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# Dual Stimuli Switching: Interconverting Cationic and Radical Polymerizations with Electricity and Light

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## SUMMARY

**Increasing demand for advanced materials that are essential to emerging technologies calls for synthetic methods which can easily generate polymers with complex structures. Multiblock copolymers display a range of material properties depending on the length and number of polymer blocks. Currently, there remains a lack of polymerization processes that can easily synthesize these multiblock structures. Herein, we report the in situ synthesis of multiblock copolymers by controlling the incorporation of vinyl ether and acrylate monomers with electrochemical and photochemical stimuli, respectively. To achieve this, we developed a cationic polymerization where polymer chain growth is controlled through the reversible electrochemical oxidation of the polymer chain end and coupled this with a compatible photocontrolled radical polymerization. This process was used to generate higher-order multiblock copolymers wherein the number of blocks and the length of each segment is controlled on demand by the two stimuli. This method, which lends itself toward automation, will aid in accelerating the rate at which next generation materials are discovered.**

## INTRODUCTION

Polymer properties are determined not only by the structures of the parent monomers but also by the final macromolecular structure. There have been numerous studies of block copolymers showing that the composition, length, and total number of blocks can be used to tune the final material function.[1-4] On this basis, there is a demand to develop methods to synthesize block copolymers with precise structural complexity to identify materials for next generation applications. To accelerate this discovery process, we envisaged an automated system where one could input any desired multiblock copolymer structure and automatically synthesize it from a single solution of reagents. This type of system would enable the facile formation of a library of block polymers with control over the number of blocks, as well as the length of each individual block in the material. To achieve this, we need a method where the selectivity for monomer incorporation could be controlled and switched during the polymerization to give the desired structure.

Externally regulated polymerizations (*e.g.*, thermal,[5-7] chemical,[8-13] mechanochemical,[14-17] electrochemical,[18-22] and photochemical[23-33]) offer an opportunity to control monomer selectivity at a growing polymer chain end.[34] Taking advantage of this strategy, the Byers[11,21] and Diaconescu[12,13] groups have independently developed chemically and electrochemically controlled ring opening polymerizations (ROP) that allow switching between incorporation of lactones and epoxides. Utilizing a combination of thermal and photochemical stimuli, You and coworkers[35] developed a polymerization wherein ROP of thiiranes could be interconverted with radical reversible addition-fragmentation chain transfer (RAFT) polymerization of acrylamides.

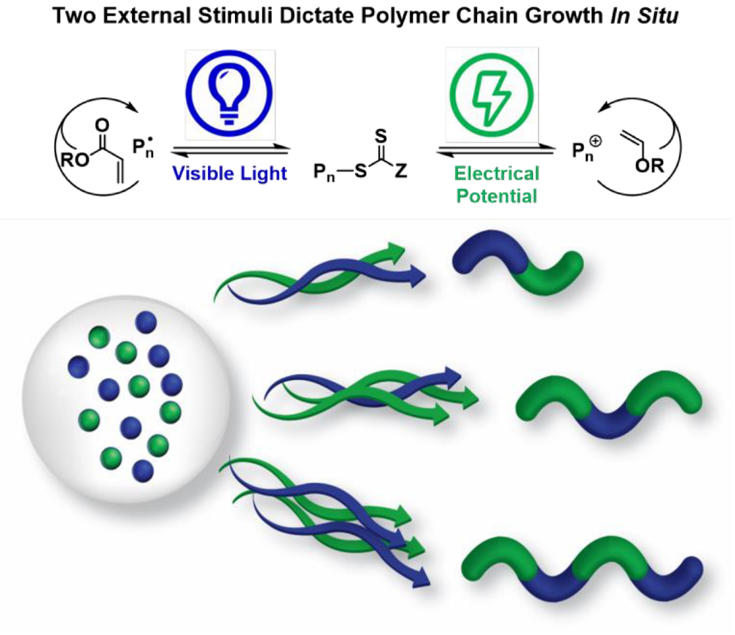


**Figure 1. Dictating polymer structure by switching between photochemically controlled radical and electrochemically controlled cationic polymerizations**

In a unique approach to control monomer selectivity, our group has developed methods that enable the stimuli controlled oxidation or reduction of a polymer chain end. This allowed us to switch between a cationic and radical RAFT polymerization mechanism, leading to the selective polymerization of vinyl ethers or acrylates, respectively. In the first system, we used both an oxidizing and reducing photocatalyst to control each polymerization. Irradiation with green light selectively promoted a cationic polymerization. However, irradiation with blue light excited both photocatalysts and led to initiation of both polymerization mechanisms simultaneously. Although this system demonstrated that polymerization mechanism could be switched by changing the stimulus, it did not give control over the synthesis of well-defined multiblock copolymers. To have deterministic control over the final structure, we needed orthogonal stimuli that allowed each polymerization to be independently promoted. To this end, we designed a second system where we coupled a photocontrolled radical polymerization of acrylates with a chemically controlled cationic polymerization of vinyl ethers.[36] This allowed for the synthesis of well-defined multiblock copolymers. However, this approach relied on the manual addition of exogenous oxidizing and reducing agents for the chemically controlled cationic polymerization, which can introduce impurities to the system and cause termination events. In order to automate this system and enable the facile synthesis of structurally precise block polymers, two completely external and orthogonal stimuli are necessary to dictate polymerization mechanism.

We hypothesized that combining a photocontrolled radical polymerization with an electrochemically controlled cationic polymerization would allow switching between acrylates and vinyl ethers without having to manipulate reagents (Figure 1). This would be ideal for an automated system where the final polymer structure could be dictated by the order and total amount of time that current and light were applied to the system. Previously, we developed an electrochemically controlled cationic polymerization of vinyl ethers mediated by 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO).[18] Unfortunately, this method would inhibit a photocontrolled radical process as the aminoxyl radical mediator, TEMPO, would couple with the propagating radical chain end and terminate the polymerization of acrylates. To address this challenge, in this manuscript we developed an electrochemically controlled cationic polymerization of vinyl ethers that uses a mediator which is compatible with a radical polymerization of acrylates and demonstrate that we can efficiently switch monomer selectivity with electrochemistry and light.

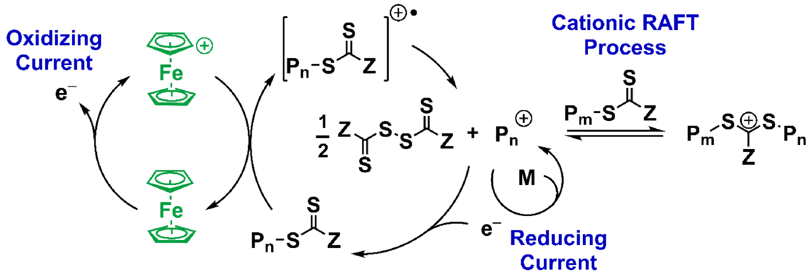


Figure 2. Proposed mechanism of electrochemically controlled cationic polymerization mediated by ferrocene (M = monomer).

## RESULTS and DISCUSSION

### Development of a Ferrocene Mediated Electrochemically Controlled Cationic Polymerization

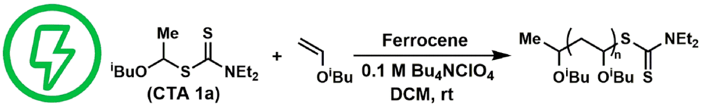
Previously, we demonstrated that ferrocenium salts (FcX) could oxidize dithiocarbonyl chain transfer agents (CTAs) to promote cationic RAFT polymerizations.[36] Therefore, we posited that ferrocene (Fc) would be an efficient electrochemical mediator for the cationic polymerization and would be compatible with the photocontrolled radical polymerization of acrylates. Specifically, electrochemical oxidation of Fc to ferrocenium would oxidize the dithiocarbonyl CTA and initiate cationic polymerization (Figure 2). Reversal of the current in the electrochemical cell will reduce the dithiocarbonyl disulfide to the anion, thereby leading to reversible termination of the growing polymer chain. Importantly this will allow chain growth to be turned on and off by the direction of current in the cell and the rate of the polymerization to be controlled by the current density applied, providing temporal control.

To test our hypothesis, we investigated the polymerization of isobutyl vinyl ether (IBVE) in a divided electrochemical cell using reticulated vitreous carbon (RVC) electrodes. Applying a constant potential to a solution of IBVE, CTA (**1a**), Fc, and tetrabutylammonium perchlorate ($Bu_4NClO_4$) in dichloromethane (DCM) initiated polymerization of IBVE. The resulting polymer displayed excellent agreement between theoretical and experimental number average molar masses ($M_n$s) and a low dispersity ($Đ$) value, demonstrating a controlled cationic polymerization (Table 1, entry 1). Removal of CTA from the reaction solution results in an uncontrolled polymerization (Table 1, entry 2). Additionally, in the absence of Fc no polymerization is observed, demonstrating that a redox mediator is required to promote the reaction under these mild oxidizing conditions (Table 1, entry 3).

By varying the monomer-to-CTA ratio, a range of $M_n$s were targeted while simultaneously retaining good agreement between experimental and theoretical molecular weights and low $Đ$s (Table 1, entries 4-7). Greater control of the polymerization is achieved by applying a constant current instead of a constant potential, thus substantially decreasing $Đ$ (Table 1, entry 5). Furthermore, changing the electrolyte counterion to either tetrafluoroborate or hexafluorophosphate results in polymers with similarly low $Đ$ values (Table 1, entries 8-9).

The polymerization kinetics were monitored over the course of the reaction by gel permeation chromatography (GPC) and $^1H$ NMR. After applying 1.5 mA of anodic current over a 15 minute period, a linear relationship between conversion and $M_n$ is observed, indicative of a chain growth polymerization (Figure 3a). Importantly, the applied current density dictates polymerization rate as the concentration of propagating cationic chain ends is directly proportional to ferrocenium concentration (see Supplemental Information, Figure S2).[37,38] This feature of the polymerization gives an additional layer of control when attempting to iteratively synthesize blocks of varying size. Additionally, it was observed that the rate of ferrocenium generation has little effect on the control over the cationic RAFT polymerization, producing poly(IBVE) with low $Đ$ and good agreement with the theoretical molecular weight (Table S1). This indicates that generating active mediator more quickly at higher current densities does not lead to a loss in control over the polymerization, while affording us the ability to alter the rate of reaction.

Table 1. Living Characteristics of Ferrocene Mediated Electrochemically Controlled Cationic Polymerization



| Entry[a] | [M]:[CTA]:[Fc] | $M_{n,Theo}$[b] (kg/mol) | $M_{n,Exp}$ (kg/mol) | $Đ$ |
|---|---|---|---|---|
| 1[c] | 100:1:1 | 10.4 | 10.2 | 1.21 |
| 2[c] | 100:0:1 | — | 46.1 | 2.25 |
| 3[c] | 100:1:0 | — | — | — |
| 4[d] | 50:1:0.2 | 5.2 | 4.7 | 1.32 |
| 5[d] | 100:1:0.2 | 10.4 | 10.6 | 1.13 |
| 6[d] | 150:1:0.2 | 16.1 | 14.5 | 1.04 |
| 7[d] | 200:1:0.2 | 20.4 | 20.9 | 1.14 |
| 8[e] | 100:1:0.2 | 10.4 | 12.9 | 1.13 |
| 9[f] | 100:1:0.2 | 10.4 | 11.6 | 1.18 |

[a] [IBVE] = 3.2 M (in DCM), $V_{tot}$ = 6 mL, [$Bu_4NClO_4$] = 0.1 M, RVC or Steel Anode, RVC or Steel Cathode (Divided cell).
[b] $M_{n,Thero}$ = [M]/[CTA] X $MW_M$ X Conversion + $MW_{CTA}$.
[c] Applied 440 mV vs. Ag Reference.
[d] Applied 1 mA of current.
[e] [$Bu_4NPF_6$] = 0.1 M.
[f] [$Bu_4NBF_4$] = 0.1 M.

## Gaining Temporal Control

In order switch polymerization mechanism *in situ*, we must be able to reversibly terminate the cationic polymerization. We posited that applying a cathodic current will reduce the disulfide to the dithiocarbonyl anion which will cap the propagating polymer chain ends and reversibly terminate the polymerization. To test this hypothesis, polymerization was initiated by applying +0.5 mA of current over 15 minutes to a solution of IBVE, Fc, CTA (**1a**), and $Bu_4NClO_4$ in DCM after which current application was halted. After 30 minutes of polymerization, –0.5 mA of current was applied to reversibly terminate the reaction. Following a 60 minute "off" period, the polymerization could be reinitiated by subjecting the reaction to anodic current—this overall process was repeated two times, demonstrating good temporal control over the polymerization (Figure 3b). Notably, in the third "on" period twice the current was passed, yielding an increased rate of polymerization; this result demonstrates the ease of controlling the polymerization rate through modulation of current density. Additionally, this new electrochemical polymerization can be applied to a large range of vinyl ether monomers of varying steric and electronic parameters, as well as *para*-methoxystyrene. In each case, polymers with low $Đ$ values and excellent agreement between theoretical and experimental $M_n$s were obtained (Table S2).

The temporal control over this electrochemically controlled cationic polymerization validates this method as a good candidate to be paired with a photochemically controlled radical polymerization for *in situ* synthesis of multiblock copolymers. Drawing from previous experience, we chose $Ir(ppy)_3$ as the photocatalyst to mediate the radical polymerization of methyl acrylate (MA).[31,36,39] It is important to note that successful switching requires that temporal control of each polymerization be retained when all reagents for both polymerizations are combined.

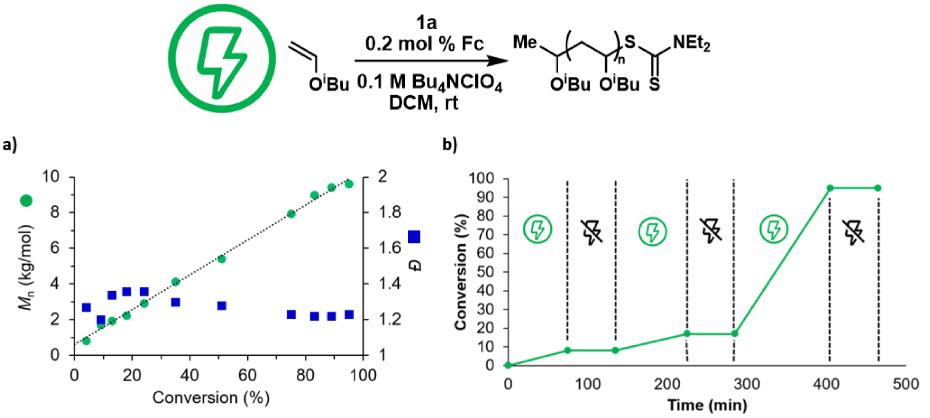


**Figure 3. (a) Relationship between Mn and conversion for the electrochemical polymerization of vinyl ethers. (b) Temporal control over polymer chain growth through application of oxidizing and reducing potentials.** [IBVE] = 3.2 M (in DCM), $V_{tot}$ = 6 mL, [Bu$_4$NClO$_4$] = 0.1 M, Steel Anode, Steel Cathode (Divided cell).

To demonstrate that the electrochemically mediated cationic polymerization is unaffected by the presence of Ir(ppy)$_3$ and MA, +0.5 mA of current was applied over 10 minutes to a solution containing Fc, Ir(ppy)$_3$, IBVE, MA, CTA (**1b**), and Bu$_4$NClO$_4$ in DCM. We observed efficient polymerization of IBVE, producing a polymer with a $M_n$ of 8.8 kg/mol and a low dispersity of 1.15. Importantly, the experimental $M_n$ aligned well with the theoretical molar mass, and the polymerization can be turned on and off by simply changing the direction of current. Unfortunately, upon irradiation of an identical reaction solution with 456 nm blue LEDs, we observed no conversion of MA over 6 hours. For comparison, the radical polymerization of MA reached 88% conversion after the same time period in the absence of ferrocene and electrolyte (Table S3). We hypothesized that Fc was quenching the excited state of Ir(ppy)$_3$, as it is known to be a triplet quencher.[40] Indeed, mM concentrations of Fc showed strong quenching of the Ir(ppy)$_3$ photoluminescence (Figure 4). This observation illustrates that the Fc is inhibiting the photochemical radical polymerization. Importantly, by substantially lowering the concentration of Fc in solution, the reaction rate of the radical polymerization could be recovered while also retaining good temporal control over both the photochemical and electrochemical polymerizations (Figure S11,S15). These results demonstrate that both the cationic and radical polymerizations are compatible with one another, which provides the opportunity to switch between polymerization mechanisms at will.

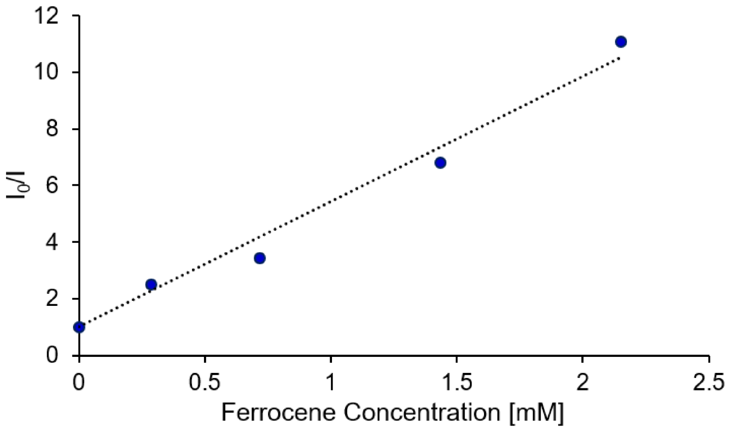


**Figure 4. Stern-Volmer plot for the fluorescence quenching of Ir(ppy)$_3$ by ferrocene ($\lambda_{ex}$ = 455 nm).**

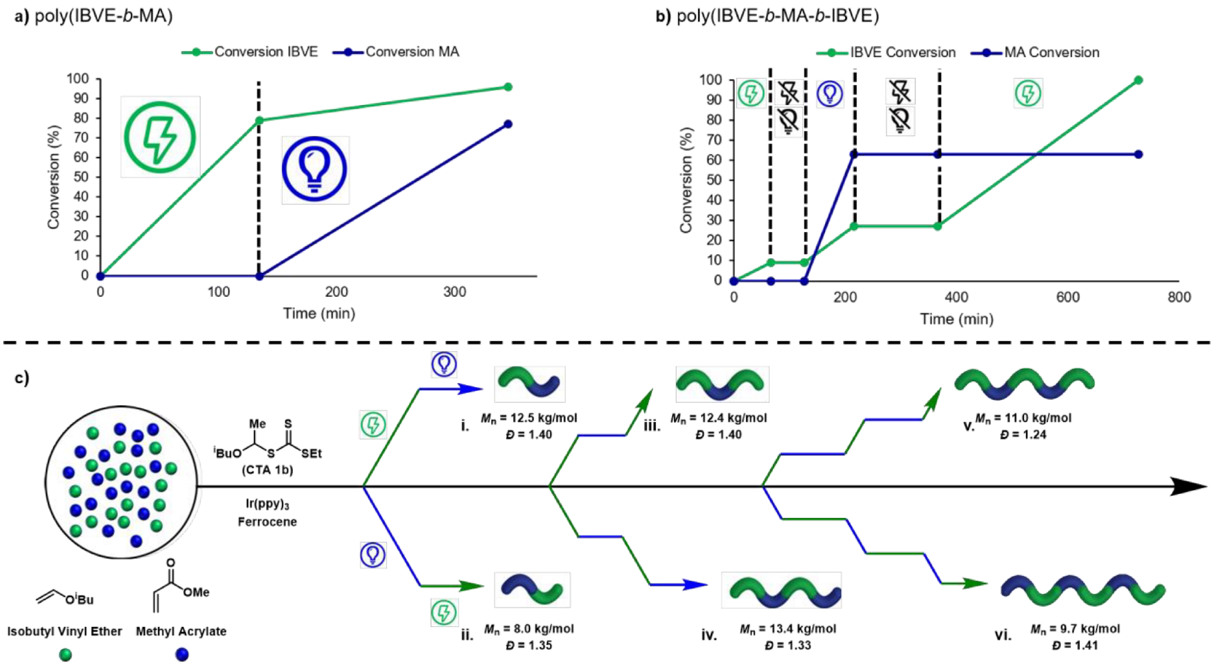


**Figure 3. Conversion of IBVE (green line) and MA (blue line) for dual stimuli switching using alternating application of photochemical or electrochemical stimuli to synthesize (a) poly(IBVE-*b*-MA) and (b) poly(IBVE-*b*-MA-*b*-IBVE). (c) Range of accessible multiblock copolymers synthesized via electro- photo- switchable RAFT polymerization: i. poly(IBVE-*b*-MA), ii. poly(MA-*b*-IBVE), iii. poly(IBVE-*b*-MA-*b*-IBVE), iv. poly(IBVE-*b*-MA-*b*-IBVE-*b*-MA), v. poly(IBVE-*b*-MA-*b*-IBVE-*b*-MA-*b*-IBVE), and vi. poly(MA-*b*-IBVE-*b*-MA-*b*-IBVE-*b*-MA-*b*-IBVE).**

## Stimuli Switching Facilitates Multiblock Polymers

With orthogonal and compatible polymerization processes in hand, we set out to make multiblock copolymers. Upon applying +0.5 mA of current to MA, IBVE, Ir(ppy)$_3$, Fc, and $Bu_4NClO_4$ in DCM, IBVE is exclusively polymerized. Following the application of –0.5 mA of current to reversibly terminate the cationic polymerization, the solution was subjected to blue light irradiation affording a well-defined poly(IBVE-*b*-MA) block polymer (Figure 5a). Importantly, from the same solution conditions, the inverse diblock polymer can be synthesized by simply changing the order of the two applied stimuli (Figure S18-19). Of note, we have previously demonstrated that we can polymerize IBVE from a poly(MA) macroinitiator; the incorporation of a small amount of IBVE during the radical polymerization results in thioacetal chain ends, which enables efficient initiation of the cationic process.[36,41]

We sought to explore the range of copolymer sequences that we could generate by alternating the order of applied stimuli. To synthesize a poly(IBVE-*b*-MA-*b*-IBVE) triblock copolymer, we first applied anodic current to promote the cationic polymerization of IBVE. The polymerization was then reversibly terminated by the application of cathodic current, which is followed by an off period in the absence of stimuli that illustrates the stability of the system. We then irradiated the solution with blue light to promote the radical polymerization of methyl acrylate, wherein a small amount of isobutyl vinyl ether is incorporated, followed by another off period upon the removal of light. Subsequent application of electrical current generated the terminal IBVE block (Figure 5b). This triblock copolymer synthesis with two alternating off periods, demonstrates the excellent temporal control and chain-end fidelity of the dual stimuli system. This methodology can be taken a step further to generate tetrablock copolymers by simply adding an additional switching event (Figure S22-23). Interestingly, while our past methodology was able to achieve the synthesis of tetrablock copolymers, the need for successive addition of exogenous ferrocenium greatly limited the number of switching events that could take place due to increased termination events and inhibition of the photochemical radical polymerization by ferrocene quenching.[36] In this electro- photo- switchable system we can maintain low concentrations of ferrocene and negate the need for any exogenous reagents facilitating enhanced control over the process. This novel polymerization methodology enables the synthesis of penta- and hexablock copolymers composed of methyl acrylate and isobutyl vinyl ether, which were previously inaccessible by any previous methodologies (Figure 5c). Significantly, the size of each block can be controlled by the length of application and intensity (*i.e.*, current density or light intensity) of each stimulus, while the number of blocks is dictated by the number of times the two stimuli are switched. The control offered by this method paves the way toward generating libraries of block polymer structures through automated switching of the applied stimuli.

## Conclusion

In conclusion, we have developed a system that enables switching of polymerization mechanisms, and thereby monomer selectivity *in situ* using two external stimuli, visible light and electrical potential. To achieve this goal, we designed an electrochemical cationic polymerization mediated by ferrocene. Pairing this electrochemical cationic polymerization with a photochemical radical polymerization enabled us to successfully switch polymerization mechanism *in situ*. A variety of well-defined multiblock copolymers were synthesized where the final structure was dictated by the order and duration of the applied stimuli. This new switchable polymerization demonstrates the power of pairing two orthogonal, external stimuli and will facilitate the synthesis of advanced polymer structures in a one-pot process; thus, accelerating the discovery of next-generation materials.

## SUPPLEMENTAL INFORMATION

Document S1. Supplemental Experimental Procedures, Figures S1–S27, Tables S1-S3, and References 1-2.

## ACKNOWLEDGMENTS

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## AUTHOR CONTRIBUTIONS

M.J.S., B.M.P., and B.P.F. designed this project. M.J.S. and B.M.P. optimized the electrochemical polymerization. M.J.S. performed the photochemical and switching experiments. M.J.S. wrote the manuscript with input from all authors.

## DECLARATION OF INTERESTS

The authors declare no competing interests.

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