CPP 27: Photoswitchable Materials

Time: Tuesday 14:00–15:45 Location: ZEU 114

CPP 27.1 Tue 14:00 ZEU 114

Kinetics of light-induced ordering and deformation in LC azobenzene-containing materials — •Vladimir Toshchevikov[1], Tatiana Petrova[2], and Marina Saphiannikova[1] — [1]Leibniz-Institut für Polymerforschung, Hohe Str. 6, 01069 Dresden, Germany — [2]Cherepovets State University, pr. Lunacharskogo 5, 162600 Cherepovets, Russia

Azobenzene-containing materials are known as effective actuators of the light energy into mechanical work [1]. We develop a theory of light-induced ordering and deformation in azo-materials starting from kinetic equations of photoisomerization. The orientation interactions between rod-like trans-isomers are taken into account. Angular selectivity of the photoisomerization leads to the light-induced ordering and deformation of the azo-material. The time evolutions of ordering and deformation are found as functions of the light intensity depending on opto-mechanical characteristics of the material: probability of optical excitation of trans- and cis-isomers, angular jump during single isomerization event, viscosity of the material, strength of the orientation interactions and angular distribution of chromophores in side chains. Found structural-property relationships are in agreement with experiments and can be used for construction of light-controllable smart materials for target practical applications.

[1] Petrova T. et al., Soft Matter 11, 3412-3423, 2015.

CPP 27.2 Tue 14:15 ZEU 114

Tris(azobenzene) star: A theoretical study of the isomerization states and self-organization of this multiphotochromic compound — •Markus Koch[1,2] and Olga Guskova[1,3] — [1]Leibniz-Institute of Polymer Research Dresden, Hohe Str. 6, 01069 Dresden — [2]Institute of Theoretical Physics, Technische Universität Dresden, 01069 Dresden — [3]Dresden Center for Computational Materials Science (DCMS), TU Dresden, 01062 Dresden

Three-arm azobenzene derivative, a star-shaped molecule with three azobenzene (azo) groups, symmetrically attached to a central unit, has potential to be a new photooptical medium for optical recording [1]. Since it contains more than one azo-group, this system exhibits multiple isomers with diverse optical properties due to irradiation with an intensity or polarization interference pattern.

Here we show the results of DFT calculations of three-arm azo isomers, considering the changes in molecular volume, dipole moment, the first static hyperpolarizability and UV-vis spectra going from all-trans to all-cis state. Using all-atom MD simulations, we show the process of self- organization of tris(azobenzene) stars in a bulk solvent and characterize the forming clusters in terms of size, shape and stability.

We highly appreciate the financial support from DFG (project GU 1510/3-1).

[1] N.S. Yadavalli, M. Saphiannikova, S. Santer, Appl. Phys. Lett. 105, 051601 (2014).

CPP 27.3 Tue 14:30 ZEU 114

Azobenzene-containing surfactants and their association with poly(methacrylic acid) at nanometer scale — •Maria Montagna[1], Markus Koch[1,2], and Olga Guskova[1,3] — [1]Leibniz-Institute of Polymer Research Dresden, Hohe Str. 6, 01069 Dresden — [2]Institute of Theoretical Physics, Technische Universität Dresden, 01069 Dresden — [3]Dresden Center for Computational Materials Science (DCMS), TU Dresden, 01062 Dresden

Light-responsive hybrid materials have been considered in several recent investigations due to their promising applications in different fields, e.g. Biomedicine and Nanotechnology. One of them is azobenzene (azo), an organic chromophore which shows a reversible isomerization process between its trans- and cis-states driven by light excitation. Furthermore, the addition of this photosensitive molecule to synthetic or biological polyelectrolytes allows for remote control of the chain conformation and consequently causes changes of the polymer functional properties. We present a study on the electrostatic interaction between the azobenzene-containing surfactants and poly(methacrylic acid) by means of an atomistic computational approach. More specifically, we used a density functional theory and classical molecular dynamics simulations to look into the structural, spectroscopic and association properties of azo-polymer complexes in order to rationalize recent experimental results on the manipulation of polymer brushes modified by photosensitive molecules.

The financial support from DFG (GU 1510/3-1) is highly appreciated.

CPP 27.4 Tue 14:45 ZEU 114

Near field induced structuring of photosensitive polymer films: SNOM and AFM measurements — •Joachim Jelken, Burkhard Stiller, Carsten Henkel, Svetlana Santer, and Dieter Neher — Institute of Physics and Astronomy, University of Potsdam, Potsdam, Germany

Here we report on structuring of photosensitive polymer films by near field intensity pattern. The near fields were generated at a nano-groove fabricated within a thin metal layer. It is well known that when the nano-groove is irradiated, a surface plasmon wave is generated within the nano-groove, that should propagate along the metal surface. We have found, that instead of propagating SP mode, a standing EM-wave is generated at the metal/dielectric interface as a result of constructive interference between propagating SP mode and transmitted light. We have analyzed this phenomenon using photosensitive azobenzene containing polymer film placed above the metal surface [1-3]. The polymer film deforms following the intensity distribution of light only in case of stationary distribution of the intensity or polarization pattern. We have analyzed the system theoretically and have found that the standing wave exist even in the absence of the polymer film. This was also supported by SNOM measurements [4]. [1] T. Papke, N. Sekhar Yadavalli, C. Henkel, and S. Santer, ACS Appl. Mater. Interfaces, 6 (2014) 14174. [2] König, T.; Tsukruk V. V.; Santer, S., ACS Appl. Mater. Interfaces, 5 (2013) 6009. [3] König, T.; Yadavalli, N. S.; Santer, S., Plasmonics 7, (2012) 535. [4] J. Jelken, diploma thesis 2015.

CPP 27.5 Tue 15:00 ZEU 114

Modeling inscription of surface relief gratings on azobenzene polymers — •Marina Saphiannikova[1] and Jaroslav Ilnytskyi[1,2] — [1]Leibniz-Institut für Polymerforschung, Hohe Str. 6, 01069 Dresden, Germany — [2]Institute for Condensed Matter Physics, Svientsitskii Str. 1, 79011 Lviv, Ukraine

Azobenzene polymers proved to be invaluable in the fields of photopatterning and photomechanics. The direction of deformation can be easily controlled by illumination with linearly polarized light. Recently we showed with the help of coarse-grained simulations that a complex process of anisotropic stochastic photoisomerization can be reduced to a deterministic orientation in a field of the effective potential [1]. Presently we mimick on a coarse-grained level inscription conditions for two intensity and one polarization interference patterns commonly used to grow the surface relief gratings (SRGs). The temperature of azo-polymer film under illumination is kept very close to its value in darkness. We observe how the azo-material gradually moves from highly illuminated spots under intensity interference patterns building a sinusoidal SRG. The SRG inscribed by the polarization pattern appears to be a superposition of two SRGs inscribed by two intensity patterns, whose superposition reproduces the polarization pattern. This explains why complicated surface patterns can be inscribed using multiple steps.

[1] J.M. Ilnytskyi, M. Saphiannikova, ChemPhysChem, 16, 3180, 2015.

CPP 27.6 Tue 15:15 ZEU 114

Switching Thin Films of Metal-Organic Frameworks with Visible Light — •Kai Müller and Lars Heinke — Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany

Stimuli responsive molecules, also referred to as smart molecules, change their properties when exposed to external signals like light and enable the preparation of smart materials. UV light, which often destroys organic materials, is typically required for activating the desired response of photoswitchable compounds, significantly limiting the potential applications of photoswitchable smart materials. Here, we present the first metal-organic framework (MOF) which enables reversible modulation of key properties upon irradiation with visible light only. The fluorinated azobenzene side groups can be reversibly switched between the trans and cis state by green and violet light, avoiding UV light. It is demonstrated that the uptake of guest molecules by these MOF films can be significantly increased in a fully remote controlled way. Furthermore, membrane separation experiments demonstrate the switching of the molecular separation factor by illumination with light of different color. The light-induced changes of the size of the pore windows result in the switching of the selection factor.

CPP 27.7 Tue 15:30 ZEU 114

Thin Films of Photoswitchable Metal-Organic Frameworks — •Lars Heinke — Karlsruhe Institute of Technology (KIT)

Metal-organic frameworks (MOFs) are nanoporous, crystalline materials, assembled from metal notes and organic linker molecules. In addition to many potential applications of the (conventional) powder MOF material, well-defined thin films seem perfectly suited for challenging uses and as unique model systems, where certain molecular and MOF properties can be precisely measured by applying surface sensitive techniques. These thin films are prepared in a layer-by-layer fashion on a solid substrate by using liquid-phase epitaxy, referred to as the SURMOF-approach. Incorporating photochromic molecules like azobenzene in the crystalline structure enables the switching of physical and chemical MOF properties by light. The trans-to-cis switching or vice versa of the azobenzene groups by UV or visible light, respectively, can be used for various uses, such as realizing the remote-controlled release of guest molecules from a nanoporous container. Furthermore, these films can be used as membranes for the separation of molecular mixtures. There, the photoswitchable MOF films enable a dynamic control of the selectivity by remote signals, thus enabling a continuous adjustment of the permeate flux. For H2:CO2, the separation factor can be tuned between 3 and 8 by switching the photochromic moieties. Moreover, by loading the MOF pores with conducting organic molecules, the conduction of the guest molecules can be controlled in the fully remote by trans-cis photoswitching of the host structure.