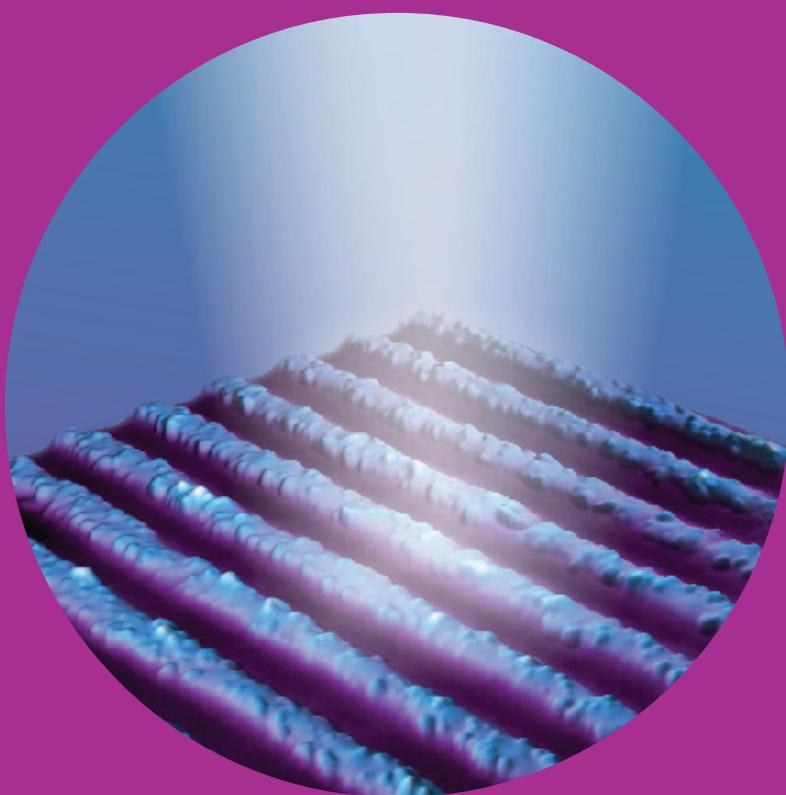


Light-fuelled motions in azobenzene-containing materials

From supramolecular design to new applications

Jenni E. Koskela



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Jenni E. Koskela

A doctoral dissertation completed for the degree of Doctor of Science (Technology) to be defended, with the permission of the Aalto University School of Science, at a public examination held at the lecture hall AS1 of the school on 23 January 2015 at 12 noon.

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Aalto University publication series

DOCTORAL DISSERTATIONS 213/2014

© Jenni E. Koskela

ISBN 978-952-60-6030-9 (printed)

ISBN 978-952-60-6031-6 (pdf)

ISSN-L 1799-4934

ISSN 1799-4934 (printed)

ISSN 1799-4942 (pdf)

<http://urn.fi/URN:ISBN:978-952-60-6031-6>

Unigrafia Oy
Helsinki 2014

Finland



441 697
Printed matter

Author

Jenni E. Koskela

Name of the doctoral dissertation

Light-fuelled motions in azobenzene-containing materials: From supramolecular design to new applications

Publisher School of Science

Unit Department of Applied Physics

Series Aalto University publication series DOCTORAL DISSERTATIONS 213/2014

Field of research Engineering Physics

Manuscript submitted 7 October 2014

Date of the defence 23 January 2015

Permission to publish granted (date) 26 November 2014

Language English

☐ **Monograph**

☒ **Article dissertation (summary + original articles)**

Abstract

Azobenzene-containing materials represent a versatile class of stimuli-responsive systems, in which light can be used to trigger a variety of fascinating phenomena. Owing to their rapid and reversible photoisomerization, azobenzenes are efficient molecular photoswitches that enable effective control over a number of properties of the host material. Moreover, the nanoscale photoisomerization reaction can actuate various large-scale molecular motions in the system, such as the light-driven macroscopic mass transport. Under certain conditions, polarized light can be used to induce macroscopic movement in a glassy material, which results in a well-defined topographic pattern on the film surface. During the past two decades, a vast amount of research has been devoted to understand the microscopic origin of these motions. On the other hand, the light-induced phenomena in azomaterials have demonstrated huge potential in numerous application areas ranging from photonics to biology. Still, many aspects of the intricate relationship between the light-triggered macroscopic effects and the material properties remain unresolved.

This thesis aims to unveil new possibilities for the light-induced motions in terms of material design and application potential. Importantly, the recent advancements in supramolecular design of light-responsive materials are exploited in order to present new implications on the surface patterning phenomenon and to explore its fundamental limits. First, hydrogen-bonded azobenzene-polymer complexes with versatile optical properties over a broad spectral range are presented. Secondly, azobenzene-oligomer complexes with extremely low azobenzene content are used to systematically seek for the lowest amount of azobenzene that is still capable of inducing mass transport. The phenomenon is also taken to another extreme, as the light-induced surface patterns are shown to occur in azobenzene-functionalized dendrimers and native biomolecules with exceptionally high molecular weight. Finally, the immense yet largely unexploited application potential of the light-induced surface patterning is discussed and the use of the patterns in the nanofabrication of plasmonic hole arrays is demonstrated. This thesis presents new means to understand the complex structure-performance relationships in azomaterials and suggests novel uses for the light-induced surface patterns.

Keywords azobenzene, polymer, light, nanostructure, surface-relief grating, plasmonics

ISBN (printed) 978-952-60-6030-9

ISBN (pdf) 978-952-60-6031-6

ISSN-L 1799-4934

ISSN (printed) 1799-4934

ISSN (pdf) 1799-4942

Location of publisher Helsinki

Location of printing Helsinki

Year 2014

Pages 130

urn <http://urn.fi/URN:ISBN:978-952-60-6031-6>

Tekijä

Jenni E. Koskela

Väitöskirjan nimi

Liikettä valolla: Supramolekyläarisistä materiaaleista sovelluksiin

Julkaisija Perustieteiden korkeakoulu

Yksikkö Teknillisen fysiikan laitos

Sarja Aalto University publication series DOCTORAL DISSERTATIONS 213/2014

Tutkimusala Teknillinen fysiikka

Käsikirjoituksen pvm 07.10.2014

Väitöspäivä 23.01.2015

Julkaisuluvan myöntämispäivä 26.11.2014

Kieli Englanti

☐ **Monografia**

☒ **Yhdistelmäväitöskirja (yhteenvedo-osa + erillisartikkelit)**

Tiivistelmä

Atsobentseeni ja sen johdannaiset ovat väriainemolekyylejä, jotka sopivalla aallonpituudella valaistaessa muuttavat muotoaan stabiilista *trans*-muodosta metastabiiliin *cis*-muotoon. Isomeroitusreaktio on nopea ja reversiibeli, mistä johtuen atsobentseeniä sisältävien materiaalien monia ominaisuuksia voidaan muokata valolla, ja niissä voidaan saada aikaan jopa makroskooppista liikettä. Erityisen kiinnostava ilmiö on pintahilan muodostuminen lasimaisen atsomateriaalikalvon pinnalle valon interferenssikuvion vaikutuksesta. Pintahiloissa atsomateriaali kasaantuu säännöllisiksi topografisiksi kuvioiksi, joiden korkeus voi olla jopa useita mikrometrejä. Pintahilat ovat kiehtoneet tutkijoita viimeisen kahden vuosikymmenen ajan, ja niille on kehitetty monentyyppisiä sovelluskohteita fotonikasta biologiaan. Yhtenevää ja kaikenkattavaa selitystä pintahilojen muodostukselle ei kuitenkaan ole vielä esitetty, ja erilaisten atsomateriaalien valovasteen monimutkaisten yksityiskohtien selvittäminen vaatii runsaasti lisätyötä ennen kuin ilmiötä voidaan tehokkaasti hyödyntää käytännön sovelluksissa.

Tämä väitöskirja esittelee kokeellista tutkimusta, jonka tavoitteena on lisätä atsomateriaalien rakenteen ja valoliikkeen välisten lainalaisuuksien ymmärrystä ja antaa ehdotuksia uusista, vielä selvittämättömistä hyödyntämismahdollisuuksista. Työssä on valmistettu uusia valoaktiivisia materiaaleja supramolekyläarista funktionalisointia hyödyntäen, minkä ansiosta pintahilojen muodostusta voidaan tutkia materiaalin rakenteeseen liittyvien ääriesimerkkien avulla. Ensinnäkin, työssä tutkitaan vetysitoutuneita bisatso–polymeerikomplekseja, joissa valon indusoimat liikkeet ilmenevät tehokkaasti laajalla aallonpituusalueella. Toiseksi, vastaavanlaisten pienimoolimassaisten atso–polymeerikompleksien avulla etsitään pienintä mahdollista atsobentseenipitoisuutta, jolla pintahiloja voidaan vielä kirjoittaa. Toisaalta pintahilojen muodostusta tutkitaan atsobentseenifunktionalisoiduissa suurimoolimassaisissa dendrimeerikomplekseissa ja osoitetaan, että pintakuviointi on mahdollista myös suurista, pallomaisista biomolekyyleistä koostuvissa kalvoissa. Lopuksi työssä selvitetään valoherätteen pintakuviointin monipuolisia sovelluskohteita, joista esimerkkinä esitellään pintakuvioiden hyödyntämistä plasmonisten kultananorakenteiden valmistuksessa.

Avainsanat atsobentseeni, polymeeri, valo, nanorakenne, pintahila, plasmoniikka

ISBN (painettu) 978-952-60-6030-9

ISBN (pdf) 978-952-60-6031-6

ISSN-L 1799-4934

ISSN (painettu) 1799-4934

ISSN (pdf) 1799-4942

Julkaisupaikka Helsinki

Painopaikka Helsinki

Vuosi 2014

Sivumäärä 130

urn <http://urn.fi/URN:ISBN:978-952-60-6031-6>

Preface

It was never my intention to get a doctoral degree, let alone in the field of Applied Physics. In retrospect, I blame my excellent high school teacher Paula Perkkalainen for making chemistry so much fun that I went on to study engineering at Tampere University of Technology instead of building a career on my artistic ambitions. However, it was only during my Master's thesis work at the Department of Biomedical Engineering, when I discovered the fascinating world of scientific research. Therefore I would like to acknowledge my back-then advisor Dr. Niina Ahola and Professor Minna Kellomäki for pushing me onto the path that has led me where I stand today.

The research presented in this thesis has been carried out at the Department of Applied Physics in Aalto University during 2010-2014. I wish to express my greatest gratitude to my supervisor Professor Robin Ras, who offered me the possibility to become his first doctoral student in what is nowadays known as the Soft Matter and Wetting group. Robin, your endless flow of ideas and enthusiasm as well as sincere belief in my work have carried me through these years. However, none of this work could have been possible without my advisor Professor Arri Priimägi, his pioneering research on the subject and his hands-on guidance and support from day one. Arri, thank you for your patience in explaining and tweaking my optical set-ups over and over, for spurring me to become a better writer and above all, for your friendship. Cheers!

I also want to acknowledge the outstanding research surroundings provided by Professors Olli Ikkala, Matti Kaivola, Janne Ruokolainen and Mauri Kostiainen. I am well aware that I have been privileged to be part of a world-class research team and able to learn from the best of the best.

I would like to thank Professor Atsushi Shishido and Professor Emeritus Jouko Korppi-Tommola for the effort of examining this thesis and their valuable comments. I also greatly appreciate Dr. Carlos Sanchez Somolinos for accepting the invitation to act as my opponent in the upcoming thesis defence.

No pain, no gain, they say. Indeed, there have been times of severe frustration and distress, but thanks to the great people I have been fortunate to work with, I have not given up. It is difficult to imagine to ever again finding such a great, mutually supporting atmosphere among so many like-minded and ambitious yet completely different people. I wish to express my sincere gratitude all my co-authors and the talented students involved in my projects,

as I never could have completed this work alone. I want to especially thank Dr. Jaana Vapaavuori for her practical guidance on my work as well as our fruitful discussions. Dr. Antti Soininen deserves to be acknowledged for the numerous times of helping me with the AFM and Dr. Juuso Korhonen for his expertise on SEM and so much more. Riikka, Jason and other roommates, thanks for being there and bearing with me. Susanna, Henna, Lahja and Virginia, you have become so much more than just colleagues, I feel humbled to have you as friends. Let's do epic things together, I can hear the glass ceilings cracking! Thank you Johanna, Marjo and Päivi for everything. Timo, thanks for facilitating my non-scientific side projects during the years.

I am much obliged to Dr. Runar Törnqvist for giving me the opportunity to join the UMK Center for New Materials as a Coordinator during the early years of my grad studies. Runar, I am forever indebted for everything you taught me about work, business and life in general and all the valuable connections that I received through this job. In a broader perspective, my time at Aalto has taught me more about one thing than all of the scientific discoveries put together – myself. For everything that I have learned from the academic world to the optimistic entrepreneurial atmosphere of the Aalto community, I am now ready, willing and able to discover and reach for my own passions.

It is undoubtedly an understatement to say that my life has been quite hectic, even chaotic, in the recent years. This adventure has only been possible with a great support system, and I wish to express thanks all my dear friends for their unconditional support, for balancing my work with lots of fun, and for keeping me grounded. Especially Petra, Veera and Katri H., Katri K., Anette and Anna-Kaisa, thank you for being there.

Äiti ja isä, arvostan kaikkea mitä olette hyväkseni tehneet enemmän kuin arvaatte. Kiitos, että olen saanut aina valita oman tieni. Mummu, tukesi on ollut mittaamattoman arvokasta monessa suhteessa, kiitos kaikesta.

Seppo, sanat eivät riitä kiittämään tuestasi ja sitoutumisestasi, joka on mahdollistanut tämän kaiken. Rakas poikani Leo, toivon, että tämä väitöskirja osaltaan auttaa minua luomaan tulevaisuudellesi parhaat mahdolliset edellytykset.

Espoo, 3 December 2014

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List of Abbreviations and Symbols

| | |
|----------|---|
| 2NHA | ((2,5-dimethoxy-4-((4-nitrophenyl)diazenyl)phenyl)-diazenyl)phenol |
| OH-DMA | 4-dimethylamino-4'-hydroxyazobenzene |
| aFT | apoferritin |
| AFM | atomic force microscopy |
| DY7 | Disperse Yellow 7, 4-(4-(Phenylazo)phenylazo)- <i>o</i> -cresol |
| DLS | dynamic light scattering |
| EO | Ethyl Orange, 4-(4-Diethylaminophenylazo)-benzenesulfonic acid |
| FTIR | fourier transform infrared spectroscopy |
| LC | liquid crystal |
| PIMD | photoinduced molecular diffusion (model) |
| POM | polarized optical microscopy |
| P4VP | poly(4-vinyl pyridine) |
| pDR1M | poly(Disperse Red 1 methacrylate) |
| SEM | scanning electron microscopy |
| SRG | surface-relief grating |
| UV-Vis | ultraviolet–visible spectroscopy |
| θ | angle between the mirror and the inscription beam in a Lloyd's mirror setup |
| r | average intermolecular distance |
| N_A | Avogadro's number |

| | |
|------------|--|
| Δn | birefringence |
| w_i | chromophore weight fraction |
| ρ | density |
| d | film thickness |
| T_g | glass transition temperature |
| Λ | grating period |
| M | molecular weight |
| N | number density of chromophores |
| I_0 | transmitted probe beam signal through an unirradiated sample |
| I | transmitted probe beam signal through a birefringent sample |
| λ | wavelength |
| M_w | weight-average molecular weight |

List of Publications

This doctoral dissertation consists of a summary and of the following publications, which are referred to in the text by their Roman numerals.

- I. **Jenni E. Koskela**, Jaana Vapaavuori, Juho Hautala, Arri Priimagi, Charl F. J. Faul, Matti Kaivola, and Robin H. A. Ras. *Surface-Relief Gratings and Stable Birefringence Inscribed Using Light of Broad Spectral Range in Supramolecular Polymer-Bisazobenzene Complexes*. The Journal of Physical Chemistry C, **2012**, 116, 2363–2370. DOI: 10.1021/jp210706n.
- II. **Jenni E. Koskela**, Jaana Vapaavuori, Robin H. A. Ras and Arri Priimagi. *Light-driven Surface Patterning of Supramolecular Polymers with Extremely Low Concentration of Photoactive Molecules*. ACS Macro Letters, **2014**, 3, 1196–1200. DOI: 10.1021/mz500616q.
- III. **Jenni E. Koskela**, Ville Liljeström, Jongdoo Lim, Eric E. Simanek, Robin H. A. Ras, Arri Priimagi, and Mauri A. Kostiainen. *Light-Fuelled Transport of Large Dendrimers and Proteins*. The Journal of the American Chemical Society, **2014**, 136, 6850–6853. DOI: 10.1021/ja502623m.
- IV. Robert J. Moerland*, **Jenni E. Koskela***, Aleksandr Kravchenko, Mikael Simberg, Stefan van der Vegte, Matti Kaivola, Arri Priimagi and Robin H. A. Ras. *Large-area Arrays of Three-dimensional Plasmonic Subwavelength-sized Structures from Azopolymer Surface-relief Gratings*. Materials Horizons, **2014**, 1, 74-80. DOI: 10.1039/C3MH00008G.

*these authors contributed equally to this work

Author's Contribution

Publication I: Surface-Relief Gratings and Stable Birefringence Inscribed Using Light of Broad Spectral Range in Supramolecular Polymer-Bisazobenzene Complexes

The work was carried out in collaboration with Dr. Charl F. J. Faul, who provided the 2NHA chromophore. The author participated in designing the study, performed majority of the experiments, analysed the results and wrote the manuscript.

Publication II: Light-driven Surface Patterning of Supramolecular Polymers with Extremely Low Concentration of Photoactive molecules

The author designed and performed the measurements, analysed the data and wrote the manuscript.

Publication III: Light-Fuelled Transport of Large Dendrimers and Proteins

The work as carried out in collaboration with Prof. E. Simanek and Ph.D. student J. Lim who provided the dendrimer materials. The author participated in designing the study, performed sample preparation, the optical experiments and microscopy imaging, analyzed the data and wrote the manuscript.

Publication IV: Large-area Arrays of Three-dimensional Plasmonic Subwavelength-sized Structures from Azopolymer Surface-relief Gratings

The author participated in designing the study, and performed majority of the sample preparation, nanostructure fabrication, and AFM and SEM characterization and analysis, partly with the help of undergraduate students M. Simberg and S. van der Vegte. A. Kravchenko performed the gold deposition and cross-sectional SEM imaging. The author also participated in the optical transmission measurements that were primarily performed and analysed by R. Moerland. The author wrote the first version of the manuscript and had a major part in compiling the final version according to other authors' comments.

1. Introduction

The important thing in science is not so much to obtain new facts as to discover new ways of thinking about them. —William Lawrence Bragg

In nature, rapid and controlled response to stimulus is vital for living organisms, in order to adjust to changes in the environment. For scientists, reversible and rapid control over the physical and chemical properties of a material has been a day dream for decades. A great amount of work has been devoted to developing tailorable and smart materials that respond to changes in, e.g., temperature, pH, light, electric field, chemicals or ionic strength, to be utilized in various areas such as nanotechnology, electronics, diagnostics and biomedicine.¹⁻³

Light, in particular, is an attractive trigger as it offers precise and fast switching and spatial control from remote distances. A simple way to prepare light-responsive materials is to utilize photochromic molecules, which, upon photon absorption undergo configurational or conformational modifications that lead to changes in material properties such as shape, phase, wettability, permeability and solubility.^{4,5} Often the design of such photoresponsive materials is inspired by complex biological systems.⁶ One example of such a light-triggered process is vision. The light-sensing ability of the eye is based on the light-induced *cis-trans* isomerization around a (C=C) double bond in *opsin*, protein in the photoreceptor cells of the retina, in which a photon of light is converted into an electrochemical neural signal by a simple change of the shape of the molecule. As the complicated cascade of subsequent events ultimately leads to perception of light, the energy of the input photon is amplified thousands of times. Yet, the process is completely reversible.⁷

Azobenzene, one of the most employed photochromic molecules, responds to light in a similar way as opsins. Azobenzenes are aromatic molecules characterized by two phenyl rings connected by an azo linkage (–N=N–), through which the chromophore undergoes efficient and reversible *trans-cis* photoisomerization.⁸ This large change of its molecular structure enables effective control over chemical, mechanical, and optical properties of the whole material system, in which the chromophore is incorporated into.⁹ Besides its use as an effective photoswitch,¹⁰ photoisomerization of

azobenzene can initiate motion on much larger length scale, even macroscopically.¹¹ Academic interest in light-responsive azobenzene-containing materials has increased enormously within the past decades, with a continuous flow of literature about new phototriggered effects both at molecular and macroscopic level, and from both fundamental and applied points of view.^{12,13} Astonishing demonstrations of the power of this small molecular motor include the reversible macroscopic deformations and helical motion in free-standing azobenzene-containing polymer films^{14–16} and light-powered nanoengines.¹⁷ The wide range of length-scales employed in these applications only hint the future possibilities of azobenzene-functionalized materials.

In spite of extensive research on azopolymers during the past decades, the complicated relationship between the light-triggered effects and the molecular architecture continues to challenge researchers across different fields. Essentially, majority of the fundamental understanding on the azobenzene-based light-induced motions has been reached using traditional, covalently-functionalized polymers. However, to truly explore and extend the limits of light-fuelled motions, alternative material platforms are needed to reach beyond what covalent synthesis tools can offer. Followed by the development of supramolecular chemistry,¹⁸ traditional azopolymers have faced serious competition to novel azobenzene-containing materials that are based on noncovalent interactions. The design of such materials is spurred, once again, by nature, as its beautiful yet highly complex systems provide inspiration to develop sophisticated chemical architectures, which are increasingly difficult to achieve by conventional synthetic strategies. In recent years, the supramolecular functionalization strategy has been employed to design a number of high-performance photoresponsive systems. In particular, supramolecular azomaterials provide simple tools for gaining fundamental understanding on the material design aspects related to the light-induced effects. In this regard, the research presented in this thesis builds on the work on azobenzene–polymer complexes initiated by Prof. Arri Priimägi¹⁹ and later continued by Dr. Jaana Vapaavuori.²⁰

Perhaps the most extensively studied light-induced movements of azomaterials are the photo-orientation of the azobenzene chromophores with polarized light and the macroscale mass transport occurring on an azopolymer film upon irradiation. The latter, in particular is a remarkable example of how the simple photoisomerization reaction can amplify into macroscopic movements and temporally stable displacement of polymer at temperatures at which, intuitively thinking, the material should not be able to flow. As it was first discovered, illuminating a thin film of azobenzene-containing material with an interference pattern of two appropriately polarized light beams induces macroscopic movement of the material that results in the formation of a

temporally stable topography grating of up to hundreds of nanometers on the film surface.^{21,22} The mass transport process is a highly complicated cascade of events that occur on different time and length scales, and a universal theory to explain all the experimental findings is still debated.²³

Taking advantage of the known benefits of supramolecular assembly, this thesis seeks to extend the knowledge on the structure-performance relationships related to the light-induced movements – especially the light-induced surface patterning phenomenon. The main results are discussed in the following three chapters. Chapter 2 gives an introduction to azobenzene-functionalized materials and the light-induced movements in these systems. Part of the results of Publication I are discussed in relation to the photo-orientation phenomenon. Specifically, hydrogen bonding is employed to construct bisazobenzene-polymer complexes with attractive optical properties and high and stable photoinduced birefringence. Chapter 3 focuses on the light-induced surface-relief gratings (SRGs), and the main findings of Publications I–III are presented after a brief overview on the current understanding of the phenomenon and related previous work on SRG-forming supramolecular materials. It is first demonstrated that efficient surface patterning can be induced in a broad range of inscription wavelengths in hydrogen-bonded bisazobenzene-polymer complexes (Publication I). Secondly, the fundamental limits of mass transport are explored by studying hydrogen-bonded polymer-azobenzene complexes with extremely low chromophore content (Publication II). Lastly, ionic interactions are employed to functionalize high-molecular-weight dendrimers and globular proteins with azobenzene to show that even very large complexes of both synthetic and biological origin can undergo light-induced mass transport (Publication III).

Even though the fundamental materials-related investigations are of great significance, it is equally important to consider their application potential and new fields where the light-induced phenomena can be utilized. Therefore, the potential applications of light-induced surface patterning are discussed in Chapter 4. As a case example, the photoinduced SRGs are utilized in the nanofabrication of plasmonic hole arrays on gold to demonstrate the use of this versatile phenomenon as a patterning tool. Finally, in Chapter 5, general remarks of the presented work are discussed, and directions for future studies are given.

2. Light-induced movements in azobenzene-functionalized materials

Azobenzene is an aromatic molecule consisting of two phenyl rings connected by an azo (--N=N--) bond, giving rise to strong absorption in the ultraviolet and visible wavelengths. It serves as a parent molecule for an extensive class of robust and chemically stable azo compounds, which have received much research attention for their versatile and fascinating response to light. In everyday life, many commercial dyes contain azo chromophores, which are characterized by their chemically tunable colors and great stability even upon continuous irradiation. In modern material science, azobenzenes are most known for the efficient and reversible *trans*–*cis* photoisomerization, which induces a substantial change in the shape and size of the molecule and affects its spectroscopic and physical properties. When incorporated into polymers and other materials, the large nanoscale force generated by the geometrical change of photoisomerization can be translated into larger-scale movements of the material system. The unique ability of azobenzene to amplify the energy of incident light into significant micron-scale and even macroscopic motion is one of the most important reasons why photoresponsive azo-containing materials hold great, yet largely unexplored, technological potential. Prospective applications are diverse, including, e.g., optical information storage and processing, photoswitching, diffractive optics, and photomechanics.

2.1 Photoisomerization

‘Azobenzenes’, or simply ‘azos’, are a class of compounds obtained by substituting the benzene rings of the parent azobenzene molecule with different substituents. The substitution pattern of an azobenzene-based molecule determines its photochemical behaviour. Thus, according to Rau,²⁴ the spectral properties stand for the basis of classification into (1) *azobenzenes*, which structurally resemble the unsubstituted azobenzene or only contain non-polar substituents such as long aliphatic chains, (2) *aminoazobenzenes*, which are para-substituted with an electron-donating group and (3) *pseudostilbenes*, which are substituted at the 4 and 4’ positions with an electron-donating and an electron-withdrawing group. As a common feature, the conjugated π system

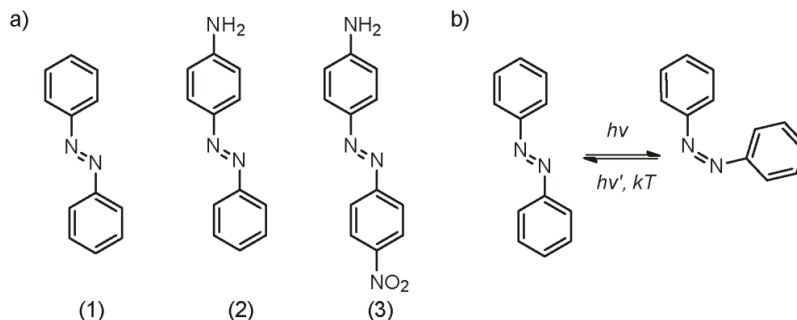


Figure 2.1. a) Example molecular structures according to Rau's classification: (1) azobenzene-type, (2) aminoazobenzene-type and (3) pseudostilbene-type chromophores. b) *Trans*–*cis* photoisomerization of azobenzene.

gives rise to a strong electronic absorption in the UV and/or visible range of the spectrum. The structural differences of the different types of azobenzenes are presented in Figure 2.1a.

Upon absorption of a photon, the azobenzene molecule crosses an energy barrier of ca. 200 kJ mol⁻¹, within a time scale of picoseconds, to isomerize from a thermally stable *trans*-form to a metastable *cis*-form, as illustrated in Figure 2.1b.^{25–27} Geometrically, the *cis*-azobenzene is characterized by 90° twisting of the phenyl rings relative to plane of the azo bond,^{28,29} and 44 % reduction in the distance between the 4 and 4' positions.^{30,31} This conformational change can proceed either via out-of-plane rotation or in-plane inversion around the nitrogen–nitrogen double bond, of which the latter is favoured due to smaller free volume needed, although compound- and environment-specific differences exist. The reverse reaction back to the stable *trans*-form occurs via thermal relaxation or illumination with light within the absorption range of the *cis*-isomer. The energy barrier for thermal isomerization is on the order of 100–150 kJ mol⁻¹.^{32,33} A fairly recent review by Bandara and Burdette⁸ is recommended for a more detailed description of the isomerization mechanisms of different types of azobenzene chromophores.

The electronic structure resulting from the substitution pattern of the molecule strongly affects the rate of thermal reversion; the *cis*-form of azobenzene-type molecules can persist for hours, while the *cis*-lifetime of aminoazobenzenes and pseudostilbenes are in the order of minutes and seconds, respectively.²⁴ Continuous illumination of a solution or solid sample with azobenzene leads to a photostationary state, in which the fraction of *trans*- and *cis*-isomers depends on the quantum yields of the two isomerization processes and on the thermal relaxation rate, being highly sensitive to the local environment and the irradiation conditions such as the illumination wavelength.⁸ The power of the azobenzene as a molecular muscle was recently elaborated by the Barrett group, by showing that photoisomerization could be induced in an azopolymer film even under high external pressure of more than 1 GPa.³⁴

The photochemical properties of the pseudostilbene-type azobenzenes are of particular interest due to their substitution with strongly electron-donating and -withdrawing groups. This structure leads to an asymmetric electron distribution, giving rise to a strong nonlinear optical response. In addition, there is substantial overlap in the absorption spectra of the *trans*- and *cis*-pseudostilbenes. Therefore a single wavelength of illuminating light can drive both isomerization directions, leading to continuous cycling between the two isomeric states that is needed for many of the photoinduced effects such as photo-orientation. For this reason, the azobenzene chromophores utilized in this thesis belong to the pseudostilbene category. On the other hand, pseudostilbene-type molecules cannot be used in photoswitching applications, in which the bistability needed is provided by azobenzene-type molecules instead.

2.2 Photoresponsive materials via azobenzene-functionalization

Azobenzene, being a robust and chemically stable molecule, can be incorporated into a wide range of material systems without compromising its ability to photoisomerize. Due to its unique photochromic behaviour, azobenzene can be exploited to induce controlled changes in the chemical, mechanical, electronic, and optical properties of the system. Numerous possibilities as the host material exist, with demonstrations including azobenzene-containing photoresponsive amorphous³⁵ and liquid-crystalline (LC) polymers,³⁶ self-assembled monolayers,³⁷ Langmuir-Blodgett films,³⁸ and sol-gel glasses.³⁹ The photoisomerization reaction is particularly useful to switch a material between two different states or phases.⁴⁰ Therefore also azo-functionalized crown ethers,⁴¹ cyclodextrins,⁴² protein-analogues,⁴³ and even DNA⁴⁴ have been prepared for example to photo-control a catalytic activity. Moreover, the solubility⁴⁵ and viscosity⁴⁶ of a polymer solution can be altered by suitable irradiation. When coupled to a self-assembled system, such as polypeptide micelles, the photoisomerization of azobenzene can be used to reversibly disaggregate an ordered structure.^{47–49} Furthermore, as the rigid and anisotropic structure of *trans*-azobenzene often results in LC behaviour but *cis*-azobenzene is a poor mesogen, the ordering of the LC phase can be reversibly switched with light.^{50–54} Similar order–disorder transitions can be photoinduced in azo-modified polypeptides.^{55–57}

From a practical point-of-view, polymeric materials offer robustness and processability needed to construct light-operated devices but also to provide a stable platform for fundamental research on the photoinduced effects. Thus, majority of the research on the light-induced photomechanical phenomena has been done with thin films of azo-containing polymers. Photoresponsive polymers are typically obtained simply by azobenzene doping or via covalent

attachment for increased stability and control. However, the characteristics of the polymer matrix as well as the mode of incorporation affect the photochemical properties of azobenzene, known as the ‘matrix effect’.^{5,9} For example, embedding the chromophores into a glassy polymer matrix may hinder the photoisomerization thus decreasing the *cis* content of the photostationary state.^{58,59} Also the rate of thermal isomerization from *cis* to *trans* will be affected by the matrix.^{60,61} In general, photochromic transitions occur slower in a polymer matrix than in solution, which can be explained by the limited free volume available, reduced segmental motion of the polymer chains and steric constraints. In addition, aggregation of the chromophores will affect the kinetic and spectral properties, hence the task of the polymer matrix is to prevent excessive interactions between neighbouring azo molecules.⁶²

The type of binding between the chromophores and the polymer matrix has a significant effect on the photoresponsive properties of the system. Simple mixing of the chromophores with a polymer is straightforward, cheap and enables effortless tuning of the azo content. Nevertheless, many of the interesting photomechanical effects are lost due to lack of interaction between the photochromic units and the matrix and due to chromophore aggregation and phase separation.^{62,63} To solve the problems of guest-host systems, covalently synthesized azopolymers have been developed.^{64–66} Most importantly, covalent functionalization allows high doping levels without phase separation, leading to superior optical performance.⁶⁵ Moreover, covalent attachment hinders the orientational relaxation of the chromophores, which is beneficial in applications that require collective alignment of the chromophores. Also the glass-transition temperature (T_g) is higher compared to corresponding guest-host systems, leading to increased thermal stability.⁶⁶

Both side-chain and main-chain azopolymers have been prepared, using either monomers bearing the azo-functionality or by post-functionalization of a pre-synthesized polymer. Many types of polymer backbones have been used, including methacrylates,⁶⁷ imides,⁶⁸ esters,⁶⁹ urethanes,⁷⁰ ethers,⁷¹ ferrocenes⁷² and polyacetylenes⁷³. As an example, Figure 2.2 presents the chemical structure of a popular, commercially available methacrylate polymer poly(Disperse Red 1 methacrylate) (pDR1m), which has been used in the study

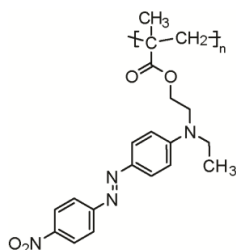


Figure 2.2. The chemical structure of poly(DR1m).

of publication IV. Also photoresponsive block-copolymers have been developed to bring the photoresponsive features of azopolymers into the microphase separation of well-defined block-copolymers.^{36,74–79} Moreover, azo-containing block-copolymers can form photoresponsive micelles and vesicles.^{80–85}

In contrast to amorphous azopolymers, azo-containing LC systems have an extraordinary ability to change their long range ordering in response to light, supported by co-operative motions between the mesogens and the photochromic units. For example, photoisomerization can drive reversible order-disorder phase transitions and order–order alignment changes.^{53,86} Furthermore, the inherent anisotropy of LC materials can amplify the mechanical power produced by photoisomerization, resulting in substantial contraction of the material upon irradiation.⁸⁷ Astonishing effects can be achieved with azo-functionalized LC elastomers, such as mechanical bending of a macroscopic film.^{14,88} Many comprehensive reviews on photo-responsive LC systems have been published.^{89,90}

Besides polymeric azomaterials, considerable amount of research has been conducted on azobenzene-containing dendrimers and molecular glasses. These materials are characteristically monodisperse, and the advantageous combination of high stability and excellent sample homogeneity with tunable solubility, aggregation, and crystallinity renders them serious competitors to azopolymers in terms of applicability. Dendrimers are highly branched globular macromolecules with a well-defined structure that can host functional groups both on the peripheral units⁹¹ and in the core.⁹² The light-responsive properties of azobenzene-functionalized dendritic structures have been studied for a variety of applications from light harvesting and optical anisotropy to film dewetting and drug release.^{93–96} On the other hand, glass forming low-molecular-weight azo-materials present a feasible choice due to their intrinsically high azobenzene loading, ability to form uniform amorphous films and small molecular size leading to fast dynamics in light-induced surface patterning.^{97–99}

Lastly, photofunctional biomaterials have been developed by modifying biopolymers or by synthesizing bioinspired macromolecules functionalized with azobenzene units.^{6,100} Whereas nature and its biological processes provide inspiration for the design of such intelligent materials, biological units and structures can serve as a platform to explore the light-induced phenomena found in synthetic materials. Publication III demonstrates this strategy with photoresponsive azobenzene-functionalized native proteins that are able to undergo macroscopic movements in response to light. In general, the ability to control a biological function on demand with light is highly interesting not only for fundamental studies but also for creating smart biomaterials for implants and medicine.^{5,101}

2.2.1 Tailored photoresponsivity via supramolecular chemistry

As noted, most of the photoresponsive materials studied until today have been prepared by covalent functionalization, as they excel in optical performance compared to guest-host systems. However, laborious organic synthesis with multiple preparation and purification steps are required for each polymer–chromophore combination, making covalently linked azopolymers considerably less attractive than guest-host systems from a practical point of view. The applicability of covalent azopolymers is further limited by the fact that specifically functionalized structures are difficult to prepare in a reproducible and simple manner combined with the lack of facile tunability over the molecular design.⁶³

To overcome the burden of covalent synthesis, an alternative route to robust photoresponsive azomaterials is available via supramolecular chemistry. In its simplest form, a supramolecular complex means a construct of two molecules stabilized by a physical bond between complementary binding sites.¹⁰² Such a complex is stable when the bond energy is high enough to surpass the energy of thermal randomization. Even though the concept of self-assembly via noncovalent interactions is relatively new to material science, these interactions played a crucial role in the development of living organisms and are essential to most molecular events in the biological systems of today.¹⁸ Supramolecular side-chain polymers are based on a covalently linked polymer backbone that contains molecular recognition units on its side-chain and can be functionalized via noncovalent interactions.¹⁰³ This clever synthesis strategy combines the simplicity of doping while retaining the stability of covalent polymers. Functional materials can be created simply by mixing of readily available components, in contrast to the time-consuming and costly organic synthesis of covalent polymer-dye systems.^{103–105} Besides cost-efficiency, supramolecular bonds serve to prevent aggregation of the chromophores, which significantly improves the optical properties.⁶² Furthermore, noncovalent bonds are highly dynamic and reversible, and are readily affected by changes in the environment.¹⁰³ In recent years, a large number of photoresponsive supramolecular polymer-azobenzene complexes have been developed. The variety of polymer architectures in these materials includes linear polymers,^{106–108} random copolymers,¹⁰⁹ linear block-copolymers,^{75,110,111} crosslinked polymers,¹¹² hyperbranched polymers,^{113,114} and dendrimers.^{95,113–115} Moreover, also low-molecular-weight azomaterials can be prepared via supramolecular assembly.^{116,117}

In this thesis, two types of noncovalent bonds are employed to construct light-responsive materials, namely hydrogen bonding and ionic interactions. According to the definition by IUPAC, “*the hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of*

atoms in the same or a different molecule, in which there is evidence of bond formation."¹¹⁸ In practice, majority of the electron density in the covalent bond **X–H** is located on the electronegative atom **X**, leaving the proton exposed. The hydrogen-bond ‘acceptor’ is an atom with a lone-pair or π -electrons that attracts the unprotected proton acting as a hydrogen bond ‘donor’. In our group, Priimagi and co-workers have consistently developed the concept of hydrogen-bonded polymer-azobenzene complexes since 2005, establishing that supramolecular concepts provide facile means to gain comprehensive understanding on the role of chromophore concentration and structure on the photoresponsive properties, aggregation behaviour in particular, of the material.^{62,119,120} In these efforts, the phenol–pyridine hydrogen bonding (bond-energy of 16-60 kJ/mol), has proven particularly feasible, as tuning of the chromophore concentration is effortless, and even equimolar complexes, with equal amounts of dye molecule and repeat units can be fabricated without excessive aggregation or phase separation.¹²¹ Due to these well-established advantages, the phenol-pyridine interaction is also employed in Publications I and II. In general, functionalization via hydrogen bonding would allow one to accessorize a polymer backbone with several different chromophores or other side units, to gain multifunctionality, or to selectively remove the azobenzene chromophores from the material if necessary.¹⁰⁹

When a supramolecular side-chain polymer is constructed via ionic interactions, the polymer and the side chain units are oppositely charged.¹⁰⁴ The cooperative nature and high strength of ionic interactions causes fundamental differences to hydrogen bonding, which is assumed to occur randomly along the polymer chains. Ionic supramolecular complex forms readily when equimolar amounts of solutions of the constituents are mixed, leading to stoichiometric complexes where practically every polymer repeat unit is bound to a side-chain molecule.¹²² Another important difference, especially application-wise, is that ionic supramolecular systems are generally prepared in water-based solutions, whereas hydrogen-bonding systems typically are soluble in organic solvents. However, the solubility in organic solvents of ionic complexes can be improved by appropriate design of the chemical structure to facilitate processing.⁹⁵ Also, high water-solubility of ionic species can compromise the stability of the complexes during preparation and decrease the persistence of the prepared materials in ambient conditions. On the other hand, ionic interactions are known to provide significant thermal stability, and for example the removal of light-induced surface patterns requires very high temperatures.¹²³ In this thesis, ionic interactions are employed in Publication III to construct azo-functionalized dendrimers and proteins. In the latter case, the water-based preparation of the materials is viewed as an advantage with respect to biological applications. However, once the ionic supramolecular bonds are formed, the resulting material may

precipitate out from the water solution, and can be subsequently dissolved into an organic solvent for further processing if necessary.

Very recently, also halogen bonding has started to gain attention as an alternative to hydrogen bonding and ionic interactions in the preparation of photoresponsive systems. Halogen bonds are highly directional noncovalent interactions, in which a halogen atom possesses a region of positive electrostatic potential to which a nucleophilic region in another (or same) molecule or atom is attracted to.¹²⁴ A unique feature of halogen-bonded systems is that the strength of the interaction can be conveniently tuned with the polarizability of the bond-donor atom, which allows one to evaluate the dependence of the photoresponsive properties on chromophore-host interaction independently of other factors.¹²⁵

The myriad of different material platforms employed to construct light-responsive films and devices highlights the versatility of azobenzene as a universal and indefatigable photoswitching molecule. Essentially, studying the light-induced effects of azobenzene in new environments can add to the fundamental understanding of the underlying mechanisms. In addition, novel azomaterials may create new possibilities for innovative combinations of different fabrication techniques.

2.3 Light-induced movements in azopolymers

The photoisomerization of azobenzene can be exploited to convert light energy into mechanical energy by inducing reversible shape and volume changes into the material. The magnitude of the nanoscale force generated by the *trans*-to-*cis* shape change is in the order of pN to nN per chromophore, as measured by single-molecule force spectroscopy experiments^{126,127} and predicted theoretically.¹²⁸ Importantly, the direction of the force can be controlled by light polarization. This photoinduced force is significant enough to be coupled to simple machinery to construct an “artificial molecular-level machine”, as demonstrated by Stoddart and co-workers.¹⁷

Following the classification of Natansohn and Rochon,⁹ light-induced motions are generally divided by their characteristic length scale into (1) *molecular-scale* motions, (2) *domain-scale* motions and (3) *macroscopic* motions, as illustrated in Figure 2.3. However, motions on different size-scales are always concurrent and inter-dependent, therefore this division is oversimplified. Motion at the molecular level is induced by linearly polarized light that only activates chromophores with dipole moment parallel to the axis of light polarization. This selectivity originates from the highly anisotropic structure of *trans*-azobenzene, and ultimately leads to anisotropic alignment of the chromophores and birefringence in the material.⁹ This has been one of the

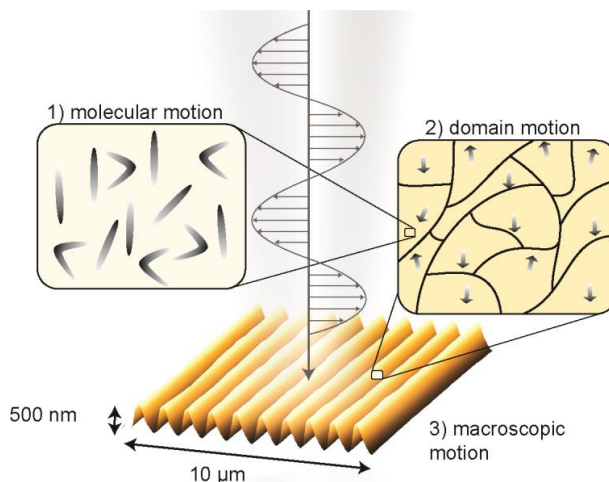


Figure 2.3. Levels of light-induced motions in azobenzene-containing materials. Adapted from Ref. [9] with permission from the American Chemical Society ©2002.

most studied photochromic effects in azo-containing polymers and will be discussed further in the next Section.

The domain-level motion, which occurs roughly on the nanometer scale, requires an interaction between the matrix material and the chromophores.⁹ Even if domain motion can be observed also in amorphous systems, it is further enhanced by some level of intrinsic order in the matrix, e.g. in the form of liquid-crystallinity, semicrystallinity or molecular alignment of a monolayer. In such systems, photoisomerization drives reorientation of whole liquid crystalline or crystalline domains, resulting in a high degree of overall orientation, much higher than in amorphous polymers.⁸⁶ This phenomenon is called ‘co-operative motion’.¹²⁹

The third level of motion occurs at a scale many orders of magnitude larger than the size of the azobenzene units, and is able to produce structural changes visible to the naked eye. In its simplest form, macroscopic motion can mean changes in the total volume of the material upon irradiation. Both contraction and expansion of amorphous azo-containing polymers have been reported to occur, even in the same material depending on the temperature.^{130,131} On the other hand, the intrinsic anisotropy of LC azomaterials enables macroscopic motion that leads to bending of a free-standing polymer film when it is irradiated only from the other side to induce contraction.^{14,88} These fascinating photomechanical effects have prompted a number of possible applications from photo-driven micromechanical devices to actuators and sensors.¹³² Yet, perhaps the most studied and also most complicated type of macroscopic motion is the light-induced surface patterning. Exposure of a thin azopolymer film to an interference pattern of two laser beams results in periodic patterns on the film surface which coincide with the light interference pattern and are several

hundreds of nanometers high.^{11,22} This intriguing phenomenon forms the core of the studies described in this thesis, and thus will be discussed separately in Chapter 3.

2.3.1 Photo-orientation

In literature, first reports on holographic gratings in azopolymers induced with a light interference pattern appeared in the 1980s.^{133–135} At first, liquid crystallinity was believed to be necessary for the light-induced alignment of the azo chromophores, known as *photo-orientation*, but by early 1990s it was realized that intrinsic order was not a prerequisite for stable photoinduced birefringence and amorphous systems could be used as holographic recording medium as well.^{136,137} Afterwards, a substantial amount of research has been dedicated to understanding the optimal conditions regarding both the material itself and the experimental setup. These efforts have resulted in a number of highly efficient materials for applications such as LC alignment, holography and reversible data storage.^{53,115,138139}

When irradiated with linearly polarized light, an azobenzene molecule will preferentially absorb light polarized along the long axis of the molecule (transition dipole axis).¹⁴⁰ In practice, this means that the absorption of molecules perpendicular to the polarization axis of the incident light is insignificant compared to the molecules positioned along the axis. Repeated cycling between the *trans* and *cis* states, which is highly efficient in pseudostilbene-type chromophores, results in reorientation perpendicular to the polarization direction(s) of incident light. Upon continuous illumination the concentration of azo molecules perpendicular to the polarization direction increases gradually before reaching a saturation level. The resulting anisotropy, which induces large and stable in-plane birefringence, can be observed in the polarized absorption spectra of the film.¹⁴¹ Irradiation with unpolarized or circularly polarized light can re-establish the original isotropic orientation, enabling many subsequent photo-reorientations.

In a typical photoinduced birefringence experiment (see Figure 2.4), a linearly polarized beam of moderate power and wavelength matching the absorption band of the chromophores is used to induce orientation of the chromophores. The evolution of orientational anisotropy is monitored by measuring the transmittance of a low-power probe beam through a polarizer/sample/analyzer configuration. The transmission direction of the polarizer/analyzer is set to $\pm 45^\circ$ with respect to the polarization direction of the writing beam to maximize the transmitted signal I . The birefringence Δn can then be calculated from

$$I = I_0 \sin^2 \left(\frac{\pi |\Delta n| d}{\lambda} \right) \quad (2.1)$$

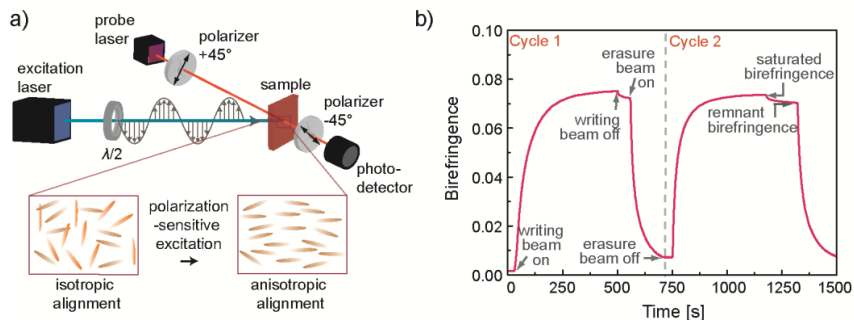


Figure 2.4. a) Schematic illustration of the experimental setup for photoinduced birefringence and the corresponding light-induced in-plane alignment of the azobenzene molecules upon excitation with linearly polarized light. b) Typical birefringence measurement as a function of writing time. Adapted from Publication I with permission from the American Chemical Society ©2011.

where d is the film thickness, λ the wavelength of the probe beam, I the signal of the probe beam transmitted through the birefringent sample (polarizer and analyzer positioned perpendicular to each other), and I_0 the signal through an unilluminated sample (polarizer and analyzer parallel). Once the irradiation is terminated, a fraction of the oriented chromophores will be randomized again due to thermal relaxation, resulting in a decrease in the birefringence.

It is known that most azobenzenes isomerize and exhibit the photo-orientation process, yet significant differences exist between different types of chromophores. The efficiency of photo-orientation in a given material is a complex result of many parameters such as chromophore structure and intermolecular interactions, type of bonding to the matrix and cooperative motions. While these factors are elaborated in the seminal review by Natansohn and Rochon⁹ and more recently in the book by Zhao and Ikeda¹³ some general rules can be listed here. First, however, one has to bear in mind that the details of the sample preparation process including the solvent, the film-casting method, and heat-treatment can have a significant effect on the ultimate photo-response of a material. Moreover, the response is also influenced by various experimental parameters such as the laser wavelength and intensity, thus a reliable and straightforward comparison between experimental results for different materials, even for the same material made by different groups or in different times of year, is rarely possible.

The nature of matrix material plays a very important role as it can either enable or restrict the motion and interactions of the chromophores. In general, photoinduced anisotropy has been reported to be higher and more stable in LC systems than in amorphous polymers due to strong cooperative movement and intermolecular interactions of the photochromic units and the mesogens.⁸⁶ Compared to simple guest-host systems, covalent attachment of the chromophores to a polymer backbone enhances the stability of orientation. However, also supramolecular systems can be designed to yield high and stable

birefringence, as shown first in ionic polymer-azobenzene complexes by Xiao *et al.*¹⁴² Later, Zhang *et al.* investigated the structure-performance relationship in similar LC systems.¹²² In both covalent and supramolecular systems the spacer length (structural units between the polymer backbone and the chromophore) strongly affects the photoinduced motion. Usually, shorter spacers restrict the chromophore's motion, leading to slower growth rate of birefringence but also improved stability.¹⁴³ Vice versa, longer spacer length facilitates chromophore motion, thus both the photo-orientation and relaxation occur faster. On the other hand, longer spacers can be used to introduce liquid crystallinity in the system, which also improves the amount and stability of the photoinduced birefringence.¹⁴⁴ Recently, Vapaavuori *et al.* made a comparison on hydrogen-bonded complexes consisting of a poly(4-vinyl pyridine) (P4VP) backbone and three different azobenzenes with varying substituents in the *para*-position of the azobenzene chromophore.¹⁴⁵ Interestingly, all the studied complexes were spacer-free, but the liquid crystallinity and the following photoresponsive properties of the system could be neatly tuned by rational chromophore design.

In terms of chromophore structure, the pseudostilbene-type molecules are an obvious choice as the photo-orientation results from many subsequent photoisomerization cycles. The chromophore bulkiness and strength of the dipole moment also play important roles. Introducing substituents on the benzene rings may hinder motion of the molecule and either decrease the level of photoinduced birefringence, or slow down the process, or both.^{9,146} The role of polarity becomes important especially when the azo content is high enough, as interactions between adjacent polar and rod-like chromophores enhance and stabilize the photoinduced birefringence.¹⁴⁷ Furthermore, it is possible to prepare supramolecular azopolymers, where the azo-containing side-groups are dendritic, leading to LC structures and improved and stable photoinduced birefringence.⁹⁶

2.3.2 Large and stable birefringence in polymer–bisazobenzene complexes (Publication I)

Many of the important factors determining the efficiency and stability of photoinduced birefringence were discussed in the previous Section. One unmentioned yet interesting aspect deals with the structure of the photochromic unit. Instead of just one azo bond, the chromophores can be extended to contain two azo groups, leading to increased conjugation length, large length-to-width ratio and low side-chain mobility. Thus, bisazo-containing polymers have been reported to yield higher and more stable photoinduced birefringence than their monoazo counterparts.^{106,148} Indeed, bisazo-based polymeric materials with extremely high birefringence have been demonstrated.^{149,150} In a study by Wu *et al.* a supramolecular bisazo-polymer was prepared by hydrogen

bonding between guest azobenzene units and azo groups of the host polymer.¹⁰⁶ In this material, extending the conjugation of the photochromic units by noncovalent interactions increased the magnitude and temporal stability of the photoinduced birefringence compared to the original azopolymer. Fairly recently, Wang and co-workers showed that the substitution pattern of the bisazo chromophore and the excitation wavelength greatly affect the photoinduced birefringence in epoxy-based bisazobenzene polymers.¹⁵¹

The aim of Publication I was to further clarify the role of chromophore polarity on the photo-orientation ability in supramolecular polymer-bisazo complexes. Taking into account the importance of polarity and substitution pattern of the chromophore, a polar bisazobenzene dye ((2,5-dimethoxy-4-((4-nitrophenyl)-diazenyl)phenyl)-diazenyl)phenol (abbreviated here as 2NHA) was synthesized. 2NHA exhibits attractive photoresponsive properties due to its molecular structure and broad absorption band, which are shown in Figure 2.5a and b, respectively. The supramolecular complex was prepared by introducing hydrogen bonds between the phenolic moieties of the 2NHA chromophore and the nitrogen atoms of a P4VP backbone. In order to make a comparison, complexes of P4VP and a commercially available bisazo chromophore 4-(4-(phenylazo)phenylazo)-*o*-cresol, i.e., Disperse Yellow 7 (DY7) were also prepared. DY7 is a significantly less polar molecule, as its structure (see Figure 2.5a) lacks an electron-withdrawing group such as the NO₂ group in 2NHA. From here on, the complexes are referred to as P4VP(2NHA)_x and P4VP(DY7)_y, where *x* and *y* denote the number of chromophores per polymer repeat unit. The formation of the complex was verified by Fourier-transform infrared (FTIR) spectroscopy similarly to previous studies, following the absorption band of the stretching mode of the free pyridine moieties at 993 cm⁻¹. Whereas the spectra of P4VP(DY7)_y complexes showed the most pronounced peak shift for the equimolar complex, for P4VP(2NHA)_{1.0} the 993 cm⁻¹ band did not fully disappear, which indicated that full complexation was slightly hindered by the lack of free space between the relatively bulky chromophores. The UV-vis absorption spectra for thin films of P4VP(2NHA)_{1.0}, P4VP(DY7)_{1.0} and uncomplexed chromophores in dilute THF solution are presented in Figure 2.5b. The absorbance spectra of the complexes did not exhibit clear signs of aggregation despite the slight broadening compared to the pure chromophores. This result indicated that the structure of both materials is amorphous in the films, which was confirmed by polarized optical microscopy (POM). Interestingly, the 2NHA complex showed two almost equally intense absorption maxima at around 375 and 510 nm, attributed to the donor-acceptor structure containing the donating methoxy groups in the central phenyl ring and the electron withdrawing NO₂ moiety in the para position of the terminal phenyl group. In contrast, the DY7 complex only had one peak, located at around 390 nm.

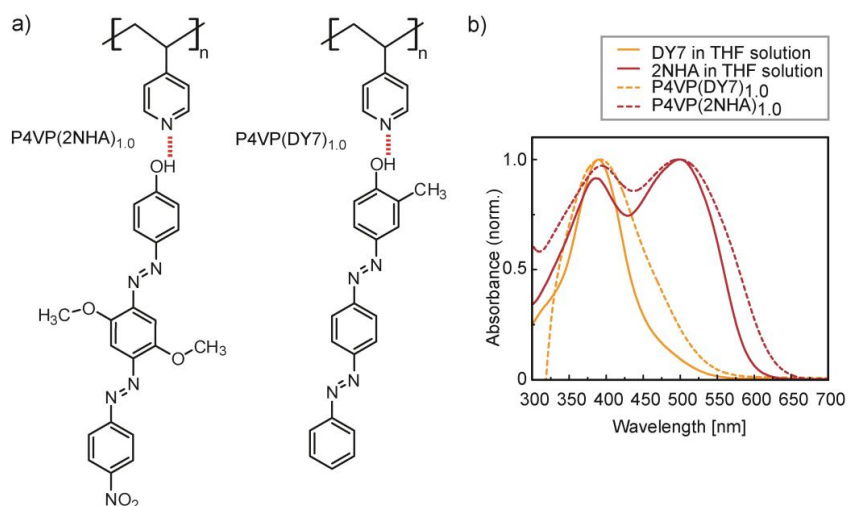


Figure 2.5. a) Chemical structures of the nominally stoichiometric P4VP(2NHA)_{1.0} and P4VP(DY7)_{1.0} complexes, and b) normalized absorption spectra of the corresponding complexes as thin films and in solution. Adapted from Publication I with permission from the American Chemical Society ©2011.

The unique spectral features of 2NHA prompted us to study the photo-orientation ability of these materials in a broad selection of irradiation wavelengths. The measurements were conducted as described in Section 2.3.1. Light-induced birefringence was inscribed into the sample films using writing wavelengths of 405 nm and 514 nm, according to the absorption maxima of P4VP(2NHA)_x, but also 633 nm was chosen to study the photoresponsivity of the material at a wavelength far from the absorption maxima.

The saturated and remnant birefringence as a function of the chromophore concentration at the writing wavelength of 405 nm are shown in Figure 2.6a both P4VP(2NHA)_x and P4VP(DY7)_y. Unsurprisingly, photoinduced birefringence of the P4VP(2NHA)_x complexes increased systematically with

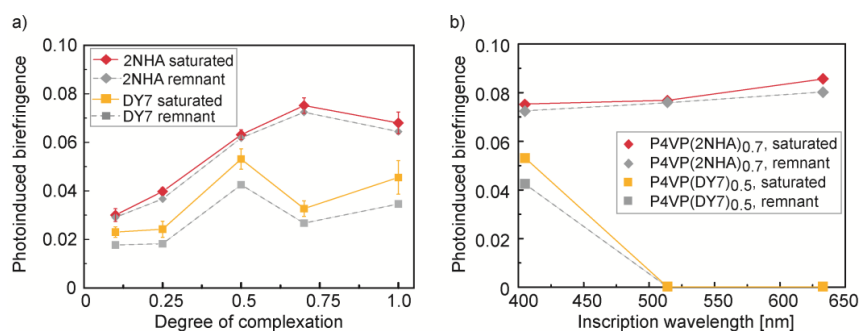


Figure 2.6. Photoinduced birefringence as a function of a) the degree of complexation at 405 nm, and b) the inscription wavelength for P4VP(2NHA)_{0.7} and P4VP(DY7)_{0.5}. Adapted from Publication I with permission from the American Chemical Society ©2011.

dye concentration, being highest for $x = 0.7$. In the equimolar P4VP(2NHA)_{1.0} complex the photoinduced birefringence was slightly decreased, which was presumably caused by less efficient complexation and less efficient *trans*–*cis*–*trans* isomerization cycling due to steric hindrance between the large chromophores. Furthermore, the 2NHA complexes showed excellent stability of the photoinduced birefringence throughout the concentration range studied. On the contrary, P4VP(DY7)_y revealed significantly lower birefringence in terms of both magnitude and stability. In contrast to previous studies where the stability of birefringence was significantly improved at higher degrees of complexation,¹⁰⁸ such effect was not observed in neither of the materials.

The photoinduced birefringence at longer wavelengths was studied in the complexes that yielded the highest birefringence at 405 nm, namely P4VP(2NHA)_{0.7} and P4VP(DY7)_{0.5}. The birefringence values for all three wavelengths are presented in Figure 2.6b. Interestingly, for P4VP(2NHA)_{0.7} the magnitude and stability of the photoinduced birefringence was nearly independent of the irradiation wavelength. This could be explained by the particularly wide absorption bands of 2NHA, for which the *trans*–*cis*–*trans* isomerization cycling, and subsequent photo-orientation is efficient over a wide range of inscription wavelengths. While dipolar interactions between polar chromophores are known to enhance photo-orientation, excessive interactions can also lead to detrimental effects. In 2NHA the methoxy spacers attached to the middle benzene ring are responsible for broadening of the absorption spectrum, increasing the mutual distance between the azo chromophores and preventing their aggregation. In contrast to 2NHA, no photoinduced birefringence was observed at the writing wavelengths of 514 or 633 nm in P4VP(DY7)_{0.5}. This rather expected behaviour was attributed to the nonpolar nature of DY7, decreasing the thermal *cis*–*trans* isomerization rate and consequently suppressing the isomerization cycling required for efficient photo-orientation in amorphous polymers.

The significant difference in the temporal stability of photoinduced birefringence between the 2NHA and DY7 complexes can be explained by the chemical structures of the chromophores. The push–pull-type 2NHA has a larger dipole moment, enabling strong interaction between the chromophores and decreasing the mobility of the chromophores. In P4VP(DY7)_y such interactions are much weaker. Moreover, in 2NHA the bulky methoxy substituents located near the photoisomerizable groups require lots of free volume, thus they hinder chromophore motion. For the same reason, the relaxation process is more difficult, thus giving rise to enhanced temporal stability. The bulkiness of 2NHA clearly serves for multiple advantageous effects. In conclusion, the molecular structure 2NHA chromophore enabled larger and substantially more stable photoinduced birefringence compared to DY7. Furthermore, the broad absorbance range of 2NHA allowed for an

expanded range of efficient writing wavelengths. In the future, the supramolecular concept combined with versatile chromophore design will open up new applications for photoresponsive materials that work on a very broad range of the visible spectrum.

3. Light-induced surface patterning in supramolecular azomaterials

One of the most remarkable light-induced effects caused by azobenzene photoisomerization is the capability of directional micron-scale mass transport of the bulk material. In 1995, two independent research groups concurrently reported that illumination of a glassy azopolymer film with a light interference pattern results in the formation of temporally stable surface patterns with modulation depths of hundreds of nanometers.^{21,22} Indeed, when a thin film of an azopolymer is subjected to a simple interference pattern of light with spatial variation of intensity and/or polarization, the photoisomerization of azobenzene invokes mass migration of the polymer over distances of several micrometers, forming high-modulation-depth sinusoidal surface-relief gratings (SRGs) at the polymer–air interface.¹¹ However, the mass transport is dictated only by the spatial intensity and/or polarization variation of the incident light, and arbitrary structures can be inscribed as well.^{11,152} This intriguing all-optical phenomenon has received considerable attention from both experimental and theoretical points of view now for almost 20 years. It has been extended to complicated illumination conditions and various material systems beyond traditional polymers, and simultaneously to the increasing fundamental understanding of the phenomenon, significant effort has been made to introduce applications for this facile, one-step method of fabrication of periodic microstructures. The surface deformation of azomaterials enables nano- and micron-scale motions to be induced by light when desired, which makes the phenomenon interesting for applications far beyond simple patterning.¹⁵³ The versatility of azobenzene-based surface patterning renders it a useful tool, e.g., in photonic applications and nanofabrication,^{154–158} and for organizing other materials such as block-copolymers and nanoparticles.^{76,159}

3.1 Experimental findings

The photoinduced mass transport phenomenon has been observed in a wide range of azo-containing material systems. As is now known, very different mechanisms apply for mass transport in amorphous and LC systems.¹⁶⁰ For clarity, the basic principles applying only to amorphous azopolymers will be

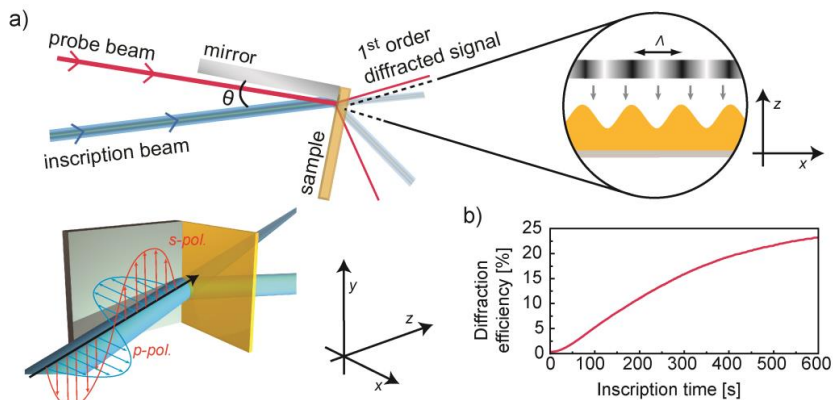


Figure 3.1. a) Schematic illustration of the SRG inscription setup and b) an example of the evolution of diffraction efficiency during inscription.

discussed here as they are more relevant for this work. By far the most studied SRG structures are obtained with a periodic intensity and/or polarization pattern formed by the interference of two polarized laser beams, as the irradiation setup is relatively simple and the periodic sinusoidal grating can be used in applications as such. In this thesis, a Lloyd's mirror interferometer²² has been used for inscribing the SRGs. As illustrated in Figure 3.1a, the interference pattern is created by reflecting half of the inscription beam from a mirror placed perpendicular to and in contact with the sample. In this setup, the grating period Λ can be conveniently tuned by adjusting the angle between the incident beam and the sample normal θ , as

$$\Lambda = \frac{\lambda}{2\sin\theta} \quad (3.1)$$

where λ is the wavelength of the inscription beam. The inscription wavelength should be within the absorption band of the material such that it induces both *trans-cis* and *cis-trans* isomerization. In other words, an efficient SRG-forming material usually contains pseudostilbene-type azo chromophores, in which the continuous illumination causes cyclic isomerization reactions. Increasing the chromophore concentration in the material is known to improve the efficiency of mass transport.¹⁶¹ The molecular weight and the T_g of the host polymer also greatly affect the SRG formation efficiency. Temporally stable SRGs can only be inscribed to polymers with T_g higher than the inscription temperature.¹⁶²

The formation of the SRG can be monitored during inscription by measuring the diffraction of a non-isomerizing probe beam that has been directed through the illuminated sample area. SRGs with an average modulation depth of a few hundreds of nanometers will appear within minutes. However, depending on the material and the illumination intensity, it may take hours for the diffraction signal to saturate. A typical measurement of the diffraction efficiency is presented in Figure 3.1b. We define the diffraction efficiency of an SRG as the

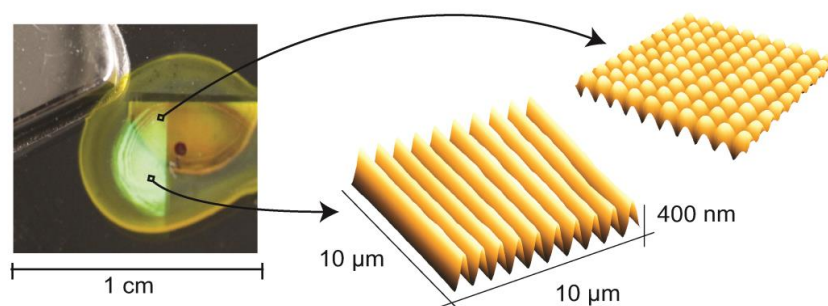


Figure 3.2. Photograph of a sample film on a glass substrate with two perpendicular SRGs and AFM height images of the sample area of a single grating (left) and at the intersection of the two gratings (right).

ratio of the first-order diffracted signal and the input signal through the sample prior to illumination. It should be noted that besides the evolving topographical pattern, also a birefringence grating may form in the bulk film to contribute to the overall diffraction efficiency.¹⁶³ Once the grating is formed, no further processing is needed and the modulation depth can be analysed by AFM.

The fact that the surface patterning process is purely light-induced is supported by several experimental findings. First, the temporally stable SRG can be erased by heating the film above its glass-transition temperature T_g , or even by suitable illumination, and subsequently the inscription-erasure process can be repeated many times.¹⁶⁴ Figure 3.2 presents a photograph of a sample film, with two gratings inscribed partially on top each other in a 90° angle. AFM images show the resulting microstructures. Secondly, SRG formation is highly dependent on the polarization of the inscription beam, and gratings will form even with a purely polarization-modulated interference pattern with constant intensity.^{163,165–168} The polarization dependence of mass transport discards the role of thermal effects in the process. It has been shown that a thermal gradient across the intensity interference pattern is only in the order of 10^{-4} K.¹⁶⁹ Furthermore, SRGs can be inscribed with notably low laser power, 1–100 mW/cm.¹⁷⁰

One of the most distinct features of the azobenzene surface patterning is that the SRG structure is 180° out of phase compared to the light interference pattern. This means that the polymer chains move away from the bright fringes and pile up on the dark fringes in the direction of the light polarization. If the intensity profile of the interference pattern is flat, but the amplitude of the electric-field component in the direction of the grating vector is modulated, the material piles up in the region of smallest amplitude. Experimental data shows that grating formation is most efficient with polarization combinations with an electric field vector component in the direction of the grating vector, such as *p*–*p* and counter- circularly-polarized beam configurations.¹¹ In amorphous systems, illumination with an *s*–*s* polarization combination produces essentially no surface pattern, even if counter-examples do exist.^{171,172} In a

recent study by Yadavalli *et al.* an AFM was combined with a two-beam interferometric setup for *in-situ* scanning of the polymer film while illumination with different polarization states of the two interfering beams.¹⁷³ This simple setup enabled the analysis of the topographic changes in relation to the variation of the electrical field vector within the interference pattern. Interestingly, an *s-p* polarization combination resulted in surface structures with half the periodicity of the optical pattern. Also, the polarization-dependent flow of azopolymers can be clearly visualized using prepatterned line arrays, which deform under irradiation.¹⁷⁴

At this point, it should be noted that the light-induced mass transport occurs also upon different types of irradiation patterns and even in the absence of a field gradient.¹¹ Under specific conditions, regularly ordered hexagons with random height distribution appear on the film surface upon irradiation with a single beam.¹⁷⁵ Such structures can be subsequently irradiated with a holographic interference pattern to organize the hexagons into a periodic grating with random roughness, resembling the wings of *Morpho* butterflies.¹⁷⁶ Furthermore, superhelix-like SRGs can be generated with a combination of elliptical polarizations,¹⁷⁷ while irradiation with three interfering beams result in the formation of hexagonally arranged troughs.¹¹ Recently, Ambrosio *et al.* showed that the direction of mass transport is sensitive to the helical wavefront handedness of a doughnut-shaped optical vortex beams, resulting in spiral-shaped surface structures.^{152,178} The multitude and complexity of these experimental findings have provoked a number of theoretical studies to explain the driving mechanism of light-induced mass transport, which will be reviewed next.

3.2 Mechanism of macroscopic mass transport

The driving mechanism behind light-induced mass transport is still debated, although it is commonly acknowledged to originate from the fast cycling between *trans* and *cis* azobenzene isomers and the subsequent modifications in the local environment of the chromophore.²³ The magnitude of stresses exerted by light-driven macroscopic motions on the host material was recently approximated to be 0.1–0.4 GPa by Yadavalli *et al.*, who deposited very thin gold layers on top of an azopolymer film and analysed crack formation in the gold layer during SRG inscription.¹⁷⁹ Different kinds of cracks were found at the crests and the hills of the grating, indicating different types of stresses experienced by the metal. Various models have been developed to explain these light-induced stresses and the subsequent macroscopic movements of azopolymers, but still none can explain all the experimental observations described in the previous Section.

Early efforts to explain mass transport focused on describing the forces that make the material move. The pressure gradient model developed by the Natansohn/Rochon collaboration proposed that the *trans*-*cis* isomerization and associated volume change causes internal stresses that result in mass transport.¹⁷⁰ However, this theory could not explain the SRG formation with purely polarization-modulated illumination. Kumar *et al.* then suggested the process to be driven by an optical gradient force and were able to adequately explain the polarization dependence,¹⁸⁰ while Lefin *et al.* introduced the concept of anisotropic worm-like diffusion of the azo chromophores.¹⁸¹ Following theories focused on addressing the mass transport process to gradients of the optical field that cause a local change of parameters such as polarization, free volume, density and molecular orientation of the azobenzene molecules, leading ultimately to diffusion of the chromophores from the bright regions to the dark regions of the illumination pattern. For example, the microscopic theory of Saphiannikova and coworkers is based on the idea that the photoinduced alignment of azobenzene chromophores creates mechanical stress along the polarization direction.¹⁸² In 2009, the photoinduced molecular diffusion (PIMD) model of Juan *et al.* could predict almost all reported light-induced motions of azo-materials in terms of the diffusional directionality of a single azobenzene molecular motion.¹⁸³ Yet, the movement of larger molecules such as azopolymers remained unexplained. Ambrosio *et al.* then developed the PIMD model further by including an additional surface-enhanced diffusion term in the mass transport vector in order to explain the spiral relief patterns observed under vortex light illumination.¹⁷⁸ However, this simplified model did not account for the chromophore photo-orientation effects at the microscopic level nor the viscoelastic couplings in the polymer at the macroscopic level, leaving the mass transport phenomenon still unsolved.

Besides the driving force of mass transport, many have focused on describing the viscous flow of the polymer.^{183–186} The PIMD model assumes that azo-induced motion can be optimized near T_g , but typical experiments are conducted at room temperature. This brings us to consider the mechanical characteristics of the host material. In general, it has been assumed that the viscosity of the polymer has to be reduced significantly, but as thermal effects have been excluded, how is the viscoelastic flow possible well below T_g ? Saphiannikova *et al.* claimed that permanent surface patterns will only form when the photo-orientation-induced stress exceeds the yield stress of the material in question, and managed to estimate these stresses in their microscopic model.¹⁸² They also found that the SRG formation efficiency is directly proportional to temperature due to competition of the photoinduced ordering of the azobenzene chromophores and temperature-induced disorder. The light-induced stress decreases with increasing temperature and above a certain temperature the effect of thermal relaxation overrules the effect of

photo-orientation, and surface deformation becomes purely elastic. However, the model of Saphiannikova *et al.* explicitly excluded the possibility of significant light-induced plasticization in the polymer material, which was suggested already by Kumar *et al.* in 1998.¹⁸⁰

To date, several studies have reported photoinduced changes in the mechanical properties of azopolymer thin films upon light irradiation. Among the first were Srihirin *et al.*, who measured the elastic compliance of thin polymer films doped with an azobenzene dye using quartz crystal resonators and described light-induced softening upon irradiation with visible light.¹⁸⁷ In 2005 Karageorgiev *et al.* utilized AFM-based indentation experiments to show that a rigid pDR1M azopolymer film can be “photofluidized” upon light irradiation, reporting a remarkable 74% decrease in elastic modulus complemented with a reduction in viscosity by many orders of magnitude. The study also confirmed the directionality of photsoftening as opposed to that induced by heat; the light-induced softening process leads to directional viscoelastic flow parallel to the light polarization. These photoinduced changes in the mechanical properties of the host material, now further supported by more experimental work^{188–190} and molecular simulations,^{191–193} likely stem from the cyclic photoisomerization reactions of the azobenzene molecules. In the future, the molecular-level mechanism of photofluidization and coupling to the optical gradients present in the material have to be further rationalized. The difficulty is that the surface patterning is highly dependent on the structural and viscoelastic characteristics of the material system, as well as the experimental conditions. Furthermore, the presented theoretical models typically deal with linear polymer materials where the azo chromophores are covalently attached to the side chains, and therefore cannot be directly applied to alternative material concepts and extreme cases, such as the ones presented here in Publications II and III. Thus, a large amount of both theoretical and experimental work is still needed in order to thoroughly understand the light-induced macroscopic motions, which is a prerequisite for efficient use of azobenzene surface patterning in applications.

3.3 Efficient mass-transport in supramolecular azobenzene-containing materials

Most results concerning SRG formation, including the initial discovery of the process, have been obtained using polymers with covalently attached azo chromophores as pendant groups. These investigations could first identify that the process is unique to azobenzene-containing systems, and provided increasing understanding of the underlying mechanisms. Further on, various photosensitive SRG materials were developed along with a host of new applications, and the importance of the wide body of studies on covalent

azopolymers should be acknowledged. However, applications demand easily processable, low-cost materials that provide good optical quality and show efficient, reproducible photoresponse. Hence, novel materials concepts with optimized optical performance are constantly being investigated. A feasible alternative to covalent systems has emerged within recent years, as the photoinduced motions in supramolecular polymer–azobenzene complexes have achieved considerable interest, leading to impressive results.

The first report on SRG formation on supramolecular hydrogen-bonded polymer–azobenzene complexes was published in 2007 by Gao *et al.*, utilizing a hydrogen bond between a pyridine group in the polymer and a carboxyl group in the chromophore.¹⁹⁴ Kulikovska *et al.* studied the photoinduced mass migration in ionic azobenzene–polyelectrolyte complexes, reporting stable SRGs with remarkable surface modulation depths up to 1.8 μm .¹⁹⁵ Later, working also with ionic complexes, Zhang and co-workers reported a correlation between the efficiency of SRG formation and the photoinduced birefringence value.¹²³ Another demonstration of light-induced mass transport in hydrogen-bonded complexes was then reported by Zettsu *et al.*, who studied SRG formation in supramolecular LC azopolymers and showed that the azobenzene chromophores can be selectively removed after grating inscription due to the dynamic nature of the hydrogen bonds.¹⁰⁹ They also elaborated the importance of binding between the chromophores and the host materials, since no SRG was formed if the hydrogen bonding was prevented. Another important advantage of the supramolecular approach was shown by Priimagi and co-workers, who demonstrated that the SRG modulation depth can be adjusted by varying the chromophore concentration.¹²⁰ Recently, Schab-Balcerzak *et al.* reported on hydrogen-bonded supramolecular azo-polyimides capable of surface patterning, and found that the SRG inscription efficiency was more dependent on the structure of the polymer than the type of bond between the polymer and the chromophores.^{107,196} Besides linear supramolecular polymers, also dendritic molecules have been shown to undergo mass transport when functionalized with azobenzene using noncovalent interactions.¹¹³

In addition to hydrogen bonding and ionic systems, surface patterning in halogen-bonded azomaterials have been very recently demonstrated with impressive results. Halogen bonding offers a unique possibility to study the effect of strength and type of the noncovalent bond between the chromophores and the host polymer on the efficiency of mass transport. Priimagi *et al.* studied grating formation in a series of materials consisting of a bond-accepting P4VP host and azo chromophores with three different halogen substituents, and concluded that the SRG formation efficiency increases with the interaction strength.¹²⁵ Furthermore, the directionality of the halogen bond was found to promote mass transport. In another study, the same researchers demonstrated a

remarkable efficiency of mass transport in an LC system constructed from non-liquid-crystalline starting materials by halogen bonding, in which the modulation depth of the inscribed grating was found to be more than twice the initial film thickness.¹¹⁷ These results demonstrate a huge potential for halogen-bonded material systems in light-induced surface patterning, both for fundamental and application-oriented work.

Inspired by the literature discussed above, the research presented in the following Sections seeks for further understanding on the influence of material-related parameters on the efficiency of mass transport. Taking advantage of the toolkit of supramolecular chemistry, we will look into the effect of the chemical structure and the concentration of the chromophore, as well as to the size and molecular shape of the host material.

3.3.1 Surface patterning in supramolecular polymer–bisazobenzene complexes over a broad spectral range (Publication I)

As described in Section 2.3.2, the magnitude and stability of the photoinduced birefringence can be improved with chromophores containing two photoisomerizable azo groups. Such bisazo-polymers can also be feasible for light-induced surface patterning, as demonstrated by Vapaavuori *et al.*¹⁹⁷ The study showed highly efficient SRG formation in the P4VP(DY7)_y complexes, which is one of the materials used in Publication I. Interestingly, surface modulation depths exceeding 600 nm could be reached with the non-polar DY7 chromophore. The authors linked the efficient mass transport to the amorphous nature of the material, as the direct, spacer-free coupling of the chromophore to the polymer disables liquid crystallinity despite the mesogenic character of DY7. However, it is known that the SRG inscription can be enhanced by using azobenzene units that are substituted with electron donor and acceptor groups, whereas DY7 has no substituents in the other benzene ring. It is therefore tempting to try to improve the efficiency of SRG inscription using similar polymer-dye complexes with such push-pull type bisazo chromophores.

In Section 2.3.2 it was already shown that the polar bisazo chromophore 2NHA exhibits high and stable photoinduced birefringence, much owing to the bulky methoxy substituents in the middle benzene ring. Besides the photoinduced birefringence, the mass-transport efficiencies of the P4VP(2NHA)_x complexes were investigated in Publication I. Surface patterns were inscribed at three different writing wavelengths with a circularly polarized beam as presented in Section 3.1. Figure 3.3 presents the average modulation depths as a function of the complexation degree for SRGs inscribed on P4VP(2NHA)_x sample films with writing wavelengths of 405 and 514 nm, which showed comparable behaviour. Similarly to the study of Vapaavuori *et al.*, the average SRG modulation depth increased as a function of the degree of functionalization up to $x = 0.5$, after which the depth growth levelled off. Even

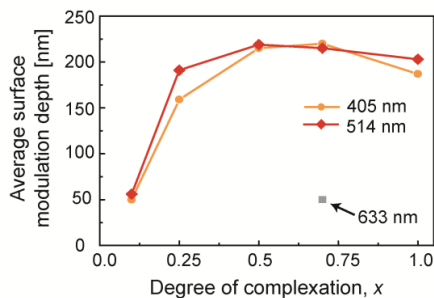


Figure 3.3. Average modulation depths as a function of the complexation degree for SRGs inscribed on P4VP(2NHA)_x sample films with writing wavelengths of 405, 514, and 633 nm. Adapted from Publication I with permission from the American Chemical Society ©2011.

if the grating depth almost reached the initial film thickness, the push-pull character of 2NHA did not provide added value in terms of inscription efficiency. It may be that the bulkiness of 2NHA restricts the movement of the chromophore compared to the rod-like DY7 molecule. In fact, it is quite surprising that both large and stable photoinduced birefringence and efficient surface patterning can be induced within the same material. Birefringence is typically high and stable in materials where chromophore-chromophore intermolecular interactions are strong, giving rise to LC behaviour and deceleration of SRG formation.²⁰ However, the bulky side groups in the polar 2NHA chromophore prevent the molecules from packing tightly together, which inhibits excessive intermolecular interactions and renders the material amorphous.

Nevertheless, the structure of 2NHA does provide an additional advantage compared to DY7 due to its broad absorption band, as it was already shown that stable photo-orientation could be inscribed at three very different inscription wavelengths. This result inspired us to study if also effective mass transport could be induced in the P4VP(2NHA)_x material at a wavelength that lies far above the absorption maximum. When it comes to SRG inscription with a red laser beam, literature remains sparse. While the SRGs inscribed with a 633 nm beam in an azo-containing molecular glass by Ozols *et al.* were the results of irreversible photodegradation, only Goldenberg and co-workers have published an efficient SRG formation at 633 nm in a low-molecular weight azobenzene-containing material that had the absorbance maximum at 495 nm.

As is shown in Figure 3.3, it was indeed possible to inscribe a surface pattern using irradiation wavelength of 633 nm, even if the inscription beam intensity used was substantially lower than at 405 and 514 nm. Obviously, the lower absorbance at the longer-wavelength side of the absorbance tail reduced the efficiency of the SRG formation, leading to modulation depth of 50 nm after 90 min inscription in the $\text{P4VP(2NHA)}_{0.7}$ sample. Improvements to the inscription setup and parameters would undoubtedly yield SRGs with higher modulation depths with the red inscription beam.

3.3.2 How much azobenzene is needed to induce mass transport? (Publication II)

As was demonstrated in Publication I, supramolecular polymer-azobenzene complexes provide a simple platform to study the relationship of the chromophore structure and efficiency of mass transport. However, general understanding on how the material parameters affect the surface patterning is still inadequate. Besides the molecular weight and the T_g of the polymer, the azobenzene content of the material is known to have a significant effect,¹²⁰ and many have investigated this aspect with intermediate or high azobenzene concentrations in order to optimize the optical performance of the material system for increased efficiency.^{161,198,199} On the other hand, exploring the effect of chromophore concentration could reveal the fundamental limits of light-induced macroscopic motion – what is the true efficiency of the azobenzene molecular motor when it comes to induction of macroscopic movements? Is it possible to define a threshold azo content for the mass transport to occur and does such a limit even exist?

To our knowledge, none of the proposed theories of the mass transport have taken into account the effect of azobenzene content on the surface-patterning mechanism, nor could we find literature to provide experimental data on the threshold azo content of SRG formation, even if this data might impact the future development of the microscopic theory of the light-induced mass transport. For example, in the studies of Andruzzi *et al.*¹⁹⁹ and Börger *et al.*¹⁹⁸, the minimum azo content was approximately 7 mol-%. With the tools of covalent synthesis, it is undeniably time-consuming if not impossible to prepare series of polymers with varying chromophore content in a reliable and systematic manner. However, the noncovalent functionalization strategy provides suitable tools to freely change the amount of chromophores while keeping the polymer backbone exactly the same. Previously, even equimolar chromophore-polymer complexes have been prepared without excessive aggregation or phase separation.¹²⁰

In Publication II, the chromophore content in a hydrogen-bonded polymer-azobenzene complex was systematically decreased to find a critical concentration limit, below which mass transport no longer occurs. The material system used for the study consisted of a P4VP backbone functionalized with 4-hydroxy-4'-dimethylaminoazobenzene (OH-DMA) (See Figure 3.4a). Based on previous studies, this material is known to be amorphous and efficient in surface patterning,¹⁴⁵ and hydrogen bonding between the constituents has been confirmed previously by FTIR.³⁴ A series of complexes with degree of complexation x from 0.005 (i.e. 0.5 mol-% azobenzene content) to 0.1 were prepared by simply mixing of solutions containing the chromophores and the polymer, as listed in Figure 3.4b with the respective chromophore concentrations as weight percentage. The UV-vis spectrum of the

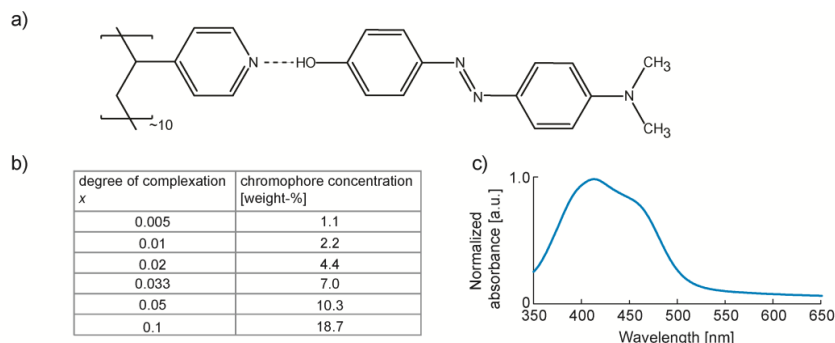


Figure 3.4. a) Chemical structure of the nominally stoichiometric P4VP(OH-DMA)_{1.0} complex, b) the chromophore concentrations as molar ratio and weight-% and c) the normalized UV-vis absorption spectrum of P4VP(OH-DMA)_{0.1}. Adapted from Publication II with permission from the American Chemical Society ©2014.

P4VP(OH-DMA)_{0.1} complex is shown in Figure 3.4c. At the smallest studied concentration of $x = 0.005$, there is one OH-DMA molecule per every 200 polymer repeat units. Since a very short polymer chain length, an oligomer of 10 repeat units, was chosen for the study to obtain fast dynamics in mass transport,¹⁴⁵ this means only one azobenzene per 20 individual oligomers. Surface patterning was performed on drop-cast films with thicknesses above 2.5 μm using circularly polarized light in the inscription setup presented in Section 3.1. The evolution of the diffraction efficiency is presented in Figure 3.5a for all the studied complexes, and the values of diffraction efficiency after 10 min inscription are shown in Figure 3.5b.

As expected, the efficiency of mass transport increased significantly when the OH-DMA concentration was increased. The average modulation depths of the SRGs obtained by AFM were in good agreement with the diffraction data, as presented in Figure 3.5b. The most important outcome of the experiment was that the light-induced mass transport occurred even in the P4VP(OH-DMA)_{0.01} complex, resulting in a SRG of 40 nm after 10 min of irradiation. When the

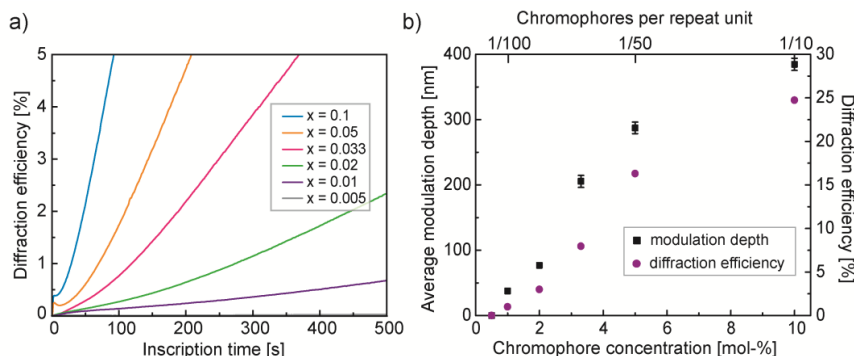


Figure 3.5. a) Diffraction efficiency as a function of inscription time for all the complexes, and b) average modulation depths (black cubes) and diffraction efficiencies (violet circles) as a function of chromophore content. The error bars denote the standard deviation in the AFM data. Adapted from Publication II with permission from the American Chemical Society ©2014.

amount of azobenzene was reduced to 0.5 mol-%, grating formation was no longer observed even upon prolonged inscription. On the other hand, when the inscription time and intensity were increased for the $\text{P4VP(OH-DMA)}_{0.01}$ complex, a considerable modulation depth of 170 nm could be reached. Within the inscription time of 90 min, the diffracted signal did not show any sign of saturation, which implies that SRG with modulation depth of hundreds of nm could be inscribed even in samples bearing negligible amount of azobenzenes if the inscription time would be further increased.

The fact that light-induced surface patterning still takes place in a material which contains nominally 1 azobenzene molecule per 100 polymer repeat units is rather astonishing. As each oligomer carries on average 10 repeat units, this means that only one out of every ten oligomers contains a chromophore while the other nine remain azobenzene-free. To visually demonstrate how little amount of azobenzene is responsible for the macroscopic mass transport, the complexes with varying degree of functionalization are schematically depicted in Figure 3.6. It should be noted that the presently found threshold concentration of 1 mol-% is likely to be very system-specific, and calls for more research using different chromophores and binding motifs, as well as polymers with varying chain lengths. Such systematic studies should be performed in the future.

In order to rationalize the light-induced mass transport at such low azobenzene content, we decided to estimate the average intermolecular distances between the chromophores to see whether intermolecular interactions play a role in the process. Taking the inverse value of the number density N of the chromophores,²⁰⁰ the volume occupied by a single chromophore can be calculated. Now the cubic root of this value gives an estimate for the average distance between the chromophores r , as

$$r = \sqrt[3]{\frac{1}{N}} = \sqrt[3]{\frac{M}{w_i \rho N_A}} \quad (3.2)$$

where w_i is the chromophore weight fraction, ρ the density of the material, N_A the Avogadro's number, and M the molar mass of the chromophore. As for the current system, the density of the material was estimated to be 1.2 g/cm³, which is slightly more than for pure P4VP.²⁰¹ We assumed the chromophores

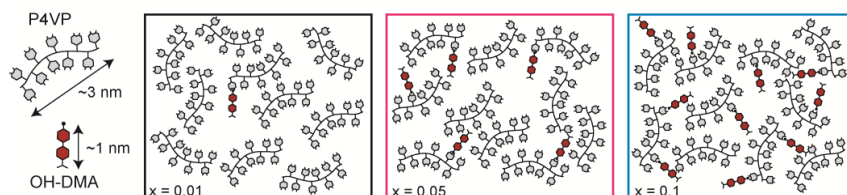


Figure 3.6 Schematic visualization of the complexes with 1, 5 and 10 mol-% of azobenzene. Adapted from Publication II with permission from the American Chemical Society ©2014.

to be uniformly distributed within the matrix, as the material was proven to be amorphous by POM. The calculated average intermolecular distances between the OH-DMA molecules as a function of degree of complexation are presented in Figure 3.7.

For P4VP(OH-DMA)_{0.01}, the estimated intermolecular distance was much larger than the value reported for the azobenzene self-assembled monolayers that suffered from excitonic coupling quenching the photoisomerization.^{202,203} Based on the proposed r^{-3} distance dependence for excitonic coupling,²⁰⁴ it was clear that the photoisomerization at very low azobenzene content is not affected by adjacent chromophores. Consequently, the light-induced mass transport had to be caused by the action of dispersed, independent azobenzene units in a polymer.

Essentially, the results pointed out that not every polymer chain has to carry a photochromic unit for the mass transport to occur, and also intermolecular interactions between the chromophores are not needed. These interesting and important findings challenge some of the previously proposed theories and thus call for further modelling on the microscopic mechanism at work. In particular, Saphiannikova and coworkers^{23,40} claimed that the light-induced stress responsible for mass transport should be above the yield stress of the material, and used relatively large chromophore number density (20 azobenzenes per each oligomer vs. in our case 0.1 chromophores per oligomer) to obtain stress values large enough. On the other hand, as the viscous flow of the polymer below T_g is believed to be enabled by photoinduced mechanical changes (described in Section 3.2), it would be important to measure the magnitude of such changes at very low azobenzene content, preferably in various systems. Moreover, the type of bonding between the chromophores and the polymer may also play an important role in the mechanism, as the photosoftening phenomenon was observed to be much more pronounced in hydrogen-bonded polymer-azobenzene complexes than in covalent systems.¹⁸⁸ Lastly, due to the dynamic nature of hydrogen bonding, it is possible that each chromophore interacts with several oligomers during the surface patterning process, which might explain why SRG formation still occurs at very low azo content.

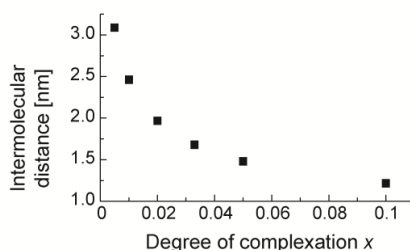


Figure 3.7. Average distance between the chromophores as a function of chromophore content. Adapted from Publication II with permission from the American Chemical Society ©2014.

3.3.3 Light-induced mass-transport in high-molecular weight dendrimers and proteins (Publication III)

In Publication II, we explored how little amount of azobenzene in the system is needed for effective mass transport. In that study, very short polymer chains were used for optimal inscription efficiency, since it is commonly believed that increasing chain length in linear polymers may hinder surface patterning due to chain entanglements. Therefore linear polymer architectures cannot be used to answer another fundamental question: is there a size limit of molecules that can be transported with light-fuelled azobenzene motions?

In contrast to linear polymers, branched molecules such as dendrimers allow for a systematic study of the effect of molecular architecture and bulkiness on the grating formation due to their well-defined monodisperse structure. However, surface patterning in azo-dendrimers has only received limited attention, and the largest molecules investigated have been generation 5 dendrimers.^{113,115,205} Generally, the azo-dendrimer studies suggest that the structure and rigidity of the dendrimer dominate over size and generation in determining the optical response. For instance, Gharagozloo-Hubmann *et al.* reported similar SRG formation efficiency in star-branched polymers with different amount of branches but otherwise similar properties.²⁰⁵ Therefore, it seems that as long as the chromophores are prevented from forming micro-phase separated domains, there is no apparent upper limit on dendrimer generation in the SRG formation process. Thus, even very large dendrimers could exhibit attractive light-responsive properties when cleverly designed.

Publication III describes a study of the light-induced surface patterning in materials consisting of high-molecular weight dendrimers as the host material and Ethyl Orange (4-(4-Diethylaminophenylazo)benzenesulfonic acid) chromophores as the photoactive units. The dendrimers utilized in the study were triazine-based molecules with molecular weights ranging from ~8000 g/mol (generation 3) to 530 000 g/mol (generation 9), for which the synthesis has been previously published.²⁰⁶ The materials were prepared by mixing of dilute aqueous solutions of the constituents. Stoichiometric complexation occurred through the electrostatic attraction between the positively charged amine surface groups of the dendrimers and the negative sulfonic acid group of the chromophores, resulting in azo-functionalized dendrimers with approximately 40 weight-% of EO. Complexation was confirmed by FTIR, UV-vis spectroscopy, dynamic light scattering (DLS) and AFM. A schematic structure of the generation 3 complex (G3-EO) is shown in Figure 3.8a, whereas the theoretical M_w and experimentally determined diameters of the dendrimers, the number of end groups per dendrimer, and the M_w of nominally stoichiometric dendrimer-EO complexes are shown in Figure 3.8b. Surface patterning experiments were performed on spin-coated thin films in a similar

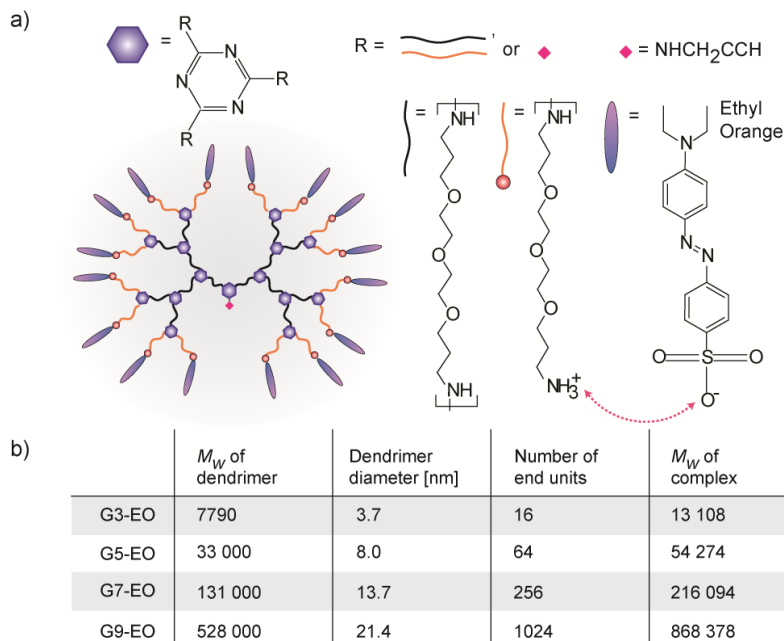


Figure 3.8. a) Schematic representation of G3-EO and the chemical structures of the constituent units and the EO chromophore. (b) Dendrimer sizes, the respective amount of end groups per dendrimer and M_w of nominally stoichiometric complexes. Adapted from Publication III with permission from the American Chemical Society ©2014.

way to Publications I and II, using sample solutions with dendrimer-EO mass fraction of 1.0.

Quite surprisingly, all the complexes were able to undergo macroscopic mass transport despite the very high molecular weight. In fact, the modulation depth of the SRGs increased with the dendrimer generation up to G7 and was equal for G7 and G9, as can be seen from Figure 3.9a. Notably, mass transport occurred even in the largest complex, G9-EO, in spite of its very large M_w of almost 900 000 g/mol. This was somewhat counterintuitive, as the greater molecular weight of the larger dendrimers was thought to result in less efficient mass transport. SRG inscription was, of course, much slower in the large dendrimer-azo complexes compared, e.g., to short polymer chains utilized in Publications I and II. As an example, the evolution of diffraction efficiency during inscription is shown in Figure 3.9b for G3-EO. AFM images of the grating on the G9-EO sample are shown in Figure 3.9c. The effective mass transport in the high-molecular weight dendritic complexes can be attributed to the structure of the material. The dendrimers consist of long hydrophilic chains connected with triazine rings, thus being highly flexible, yet the globular shape of the molecule prevents them from forming intermolecular entanglements that would decrease mobility. The EO chromophores, on the other hand, are rigid and polar molecules, but as they are strongly bound to the peripheral groups of

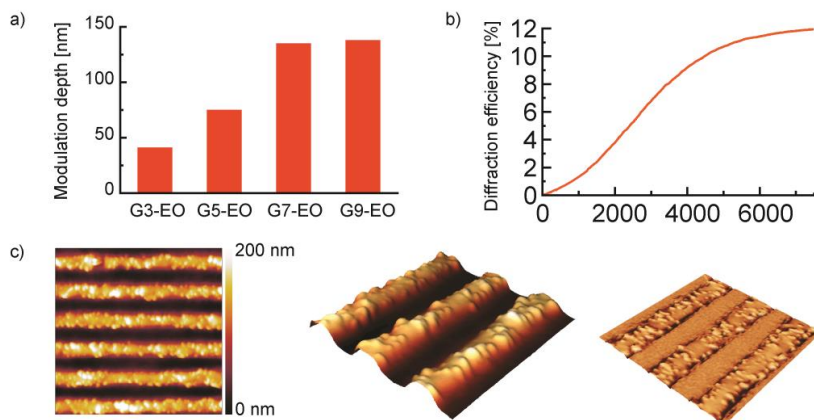


Figure 3.9. a) Average modulation depths of the SRGs on the dendrimer–azobenzene complexes, b) diffraction efficiency as a function of inscription time in G3-EO, and c) a 5x5 μm AFM height image of an SRG on G9-EO with the corresponding 3D height and phase images. Adapted from Publication III with permission from the American Chemical Society ©2014.

the dendrimers, excessive intermolecular interactions between the chromophores are prevented. Thus, there are no steric constraints on photoisomerization that would compromise the SRG inscription process. Also, as the bulky chromophores are assumed to be uniformly arranged around the globular dendrimers, they further decrease the likelihood of entanglements.

The surfaces of the SRGs revealed an unusual bumpy texture, which might be related to the globular structure of the complexes. The same texture could be observed also in the AFM phase image of the grating, but was not found on the unilluminated areas of the samples. This additional surface texturing of the SRG patterns could be exploited for instance in applications in directed cell growth as cells can sense and react even to very small topographical differences.

At this point, it was clear that mass transport can occur in a material that consists of very large yet flexible globular molecules, which carry chromophores on their surfaces. It was then interesting to see what happens to the SRG inscription efficiency if we introduce more rigidity to the structure of the globules. Even if the properties of the dendrimers could be varied via synthetic tools, there is a way to avoid such excessive laboratory work. Suitable and functionalization-ready materials of globular shape can be found abundantly in nature, such as viruses and proteins. For Publication III, we chose a ubiquitous intracellular iron-storage protein *ferritin*, which is a hollow globular shell (*apoferritin*, aFT) with diameter of 12 nm (see Figure 3.10). The motivation for this choice was two-fold. Firstly, the protein can be similarly functionalized with negatively-charged EO chromophores, as the surface carries a net positive charge at pH below the pI of the protein (~ 4.5). Ferritins, like other protein cages, can be viewed as nanoparticles with a well-defined

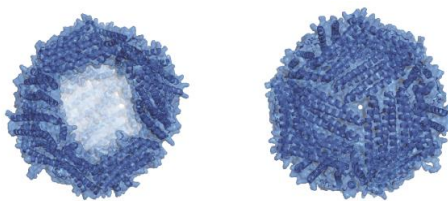


Figure 3.10. Three-dimensional presentations of the aFT structure with a cut-out showing the hollow shell (left) and through the three-fold symmetry axis (right). Adapted from Publication III with permission from the American Chemical Society ©2014.

hollow structure and ability to encapsulate various synthetic and biological materials.^{207,208} Secondly, the biological applications of azobenzene-based surface patterns have only started to emerge,^{209–211} yet no reports on SRG inscription on biological material could be found in literature.

The molecular weight of aFT, 450 000 g/mol, falls between the G7 and G9 triazine dendrimers, while it differs significantly in terms of structure and rigidity. The protein consists of tightly arranged subunits, which makes it more of a hard, rigid sphere than a soft, flexible globule. As with the dendrimers, ionic complexation between the EO chromophores and the protein was verified by DLS. Although aFT is known to form well-defined higher-order structures at suitable conditions, the films prepared for the current study were amorphous based on small-angle X-ray scattering experiments. Thin films of aFT-EO were prepared by spin-coating from aqueous solution and patterned using the previously described method.

First of all, also the azo-functionalized protein complexes were able to undergo light-induced mass transport. If compared to the dendrimer samples, the growth of the diffraction efficiency levelled off significantly sooner, at around 30 min, whereas it took over 2 hours for the SRG inscription process to saturate in the dendrimer complexes. AFM revealed an SRG structure with an average modulation depth of approximately 50 nm (see Figure 3.11), which is significantly less than for the SRGs inscribed in the dendrimer-EO complexes. The bumpy surface texture of the dendrimer gratings was not observed on the protein-EO samples, which further indicated that the dynamics of SRG



Figure 3.11. 10×10 μm AFM height image of an SRG on the aFT-EO film, with the corresponding phase image and a 3D presentation. Adapted from Publication III with permission from the American Chemical Society ©2014.

formation differ considerably between the protein and the dendrimer complexes due to their structural differences. However, this was the first demonstration of SRG inscription on a native biomaterial, and an important step towards biological applications. In the future, the intrinsic capability of aFT to host other materials inside its cage could be used to introduce chemical triggers to combine with the physical cues provided by the topography. The facile fabrication of such multifunctional surfaces would be highly interesting for instance to guided cell growth.

From a fundamental point of view, it has now been established that thin azobenzene-containing films comprising both flexible and rigid globular particles of large diameter can be moved with light. In the future, it would be highly interesting to extend the concept of light-induced patterning into other types of spheres of both synthetic and biological origin, such as nanoparticles and viruses. It would also be pertinent to compare the performance of such systems constructed via noncovalent functionalization to their covalently synthesized equivalents – if possible – in order to investigate the role of dynamic binding in the mass transport process.

4. Applications of light-induced mass transport

Many of the materials-related aspects of the light-induced surface patterning in azomaterials will require more fundamental research for years to come. Even if such studies are highly important for gaining further understanding on the prevailing molecular-level mechanisms, it is equally relevant to consider the application potential and new fields where the photoresponsive systems could be used. Indeed, the unique photoresponse of azomaterials allows for the fabrication of large-area periodic micro- and nanostructures in an exceptionally simple way. The surface patterns can be used either directly as functional optical structures for photonic applications and devices or, indirectly, by using them to structure and organize other materials. The aim of this Chapter is to briefly review and highlight some of the demonstrated and yet anticipated applications of the photoinduced mass transport phenomenon. Also, the advantages of this method as a nano- and micropatterning tool are elaborated. The photoinduced SRGs exhibit widespread potential in nanofabrication of complex structures for photonics and plasmonics. In this regard, the light-induced SRG structures are used to prepare gold nanohole arrays with non-trivial optical transmission properties (Publication IV). Finally, novel uses beyond periodic patterning as well as future directions will be shortly discussed.

4.1 Applications of light-induced surface-relief patterns

The general interest in micro- and nanofabrication of periodic surface gratings stems from the fact that such structures can be used to induce interesting optical phenomena such as diffraction and surface plasmon polaritons.^{212,213} Also, well-ordered gratings are employed as the basic structural units in integrated electronic and energy devices.²¹⁴ Conventionally, surface patterns with controlled dimensions at the micro- and nanoscale have been realized by fabrication techniques such as photolithography and scanning beam lithography. While these methods offer high resolution and freedom in design, they typically require cleanroom conditions and multiple fabrication steps with high processing and maintenance costs. Optical lithography relies on

photoresist materials that usually require restricted lighting conditions and high-precision UV exposure. Additional photoresist development and lift-off steps that are needed immediately after the exposure increase the overall fabrication time.¹⁵⁷ Moreover, patterning of large surface areas is cost-inefficient with these conventional methods, which also do not offer the possibility to rapidly change the design of the structure when desired. To overcome these restrictions, other less common fabrication methods have been developed, including soft lithography,^{215,216} nanoimprint lithography, nanosphere lithography,²¹⁷ block-copolymer lithography,²¹⁸ interference lithography²¹⁹ and dip-pen nanolithography.^{220,221} However, also these methods suffer from limitations such as inherent defects, hence cannot surmount all the problems of the conventional fabrication strategies.²³

Compared to the above-mentioned fabrication techniques, the photoinduced surface patterning of azomaterials offers several advantages. Firstly, the size of the patterned area only depends on the dimensions of the incident light beam and the film, thus wafer-scale fabrication of light-induced surface patterns is possible. The patterning occurs uniformly and simultaneously over the illuminated area, and the quality of the inscribed structure depends mainly on the smoothness of the film and the optical quality of the laser beam. Secondly, azopolymers do not require highly controlled humidity, temperature, and lighting conditions during fabrication, which are typical requirements for traditional photoresist materials used in lithography. Once inscribed, the surface patterns will persist at least over several years under ordinary storage conditions. Furthermore, azopolymers typically absorb at the visible wavelength range; thus no UV light sources are required, nor is the use of master molds, mask aligners or any post-processing. The listed benefits apply to both conventional covalently-functionalized azopolymers as well as to the supramolecular materials. However, the commercially available azopolymers are typically rather expensive whilst the noncovalent systems can be prepared from cheaper constituents, rendering the supramolecular azomaterials attractive also from the application point of view.

The potential of the light-induced SRG structures in optics and photonics was acknowledged early on. Until today, myriad of photonic applications for the SRG patterns have been proposed, including diffractive optical elements,²²² optical polarizers,²²² angular or wavelength filters,^{223–226} couplers for optical devices,²²⁷ and even tunable polymeric lasers.^{158,228–230} Furthermore, the mass transport phenomenon can be exploited as an optical data storage and holographic recording mechanism.^{231–233} One of the most beneficial features of the light-induced patterning is the fact that the material is not chemically modified during the process, unlike photoresists that are typically irreversibly ablated or crosslinked upon light exposure. Therefore the surface can be re-patterned several times. This reversibility allows multiple gratings to be

superimposed, to create multilayered structures,²³⁴ but it also renders the surface patterns suitable for rapid prototyping of optical elements that can be generated or modified quickly and during device operation.²³⁵ For a comprehensive outlook on the applications in photonics, a recent review by Priimagi and Shevchenko is recommended.¹⁵⁴

In addition to the direct use of the structured azo-containing films, light-induced patterns have been employed as molds for structuring other materials at the micro- and nanoscale. Use of the grating structure as a master to create replicas is a facile and cost-effective approach for creating periodic structures of variable shape out of basically any material. For example, this method has been utilized to improve efficiency of organic solar cells, since the periodic SRG structure enhances light-trapping in the solar-cell body.^{236–240} Besides molding, the light-induced SRGs can be used as etch masks for periodic structuring of the underlying substrate material over a wide periodicity range of 250 nm to 10 μm . Figure 4.1 presents a schematic illustration of the fabrication process using SRG etch masks and examples of silicon nanostructures fabricated with the process.¹⁵⁷ Also gold nanostructures can be fabricated in a similar fashion.^{241,242}

Azopolymer SRGs have also been employed as templates for controlled assembly of colloidal spheres²⁴³ and subsequent fabrication of sintered nanowires.²⁴⁴ Given that significant mechanical forces arise and act upon the light-induced mass transport, would it be possible to displace and organize such exogenous objects on the surface of an azomaterial film? It has previously been shown that the photoinduced softening of an azopolymer film enables the immobilization of nanospheres and proteins physically onto the surface.^{245,246} As the polymer softens upon irradiation, the particles sink partially into the film and become physically trapped. Taking this phenomenon one step further, Snell *et al.* recently showed that polystyrene nanoparticles can be organized

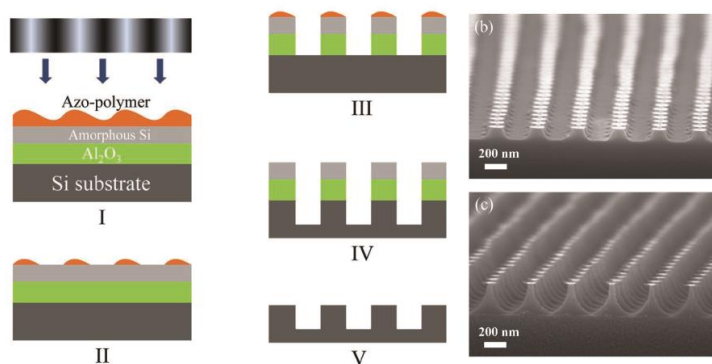


Figure 4.1. Nanopatterning of silicon using an azopolymer SRG as an etch mask. The azopolymer pattern is first transferred to the amorphous silicon using reactive ion etching and then to the alumina layer using wet etching and finally to the silicon. The SEM images present silicon structures fabricated in this way. Adapted from Ref. [157] with permission from Wiley ©2011.

into well-ordered structures as a result of SRG formation in the underlying azo-containing film.¹⁵⁹ If the particles were deposited before SRG inscription, they became embedded and aligned along the fringes. The authors envisioned that the method enables light-driven assembly of individual nano-objects over large areas, yet the influence of the particle size and material density onto the mass transport needs to be investigated more thoroughly.

A very promising, yet largely unexplored application area for the SRGs is the manipulation of living cells. Indeed, light-induced surface patterning offers precise topography control at a length scale well-suited to study the relationship between the cells and the surface geometry of the cell culture substrate, which greatly affects the adhesion, differentiation, proliferation and migration of the cells.²⁴⁷ The use of azobenzene-based surface patterns as cell culture substrates was first reported already in 2004, when Baac *et al.* introduced SRGs as submicron-scale topographical control for human astrocytes. The cells would preferentially attach onto the SRG surface and elongate along the groove direction. However, surprisingly few publications have emerged since in spite of the evident advantages of the all-optical patterning in cell culture applications.^{210,211,248,249} Figure 4.2 presents the work of Barillé *et al.*, who studied SRG inscription through a buffer solution *in vitro* and used the inscribed patterns for culturing of neuronal cells.²¹¹ More recently, Rocha *et al.* demonstrated the possibility to influence cell growth by changing the chemical architecture of the azo-containing material in addition to the topographical cues.²⁴⁹ Moreover, one of the most anticipated benefits in contrast to traditional micro- and nanofabrication is that azobenzene-based patterning enables reversible real-time control of the topography during the cell growth experiment. Furthermore, the azobenzene photoisomerization induces mechanical stress at the film surface, which could be exploited as an additional manipulation signal for the cells. Even if these aspects remain to be demonstrated, the existing studies combined with the newfound fact that SRGs can be inscribed also on films comprising native biomolecules (as shown in Publication III) indicate great potential for the light-induced surface patterning in tissue engineering. Specifically, the prospect of patterning cells into highly

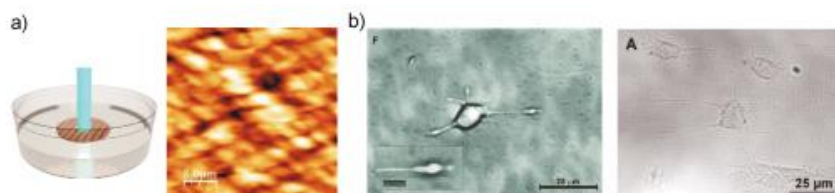


Figure 4.2. Azopolymer SRG patterns as cell culture substrates. a) Light-induced surface patterning *in vitro* through a buffer solution and an AFM image of the resulting SRG structures. b) When neuronal cells were cultured on the SRG, they grow and elongate neurites along the grooves. Adapted from Ref. [211] with permission from Elsevier ©2011.

organized networks would allow for cell-based assays for drug discovery as well as precise artificial control of electrical signalling between neuronal stem cells.²⁵⁰

4.1.1 Fabrication of plasmonic hole arrays in gold via azopolymer patterning (Publication IV)

In plasmonics, confinement and control of light at the nanoscale can be realized using structured metallic surfaces. Interactions between incident light and electrons in the metal give rise to surface-plasmon polaritons, which bring about fascinating phenomena such as the enhanced transmission of light through an array of nano-sized holes.²⁵¹ However, increasingly complicated nanofabrication techniques are required to prepare such complex structures and to enable the theoretically predicted non-trivial light-matter interactions to be realized experimentally. Nanoscale holes or particle arrays, in particular, have typically been prepared by electron-beam lithography²⁵² or focused ion beam milling,²⁵³ in which each structural feature is fabricated individually in a sequential manner. These direct-write methods offer high resolution and freedom in structure design, yet they are costly, time-consuming and limited to small patterning areas, thus being unsuitable for high-throughput production.

Large-scale patterning is warranted for practical uses as larger metal surfaces are easier to implement into sensor devices and other applications. Consequently, interference lithography with photoresist materials, as well as colloidal lithography has been proposed as alternative methods.^{254–256} However, the structure has to remain uniform over the surface in order not to compromise the sensitivity of the plasmonic response, and yet these techniques suffer from limitations related to large-scale fabrication of non-planar structures, simplicity and cost-effectiveness of fabrication or inherent defects. In Publication IV, an intrinsically three-dimensional method for fabricating such hole and particle arrays was proposed. Facile, large-area patterning of arrays of tapered holes and subwavelength-sized particles with variable size and shape was demonstrated using gold as the plasmonic material.

The fabrication process is schematically illustrated in Figure 4.3. The process began with spin-coating a thin azopolymer film on a suitable substrate. Next, a sinusoidal SRG was inscribed on the film in similar manner to Publications I–III. Another exposure, but in a 90° angle with respect to the first SRG, resulted in a tetragonal array of crests, or “a double grating”. The inscribed film was then coated with gold using electron-beam deposition. Finally, broad-beam (non-focused) ion milling at a low angle of ion incidence was employed to horizontally cut the crests of the SRG structure to the desired depth. The unit cell of the structure remained constant throughout the pattern because the ion milling removes the material at a constant rate while the substrate is spinning around its center. This fabrication scheme resulted in a

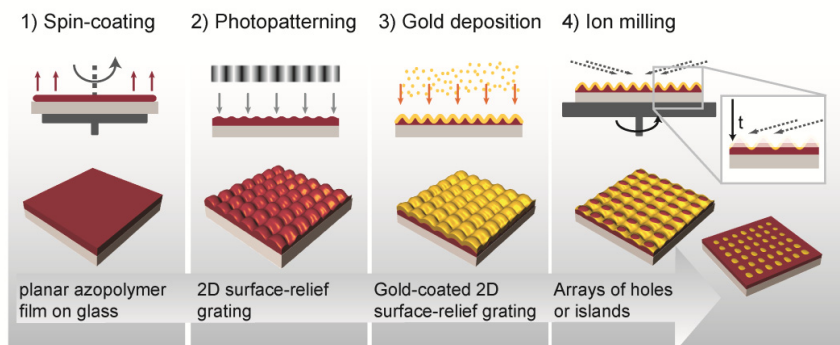


Figure 4.3. Schematic representation of the fabrication method, which results in periodic arrays of nanosized holes in a gold film or isolated gold particles on the azopolymer film. Adapted from Publication IV with permission from the Royal Society of Chemistry ©2014.

regular array of nano-sized structures ranging from holes in the gold film to isolated gold islands laying on top of the azopolymer, depending on the duration of the ion milling.

Figure 4.4 shows scanning electron microscope (SEM) images of a variety of gold nanostructure arrays that were fabricated using the presented method, ranging from small holes to isolated islands. Tuning of the structure symmetry could be done by adjusting the duration of the two exposures leading to SRG formation. The exposure time of the two gratings could be optimized to yield symmetric structures, such as the ones presented in the top row of images in Figure 4.4, whereas asymmetric structures stemmed from an azopolymer double grating in which the modulation depths were not equal in both directions. It should be noted that the method is by no means restricted to the

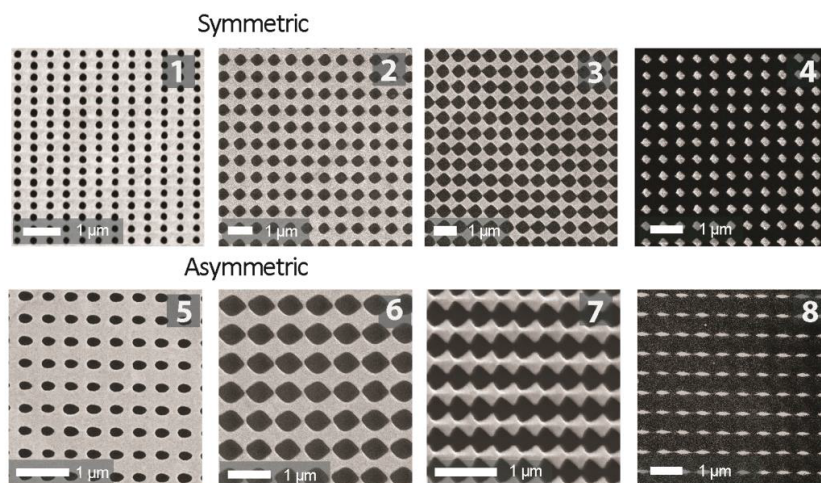


Figure 4.4. Collection of SEM images of the fabricated array structures. Images in the top row represent structures where the exposure time of the two gratings was optimized to yield a symmetric structure, whereas in the bottom row the asymmetry of the structures was introduced on purpose. Adapted from Publication IV with permission from the Royal Society of Chemistry ©2014.

tetragonal nanostructure arrays presented here. Several kinds of surface patterns can be realized on azopolymers films, which only adds to the versatility of the method.

The main advantages of the proposed method are (i) adjustable structure size, shape and periodicity, (ii) uniform patterning throughout a large sample area up to several square-centimeters and (iii) inherently three-dimensional structures. In fact, the largest possible size of the patterned area depends merely on the size of the optical inscription beam and the ion milling device used, both of which are scalable. Broad-beam Ar^+ ion milling has been used for example to polish meter-scale telescope mirrors,²⁵⁷ whereas the optical setup can easily be adjusted to pattern area over at least several square centimetres. Fundamentally, the only restraining factor for feature size is the diffraction-limited periodicity of the SRG, but even this limitation can be overcome with certain polarization combinations or possibly the use of evanescent-wave interference patterns.¹⁷³ The homogeneity and quality of the patterns depend primarily on the regularity of the SRG template. When the initial roughness of the polymer film is only a few nanometers and a highly collimated beam is used for inscription, very high-quality nanostructures can be obtained.

Importantly, any azomaterial with the intrinsic capability for mass transport can be used for the method. For example the supramolecular systems presented in Publications I and II, which are easy and relatively cheap to prepare, could be used to prepare the films. When compared to the conventional ways of fabricating plasmonic nanostructures, the presented method is fast and cost-effective. Molding, UV light sources or mask aligners are not needed, nor does it require any post-processing steps such as photoresist development.

A collection of SEM images of structure nr. 5 (as in Figure 4.4) are presented in Figure 4.5a, in order to prove that the structure really was uniform over a large area. The holes exhibited very smooth edges with no sign of distortion or roughness, and the size of the holes was uniform. Due to the three-dimensional character of the double grating, the holes were tapered, which could be exploited, for example, to enhance the extraordinary optical transmission effect.²⁵⁸ A cross-sectional SEM image of the hole array is shown in Figure 4.5b. In Publication IV the difference between planar and tapered holes, schematically depicted in Figure 4.5c, was further clarified by calculations of the plane-wave transmission of an array of tapered holes and an array of holes in a planar gold film with the same periodicity and hole diameter. It was shown that the array of tapered holes exhibited higher transmission than the planar arrays of holes, and the characteristic dip in the transmission spectrum was significantly narrower for the tapered holes than for the planar counterparts. Both of the features of tapered holes can be beneficial application-wise, for instance in the detection of small changes in refractive index for sensing purposes.²⁵⁹

As the proposed method was originally aimed at the fabrication of plasmonic structures, it was pertinent to demonstrate the real application potential of the fabricated structures. When comparing measured and simulated optical transmission through a symmetric hole array (structure nr. 1), it could be noted that, overall, the spectra matched fairly well (see Publication III). The simulation could reproduce all of the characteristic spectral features of the real sample, implying that the structure worked as expected. In a similar measurement of the subwavelength-sized gold islands (structure nr. 4) a clear narrow dip appeared in the transmission spectrum as a result of surface lattice resonance. Also for this type of an array, the spectrum could be satisfactorily approximated through simplified simulations. Even if further modelling is needed to precisely characterize the spectral features of the fabricated structures, the method was proven as a suitable tool to produce periodic nanostructures that exhibit non-trivial optical transmission properties.

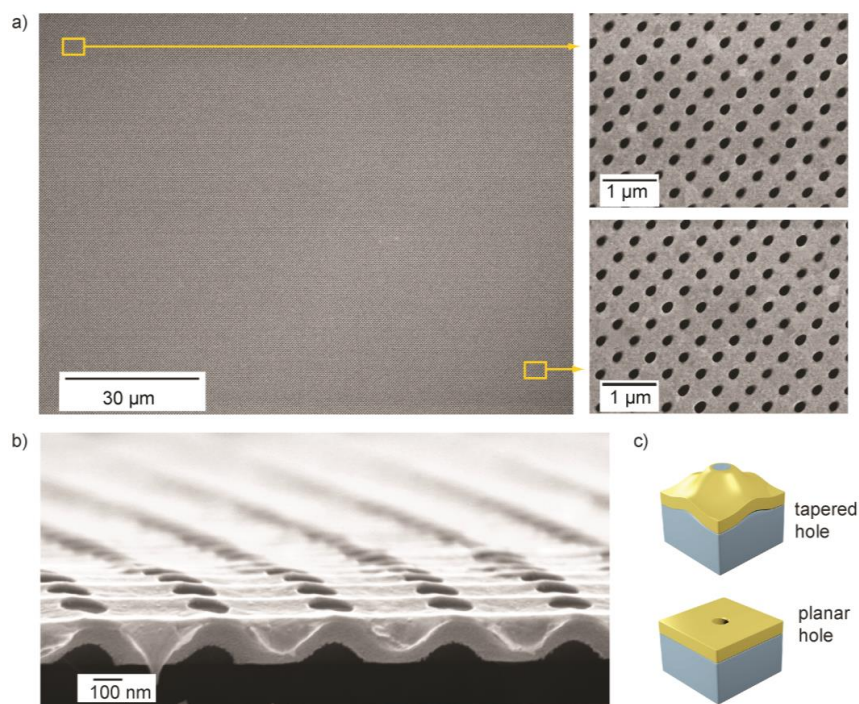


Figure 4.5. a) SEM images of a hole array structure (nr. 5 in Figure 4.2) at low and high magnification displaying a homogeneous array of holes with uniform size and periodicity over a large area, b) a cross-sectional SEM image of the hole array and c) a schematic visualization of the unit cell of a tapered-hole array and a planar hole array. Adapted from Publication IV with permission from the Royal Society of Chemistry ©2014.

4.2 Applications beyond surface-relief gratings

It is important to recognize that the use of light-induced macroscopic motions is not limited to applications of periodic patterning. For example, the photofluidic movements of azomaterials can be exploited in the post-modification of arbitrary nanostructures. Polymeric nanostructures are conventionally post-modified by a technique called “self-perfection by liquefaction”, in which the polymer is melted isothermally to improve or modify the shape and dimensions of the nanostructures.²⁶⁰ As opposed to this method, which is inherently isotropic, azobenzene-containing materials provide an additional degree of control through the directional photofluidization caused by photoisomerization. Lee *et al.* demonstrated nanofabrication by photofluidization lithography in a series of articles, in which the azopolymer films is prepatterned by soft lithography and subsequently reconfigured via single- or interfering-beam irradiation.^{155,261–263} Importantly, the direction of movement of the material is determined by polarization, thus the fabrication of a variety of complex nanostructures is simple yet precisely controlled by a distant light source.²⁶² Using this versatile post-processing method, the authors were able to prepare, e.g., large-area plasmonic nanofunnel arrays for electromagnetic field enhancement.²⁶¹ In similar experiments, Gritsai *et al.* studied the effect of polarization direction on the light-induced manipulation of pre-fabricated structures on various azomaterials.¹⁵⁶ Complicated microstructures could be fabricated for optical applications, but even more importantly, the method proved to be useful for understanding of the light-induced mass transport as the flow of material is much easier to visualize using disconnected structures or line arrays instead of homogeneous films.

Another emerging application area for the light-induced mass transport is the simultaneous near-field imaging of large samples with remarkably high resolution beyond the diffraction limit. The imaging of the optical near-field intensities resulting from the interaction of light with nanostructured materials and devices at continuously decreasing lengths scales is crucial for both optical technologies and fundamental understanding. The potential of azopolymer mass transport in near-field imaging was found when an azopolymer film with dielectric spheres cast on it deformed in a non-trivial manner upon irradiation.²⁶⁴ When the spheres were small enough, the shape of the dents in the film could not be explained simply by photosoftering. Indeed, the polarization-sensitive photofluidization of azomaterials can be employed to visualize complex optical-field distributions at the vicinity of nanostructures.¹⁵³ For example, the plasmonic-excited near-fields in an array of silver nanoantenna can be visualized by a layer of azopolymers that responds to the polarization and intensity by directional deformations.²⁶⁵ The final image of the near field is then obtained by AFM and numerical modelling as shown in Figure 4.6. When compared to existing scanning probe imaging techniques, the

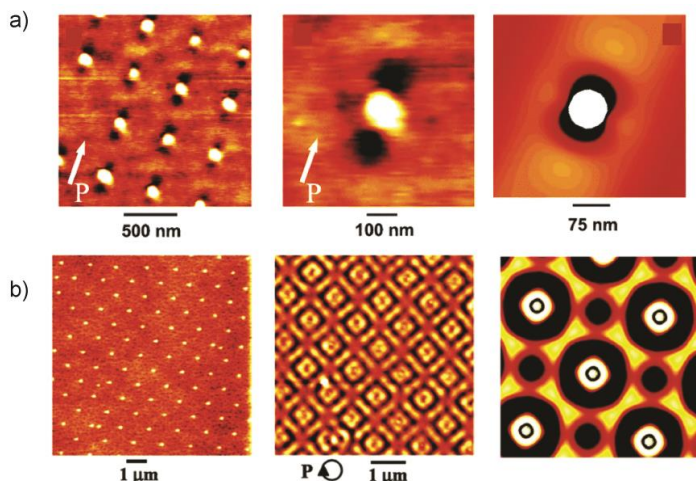


Figure 4.6. Topographic AFM images and theoretical calculations of optical near fields around silver nanoparticles using a) linearly polarized and b) circularly polarized irradiation. Reproduced from Ref. [265] with permission from the American Chemical Society ©2005.

presented method provides scalability over large imaging areas at once. However, the ultimate spatial resolution, which has now been demonstrated down to 20 nm,²⁶⁵ needs to be defined and explained. After all, the method utilizes similar mass transport mechanisms as the inscription of periodic surface-relief gratings, just with more complex illumination conditions.

To summarize, the light-induced mass transport phenomenon in azobenzene-containing materials, characterized by reversibility and nearly arbitrary directionality, has already found several application areas in photonics and nanofabrication. Importantly, the photofluidic motions allow for the design of large-area, well-defined micro- and nanoscale structures that are difficult to achieve with established lithographic approaches, such as the plasmonic structures presented in Publication IV. Even so, the light-induced mass transport is not only suitable for simple patterning, proven by the clever new uses, e.g., in near-field imaging and physical immobilization of nanoparticles.

5. Conclusions and outlook

The work presented in this thesis has dealt with azobenzene-containing materials and their fascinating photoinduced phenomena. A special focus was set on the light-induced surface patterning of thin films. Recall that the macro-scale mass transport in azopolymers is a complicated chain of physicochemical phenomena that originates from the photoisomerization of the azobenzene molecules. The chromophores respond to the incident optical field in a unique manner, which leads to viscous flow of the originally glassy material. Ultimately, the spatial field distributions, for example those of an interference pattern, are reproduced as a topographical surface structure. However, previous theoretical models developed to explain the microscopic observations have only provided a scattered and indefinite picture of the detailed molecular-scale processes. It is obvious that more theoretical and modelling work is still required to obtain a comprehensive understanding on the molecular and macroscopic motions. Alternatively, experimental studies related to the structure and properties of the material can provide new insight into the photoinduced effects, as is shown in this thesis. In particular, we have explored the light-induced surface patterning in some extraordinary azobenzene-containing materials. The presented findings revealed new fundamental aspects of the light-induced mass transport that have not been considered before. Moreover, the thesis showed that new material concepts can generate innovative uses for the unique photoresponsive properties of azobenzene-containing systems.

The main findings of the current work can be divided into two parts. Publications I-III comprise the main part, which confirmed that supramolecular functionalization provides **(i)** *a facile way to build and modify light-responsive materials* with variable composition and versatile photoresponsive properties. Specifically, supramolecular hydrogen-bonded azobenzene-polymer complexes were used as **(ii)** *a tunable platform to investigate some of the very fundamental aspects related to the photoinduced macroscopic mass transport*. It was established that **(iii)** *light-fuelled mass transport can occur even in a material where only one polymer chain out of ten carries a single photoactive molecule*. Even if the critical azo concentration of 1 mol-% was most likely

specific to this particular material system, the results are important for the basic understanding on the light-induced mass transport and call for theoretical modelling and systematic experimental studies with different chromophores and binding motifs to be performed in the future. For example, it might be possible to build similar low-azobenzene-content systems from so-called end-functionalized polymers, where the photoactive molecule would be covalently attached only to the end of the polymer chain. Such a system would provide a meaningful comparison on the efficiency and onset concentration of mass transport in covalently-functionalized materials, in order to explore the role of hydrogen-bonding dynamics in the process. It would also be pertinent to perform a similar study with halogen-bonded complexes, as they have been reported to excel hydrogen-bonded complexes in mass transport efficiency.¹²⁵

Furthermore, the limits of light-induced mass transport were taken to another extremity as it was discovered that **(iv)** azobenzene-functionalized materials comprising *both flexible and rigid globular particles of very high molecular weight can be made to move in response to light*. In the future, the effect of azobenzene concentration and size of the photopassive units on the efficiency of mass transport could be investigated in parallel if the dendrimers of various generations were coupled to the azobenzene units with hydrogen bonds to allow free tuning of the chromophore concentration.

Additionally, **(v)** photoinduced *surface patterns were inscribed on material of purely biological origin* for the first time. The importance of this result is two-fold. On one hand, nature offers innumerable possibilities as material templates for fundamental studies on many light-induced effects, not only the mass transport phenomenon. On the other hand, this demonstration offers new possibilities for the yet marginally explored biological applications of azobenzene surface patterning. Future studies could consider creating patterned surfaces from other types of azo-functionalized native biomolecules such as viruses, as well as synthetic spheres such as metal nanoparticles. Also, it would be particularly interesting to see if such light-responsive spheres were distributed on a substrate to form a random monolayer, and the spheres could be made to move and align into well-defined structures upon irradiation. Such studies are envisioned to open up completely new pathways to advanced micro-and nanofabrication.

The second part of the thesis discussed the possible uses for the light-induced mass transport and presented the results of Publication IV. It could be concluded that the phenomenon is especially suited for large-area micro- and nanofabrication of periodic complex structures. The main finding of this part was that **(vi)** the light-induced SRGs can be employed to fabricate *periodic large-area arrays of gold nanostructures with non-trivial transmission properties suited for plasmonic applications*. However, the presented method is not restricted to gold. For example inorganic materials such as TiO₂ could be

deposited on the grating using atomic layer deposition,¹⁴⁵ or another polymer layer can be spin-coated on the SRG and subsequently patterned with the proposed method. Also, the ion milling process can be merged with other fabrication methods to yield very interesting new structures, thus the potential applications are manifold also outside the plasmonics or nanophotonics fields. Importantly, any type of SRG-forming azomaterial can be used in the fabrication process. It is also worth emphasizing that the azopolymer layer is an integral part of the structure, thus the photo-alignment ability of the azobenzene molecules could offer an additional degree of control to modify the optical transmission properties of the structures. Nevertheless, future studies would greatly benefit if the ion milling process was quantitatively modelled, as for now the milling times were determined purely empirically. Such calculations may be possible, and would enable better control over the resulting nanostructures. It is also warranted to carefully study the effects of the ion bombardment on the material, such as possible crosslinking, especially if the ion-milled surface is subject to chemical post-functionalization.

In the future, perhaps the most promising new uses for the light-induced surface patterns will appear in the field of biology, as there seems to be a growing interest in developing novel light-responsive and biocompatible materials. For example protein arrays, which are used in biosensing and studying biointeractions,²⁶⁶ could be fabricated on functionalized SRG templates or via direct patterning such as presented in Publication III. On the other hand, the large-area arrays of isolated gold structures of Publication IV could serve as a basis for further chemical functionalization and use in bioassays.²⁶⁷ In addition, supramolecular chemistry can be used to equip existing biopolymers with the capability of light-induced surface patterning, which would further facilitate the use of the SRG structures in tissue engineering applications.

Overall, this thesis has presented new ways to investigate and utilize the intriguing light-induced effects of azobenzene-containing materials. The studies have not tried to simply solve the puzzle of the intricate structure-performance relationships, but they have also introduced new, unfitting pieces that reach beyond existing knowledge. One of the key factors that limit the practical utilization of the light-fuelled macro-scale motions is still the inadequate fundamental conception of the core molecular mechanisms in various material systems. Improving our understanding on the directionality and the photosoftering of azomaterials will help to put the phenomenon to the real use in existing and yet unknown application areas.

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ISBN 978-952-60-6030-9 (printed)
ISBN 978-952-60-6031-6 (pdf)
ISSN-L 1799-4934
ISSN 1799-4934 (printed)
ISSN 1799-4942 (pdf)

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