET, on the other hand, does not shift the energy bands of the chromophores. Hence, the observed UV-Vis spectral shifts must be accounted

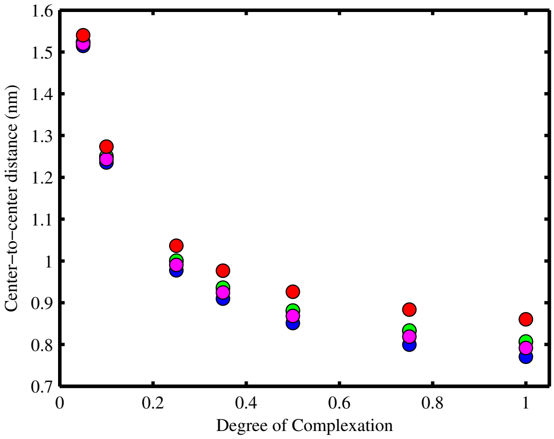

Figure 4.2. Center-to-center distance of the chromophores **1** (green), **2** (magenta), **3** (cyan), **4** (blue) and **5** (red) in P4VP complexes as a function of the degree of complexation. The cyan spheres are totally covered by the green ones, because the molar masses of **1** and **3** differ only by 1.91 g/mol.

for by chromophore-chromophore interactions causing excitonic splitting.

In excitonic splitting, the energy levels of the excited states of two adjacent molecules fuse into two common excited states, one having higher and the other lower energy than the monomer level. In the case of an excitonic dimer, this energy difference from a van der Waals corrected monomer level can be calculated from

$$\Delta E = \frac{2|\mu|}{r^3}(1 - 3\cos^2\theta), \tag{4.3}$$

where μ is the transition dipole moment of the monomer, r is the center-to-center distance between the molecules, and θ is an angle that depends on the positions of the monomers with respect to each other [138], as shown in Fig. 4.3.

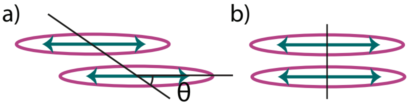

Figure 4.3. a) The angle, θ, between the transition moments and the center-to-center line of the dimer, and b) the sepcial case of θ being 90° leading to side-by-side packing and H-aggregation.

Depending on the geometric configuration of the monomers, transition to only one of the two states is allowed. If the angle θ is more than 54.7°, only the higher energy state is allowed resulting in a blue shift of the absorption maximum (H-type aggregation). When θ is in the range of 0°-54.7°, a red shift, referred to as J-aggregation, is observed. This model can easily be generalized to multiple interacting chromophores [39, 140].

Now that we have established the conceptual background for the spectral changes, it is time to explore the actual spectra measured from the spin-coated films of the polymer-azobenzene complexes. The UV-Vis spectra for the degrees of complexation of $x = 0.05$ (every 20th polymer repeat unit occupied by a chromophore) and $x = 1.0$ (each polymer repeat unit occupied) for P4VP(**1**)$_x$ and P4VP(**3**)$_x$ are shown in Fig. 4.4. This figure demonstrates that a hypsochromic shift occurs in P4VP(**1**)$_x$, whereas no shift of the absorption maximum is observed for P4VP(**3**)$_x$, the spectrum of which is only broadened as a function of increasing degree of complexation.

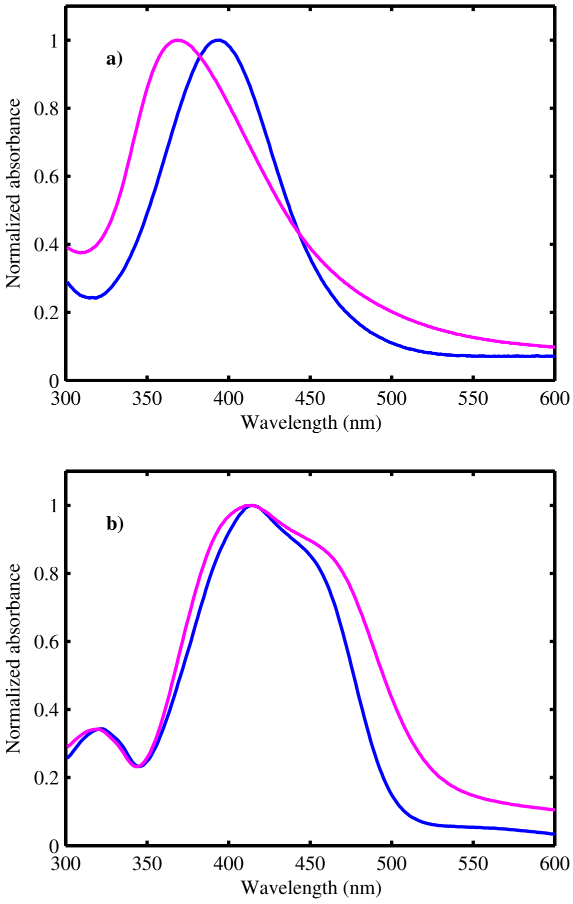

Figure 4.4. Top: The spectra of P4VP(**1**)$_{0.05}$ (blue) and P4VP(**1**)$_{1.0}$ (magenta). Bottom: The spectra of P4VP(**3**)$_{0.05}$ (blue) and P4VP(**3**)$_{1.0}$ (magenta).

Table 4.1 lists the hypsochromic shifts of the absorption maxima for all the monoazo-based complexes when comparing the degrees of complex-

Table 4.1. Wavelength differences of the absorption maxima of the P4VP(X)$_{0.05}$ and P4VP(X)$_{1.00}$ complexes.

Chromophore	Hypsochromic shift (nm)
1	25
2	24
3	1
4	4

ation x = 0.05 and x = 1.0, studied in publications I-II. From this table we see that the hypsochromic shift of P4VP(**2**)$_x$ is identical to that of P4VP(**1**)$_x$, and negligible for P4VP(**3**)$_x$ and P4VP(**4**)$_x$. This difference systematically follows the features presented in Chapter 4.1: dipolar and rod-like molecules undergo pronounced excitonic coupling, whereas for (i) apolar or (ii) dipolar but bulky chromophores the intermolecular interactions are less significant.

The above-mentioned observation seems inconsistent with the calculated results shown in Fig. 4.2, which claim that the center-to-center distance for molecules **1**-**4** is approximately the same. Indeed, taking into account also their comparable transition dipole moments, one would expect similar kinds of spectral shifts to occur for all the molecules. This discrepancy points out that dipolar and planar molecules pack more tightly into a complex, rendering the approximation of constant density in the calculations too simplified.

The notion that all the chromophores **1**-**5** are of mesogenic character, i.e. rigid and anisotropic [141], made us to study the formation of LC mesophases in the complexes. When a chromophore hydrogen-bonds to P4VP, an interplay between the tendency of the mesogenic segments to self-align and the polymer to adopt a random-coil configuration takes place. As the degree of complexation increases, the balance of this competition changes to favor the self-alignment – particularly for polar rod-like chromophores such as **1** and **2**. Figure 4.5 shows a polarized optical micrograph of a thin film of P4VP(**2**)$_{1.0}$, clearly indicating the anisotropic ordering of the material into small birefringent domains. Similar birefringent textures were also observed for the P4VP(**1**)$_{1.0}$ complex. Hence, these spacerless polymer-azobenzene complexes seem to form a small-domain mesophase, which cannot be unambiguously assigned to any LC phase. When the pendant groups are less polar (like **4** or **5**), or when they bear slightly bulkier substituent groups (such as **3**), mesophase formation is restricted and the complexes remain isotropic even at the equimolar degree of complexation.

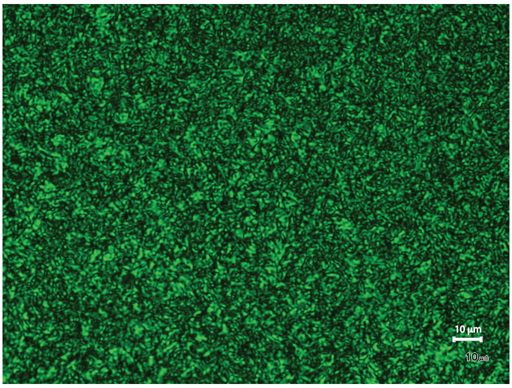

Figure 4.5. Polarized optical micrograph image of P4VP(**2**)$_{1.0}$.

Typically, a flexible spacer between the polymer and the rigid mesogen units is required to allow for sufficient mobility of the side-chain groups to exhibit LC mesophases [142, 143]. Evidence of the advantageous effect of the long alkyl segments in the formation of well-ordered structures is given by de Wit and co-workers, whose phenol-pyridine hydrogen-bonded polymer-azobenzene complexes are similar to ours, save the flexible alkyl tails of the chromophores [117]. Their complexes self-assemble into well-defined smectic A mesophase, whereas the self-assembly of our complexes can be frustrated due to the lack of any plasticizing units. We also note that very similar rigid molecules hydrogen-bonded to a slightly more plasticized systems, such as a copolymer of 4-vinyl pyridine and butyl acrylate [144] or a polyacrylate-based homopolymer [145], result in nematic orientation. Based on these results, we claim that in order to obtain a larger-domain-size LC structure for the P4VP(**1**)$_{1.0}$ and P4VP(**2**)$_{1.0}$ complexes, more plasticizing units would be needed. Also the immense impact of adding monoalkyl or longer branching units to destruct the self-assembly through sterical hindrance is observed in the literature [146], and this observation correlates well with the amorphous phase obtained for P4VP(**3**)$_{1.0}$.

When comparing the self-assembly of P4VP(**1**)$_{1.0}$ and P4VP(**2**)$_{1.0}$ to the ionic equimolar complexes introduced by Xiao *et al.* and Zhang *et al.* [123, 124], an interesting difference is observed. Both groups obtained a smectic A mesophase in their charged polyelectrolyte-azobenzene complexes, whereas the ordering of our spacerless hydrogen-bonded complexes is not so well defined. This discrepancy can be reasoned by the fact that ionic polymers tend to exist in a more straight conformation than uncharged polymers such as P4VP due to the repulsion by similarly charged units of the polymer.

4.3 Optical properties of the polymer-azobenzene complexes: remarks on the photoinduced birefringence and surface-relief grating formation

As discussed in Section 4.2, there is a systematic difference between the spectral behavior of the P4VP($\mathbf{1}$)$_x$ and P4VP($\mathbf{2}$)$_x$ compared to P4VP($\mathbf{3}$)$_x$ and P4VP($\mathbf{4}$)$_x$ as a function of azobenzene concentration. A systematic difference between these materials was also observed in photoinduced birefringence measurements. At high degrees of complexation (x > 0.5), the complexes based on **1** and **2** exhibit strongly enhanced and stabilized birefringence, whereas in the **3**- and **4**-based complexes such enhancement is not observed (see Fig. 4.6a). More specifically, P4VP($\mathbf{1}$)$_{1.0}$ and P4VP($\mathbf{2}$)$_{1.0}$ gave rise to saturated birefringence exceeding 0.1 with excellent long-term stability, thus reaching or even surpassing the performance of the corresponding covalently-functionalized polymers [10].

Taking into account the appearance of the small-domain LC mesophase in these complexes and the generally-accepted concept that collaborative effects in LC materials enhance the photo-orientation as compared to amorphous materials [10], we studied the contribution of a single chromophore on the photoinduced birefringence. This was done by dividing the saturated birefringence by the number density of the chromophores. For P4VP($\mathbf{1}$)$_x$ and P4VP($\mathbf{2}$)$_x$, the contribution of a single chromophore to the overall birefringence is remarkably increased at high degrees of complexation, compared to the case of "individual" chromophores at low degrees of complexation. A similar increase and stabilization of the saturated birefringence at high azobenzene concentration was observed by Wu and coworkers, who also studied phenol-pyridine hydrogen-bonded complexes, and linked the observed enhancement to the interplay between hydrogen bonding and chromophore-chromophore interactions [100].

The excellent correlation between the increased chromophore-chromophore interactions observed in the UV-Visible spectra, the appearance of the LC phase, and the enhancement and stabilization of photoinduced birefringence, indicate that the optical response can be conveniently con-

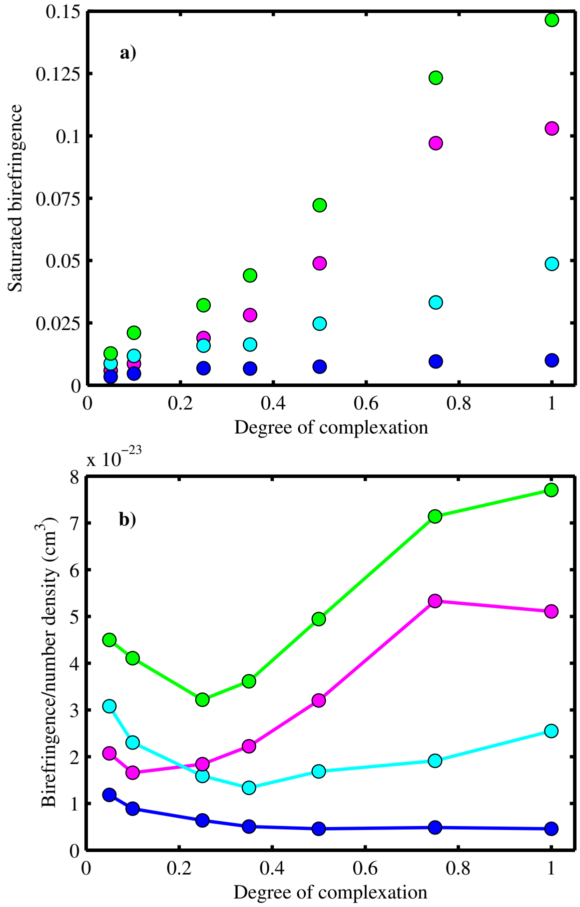

Figure 4.6. a) The saturated photoinduced birefringence and b) the contribution of a single cromophore to saturated photoinduced birefringence as a function of degree of complexation in P4VP(**1**)$_x$ (green), P4VP(**2**)$_x$ (magenta), P4VP(**3**)$_x$ (cyan) and P4VP(**4**)$_x$ (blue) complexes. Lines are drawn to guide the eye.

trolled by tuning the mixing ratio of the constituents. This correlation also suggests that the photo-orientation behavior of P4VP(**1**)$_x$ and P4VP(**2**)$_x$ complexes at high degrees of complexation can be linked to collaborative movements of the azobenzene molecules. A natural question then arises, whether the collaborative motions are driven purely sterically, by dipole-dipole interactions, or by multiple isomerization events due to sharing the energy of one photon over the exciton band. To tackle this question, Natansohn and co-workers synthesized two copolymers bearing a photoactive Disperse red 1 -containing monomer and either a polar or an apolar photo-inert co-monomer. They concluded that polarity of the used monomers is essential for obtaining co-operative photoalignment upon irradiation [147, 148], as reported also by Fukuda and co-workers [149] and Saishoji and co-workers [150]. In addition, Gahl and co-workers reasoned that excitonic sharing of an electron, which occurs at femtosecond timescales, easily inhibits the photoisomerization, known to happen in picosecond timescales [140]. Therefore, our results support the concept of collaborative photo-orientation caused by dipole-dipole interactions between the dye molecules. This brings us to our first intermediate conclusion: *(i) The interplay between hydrogen bonding and the chromophore-chromophore intermolecular interactions leads to enhancement and stabilization of the photoinduced birefringence.*

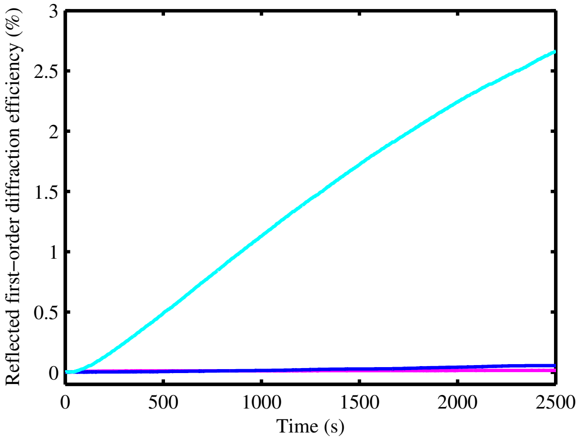

Figure 4.7. The first-order diffraction efficiency upon SRG inscription for P4VP(**2**)$_{1.0}$ (magenta), P4VP(**3**)$_{1.0}$ (cyan) and P4VP(**4**)$_{1.0}$ (blue).

As opposed to the performance in photoinduced birefringence measurements, P4VP(**3**)$_x$ and P4VP(**5**)$_x$ were by far the most efficient complexes in terms of photoinduced SRG formation. Figure 4.7 presents the first-order diffraction efficiency of P4VP(**2**)$_{1.0}$, P4VP(**3**)$_{1.0}$ and P4VP(**4**)$_{1.0}$ upon SRG inscription as a function of time. The response of P4VP(**3**)$_{1.0}$, containing polar, but bulky azobenzenes, by far overwhelms the other monoazobenzene complexes. In 2008, Elbing and colleagues observed that rigid and rod-like molecules pack much more tightly than their analogues bearing two methyl side groups [146]. Following their logic, there might be much less free volume around the rigid and rod-like molecules in the complexes P4VP(**1**)$_{1.0}$ and P4VP(**2**)$_{1.0}$ than in P4VP(**3**)$_{1.0}$. Also the higher tendency of these complexes to photo-orient might counteract the SRG formation process in these materials, even if also counterexamples exist [33, 124]. To sum up, this brings to us to our next conclusive argument: *(ii) The chromophore-chromophore interactions in P4VP(**1**)$_{1.0}$ and P4VP(**2**)$_{1.0}$ de-*

celerate the SRG formation.

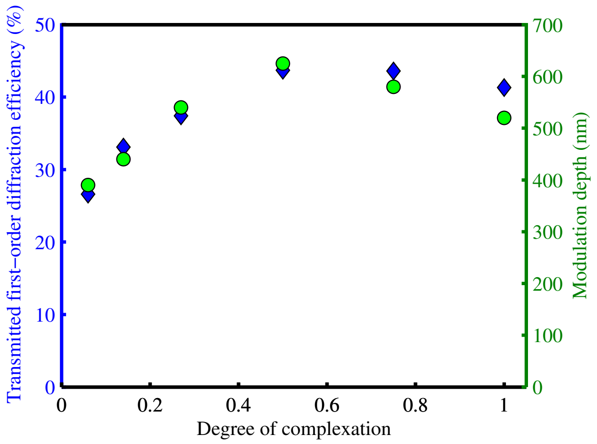

Figure 4.8. The saturated first-order diffraction efficiency (blue) and the modulation depth (green) for P4VP(**5**)$_x$ complexes.

Figure 4.8 presents the maximum first-order diffraction efficiency and the modulation depths of the obtained SRGs for P4VP(**5**)$_x$ complexes studied in publication III. We note that we were able to inscribe SRGs with a modulation depth of 400 nm in the P4VP(**5**)$_{0.06}$ complex, in which less than every 15th repeat unit is occupied by a chromophore. For the polymer chains we used, this means that there were on average only three "molecular azobenzene motors" driving the formation of the SRGs in one polymer chain. We also note that we have not yet explored the lower limit of the degree of complexation needed for efficient SRG formation. As already speculated in the previous paragraphs, the more spacious packing of the molecules leading to amorphous character of the materials is one reason behind efficient SRG formation. Another beneficial factor is related to the structure of the complexes, namely to the lack of a flexible spacer between the polymer and the azobenzenes.

The transfer of kinetic energy from an isomerizing azobenzene unit to passive polymer chains remains an open question, and is still very challenging to approach experimentally, although the forces exerted by the contraction of a single azobenzene unit upon irradiation have been successfully measured [151, 152]. It has also been shown that the rigidity of the main-chain azopolymer is a key factor for obtaining a large photoinduced decrease of viscosity in solution [153]. In addition, Zhang and co-workers [86] discovered that the most efficient energy transfer and SRG formation in their ionically bonded side-chain polymers occurred in the most rigid MO/PVP complex, which did not have any spacer and the SRG formation efficiency diminished with an increase in the alkyl spacer length. These results suggest that a similar relation for amorphous materials might exist.

Publication IV attempts to further elucidate the reasons behind the efficient SRG formation in P4VP(**5**)$_x$. The mechanical properties in two different amorphous materials, P4VP(**5**)$_{0.5}$ and the well-known covalently-functionalized polymer, poly(Disperse Red 1 acrylate) (pDR1A), are probed in darkness and under light illummination by nanoindentation. Clear photoinduced softening was observed in both cases (as illustrated in Fig. 4.9 for P4VP(**5**)$_{0.5}$), but the effect was markedly stronger for the spacerless polymer-azobenzene complex than for the conventional side-chain polymer bearing an ethylene spacer.

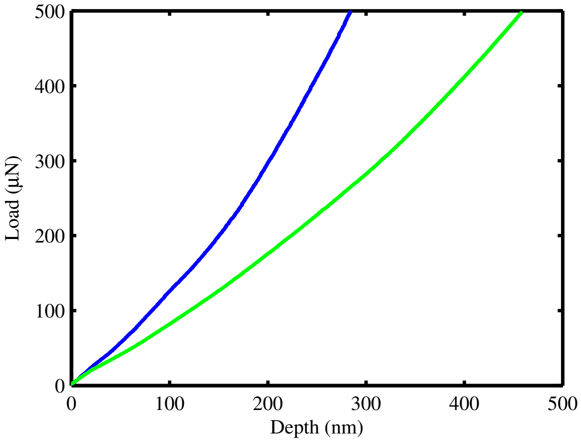

Figure 4.9. Load-depth curves for nanoindentation experiments for thin films of P4VP(**5**)$_{0.5}$ in dark (blue) and under illumination (green).

By varying the stress loading rate on the two materials in dark and upon illumination, we were able to grasp the rate-dependent mechanical properties of the materials, which in simplified models are related to viscosity. Our data suggest that in P4VP(**5**)$_{0.5}$, far less light energy is needed to induce a much greater photosoftening than in pDR1A. Although there are also other possible explanations for the larger photoplasticization of the no-spacer complex, the lack of energy-dissipating alkyl chains is likely to have a positive contribution to the observed photosoftening.

This leads us to the next intermediate conclusion: *(iii) The no-spacer-structure seems to translate the kinetic energy of the azobenzene molecule more efficiently to the polymer chain compared to materials containing* *flexible spacers between the isomerizing units and the polymer, thus making the photosoftening effect larger.*

Another important conclusion can be drawn by comparing the SRG formation efficiency of the apolar P4VP(**4**)$_x$ and P4VP(**5**)$_x$ complexes. The negligible SRG formation in P4VP(**4**)$_x$ is well in line with the earlier observation of Ho and co-workers who reported that efficient *trans-cis-trans* isomerization cycling is not induced in polymers containing apolar chromophores as side groups [44]. In this context, the efficient mass-transport in P4VP(**5**)$_x$ is surprising. However, the existing literature is not completely consistent on the role of the polarity of a molecule to produce efficient SRGs, since Seki and colleagues have demonstrated that in many apolar side-chain polymers SRG formation can be extremely efficient [73, 125, 126]. We anticipate the reason for the striking difference in the SRG formation in these two complexes to be related to the presence of the two isomerizable units in P4VP(**5**)$_x$, since the chromophores are otherwise very similar. Upon the isomerization of one of the units, the dipole moment of the molecule increases, and thus the second isomerization can be considered to be an isomerization of a polar molecule (the *cis*-azobenzene, when attached to *trans*-azobenzene, may be viewed as a polar substituent). This suggestion brings us to our final conclusion concerning the linear hydrogen-bonded polymer-azobenzene complexes: *(iv) Placing an additional photoresponsive unit to a chromophore can drastically alter the photoresponsive properties.*

4.4 A case study: photoinduced SRG formation in cationic dendrons, dendrimers and dendronized polymers complexed with Ethyl Orange

Publication V differs from publications I-IV by the fact that it uses branched dendritic host materials ionically complexed with Ethyl Orange (EO) guests. The results obtained using ionic azo-containing dendrons (DDx-EO) and dendrimers (DMx-EO), both comprising three generations (x=1-3) (see Fig. 4.10), nicely complement the statements made based on the linear polymer-azobenzene complexes.

Dendritic molecules, due to their perfectly-defined monodisperse structure, allow us to systematically study the effect of molecular architecture and bulkiness on the mass-transport properties. An additional advantage of the dendritic structures is their capability to accommodate densely many functional groups on their periphery [154]. The molecular weights and number of peripheral units of the cationic host molecules used are listed in Table 4.2, alongside with the mass fraction of the photoactive EO molecules and the absorption maxima of the complexes.

Table 4.2. Molecular weight and the number of the peripheral units of uncomplexed dendritic molecules, weight percentage of EO units in the complexed molecules and the absorption maxima of the complexes.

Code	Molecular weight (g/mol)	Number of peripheral units	EO fraction (et%)	λ_{max} (nm)
DD1-EO	282.3	2	70.2	414
DD2-EO	752.9	4	63.9	429
DD3-EO	1603.8	8	62.4	435
DM1-EO	1048.3	6	65.6	423
DM2-EO	2550.0	12	61.0	423
DM3-EO	5144.8	24	60.8	430

Small-angle X-ray scattering analysis revealed that out of the six complexes treated here, only DD1-EO, the first-generation dendron complex, formed a well-ordered microphase-separated structure, whereas the other five complexes were rather poorly organized. The lack of well-ordered structures can be explained by the absence of softening alkyl chains in the EO surfactant, which makes the complexes very rigid. The microphase separation of DD1-EO also gives rise to a clear hypsochromic shift in the absorption maximum (see Table 4.2), indicating excitonic coupling between the adjacent azobenzene units. DD2-EO, DD3-EO, and all the dendrimer-based complexes, DMx-EO, show a single broad low-intensity scattering peak, implying a rather poor organization.

The evolution of the first-order diffracted signal during the SRG inscription is plotted in Fig. 4.11a for the dendron-based and in 4.11b for the dendrimer-based complexes. Our first observation was that the microphase-separated DD1-EO complex exhibited remarkably inefficient SRG inscription compared to the other, disordered, complexes. This is well in line with our observations made with the polymer-azobenzene complexes, as the complexes exhibiting liquid crystallinity (e.g. P4VP(**2**)$_{1.0}$) need far more energy to undergo mass transport than the more disordered complexes, such as P4VP(**3**)$_{1.0}$.

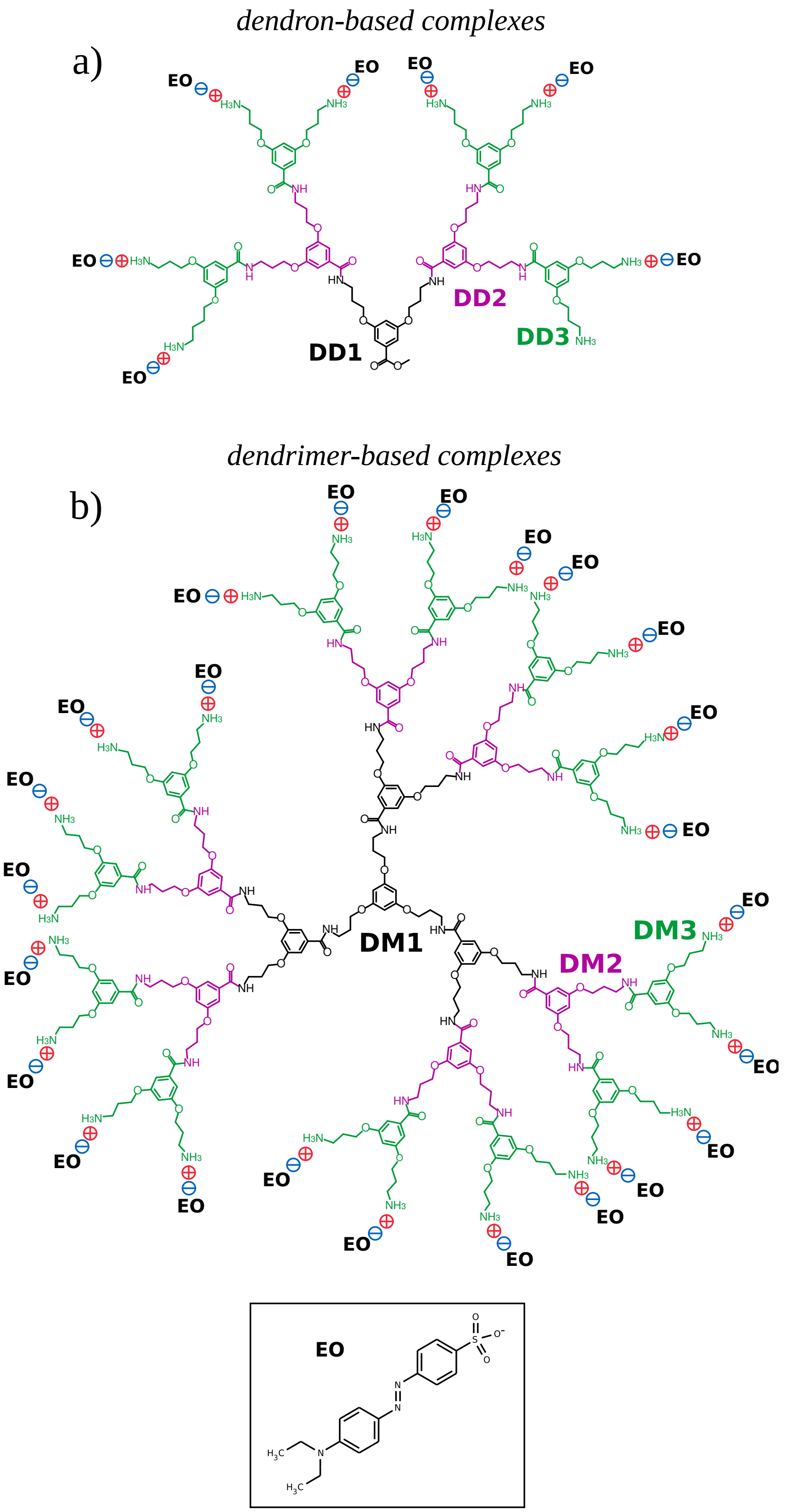

Figure 4.10. The structures of the a) dendrons and b) dendrimers, and Ethyl Orange (EO) used in publication V.

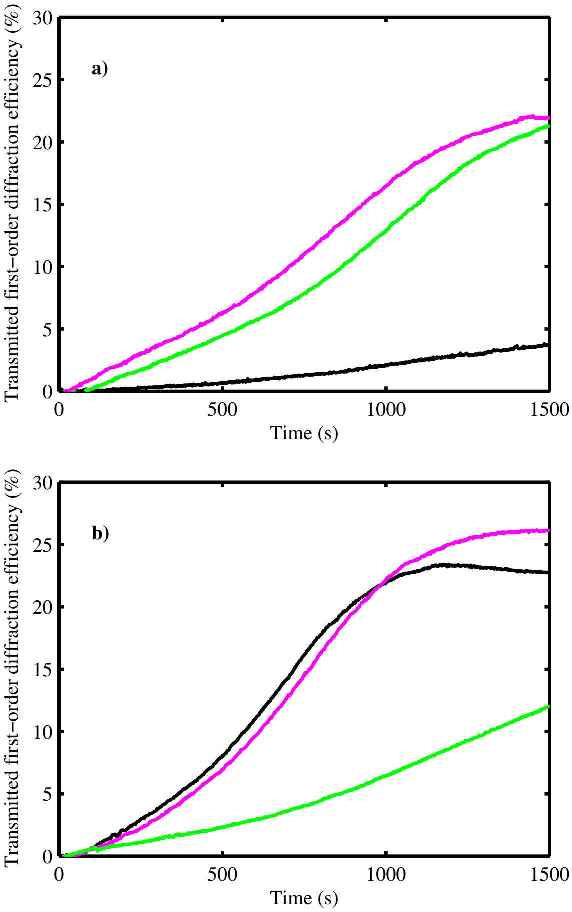

Figure 4.11. The first-order diffraction efficiency for a) DDX-EO and b) DMX-EO complexes upon SRG inscription. Black, magenta and green indicate the 1st, 2nd and the 3rd generation, respectively.

No common consent exists on the effect of microphase separation on the mass transport ability of the material: Morikawa and colleagues have shown that SRG formation is a clever way to manipulate self-assembled block-copolymer structures [155, 156] and efficient SRG formation has been demonstrated in self-assembled supramolecular side-chain LC homopolymers [87, 123]. On the other hand, Frenz and co-workers noticed that self-segregated di-block-copolymer structures suppress SRG formation compared to similar but disordered random copolymers [157]. The observation that the microphase separation inhibits the SRG formation agrees well with the latter mentioned report as well as with our intermediate conclusion *(ii)*, arguing that chromophore-chromophore interactions decelerate SRG formation.

As noted already by Gharagozloo-Hubmann and colleagues, the benefit of moving from linear polymer architectures towards more branched molecules makes it possible to differentiate between the effects of increasing polymer entanglement and molecular weight, which, for linear architectures, are interrelated [158]. The five disordered complexes, DD2-EO, DD3-EO, DM1-EO, DM2-EO, and DM3-EO, form an excellent basis for studying the effect of molecular weight of the complexes on the mass-transport efficiency since they bear approximately the same mass percentage of photoactive EO molecules. The molar mass of an uncomplexed DM3 molecule is 5144.8 g/mol, whereas the masses of the other complexes fall in the range of 752.9 g/mol - 2550.0 g/mol (see Table 4.2). On the other hand, the SRG inscription in the heavier DM3-EO complex is significantly less efficient than in the other complexes (see Fig. 4.11), which indicates that alike microphase separation, overly large size of the migrating units destructs the SRG formation process. This leads us to our final conclusive statement: *Dendritic molecular architectures provide complementary information to the studies made with linear polymer architectures, since the molecular weight can be controlled without chain entanglement, while keeping the aggregation state of the photoactive molecules the same.*

5. Conclusions and outlook

The results presented in this dissertation can be divided into two parts. The main part comprises a comparative study of the photoinduced properties of five different hydrogen-bonded polymer-azobenzene complexes. The complementary part consists of a case study exploring ionic complexes formed of azobenzenes and dendritic host molecules. This work is an ode to supramolecular binding strategies in preparation of future photonic and photoresponsive materials, as herein, both hydrogen bonding and ionic bonding provided state-of-the-art materials with efficient photoalignment and surface-relief grating formation capacity. One of the key advantages of hydrogen-bonded complexes in comparison to ionic systems is the ease of varying the relative amount of photoactive units, which enabled us to study the effect of packing density on the material properties.

The main findings concerning the studied phenomena, photoinduced birefringence and photoinduced surface-relief grating formation, are collected into five conclusive arguments, referred to by their roman numerals below. When polar and rod-like azobenzene derivatives are complexed with a polymer, chromophore-chromophore excitonic coupling comes into play when a certain threshold degree of complexation is exceeded. The interplay between the hydrogen-bonding and chromophore-chromophore interactions leads to *(i) enhancement and temporal stabilization of the photoinduced birefringence* and to *(ii) deceleration of the surface-relief grating formation.* The balance between these intermolecular interactions should be taken into account when designing materials for a specific application, which can easily be done by controlling the polymer-chromophore interaction, and the nature and the relative concentration of the azobenzene units.

One of the advantages of our polymer-azobenzene complexes is the lack of flexible spacer-units between the host polymer and the azobenzene guests brought up by the supramolecular functionalization. This particular feature leads us to the next conclusive remark: *(iii) The spacerless structure seems to translate the kinetic energy of the azobenzene molecules efficiently to the polymer chains*, which gives rise to pronounced light-induced softening of the spacer-free supramolecular complex compared to a covalent polymer, which contains a short ethylene spacer between the photoactive units and the polymer backbone. By comparing the surface-relief grating formation efficiency in polymer complexes of corresponding monoazo and bisazo derivatives, we found that *(iv) placing an additional photoresponsive azo unit to a chromophore can drastically change the photoresponsive properties*. A fundamental study of the effect of two azo groups on the photochemistry of bisazobenzenes is yet to be done.

To explore the effect of the architecture of the host molecule on the surface-relief grating formation, we extended our studies from linear hydrogen-bonded homopolymer-azobenzene complexes to ionically-bonded complexes between azobenzenes and dendritic structures. Such more branched structures are beneficial, because *(v) they provide complementary information to the knowledge gained with linear polymers on the surface-relief grating formation, such as the effect of molecular weight.* Microphase-separation, driven by chromophore-chromophore intermolecular interactions, was observed to clearly decelerate SRG formation, which strongly supports the remark *(ii)* derived from linear homopolymer-azobenzene complexes.

The results of this thesis depict relationships between material parameters and the optical phenomena in the special cases of photoinduced birefringence and surface-relief grating formation; yet little is concluded on the applicability of these results to other light-driven motions. Since the knowledge about the connection between the different light-induced phenomena is not yet well-established, we admit the challenge in extrapolating these guidelines. To elucidate this issue, it will be necessary to conduct more fundamental studies on the links between the material parameters and the macroscopic phenomena. Nevertheless, we have shown that supramolecular approaches enable a facile comparison of different material parameters, ranging from simple physical parameters, such as polarity of a single azobenzene molecule, to holistic properties of the material system, such as the packing density of the chromophores. The use of these techniques is not limited to the investigation of these particular optical phenomena, and accordingly the supramolecular approach can be generalized to any study in which accurate control and variation of material parameters is needed, such as non-linear optical materials or photoluminescence-based applications.

Naturally, the picture we have formed of the design of efficient photoresponsive materials based on the five arguments given above, is far from complete. The current knowledge could be further deepened by examining a few more material parameters. For instance, the free volume of the polymer, which is likely to have a significant influence on the photoisomerization efficiency, could be measured by means of positron annihilation spectroscopy. In addition, accurate density measurements of the polymer-azobenzene complexes as a function of azobenzene concentration could confirm the claims about the polar, rod-like chromophores being more tightly packed than more bulky chromophores. These studies could also greatly benefit from computational support: for example, calculation of the interaction strengths and bond angles within the supramolecular complexes could be of great importance in understanding the photomechanical response of azobenzene-based materials. In addition, the excitonic coupling of the molecules could be modeled and compared to the observed spectral changes.

As mentioned in Chapter 2, the surface-relief grating formation still lacks a detailed explanation. We call for the development of a more accurate model on this fascinating phenomenon and anticipate that through a more comprehensive theoretical understanding, the optimization of the materials will further improve. Additionally, more detailed experimental research on light-induced softening of the azobenzene-containing polymers might reveal fundamental connections between the surface-relief grating formation, macroscopic actuation, and light-induced changes in the mechanical properties of the materials. Such experiments may also deepen the understanding of the conditions, which inhibit the light-induced mass transport process.

As discussed in the Introduction, we believe that several cross-disciplinary fields may benefit from our results. In the context of liquid-crystal-based optical devices, we have recently observed that the optical response of the material can be greatly enhanced, when employing polymer-azobenzene complexes instead of single azobenzene units as dopants in liquid crystals. Also the interface between biology, medicine, and photoresponsive materials research is of considerable interest. The search for externally-controllable drug release systems might be addressed by supramolecular micellar structures that can change their geometry upon illumination.

Overall, the model systems presented in this research are extremely simple as compared to the complexity of the supramolecular structures in nature. Many challenges that today seem unsurmountable, may be solved by taking into account the guidance of nature as an endless source of ideas and inspiration as well as the versatility of supramolecular strategies. If we keep our eyes and minds open, perhaps one day our photoresponsive materials are as optimized as the survival strategies of archeons, which are the masters of adapting to the most extreme conditions on this globe.

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