

# Frontiers of Photoactive Soft Matter 2017



## manipulating soft matter with light

September 21-22, 2017, University of Colorado Boulder

**a two-day workshop for exploring and advancing  
the molecular, nanoscale, and macroscopic science  
and applications of photo-softening and  
photo-manipulation of material shape**



Organized by the Soft Materials Research Center,  
an NSF Materials Science and Engineering Center  
at the University of Colorado Boulder





# Frontiers of Photoactive Soft Matter Workshop

September 21–22, 2017



Thursday, September 21, 2017

8:30 AM	Registration
Session 1	Chair: Robert McLeod
9:00 AM	<b>O1: Marina Grenzer (Saphiannikova)</b> Leibniz Institute for Polymer Research, Dresden, Germany <i>Giant photomechanical stress from orientation of azobenzene in glass materials</i>
9:35 AM	<b>O2: Noel Clark</b> Department of Physics, University of Colorado Boulder <i>Photo-dynamics of a 2D XY orientational glass: from orientational work hardening to athermal photofluidization</i>
10:15 AM	Coffee Break
Session 2	Chair: Matthew Glaser
10:45 AM	<b>O3: Timothy White</b> Air Force Research Laboratory, Wright-Patterson Air Force Base <i>Photomechanical effects in azobenzene-functionalized polymer networks and elastomers</i>
11:20 AM	<b>O4: Dmitry Bedrov</b> Department of Materials Science and Engineering, University of Utah <i>Molecular dynamics simulations of photo-induced and thermal relaxations in surface-grafted azobenzene-based monolayers</i>
12:00 PM	Lunch
Session 3	Chair: Bohdan Senyuk
1:30 PM	<b>O5: Chris Kloxin</b> Department of Materials Science and Engineering, University of Delaware <i>Photo-induced modulus modulation in an elastomer substrate</i>
2:05 PM	<b>O6: Brian Donovan</b> Air Force Research Laboratory, Wright-Patterson Air Force Base <i>All-optical control of shape in ortho-fluorinated azobenzene-functionalized liquid crystalline elastomers</i>
2:40 PM	<b>O7: Devatha Nair</b> Department of Craniofacial Biology, University of Colorado Anschutz Medical Campus <i>Engineering photoresponsive azobenzene networks for biological applications</i>
3:15 PM	<b>O8: Ivan Smalyukh</b> Department of Physics, University of Colorado Boulder <i>Photo-responsive colloids and solitons</i>
4:00 PM	Coffee and Posters, 11th Floor of Gamow Tower

Friday, September 22, 2017

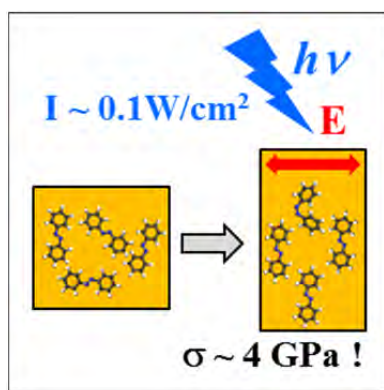
Session 4	Chair: Eva Korblova
9:00 AM	<b>O9: Anne Helene Gelebart</b> Department of Chemical Engineering and Chemistry, Technical University of Eindhoven, Netherlands <i>Sustained motions in liquid crystalline polymers induced by light</i>
9:35 AM	<b>O10: Frank Giesselmann</b> Institute of Physical Chemistry, University of Stuttgart, Germany <i>Photoresponsive liquid crystalline ferroelectrics and soft microrobots</i>
10:15 AM	Coffee Break
Session 5	Chair: David Walba
10:45 AM	<b>O11: Seungwoo Lee</b> Department of Nano Engineering & School of Chemical Engineering, Sungkyunkwan University, Korea <i>Directional photofluidization lithography: recent progress and perspectives</i>
11:20 AM	<b>O12: Michael Dickey</b> Department of Chemical and Biological Engineering, North Carolina State University <i>Light actuated polymers via photothermal strain relaxation</i>
12:00 PM	Lunch
Session 6	Chair: Joseph MacLennan
1:30 PM	<b>O13: Quan Li</b> Liquid Crystal Institute, Kent State University <i>Light-directing self-organized liquid crystalline nanostructures enabled by chiral molecular switches or motors: from 1D to 3D photonic crystals</i>
2:05 PM	<b>O14: Matthew McBride</b> Department of Chemical and Biological Engineering, University of Colorado Boulder <i>Spatiotemporal control over shape and mechanical properties in light facilitated covalent adaptable networks</i>
2:40 PM	<b>O15: Robert McLeod</b> Department of Electrical, Computer, and Energy Engineering, University of Colorado Boulder <i>Mechanical and optical property modification via mass transport in photo-responsive polymer gels</i>
3:15 PM	Wrap-Up

## Giant Photomechanical Stress from Orientation of Azobenzenes in Glassy Materials

Marina Grenzer (Saphiannikova)

*Leibniz Institute of Polymer Research, Theory of Polymers, Dresden, Germany*

To make a polymer-based material photosensitive, it is usually modified by inclusion of azobenzene chromophores. Their reaction to the light via photoisomerisation leads to conversion of absorbed energy into mechanical work. In many cases, the light-induced deformation occurs below the glass-transition temperature of the polymer. This glassy state remains nearly unaffected under illumination [1]. Recent experiments show that light-induced stress can reach a giant value of 2 GPa and is able to break the metallic layer on the surface of a glassy azopolymer as well as to deform covalent bonds [2-3].



I will present an explanation for the photomechanical stress of such a giant magnitude. Starting from kinetic equations of photoisomerization, we show in [4] that the light acts as the effective potential, which reorients chromophores perpendicularly to the polarization direction. The strength of the potential is defined by optical and viscous characteristics of the material. The potential can generate the stress up to 4 GPa, in accordance with recent experimental findings for azobenzene materials deep in a glassy state [2-3]. Whether a sample expands or contracts along the polarization vector is defined by the chemical structure of the material.

- [1] V. Toshchevnikov and M. Saphiannikova. *J. Soc. Inf. Disp.* **23** (2015) 146
- [2] N.S. Yadavalli et al. *ACS Appl. Mater. Interfaces* **5** (2013) 7743
- [3] G. Di Florio et al. *Nano Lett.* **14** (2014) 5754
- [4] V. Toshchevnikov et al. *J. Phys. Chem. Lett.* **8** (2017) 1094; *Soft Matter* **13** (2017) 2823

**Photo-Dynamics of a 2D XY Orientational Glass:  
from Orientational Work Hardening to Athermal Photofluidization**

Noel A. Clark<sup>1</sup>, Guanjiu J. Fang<sup>1</sup>, Joseph E. Maclennan<sup>1</sup>, Youngwoo Yi<sup>1</sup>, Matthew.A. Glaser<sup>1</sup>,  
Matthew Farrow<sup>2</sup>, Eva Korblova<sup>2</sup>, David M. Walba<sup>2</sup>, and Thomas E. Furtak<sup>3</sup>

<sup>1</sup> *Department of Physics and Soft Materials Research Center, University of Colorado Boulder, Boulder, Colorado, USA.*

<sup>2</sup> *Department of Chemistry and Biochemistry and Soft Materials Research Center, University of Colorado Boulder, Boulder, Colorado, USA.*

<sup>3</sup> *Department of Physics, Colorado School of Mines, Golden, Colorado, USA, and Soft Materials Research Center, University of Colorado Boulder, Boulder, Colorado, USA.*

Azobenzene and its derivatives are among the most important organic photonic materials, with their photo-induced trans–cis isomerization leading to applications ranging from holographic data storage and photoalignment to photoactuation and nanorobotics.

Here we analyze the orientational relaxation dynamics of a dense monolayer of azobenzene-based molecules tethered by flexible links to a glass surface. The tethering makes the monolayer a two-dimensional liquid crystal orientational glass, having an orientational viscosity  $\sim 10^{11}$  times larger than a comparable untethered monolayer. Orientational ordering of the monolayer is induced by polarized green laser light, orientational disordering induced by circularly polarized green laser light, and relaxation dynamics are probed with red light by measurement of the in-plane birefringence, and thereby orientational order parameter, using an ultrasensitive polarimeter.

The measurements provide evidence for photon-assisted barrier hopping (athermal photofluidization), in which the orientational viscosity becomes precisely inversely proportional to the incident green intensity. They also enable a measurement of the transient local effective temperature at which a photo-isomerizing molecule attacks its orientationally confining barriers. This temperature ( $T_{\text{local}} \sim 800$  K) leads directly to photofluidization, as each absorbed photon generates an event in which a local glass transition temperature is exceeded, enabling collective confining barriers to be attacked with near 100% quantum efficiency. This enables illumination that produces only a sub-Kelvin increase in average temperature to reduce, by many orders of magnitude, the viscosity of an organic glassy host at temperatures more than 100 K below its thermal glass transition.

Illumination of the monolayer with polarized light generates long-time dynamics in which the orientational order parameter increases with writing time as  $\log(t)$ . Such behavior is related to that of the logarithmic creep of strain in semi-soft metals under stress and can be understood in terms of the increase in the height of the typical Arrhenius barrier which has been crossed with increasing illumination time  $t$ .

\* Work supported by NSF MRSEC Grants DMR 0820579 and 1420736.

**Photomechanical Effects in Azobenzene-functionalized Polymer Networks and Elastomers**

Timothy White

*Air Force Research Laboratory**Wright-Patterson Air Force Base, Dayton, Ohio, USA*

Photomechanical effects in materials, composites, or systems are a promising way to transduce input light energy into useful work. This talk will summarize our long-standing activities in the area that have generally focused on assessing and enhancing the energy conversion and localizing the stimulus response of azobenzene-containing polymeric materials. The talk will focus extensively on this latter topic, detailing the all optical deformation and recovery of complex topographical features within elastic sheets composed of azobenzene functionalized liquid crystalline elastomers (azo-LCEs). Exposing the blueprinted LCE films to light as an actinic stimulus generates a photomechanical response which yields reversible shape changes between 2D and 3D shapes. Blueprinting complex director profiles within azo-LCEs yield reconfigurable elastic sheets that can be addressed both remotely and selectively which may have benefit in a variety of applications in aerospace, medicine, and optics.

**Molecular Dynamics Simulations of Photoinduced and Thermal Relaxations  
in Surface-grafted Azobenzene-based Monolayers**

Dmitry Bedrov and Justin B. Hooper

*Department of Materials Science & Engineering  
University of Utah, Salt Lake City, Utah, USA  
and  
Soft Materials Research Center  
University of Colorado Boulder, Boulder, Colorado, USA*

Matthew A. Glaser and Noel A. Clark

*Department of Physics and Soft Materials Research Center  
University of Colorado Boulder, Boulder, Colorado, USA*

This talk will discuss application of classical molecular dynamics (MD) simulations to investigation of relaxation processes in photo-responsive molecular systems. Specifically, we will discuss extensive atomistic MD simulations that focused on the analysis molecular orientational relaxation of azobenzene-based monolayers grafted to a solid substrate. Biased simulations that model single-molecule thermal excitation and conformational isomerization have been conducted to obtain insight into the mechanisms for photo-induced athermal fluidization and monolayer reorganization observed experimentally in this system. Our simulations clearly indicate that *trans-cis* conformational isomerization transitions of azobenzene units can lead to reorientation of mesogens and to the formation of a monolayer with strong macroscopic in-plane nematic order. While local heating created by excitation process can facilitate this process, thermal excitation alone is not sufficient to induce ordering in the monolayer. Instead, the work done by a molecule undergoing *cis-trans* isomerization on the cage of neighboring molecules is the key mechanism for photo fluidization and orientational ordering in azobenzene-based monolayers exposed to linearly polarized light.

## **Photo-induced Modulus Modulation in an Elastomer Substrate**

Chris Kloxin

*Department of Materials Science and Engineering  
University of Delaware, Newark, Delaware, USA*

The mechanical properties of polymer networks are readily tuned via the extent of crosslinking and chemical composition. We will explore the use of light to modulate network connectivity to local affect the state of stress within the material. We will discuss briefly the use of reversible covalent linkages, but we will focus on the ability to spatioselectively enhance the modulus to induce mechanical instabilities, particularly at the interface. By confining a secondary photopolymerization at the surface, we can dictate where wrinkles form. Moreover, the patterned surface provides a boundary condition that direct wrinkle orientation. Finally, wavelength selection enables control over the depth of cure: Short wavelengths (365 nm) isolate the modulus enhancement to the surface whereas longer wavelengths (435 nm) enables bulk cure of the film. More broadly, the materials fabrication concepts presented here enables the creation of designer surfaces for a number of applications, including cell culture, biomedical implants, tunable lenses, adhesive surfaces, and antifouling coatings.

## **All-Optical Control of Shape in Ortho-fluorinated, Azobenzene-functionalized Liquid Crystalline Elastomers**

Brian Donovan

*Air Force Research Laboratory*

*Wright-Patterson Air Force Base, Dayton, Ohio, USA*

Liquid crystal elastomers (LCEs) are a unique class of materials exhibiting long range order of the mesogenic units within the macromolecule. Stimuli-induced (heat, light, electrical) disruptions of the organization of these materials amplifies the mechanical response, resulting in a dynamic shape change. Photo-induced deformations have gained increased attention due to the rapid nature of photo-induced processes, and due to the improved spatial and temporal control afforded by light. Azobenzene monomers are the most frequently employed chromophores used to induce a photoresponse in a liquid crystalline material due to their strong UV light absorbance, which results in a reversible trans-cis isomerization, and their rod-like structure, which allows the molecule to orient within the LC field. Upon irradiation, the trans-cis isomerization induces a deformation of the local network leading to a macroscopic shape change. Recently, o-fluorinated azobenzene monomers have been synthesized that display reversible isomerization using only visible light, and a very long-lived cis-isomer. Here, we present on the development of an o-fluorinated azobenzene LCE film that displays a persistent shape deformation upon exposure to light. Films were prepared using a radical chain transfer mechanism that affords optically transparent and uniform films under mild polymerization conditions. The isomerization kinetics and photomechanical behavior of the o-fluorinated azobenzene films were studied and compared to non-fluorinated and m-fluorinated azobenzene control films. Additionally, the photopolymerization kinetics, phase behavior, and X-ray structure of the LCE films were investigated to further establish the conditions necessary for the preparation of well-defined, photoresponsive polymer films.



## **Engineering Photoresponsive Azobenzene Networks for Biological Applications**

Devatha P. Nair

*School of Dental Medicine*

*University of Colorado – Anschutz Medical Campus, Denver, Colorado, USA*

We explore the ability of azobenzenes to function as smart biofilm removal systems. Biofilm-associated bacterial infections such as dental plaque, lung infections and infections related to the use of medical devices such as urinary catheters are ubiquitous. Within dental materials, biofilm formation on the surface of dental restorations is a critical step in the development of secondary caries and is responsible for 70-80% of the recorded failures among the hundreds of millions of restorations performed each year. The proposed research will provide a novel approach to prevent oral biofilm formation on composite restorations and can be implemented within current clinical techniques by engineering photo-responsive coatings that can repeatedly detach biofilms from the surface of the restoration on command. Additionally, as biofilms are currently implicated in over 2 million nosocomial (hospital acquired) infections and is the fourth leading cause of death in the U.S., these studies have the potential to offer a paradigm-shifting approach in biofilm prevention and disruption.

**Photo-responsive Liquid Crystal Colloids and Solitons**

Ivan I. Smalyukh

*Department of Physics  
Department of Electrical, Computer, and Energy Engineering  
Materials Science Engineering Program  
Renewable and Sustainable Energy Institute  
Soft Materials Research Center  
University of Colorado Boulder, Boulder, Colorado, USA*

*National Renewable Energy Laboratory, Golden, Colorado, USA*

A promising approach of designing mesostructured materials with novel physical behavior is based on combining unique optical and electronic properties of solid nanoparticles with long-range ordering and facile switching of soft matter. This lecture will describe how we practically realize photo-responsive molecular-colloidal organic-inorganic composites formed via multi-scale self-assembly in dispersions of anisotropic inorganic nanoparticles in liquid crystals. These composites are pre-engineered to exhibit novel plasmonic, luminescence, photon-up-converting, and other unusual optical properties controlled by low-voltage fields and light itself.

## **Sustained Motions in Liquid Crystalline Polymers induced by Light**

Anne Helene Gelebart

*Department of Chemical Engineering and Chemistry  
Technische Universiteit Eindhoven, Eindhoven, The Netherlands*

Photo(-thermal) response of liquid crystalline networks (LCN) can be highly influenced by the photo-physical properties of the chromophore used. By using fast relaxing azoderivative dyes, a polymeric film can quickly deform and restore to its initial position upon turning on and off the light. By implementing a feedback-loop driven by self-shadowing, sustained motions can be obtained in a “hands-off” fashion. The contribution of heat in the photo-response mechanism is significant and will be highlighted. Following this approach, three type of sustained motions will be discussed; (i) oscillation of a beam, (ii) rotation of a mill, and (iii) wave propagation through a polymer stripe.

## Two Aspects of Photoactive Soft Matter: Photoresponsive Liquid-crystalline Ferroelectrics and Soft Microrobots

Frank Giesselmann

*Institute of Physical Chemistry  
University of Stuttgart, Stuttgart, Germany*

In the first part of this contribution we will review earlier work on photoresponsive ferroelectric liquid crystals (FLCs). Photoferroelectrics are materials, the spontaneous electric polarization of which can be changed by exposure to light.<sup>1</sup> In the liquid-crystalline state of matter photoferroelectricity can be achieved by dissolving photoisomerizable dyes in a FLC matrix, *i.e.* a chiral smectic C (SmC\*) host phase.<sup>2</sup> On exposure to light, the photochemical formation of *cis*-isomer molecules modifies the liquid-crystalline ordering of the SmC\* host and thereby induces a change of its spontaneous polarization. The photostationary response of these photoferroelectric liquid crystals as well as the dynamics of the photoferroelectric effect and its connection to the kinetics of the molecular *cis* – *trans* isomerization will be discussed.<sup>3</sup> The different impacts of two classes of photoisomerizable dopants, namely azobenzene and thioindigo compounds, will be compared and lead to insights into the molecular mechanism of the photoresponse. Finally, a potential application in photoferroelectric solar to electrical energy conversion proposed by Knežević and Warner<sup>4</sup> will be discussed.

In the second part of this contribution we will report recent results on the biomimetic swimming and versatile locomotion of soft microrobots consisting of photoresponsive liquid crystalline elastomers (LCEs).<sup>5</sup> We fabricated LCE microrobots in the form of long cylinders, and flat discs of submillimeter size. The photoresponse arises when the covalently bound azobenzene dye in the LCE absorbs the light, driving the elastomer through the nematic-to-isotropic phase transition which leads, under homogeneous illumination, to axial contraction and simultaneous radial expansion of the LCE cylinders. We show that these LCE microrobots can perform complex sophisticated motions if addressed with structured monochromatic light fields, the intensity of which is spatially and temporally modulated by a digital mirror device (DMD) system. In particular, we demonstrate biomimetic swimming of LCE cylinders driven by light-induced travelling wave deformations and in-place rotation of LCE discs driven by rotating fan-shaped light patterns.

Financial support by the *Deutsche Forschungsgemeinschaft* (DFG) is gratefully acknowledged.

[1] V. M. Fridkin, Photoferroelectrics (Springer Series in Solid State Sciences Vol. 9, Springer, Berlin 1979).

[2] T. Ikeda, T. Sasaki, K. Ichimura, *Nature* **361**, 428 (1993).

[3] A. Langhoff, F. Giesselmann, *ChemPhysChem* **3**, 424 (2002); A. Langhoff, F. Giesselmann, *J. Chem. Phys.* **117**, 2232 - 2237 (2002); A. Saipa, M. A. Osipov, K. W. Lanham, C. H. Chang, D. M. Walba, F. Giesselmann, *J. Mat. Chem.* **16**, 4170 (2006); P. Beyer, M. Krueger, F. Giesselmann, R. Zentel, *Adv. Funct. Mater.* **17**, 109 (2007).

[4] M. Knežević, M. Warner, *Appl. Phys. Lett.* **102**, 043902 (2013).

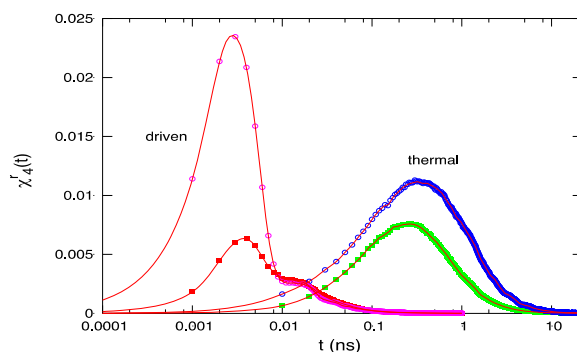
[5] S. Palagi, A. G. Mark, S. Y. Reigh, K. Melde, T. Qiu, H. Zeng, C. Parmeggiani, D. Martella, A. Sanchez-Castillo, N. Kapernaum, F. Giesselmann, D. S. Wiersma, Eric Lauga, P. Fischer, *Nat. Mater.* **15**, 647–653 (2016).

## Directional Photofluidization Lithography: Recent Progress and Perspectives

Seungwoo Lee

*SKKU Advanced Institute of Nanotechnology (SAINT)  
Department of Nano Engineering & School of Chemical Engineering  
Sungkyunkwan University (SKKU)  
Republic of Korea*

I newly introduced the distinct concept of “directional photofluidization lithography (DPL)” at 2010, when I was PhD student at Korea Advanced Institute of Science and Technology (KAIST); over the last 7 years, I have undertaken the significant efforts to make DPL to be a general solution for various lithographic issues. The key of DPL is to use light-malleable azobenzene materials as general lithographic resists; by benefitting from their exotic properties including light-powered, 2D/3D directional transformation, the pristine pattern over the wafer-scale can be uniformly reconfigured into the peculiar shaped micro/nanostructures, which would be difficult to achieve with conventional monolithic micro/nanofabrications and unconventional assembly techniques. Its unprecedented ability to remotely reconfigure micro/nanoarchitectures can enable the innovations of various fields including plasmonics, surface wetting, energy-harvesting devices, wearable electrical devices, and so on. In this talk, I’ll briefly introduce the fundamentals of DPL together with its recent progress and perspectives.



*Reduced 4-point dynamic susceptibility, measuring the cooperative motions inside the medium. Comparison of the spontaneous (thermal) and isomerization-induced (driven) values near the azobenzenes (larger curves) and in the whole system.*

- [1] P.W. Anderson, *Science* **267**, 1610 (1995)
- [2] G.J. Fang et al., *Nature Communications* **4**, 1251 (2013)
- [3] L. Berthier et al., *'Dynamical Heterogeneities in Glasses, Colloids and Granular Media'* Oxford University Press, Oxford 2011
- [4] J.P. Garrahan, D. Chandler, *Phys.Rev.Lett.* **89**, 035704 (2002)
- [5] D. Chandler, *'Introduction to Modern Statistical Mechanics'*, Oxford University Press, New York 1990.
- [6] V. Teboul et al., *Phys.Rev.Lett.* **103**, 265701 (2009); V.Teboul, J.B. Accary, M. Chrysos, *Phys.Rev.E* **87**, 032309 (2013); V.Teboul, J.B.Accary, *Phys.Rev.E* **89**, 012303 (2014)
- [7] J.B. Accary, V.Teboul, *J. Chem.Phys.* **139**, 034501 (2013)
- [8] S. Ciobotarescu et al., *Phys.Rev. E* (submitted)

## **Light Actuated Polymers via Photothermal Strain Relaxation**

Ying Liu, Robin Mays, Amber Hubbard, Duncan Davis, Russel Mailen, Mohammed Zikry,  
Jan Genzer, Michael D. Dickey

*Department of Chemical and Biomolecular Engineering  
North Carolina State University, Raleigh, NC, USA*

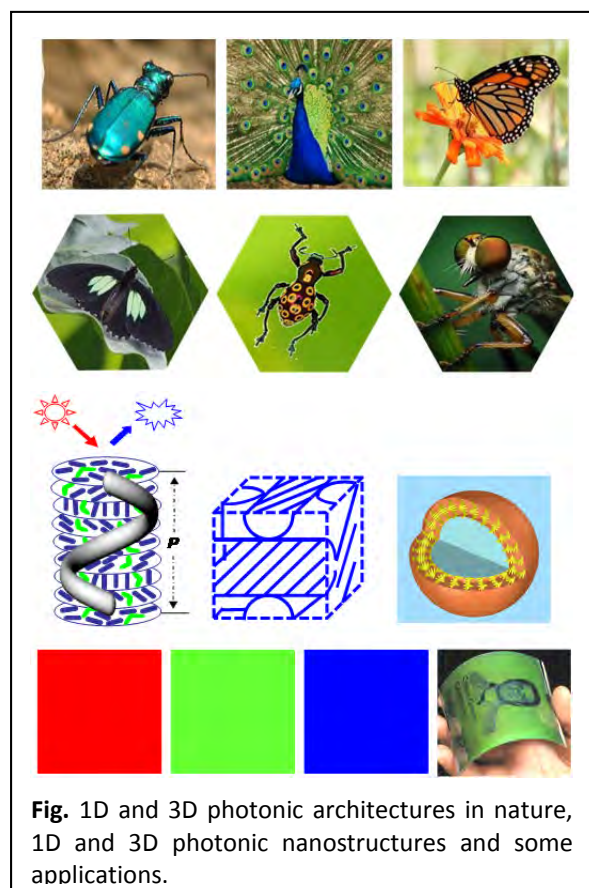
This talk will describe the use of light to from a light bulb to induce self-folding of polymer films. Regions of black ink patterned on sheets of pre-strained polymer absorb the light and heat up due to the photothermal effect. The heat causes the polymer to relax and therefore shrink, which can induce self-folding. By changing the color of the ink and the wavelength of light, it is possible to control the sequence of folding to form more complex shapes. Self-folding is similar to origami but is done without direct human intervention. The appeal of this approach is that it utilizes two dimensional patterns to create a variety of complex three dimensional objects. In essence, it allows shape memory polymers to be programmed using a variety of two dimensional patterning techniques and triggered using only light. The talk will discuss the use of light, lasers, and other electromagnetic radiation (e.g., microwaves) to induce folding, as well as the use of color to control sequence of folding.

## Light-Directing Self-Organized Liquid Crystalline Nanostructures enabled by Chiral Molecular Switches or Motors: from 1D to 3D Photonic Crystals

Quan Li

*Liquid Crystal Institute, Kent State University, Kent, Ohio, USA*

Liquid crystals (LCs) represent a fascinating state of matter which combines order and mobility



**Fig. 1D and 3D photonic architectures in nature, 1D and 3D photonic nanostructures and some applications.**

on a molecular and supramolecular level. The unique combination of order and mobility results in that LC is typically “soft” and responds easily to external stimuli. The responsive nature and diversity of LCs provide tremendous opportunities as well as challenges for insights in fundamental science, and open the door to various applications. Conventional nematic LCs have become the quintessential materials of LC displays. With the LC displays ubiquitous in our daily life and annual ~\$200 billion market, the research and development of LCs are moving rapidly beyond display applications and evolving into entirely new and fascinating scientific frontiers. In my talk, I will focus on our recent research and development on light-directing self-organized liquid crystalline nanostructures enabled by chiral molecular switches or motors: from 1D to 3D photonic crystals.

Q. Li (Ed.), *Functional Organic and Organic Hybrid Nanostructured Materials: Fabrication, Properties, and Applications*, Wiley-VCH, **2017**; Q. Li (Ed.), *Nanomaterials for Sustainable Energy*, Springer, **2016**; Q. Li (Ed.), *Anisotropic Nanomaterials: Preparation, Properties, and Applications*, Springer, **2015**; Q. Li (Ed.), *Nanoscience with Liquid Crystals: From Self-Organized Nanostructures to Applications*, Springer, **2014**; Q. Li (Ed.), *Intelligent Stimuli Responsive Materials: From Well-defined Nanostructures to Applications*, John Wiley & Sons, **2013**; Q. Li (Ed.), *Liquid Crystals Beyond Displays: Chemistry, Physics, and Applications*, John Wiley & Sons, **2012**; H. K. Bisoyi and Q. Li, “Liquid Crystals” in *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, 2014 edition; Z. Zheng, C. Yuan, W. Hu, H. K. Bisoyi, M. Tang, Z. Liu, P. Sun, W. Yang, X. Wang, D. Shen, Y. Li, F. Ye, Y. Lu, G. Li, and Q. Li, *Adv. Mater.* **2017**, 29; Z. Zheng, R. S. Zola, H. K. Bisoyi, L. Wang, Y. Li, Y. Wang, T. J. Bunning, and Q. Li, *Adv. Mater.* **2017**, 29, 201701903; L. Zhang, L. Wang, U. S. Hiremath, H. K. Bisoyi, G. C. Nair, C. V. Yelamaggad, A. M. Urbas, T. J. Bunning, and Q. Li, *Adv. Mater.* **2017**, 29, 1700676; L. Wang, H. K. Bisoyi, Z. Zheng, K. G. Gutierrez-Cuevas, G. Singh, S. Kumar, T. J. Bunning, and Q. Li, *Mater. Today* **2017**, 20, 230; H. K. Bisoyi and Q. Li, *Chem. Rev.* **2016**, 116, 15089; Z. Zheng, Y. Li, H. K. Bisoyi, L. Wang, T. J. Bunning, and Q. Li, *Nature* **2016**, 531, 352; K. G. Gutierrez-Cuevas, L. Wang, Z. Zheng, H. K. Bisoyi, G. Li, L. Tan, R. A. Vaia, and Q. Li, *Angew. Chem. Int. Ed.* **2016**, 55, 13090; H. K. Bisoyi and Q. Li, *Angew. Chem. Int. Ed.* **2016**, 55, 2994; L. Wang, H. Dong, Y. Li, R. Liu, Y. Wang, H. K. Bisoyi, L.-D. Sun, C.-H. Yan, and Q. Li, *Adv. Mater.* **2015**, 27, 2065; J. Fan, Y. Li, H. K. Bisoyi, R. S. Zola, D. Yang, T. J. Bunning, D. A. Weitz, and Q. Li, *Angew. Chem. Int. Ed.* **2015**, 54, 2160; H. K. Bisoyi and Q. Li, *Acc. Chem. Res.* **2014**, 47, 3184; L. Wang, H. Dong, Y. Li, C. Xue, L. Sun, C. Yan, Q. Li, *J. Am. Chem. Soc.* **2014**, 136, 4480; Y. Li, C. Xue, M. Wang, A. Urbas, Q. Li, *Angew. Chem. Int. Ed.* **2013**, 52, 13703; T.-H. Lin, Y. Li, C.-T. Wang, H.-C. Jau, C.-W. Chen, C.-C. Li, H. K. Bisoyi, T. J. Bunning, and Q. Li, *Adv. Mater.* **2013**, 25, 5050; Y. Li, M. Wang, T. J. White, T. J. Bunning, and Q. Li, *Angew. Chem. Int. Ed.* **2013**, 52, 8925; Y. Li, A. Urbas, and Q. Li, *J. Am. Chem. Soc.* **2012**, 134, 9573; Y. Wang, A. Urbas, and Q. Li, *J. Am. Chem. Soc.* **2012**, 134, 3342; Y. Wang and Q. Li, *Adv. Mater.* **2012**, 24, 1926.

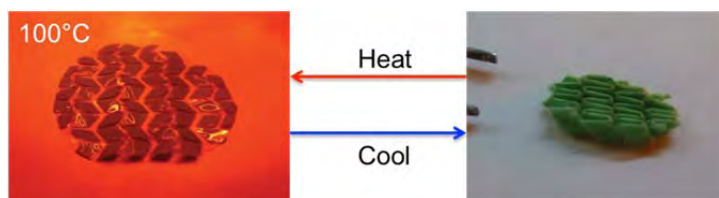
## Spatiotemporal Control over Shape and Mechanical Properties in Light Facilitated Covalent Adaptable Networks (CANs)

Matthew McBride<sup>1</sup>, Alina Martinez<sup>1</sup>, Brady Worrell<sup>1</sup>, Matthew Hendrikx<sup>2</sup>, Danqing Liu<sup>2</sup>, D.J. Broer<sup>2</sup>, and Christopher Bowman<sup>1</sup>

<sup>1</sup>*Department of Chemical Engineering, University of Colorado Boulder, Boulder, Colorado, USA*

<sup>2</sup>*Department of Chemical Engineering and Chemistry, Technische Universiteit Eindhoven, The Netherlands*

Light stimulated covalent adaptable chemistry presents a unique opportunity to fully control the bond exchange process leading to unique control over shape and mechanical properties of crosslinked polymeric materials. In this work, two such light sensitive chemistries will be discussed. First, light facilitated reversible-addition fragmentation chain-transfer (RAFT) chemistry was implemented into liquid crystalline networks (LCNs). The radical mediated bond exchange is initiated by cleavage of photoinitiators and only occurs while the light is on. In LCNs, the RAFT bond exchange was decoupled from the thermotropic behavior of the liquid crystalline behavior, which enables programming and disruption of alignment in a repeatable manner with multiple cycles of programming and erasing achievable. Controlled, thermoreversible shape changes were developed by simply mechanically molding polydomain LCNs followed by light exposure to fix the shape through bond exchange. Subsequent heating and cooling cycled the LCN from a high temperature shape associated with the isotropic polymer network and low temperature shape programmed in the LC alignment, both were programmable through RAFT. Second, anionic mediated thiol-thioester exchange was implemented into photopolymerizable thiol-ene networks. The thiol-thioester exchange occurs quickly at room temperature and is catalyzed by a broad range of organic bases and nucleophiles. The exchange is sensitive to a variety of controllable parameters including the presence of catalyst, free thiols, and thioesters. Removal of one of these components results in turning the exchange off. We employed photo switchable bases and acids to demonstrate spatial and temporal control over the exchange with light effectively changing whether the material behaves elastically or plastically in response to stress. Thioester networks were further demonstrated to be recyclable and healed without the need for heat. Both of these light facilitated bond exchange chemistries present unique opportunities to alter the covalent structure of polymer networks *post-polymerization*.



**Fig 1.** Thermoreversible shape change enabled by RAFT-LCNs. The folded shape was programmed by folding at room temperature and irradiating with 320–500 nm light for 100 seconds. The structure repeatedly unfolded and folded upon heating and cooling respectively.



**Mechanical and Optical Property Modification via Mass Transport  
in Photo-responsive Polymer Gels.**

Robert R. McLeod

*Department of Electrical, Computer, and Energy Engineering  
and  
Soft Materials Research Center  
University of Colorado Boulder, Boulder, Colorado, USA*

Photopolymer gels are a state of soft matter consisting of a solid polymer network, swollen with a liquid such as a monomer. These can exhibit complex local response to light through choices of functional groups on both the solid and liquid components. These reactions in turn lead to exhibit complex coupled chemical, optical, electronic and mechanical behavior through the interaction of typically solid-phase properties (e.g., long range positional order and percolation) and liquid-phase properties (e.g., rapid chemical reactions and transport). I will exhibit the richness of such systems via a liquid-solid polymerization reaction for 3D control of refractive index and a solid-solid polymerization resulting in folding and glassy polymer origami.

## Acknowledgements

The Soft Materials Research Center is supported by the Division of Materials Research at the National Science Foundation.



The organizers are grateful to the Department of Physics, the Department of Chemistry and Biochemistry, the School of Arts and Sciences, and the Graduate School (RIO), all at the University of Colorado Boulder, for their generous support of this workshop.

