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## Report Title

Final Report: Fluxional Mechanocatalysis

### ABSTRACT

During the final, no-cost-extension period of the grant, we continued with our modified experimental plan that leveraged the photoswitchable tension generators developed by Boulatov. This strategy allowed us to demonstrate the concept in a way that can be quantified while in parallel optimizing the reversible actuating platform for covalent mechanochemistry. Pursuant to the three goals described above, we have three principle achievements from the past reporting period:

- (1) we have quantified the force-activity relationship for MeO-BIPHEP ligands in asymmetric Heck arylations and Trost asymmetric alkylations whose behavior we had qualitatively established previously.
- (2) we have expanded the utility of our PDMS shape recovery platform and shown that it can function efficiently and effectively in new mechanochemically active electroactive devices and displays.
- (3) we have quantified the forces required for probe activation in the PDMS material and found it to be very similar to the forces required for catalyst actuation.

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**Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:**

**(a) Papers published in peer-reviewed journals (N/A for none)**

<u>Received</u>	<u>Paper</u>
01/29/2015 1.00	Sergey Akbulatov, Yancong Tian, Ross A. Widenhoefer, Roman Boulatov, Stephen L. Craig, Zachary S. Kean. Photomechanical Actuation of Ligand Geometry in Enantioselective Catalysis, <i>Angewandte Chemie International Edition</i> , (12 2014): 0. doi: 10.1002/anie.201407494
01/29/2015 2.00	Gregory R. Gossweiler, Gihan B. Hewage, Gerardo Soriano, Qiming Wang, Garrett W. Welshofer, Xuanhe Zhao, Stephen L. Craig. Mechanochemical Activation of Covalent Bonds in Polymers with Full and Repeatable Macroscopic Shape Recovery, <i>ACS Macro Letters</i> , (03 2014): 0. doi: 10.1021/mz500031q
01/29/2015 3.00	Qiming Wang, Gregory R. Gossweiler, Stephen L. Craig, Xuanhe Zhao. Cephalopod-inspired design of electro-mechano-chemically responsive elastomers for on-demand fluorescent patterning, <i>Nature Communications</i> , (09 2014): 0. doi: 10.1038/ncomms5899
<b>TOTAL:</b>	<b>3</b>

Number of Papers published in peer-reviewed journals:

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**(b) Papers published in non-peer-reviewed journals (N/A for none)**

Received

Paper

**TOTAL:**

**Number of Papers published in non peer-reviewed journals:**

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**(c) Presentations**

- “Covalent Mechanochemistry in Stress-Responsive Polymers”, Vistakon (J&J), Jacksonville, FL, Nov. 13, 2014.
- “Polymer Mechanochemistry: From Self-strengthening Rubbers to Soft Robots”, Case Western Reserve University, Cleveland, OH, Nov. 7, 2014.
- “Covalent Mechanochemistry in Stress-Responsive Polymers”, MIT, Cambridge, MA, Oct. 22, 2014.
- “Stress-responsive Polymers and Polymeric Systems”, ACS National, Division of Polymer Chemistry, San Francisco, CA, August 11, 2014.
- “Polymer Mechanochemistry in Self-strengthening Rubbers and Soft Robot Camouflage”, Michelin Research Center, Clermont-Ferrand, France, July 3, 2014.
- “Mechanochemistry for Stress Responsive Materials and Devices”, ESPCI, Paris, France, June 25, 2014.
- “Mechanochemical Remodeling: From New Reactions to Adaptive Materials”, Department of Chemistry, The Pennsylvania State University, University Park, PA, April 7, 2014.
- “Mechanochemical Remodeling: From New Reactions to Adaptive Materials”, Department of Chemistry, University of Michigan, Ann Arbor, MI, March 11, 2014.
- “Mechanochemical Remodeling: From New Reactions to Adaptive Materials”, Department of Chemistry, University of Washington, Seattle, WA, Feb. 19, 2014.
- “Mechanochemical Remodeling: From New Reactions to Adaptive Materials”, Department of Chemistry, Vanderbilt University, Nashville, TN, January 27, 2014.
- “From Rubber to Robots: the Past, Present, and Possible Future of Polymer Mechanochemistry”, Akron Section Award Address, Akron, OH, Nov. 26, 2013.
- “Mechanochemistry: From Trapped Transition States to Stress-Strengthening Materials”, University of Akron, Akron, OH, Nov. 26, 2013.
- “How Weaker Bonds Can Make For Stronger Polymers”, Southeast Regional Meeting of the ACS, Atlanta, GA, Nov. 15, 2013.
- “Mechanochemical Remodeling of Synthetic Polymers”, Eastman Chemical, Kingsport, TN, Oct. 15, 2013.
- “Mechanochemical Devices”, ACS National Meeting, Sept. 8, 2013.
- “Mechanochemical Remodeling of Synthetic Polymers”, Milliken Corp., Spartanburg, SC, June 18, 2013.
- “From Trapped Transition States to Self-Healing Polymers”, Department of Chemistry, Colby College, April 12, 2013.

**Number of Presentations:** 17.00

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**Non Peer-Reviewed Conference Proceeding publications (other than abstracts):**

Received

Paper

**TOTAL:**

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

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**Peer-Reviewed Conference Proceeding publications (other than abstracts):**

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Paper

**TOTAL:**

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

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**(d) Manuscripts**

Received

Paper

**TOTAL:**

Number of Manuscripts:

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**Books**

Received

Book

**TOTAL:**

Received

Book Chapter

**TOTAL:**

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**Patents Submitted**

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**Patents Awarded**

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**Awards**

Editorial Advisory Board, ACS Macro Lett. and Macromolecules

Co-Organizer, 5th International Conference on Self-Healing Materials, Durham, NC, June, 2015.

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ESPCI ParisTech-Michelin Chair for Visiting Professorship, ESPCI, Paris (Summer 2014)

Fellow, AAAS (2014)

Arthur K. Doolittle Award, PMSE Division, ACS (2013)

Akron Section Award of the ACS (2013)

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**Graduate Students**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Bobin Lee	0.21	
Zachary Kean	0.03	
Gregory Gossweiler	0.10	
Seong Du Lee	0.36	
Bradley Robertson	0.28	
<b>FTE Equivalent:</b>	<b>0.98</b>	
<b>Total Number:</b>	<b>5</b>	

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**Names of Post Doctorates**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Zhenbin Niu	0.06
<b>FTE Equivalent:</b>	<b>0.06</b>
<b>Total Number:</b>	<b>1</b>

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**Names of Faculty Supported**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Stephen Craig	0.03	
Ross Widenhoefer	0.04	
<b>FTE Equivalent:</b>	<b>0.07</b>	
<b>Total Number:</b>	<b>2</b>	

**Names of Under Graduate students supported**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

**Student Metrics**

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: ..... 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense ..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

**Names of Personnel receiving masters degrees**

<u>NAME</u>
<b>Total Number:</b>

**Names of personnel receiving PHDs**

<u>NAME</u>
Seong Du Lee
<b>Total Number:</b> 1

**Names of other research staff**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

**Sub Contractors (DD882)**

**Inventions (DD882)**

**Scientific Progress**

See Attachment



## **Technology Transfer**

We completed a collaborative research agreement with Bridgestone on mechanochemistry in rubber tires, and are in discussions with Michelin, Johnson & Johnson, and an unknown company via NineSigma about translating our understanding into industrial collaborations in the near future.

## Foreword

This report describes three separate accomplishments in catalyst design, material design, and force-activity studies that, when combined, establish the first viable experimental platform for macroscopic fluxional mechanocatalysis.

## List of Tables and Figures.

**Figure 1.** Mechanocatalysis through photoswitching.

**Table 1.** Asymmetric allylic alkylation: 1,3-diphenylpropenyl acetate (DPA)

**Table 2.** Asymmetric allylic alkylation: pentenyl acetate (PA)

**Table 3.** Asymmetric Heck Reaction: 2,3-dihydrofuran with phenyl triflate (PhOTf)

**Table 4.** Asymmetric Heck Reaction: 2,3-dihydrofuran with naphthyl triflate (NapOTf)

**Figure 2.** Quantifying force-selectivity relationships in Heck arylations

**Figure 3.** Covalent activation with full shape recovery

**Figure 4.** An electro-mechanochemically responsive elastomer device

**Figure 5.** Single molecule force spectroscopy of spiropyran ring opening

## Statement of the Problem Studied

The overarching goal of our project is to address several fundamental challenges that would enable reversible mechanical changes in the ligand sphere surrounding an active transition metal catalyst, in a way that alters the activity or selectivity of the catalyst in response to the stress/strain state of the material. This broad goal is subdivided into three specific research questions:

- (1) What forces are required to alter the activity of a given catalyst, and what are the force-activity relationships?
- (2) What material architectures, if any, allow for meaningful covalent mechanochemistry to take place with full shape and property recovery?
- (3) What are the molecular level forces that are transmitted to mechanophores with such a material, and how do they compare the forces necessary to alter catalyst activity?

As described in previous reports, our ultimate ligand design incorporated a chiral bisphosphine ligand such that the application of a mechanical force to the ligand would perturb the ligand dihedral angle. Chiral atropisomeric biaryl bisphosphines such as BINAP, BIPHEP, and MeOBIPHEP are effective ligands in many asymmetric catalytic reactions, and extensive studies on modifying those ligands have been performed to achieve high reactivity and stereoselectivity in asymmetric catalytic reactions for decades. In our case, the polymer-embedded ligand stretches to change its geometry and increase dihedral angle ( $\theta$ ), which we expected to reversibly change its catalytic reactivity through a general

phenomenon we have coined “fluxional mechanocatalysis.” It is this system that provides the specific context for the problem as defined above.

### Summary of Accomplishments

During the final, no-cost-extension period of the grant, we continued with our modified experimental plan that leveraged the photoswitchable tension generators developed by Boulatov. This strategy allowed us to demonstrate the concept in a way that can be quantified while in parallel optimizing the reversible actuating platform for covalent mechanochemistry. Pursuant to the three goals described above, we have three principle achievements from the past reporting period:

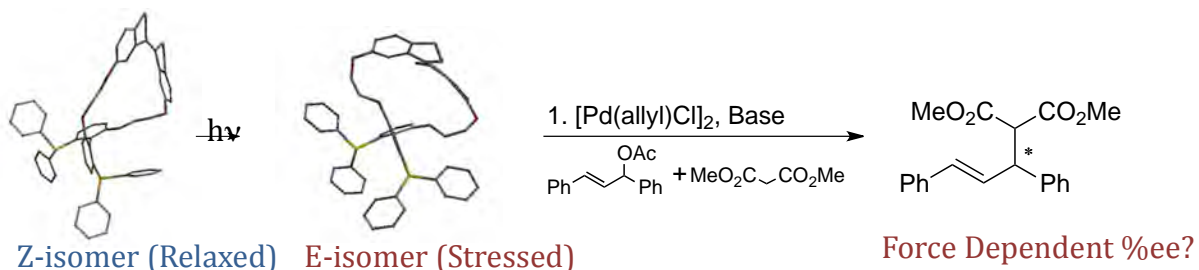
(1) we have quantified the force-activity relationship for MeO-BIPHEP ligands in asymmetric Heck arylations and Trost asymmetric alkylations whose behavior we had qualitatively established previously.

(2) we have expanded the utility of our PDMS shape recovery platform and shown that it can function efficiently and effectively in new mechanochemically active electroactive devices and displays.

(3) we have quantified the forces required for probe activation in the PDMS material and found it to be very similar to the forces required for catalyst actuation.

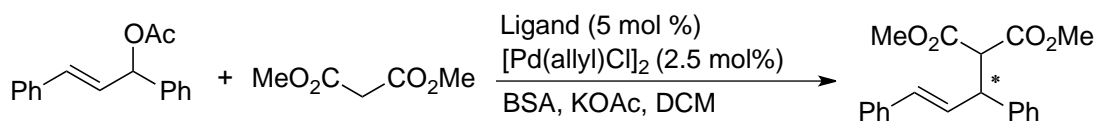
### Accomplishment 1. Quantifying tension-responsive catalysis.

The concept is shown below. A remote stiff stilbene photoswitch transmits tension to the bisphosphine ligand, actuating its extension into an extended conformation. The basic scheme is shown below for one of our target reactions:



**Figure 1.** Mechanocatalysis through photoswitching.

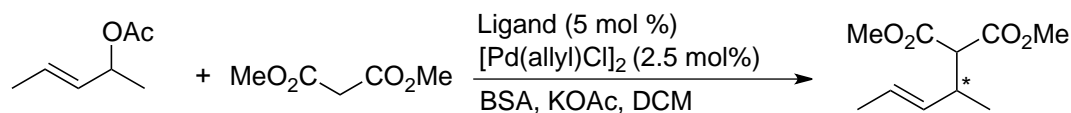
The following asymmetric reactions were tested with (S)-MeoBiphep, C3Z, and C3E ligands. Two asymmetric allylic alkylations were performed on allyl acetate substrates (diphenylpropenyl acetate [DPA], and pentenyl acetate [PA]) with dimethyl malonate as the nucleophile. Two asymmetric Heck reactions were performed on dihydrofuran with phenyl triflate [PhOTf] and naphthyl triflate [NapOTf] respectively. All reactions were prescreened with (S)-MeoBiphep and rac-Binap to establish characterization methods. In all cases E and Z ligands were run side-by-side on identical scale.



**Table 1.** Asymmetric allylic alkylation: 1,3-diphenylpropenyl acetate (DPA)

	ee (%)	conversion (%)
(S)-MeoBiphep	93	>99
C3Z	93	>99
C3E	92	>99

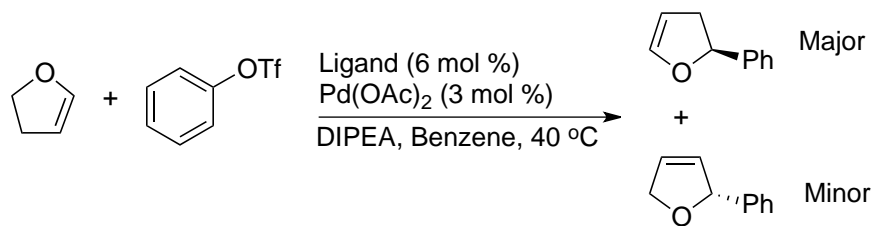
\*conversion by  $^1\text{H}$  NMR, %ee by chiral HPLC



**Table 2.** Asymmetric allylic alkylation: pentenyl acetate (PA)

	ee (%)	conversion (%)	isolated yield (%)
(S)-MeoBiphep	42	>99	95
C3Z	46	>99	89
C3E	39	>99	89

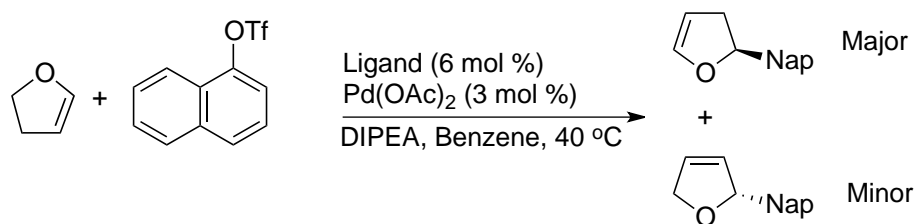
\*conversion by  $^1\text{H}$  NMR, %ee by  $^1\text{H}$  NMR with  $\text{Eu}(\text{hfc})_3$  chiral shift reagent.



**Table 3.** Asymmetric Heck Reaction: 2,3-dihydrofuran with phenyl triflate (PhOTf)

	ee (%) major	ee (%) minor	dr
(S)-MeoBiphep	90	67	95:5
C3Z	96	17	95:5
C3E	83	31	94:6

\*%ee by chiral GC

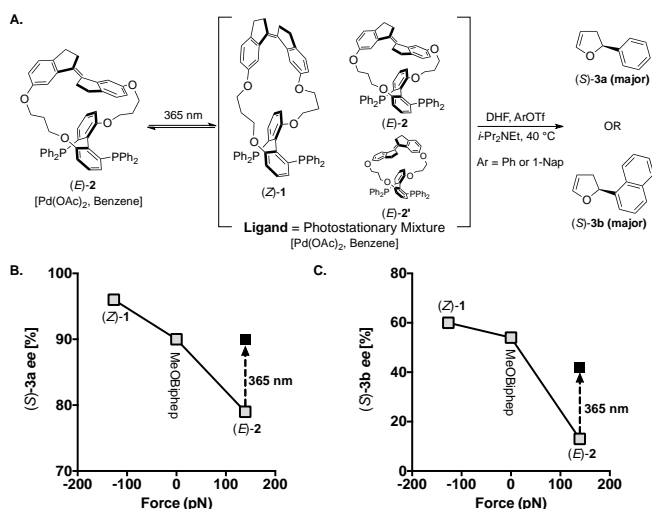


**Table 4.** Asymmetric Heck Reaction: 2,3-dihydrofuran with naphthyl triflate (NapOTf)

	ee (%) major	dr
<b>(S)-MeoBiphep</b>	38	94:6
<b>C3Z</b>	52	92:8
<b>C3E</b>	18	94:6

\*%ee by chiral HPLC.

While purely geometric ligand photoswitching might be useful in its own right, our goals were to frame the observed effects in the context of an applied mechanical distortion. Following previously described methodology, calculations at the B3LYP/6-311+G(d) level of DFT on complete conformational ensembles of MeOBiphep with constraining potential imposed across the C atoms of the Me groups yielded a calibration curve that relates the O...O bond distance to the force applied to adjacent carbon atoms for the different stereoisomers of the macrocyclic ligand. The O...O bond distance was chosen because it best represents the pulling coordinate through which the dihedral angle is compressed or widened by stiff stilbene. This approach has been validated previously against single molecule force spectroscopy data in the context of gem-dibromocyclopropane ring opening. The compression of the dihedral angle to 83° requires the equivalent of 130 pN of compressive force applied to MeOBiphep, whereas the extension of the dihedral angle to 106° would be observed if a tensile load of 140 pN were applied in the opposite direction. In the case of the Heck arylation (Figure 2), we find that this amount of force triggers changes in reaction ee of up to 40%.



**Figure 2.** a) Irradiation of catalyst solution [(E)-2, Pd(OAc)<sub>2</sub>, in benzene] *in situ* at 365 nm yields a proposed photostationary mixture of ligands in asymmetric Heck arylations b) and c) summarize the *ee* of (S)-3a and (S)-3b respectively for ligands used in this study. Dashed arrow illustrates change in *ee* of ligand (E)-2 with irradiation (+ 365 nm).

*The major finding of this work is that forces on the order of 100-200 pN are sufficient to enact substantial and measurable changes in reaction selectivity (here, ee). This work has recently been published (Z. S. Kean et al., "Photomechanical Actuation of Ligand Geometry in Enantioselective Catalysis," Angew. Chem. Intl. Ed., 2014, 126, 14736-14739).*

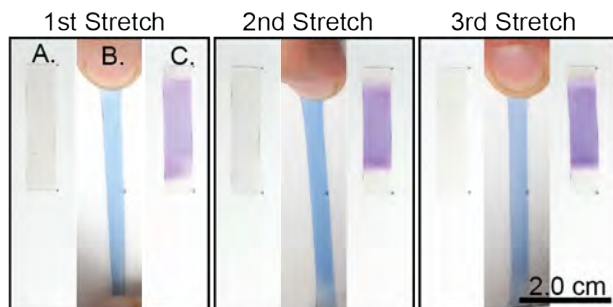
## Accomplishment 2. Platform for reversible covalent mechanochemical activation.

We reasoned that filled PDMS might be an ideal platform for reversible covalent mechanochemistry. PDMS is tough, highly elastic, compatible with a wide range of chemistry, and the surface of filler particles provides a potential site of stress concentration. We were further attracted to filled PDMS as a platform because of its relatively high stretchability, high mechanical strength, optical transparency, and high functional group tolerance. These traits make it well suited for potential catalytic functionality. In addition, PDMS is a platform material for microfluidic and electrolithographic devices, pneumatically powered soft robotics, and biomedical engineering applications, and we speculated that, if shown to be accessible, covalent mechanochemical activation might provide a route to adding new responsive chemical functionality to an already highly functional material.

To test this idea, we initially turned to the colorimetric mechanophore spiropyran, developed previously by Moore, Sottos, *et al.* Spiropyran reversibly opens in response to an appropriately coupled force, resulting in a colored merocyanine form. Force induced isomerization of the molecule allows for direct spatial and temporal visualization of stress accumulation in an otherwise insoluble network. In the final reporting period, we completed our initial assessment of this platform.

We covalently incorporated a bis-alkene functionalized-spiropyran into PDMS (0.5-0.7 wt %) via platinum cure hydrosilylation, the same chemistry used to form the covalent network. Further details of fabrication can be found in the Supporting Information. Solvent-cast films resemble the nascent PDMS material, but have pale yellow coloration from the

embedded spiropyran. Stretching the films by hand generates a vibrant color change (Figure 3) that persists once the film is relaxed (interestingly, a tension-coupled secondary color change during relaxation was also observed). Notably, the length of the relaxed film returns to that of the initial film, in marked contrast to prior reports of spiropyran activation in bulk materials. No activation was observed in control films containing a bis-functional, mechanically inactive control.



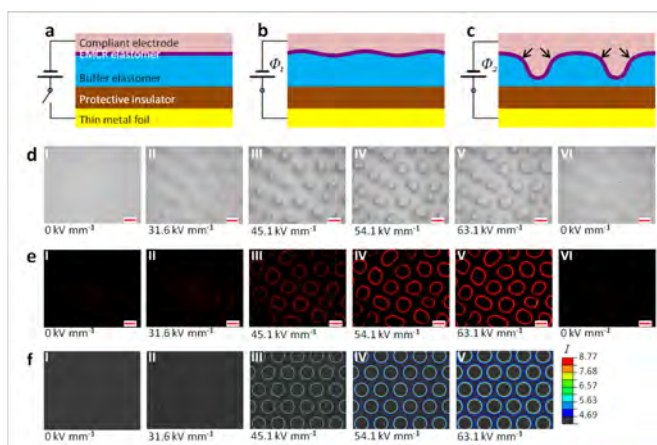
**Figure 3.** Covalent bond activation with full shape recovery. The original sample is clear and colorless under ambient conditions (A), but turns blue when stretched (B). When released, the material regains its initial shape (as indicated by the black reference spots), and the color switches to purple (C). Activation and shape recovery are repeatable over multiple cycles, as shown.

One of the most exciting follow-ups to this demonstration was the incorporation of the PDMS elastomer into electroactive devices. We showed that a soft material system that employs spiropyran functionalized PDMS can function as an electro-mechano-chemically responsive (EMCR) elastomer as an “artificial chromatophore” (inspired the camouflaging capability of numerous cephalopods) and uses electric fields to trigger self-assembled patterns of color and fluorescence on demand. We integrated the PDMS based EMCR elastomer into a display panel that can be remotely controlled. Voltages applied to the display panel induce various patterns of large deformation on the surface of the EMCR elastomer, and the induced stresses in turn lead to a versatile range of fluorescent patterns including lines, circles and letters on demand. The activation of EMCR elastomer and fluorescent patterning are reversible and repeatable over multiple cycles, in contrast to the irreversible plastic deformation or fracture required for activating most existing mechanoresponsive polymers. By integrating diverse fluorescent patterns, remote control by voltages, and reversibility over multiple cycles, the new cephalopod-inspired EMCR elastomers open promising avenues for creating flexible devices that combine deformation, colorimetric and fluorescent response with topological and chemical changes that might eventually be useful in a variety of applications in soft/wet environments, including flexible displays, optoelectronics, biomedical luminescent devices, and dynamic camouflage coatings.

On-demand fluorescent patterns are achieved by integrating the EMCR elastomer into a display panel under the control of applied electric fields. Figure 4 demonstrates the design and working mechanism of the display panel. The EMCR elastomer film is bonded to an underlying buffer elastomer whose shear modulus is lower than that of the EMCR elastomer. To protect the whole system from electric breakdown, the elastomer bilayer is laminated onto a protective insulator with much higher electric strength and modulus than the elastomers. An electric field is applied to this laminate through an external direct-current

voltage that is connected to a thin gold layer coated on the bottom surface of the protective insulator, and a compliant electrode is used to cover the top surface of the elastomer bilayer. The compliant electrode, NaCl solution, is transparent and can deform conformally with the elastomer bilayer surface.

Once an applied electric field reaches a critical value, the initially flat surface of the EMCR elastomer becomes unstable and forms a pattern of wrinkles. The pattern of wrinkles resembles those observed in bilayer systems induced by thermal expansion, swelling and UV or ion irradiation treatment. As the applied electric field further rises, the valleys of the wrinkles are pinched down, forming a pattern of craters. Once the electric field is withdrawn, the instability pattern spontaneously disappears upon elastic recovery and the surface of the EMCR elastomer returns to the flat state. Since the deformation of the EMCR film is relatively low in the flat and wrinkled states, the fluorescence intensity remains at background levels at the corresponding electric fields. At higher electric fields, however, the formation of craters involves large deformations ( $I > 6$ ) in the EMCR film around the crater edges, and the mechanophores are activated and emit strong fluorescent signals. Fluorescent patterns of rings are formed around the craters, and the fluorescent intensity becomes stronger with increasing electric field. As a control experiment, the fluorescence of a Sylgard elastomer film incorporating a bis-functionalized and mechanically inactive spiropyran (i.e., molecular elongation does not lead to ring-opening) remains low under the same applied electric fields, confirming that electro-mechano-chemical coupling to stress-bearing polymer subchains is necessary to activate the mechanophores. Nearly full reversibility and repeatability of the whole pattern is seen over multiple on/off cycles. Remarkably, the reversible patterning can be repeated over 100 cycles.



**Figure 4.** Electro-mechanical activation of EMCR elastomer films. Schematic illustrations of (a) the experimental setup, (b) wrinkle initiation, and (c) crater formation. The arrows in (c) indicate the locations of large deformation in the EMCR film. The fluorescence intensity of the EMCR film is first equilibrated to a force-free photostationary state by being exposed to green light for 3 min, and then activated with ramping electric field. (d) Optical microscope and (e) fluorescent microscope images of the EMCR film under varied electric fields. Image VI of (e) is the EMCR film illuminated by the green light for 3 min. The thicknesses of EMCR elastomer, buffer elastomer, and protective insulator are  $\sim 21 \mu\text{m}$ ,  $\sim 106 \mu\text{m}$  and  $125 \mu\text{m}$ , respectively. The applied voltages through (dI-dV) are 0 kV, 3 kV, 10 kV, 12 kV and 14 kV, respectively. The scale bars in (d) and (e) denote  $250 \mu\text{m}$ . (f) Finite-element calculations of the first invariant in the EMCR film under increasing electric field.



Relevant publications:

G. R. Gossweiler, G. B. Hewage, G. Soriano, Q. Wang, G. W. Welshofer, X. Zhao, and S. L. Craig, "Mechanochemical Activation of Covalent Bonds in Polymers with Full and Repeatable Macroscopic Shape Recovery", *ACS Macro Lett.*, **2014**, *3*, 216-219.

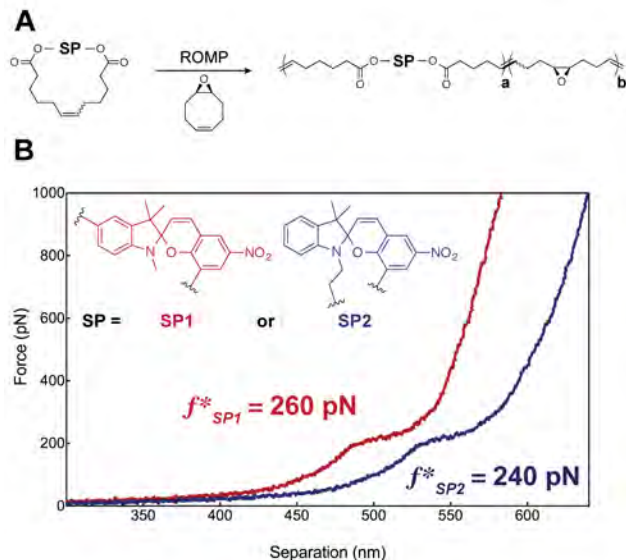
Q. Wang, G. R. Gossweiler, S. L. Craig, and X. Zhao, "Cephalopod-inspired Design of Electro-mechano-chemically Responsive Elastomers for On-demand Fluorescent Patterning", *Nature Commun.*, **2014**, *5*, 4899.

### **Accomplishment 3. Quantifying activity in the PDMS platform.**

From the prior accomplishments, we know that sufficient forces can alter catalyst activity, and we know that forces sufficient to activate spiropyran can be obtained within reversible deformation of PDMS. The missing piece was to compare those two forces. From our molecular force probe work, we know that forces on the order of 100 pN are needed to have a consequential effect on biarylphosphine dihedral angle in organometallic catalysts, and so we set out to quantify the forces at play in the activation of spiropyran.

We chose to characterize two spiropyran force probes, the seminal isomer introduced by Davis *et al.*, and a second isomer, SP2, possessing attachment points similar to a number of other demonstrations. Our approach follows that employed in our recent studies of other mechanophores. We began by synthesizing copolymers of varying SP content through an entropically driven ring opening metathesis copolymerization of SP-containing macrocycles SP1 and SP2 with 9-oxabicyclo[6.1.0]non-4-ene (epoxy-COE). The co-monomer is employed because it has been found previously to promote adhesion with the AFM tip. The copolymers are deposited onto a surface upon evaporation of a dilute polymer solution of THF.

Approach/withdraw cycles at varying velocity result in force curves that undergo a characteristic transition around  $260 \pm 15$  pN and  $240 \pm 15$  pN, respectively, for the two isomers (Figure 5). This transition is due to the mechanical conversion of SP to MC, as supported by the following observations: extension scales with initial contour length, extension is proportional to SP content, and extension matches theoretical values from computational simulations.



**Figure 5.** Macrocycles incorporating SP1 or SP2 are copolymerized with epoxy-COE to obtain a series of copolymers of varying spiropyran content (A). Representative single molecule force-extension curves of copolymers containing SP1 (Red) or SP2 (Blue) of a 1:1 ratio SP:epoxyCOE (B). The plateau shown is characteristic of the mechanically induced ring-opening of SP to the extended MC form. Values of  $f^*$  correspond to the average value of the midpoint of the plateau for multiple force extension curves (tip velocity =  $300 \text{ nm}\cdot\text{s}^{-1}$ ).

The significant point here is that we can fit the curves to kinetic models, and find that activation of spiropyran on the timescale of seconds (as is present in the PDMS work) corresponds to forces of  $\sim 150\text{-}200 \text{ pN}$ . In other words, the forces active in reversibly deformed PDMS are sufficient to enact substantial changes on catalyst selectivity. Taken in combination, this work validates our initial hypothesis and provides baseline fundamental insights for the development of fluxional mechanocatalysts, an area of inquiry that offers great promise and that we hope to continue to pursue.