Reversible Thermochromic Photonic Coatings with a Protective Topcoat

Weixin Zhang, Albert P. H. J. Schenning, Augustinus J. J. Kragt, Guofu Zhou,* and Laurens T. de Haan*

ABSTRACT: The fabrication of reversible and robust thermochromic coatings remains challenging. In this work, a temperature-responsive photonic coating with a protective topcoat is fabricated. A cholesteric oligosiloxane liquid crystal possessing a smectic-to-cholesteric phase-transition temperature response is synthesized. A planar alignment of its cholesteric phase is possible with blade coating. By stabilizing with 3 wt % of a crosslinked liquid crystal network, the photonic coating shows a color change ranging from red to blue upon heating. High transparency is retained, and the structural color changes are fully reversible. A transparent polysiloxane layer can be directly applied on top of the cholesteric coating. By stabilizing with 3 wt % of a crosslinked liquid crystal mixture encapsulated by a polymer topcoat, the photonic coating shows about 600 nm of reflection band shift, based on the pre-transitional effect, which permits easy processability, coating robustness, and a reversible temperature response.

KEYWORDS: cholesteric liquid crystals, reflective coatings, thermochromic polymers, stimuli-responsive photonic materials, structural color changes

INTRODUCTION

Temperature-responsive photonic polymers are able to change their structural reflective color upon temperature fluctuations. These “smart” materials have potential applications as temperature indicators, aesthetics, and heat-regulating windows. For these applications, polymer coatings are desired that are easily processable, robust, and have a reversible thermochromic response. Many responsive photonic polymer systems are based on hydrogels and liquid crystals. A large and reversible optical response often relies on small molecules such as water or low-molar-weight liquid crystals, which are less suitable for coating applications.

Cholesteric liquid crystal (Ch–LC) polymers have been successfully applied as thermochromic photonic coatings. The photonic properties of Ch–LCs stem from their intrinsic helical structure, with a selective reflection of light that is related to the length of the helical pitch. When in proper planar alignment, Ch–LCs are highly transparent to light outside the reflection band. Temperature-responsive color change in Ch–LCs is caused by a change in the pitch length. However, the existing examples of Ch–LC polymer coatings do not show a large thermochromic response due to a high crosslink density. Mechanically compressed elastomeric Ch–LC coatings show a large change in the reflection band upon heating above the glass-transition temperature, due to the recovery of the original pitch length. However, this response is irreversible. Semi-interpenetrating polymer network coatings have been reported that showed reversible thermochromic changes, but the response was slow (i.e., in the order of hours). In addition, responsive Ch–LC polymers based on thermal deformations only show obvious color changes over a large temperature range (i.e., from room temperature up to 200 °C).

A way to achieve large reflection band shifts over a small temperature range is by utilizing a smectic A (Sm) to cholesteric phase transition, which causes dramatic and reversible unwinding of the helix, known as the “pre-transitional effect,” and results in a large thermochromic response. Ranjeksh et al. recently succeeded in fabricating thermochromic coatings based on the pre-transitional effect, which consist of a low-molecular-weight Ch–LC mixture encapsulated by a polymer topcoat. However, the color is irreversibly lost when the device is heated to the isotropic phase, and the alignment can only be brought back by shear alignment. We have reported on a polymer stabilized Ch–LC siloxane photonic coating that shows about 600 nm of reflection band shift, based on the pre-transitional effect. However, the coating was not mechanically robust at working temperatures.

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and its transparency was irreversibly lost from the isotropic phase as well.

We now report on a new approach for the preparation of temperature-responsive Ch–LC photonic coatings with full thermal reversibility from the Ch-to-Sm and Ch-to-I transitions, which also show a fast response and good optical transparency. We synthesized a temperature-responsive siloxane Ch–LC oligomer with a Sm-to-Ch–LC transition (siloxane 2, Scheme 1), which can be directly blade-coated on glass. By introducing 3 wt % of a crosslinked LC network into siloxane 2 coating, the optical properties of the coating become fully reversible even when passing the smectic and isotropic phase transitions, due to the stabilization of the planar alignment by the LC network. On top of the photonic coating, a transparent protective polymer layer was added for protection. The thermochromic response of the LC layer is unaffected by the topcoat, showing a reversible and continuous color change from blue to red between 53 °C and room temperature. Since the thermochromic response can take place at moderate temperatures, such kind of material has potential for daily-life applications (e.g., as temperature sensors, aesthetics, and heat-regulating windows).

**EXPERIMENTAL SECTION**

**Materials.** The initiator Irgacure 184 was purchased from Ciba Specialty Chemicals, Inc. Diacrylate 1 was purchased from Merck. Sylgard 184 was purchased from Dow Corning. For details on materials and methods for the synthesis of siloxane 2, see the Supporting Information.

**Ch–LC Coating Mixture.** In a tan glass vial was weighed siloxane 2, diacrylate 1, and the initiator in a weight ratio of 100 — r/r/0.05, in which r = 1, 2, 2.5, 3, or 4. Diacrylate 1 and the initiator were added to the mixture via a diluted toluene solution in volumetric flasks. More toluene was then added and the mixture was homogenized by stirring. The total solute comprises about 45 wt % of the mixture.

**Topcoat Mixture.** In a vial was added the Sylgard 184 base and the corresponding curing agent in an 8:1 weight ratio. The mixture was stirred vigorously to blend the components and then degassed in vacuum at room temperature.

**Preparation of Rubbed Polyimide-Coated Glass Substrates.** Glass substrates of 3 × 3 cm² size were prepared following a previously reported method.41 Those of 9 × 9 cm² size were treated according to a similar procedure but using a different spin-coating rotation speed of 2000 rpm for 90 s.

**Preparation of Coatings.** An RK PrintCoat Instruments K control coater was used to prepare the coatings. Below is given an example of the fabrication procedure of a siloxane 2 coating with a crosslinked network and with a Sylgard topcoat.

On a 9 × 9 cm² size glass substrate with rubby polyimide was loaded 45 μL of the mixture, and it was placed at 100 °C for 40 min to evaporate the solvent. Then, the coating was applied using a 25 μm gap (four-sided applicator, ZFR 2040, Zehntner), which was pushed forward over the mixture automatically by the coater at 60 °C on the substrate surface. The speed of the applicator movement was about 0.5 cm/s. The coating was then cooled down to 46 °C at the surface and was UV-cured using an EXFO Omnicure S2000 mercury lamp at an intensity of 20 mW/cm² for 10 min at 46 °C in a nitrogen environment. Afterward, the coating was kept under a nitrogen atmosphere at the same temperature for 30 min for post-curing. For application of the protective topcoat, the coating was transferred back to the coater. The freshly prepared Sylgard mixture was loaded onto the LC layer, and the layer was applied using a 60 μm gap (four-sided applicator, ZFR 2040.8030, Zehntner) at 44 °C. The speed of the applicator movement was about 0.5 cm/s. After the application, the coating was kept at 44 °C for 24 h to cure the Sylgard and was then cooled to room temperature. The entire piece of coating was cut into several pieces for different tests using a glass cutter. The samples were annealed by a slow heating—cooling process from room temperature to a maximum of 49 °C (Ch–LC phase) prior to the tests. The heating and cooling rates of annealing were approximately 0.07 °C/min.

For coatings without a Sylgard topcoat, the fabrication was finished by cooling the sample down to room temperature after the UV-curing step.

To prepare a coating without a network, a 3 × 3 cm² glass substrate was used. Siloxane 2 was loaded on the substrate without the aid of solvents, and the coating was applied directly by the coater, using the same procedure as for the Ch–LC layer described above. This procedure was assisted by other glass plates of equivalent thickness, as the applicator is larger in width than that of the substrate. Afterward, the coating was brought to the pre-heated spectrophotometer immediately for transmission spectra measurements.

**Preparation of Ch–LC Cells.** Cells were prepared by gluing together two 3 × 3 cm² glass substrates with rubbed polyimide. The glue contained glass bead spacers of 10 μm diameter.

The cell containing siloxane 2 was filled at 58 °C in the Ch phase. After filling, the cell was brought to the pre-heated spectrophotometer immediately for transmission spectra measurements.

The cell containing siloxane 2 and 3 wt % of network was filled in the Ch–LC phase without solvent and UV-polymerized at 46 °C using the same conditions as for the coatings.

**Characterization.** Proton nuclear magnetic resonance (1H NMR) spectra were recorded on a 400 MHz Bruker Avance III HD spectrometer. Gel permeation chromatography (GPC) was performed on a Shimadzu LC-203OC 3D instrument equipped with a PDA-254 nm detector, using tetrahydrofuran as the eluent and monodisperse polystyrene calibration standards. Differential scanning calorimetry (DSC) curves were measured with a DSC Q2000, TA Instruments. Transmission optical microscopy (POM) images were acquired on a Leica microscope DM2700 in transmission mode, equipped with crossed polarizers. Thicknesses of the coatings were examined using a Forgale Zoomsurf 3D interferometer.

Transmission spectra were recorded using a PerkinElmer LAMBDA 750 UV/Vis/NIR spectrophotometer with a 150 nm integrating sphere detector. Temperature control of the samples was realized via a Linkam THMS600 hot stage with a customized aperture diameter of 6 mm. Heating and cooling of the hot stage were programed using a Linkam T96 controller.
Scheme 2. Chemical Structure of the Sm–Ch Polymer Siloxane 2 and the Fabrication of the Network-Stabilized Coatings with a Protective Topcoat

**Temperature Calibrations.** Temperature calibrations of the transmission spectra were performed using a Kane-May KM34O thermocouple with 1 °C precision. The temperature recorded on the surface of a blank glass plate mounted on the hot stage was considered as the actual temperature of the sample. When acquiring the photographic images, the temperatures were recorded simultaneously. For the transmission spectra, the temperature was pre-calibrated, resulting in a linear relationship between the actual sample temperature ($T_s$ °C) and “controller temperature ($T_c$ °C)” settings, as $T_s = 0.8014T_c + 1.1203$ ($R^2 = 0.9997$, $T_s > 30$ °C). The actual temperature of the samples were calculated from the controller setting using this formula. Nevertheless, due to the differences in calibration methods and changes in the environmental temperature, 1–3 °C of difference in temperature designation among each test is expected.

**RESULTS AND DISCUSSION**

**Synthesis and Characterization of the Sm–Ch–LC Oligosiloxane LC (Siloxane 2).** For the fabrication of the polymer-stabilized liquid crystal coating, we synthesized a side-chain oligosiloxane LC with a low-glass-transition temperature and a Sm-to-Ch transition (siloxane 2, Scheme 1) using a one-step hydrosilylation reaction. The resulting oligomer is a random co-oligomer of mesogenic units P1 (90 mol %) and chiral units P2 (10 mol %, Scheme 1). The length of the siloxane oligomer backbone ($n_{avg}$) of OMHS was designed to be short ($n_{avg} ≈ 4$) in order to obtain a moderate viscosity. This way, it can be aligned in the Ch–LC phase by coating, still has a fast response, and is solid enough to apply the topcoat without affecting the alignment (vide infra). The $^1$H NMR spectrum of siloxane 2 confirms its molecular structure and the correct ratio of P1/P2 and revealed an $n_{avg}$ of about 6.5 (Figure S1). This increase of $n_{avg}$ is presumably due to the loss of the low-molar fraction during precipitation, which is supported by the yield of 78%. When measured with GPC, siloxane 2 shows a polydispersity of 1.18 and a molecular weight $M_w$ of 3.8 kDa (see the Supporting Information Synthesis section and Figure S2 for details). The $n_{avg}$ calculated from the GPC result (~9.4) is higher than that obtained by NMR spectroscopy and might be less accurate as a polystyrene calibration standard is used. The oligomer undergoes an isotropic transition ($T_i$) at 66 °C, a Sm-to-Ch transition ($T_{Sm-Ch}$) around 35 °C, and a glass transition ($T_g$) around ~6 °C (Figure S3). Transmission spectra of siloxane 2 filled into a cell with planar alignment layers (Figure S4a) show a clear reflection band below $T_i$. In the cholesteric LC phase, the central reflection wavelength shifted from 550 to 902 nm as the temperature decreased from 53 to 32 °C (Figure S3), revealing the existence of the pre-transitional effect. Below 31 °C, the reflection band disappeared suddenly, followed by a loss of transparency (Figure S4a). POM reveals that this scattering state is a result of a multidomain texture (Figure S5). Hence, the disappearance of the reflection band and strong scattering are caused by the formation of the multidomain state of the Sm phase.43,44 Despite having two alignment layers, the initial cholesteric alignment of siloxane 2 does not recover completely upon heating back to the Ch–LC phase (Figure S4b) or upon cooling from the isotropic phase (Figure S4c). When siloxane 2 is applied as a coating, the Ch alignment is also lost when passing the phase transition temperatures (Figure S6). When heated up to the isotropic phase, apart from losing the Ch alignment, the coating irreversibly dewets (Figure S6e).

**Polymer-Stabilized Siloxane 2 Coatings.** To stabilize the planar cholesteric alignment of siloxane 2, we added a small amount of crosslinked LC network (Scheme 2). A nematic diacrylate reactive mesogen (diacrylate 1) was chosen as the monomer to prepare the network. We mixed diacrylate 1 with siloxane 2 in different ratios (1–4 wt %) in order to study the stabilizing effect of different amounts of network. A photoinitiator was added to the mixture to initiate the network formation. The mixtures were blade-coated on glass substrates with planar alignment layers at the cholesteric temperature of 60 °C and then cured with UV irradiation to crosslink diacrylate 1 and generate the network. The thickness of these coatings is about 10 to 12.5 μm, as determined by interferometry. DSC measurements of these network-stabilized coatings (Figure S7) show that their $T_{Sm-Ch}$ and $T_i$ are preserved after crosslinking. As the network ratio is increased, $T_{Sm-Ch}$ and $T_i$ decrease slightly from 31 to 26 and from 61 to 57 °C, respectively.

The thermo-optical responses of the network-stabilized coatings containing 1, 2, 2.5, 3, and 4 wt % of diacrylate 1 were investigated by UV–Vis–NIR spectroscopy over multiple rounds of heating and cooling from room temperature (Sm phase) to 61 °C (isotropic phase, Figures S8–S12). The stabilizing effect of the network was investigated by comparing the transparency levels of the coatings at room temperature before and after the first temperature cycle. We chose the transmission of 500 nm light as an indication of transparency. Notably, the coatings with a crosslinked network have a higher transmission of ~86% before the temperature cycle compared to a film without a network, which has a transmission of only ~72% (Figures S6a vs S8a). Even having 1 wt % of network significantly improves the transparency, with a clear reflection band (centered at ~1400 nm, see Figure S8) at room temperature (Sm phase). However, after bringing it to the isotropic phase and cooling it back down, the transparency of this film drops to 32% due to scattering, indicating that 1 wt % of network is not enough to gain reversibility from the isotropic phase. Increasing the network content significantly
improves the transparency of the coating after being cooled from isotropic to 66, 77, 82, and 88% for 2, 2.5, 3, and 4 wt % of network, respectively.

Subsequently, we analyzed the temperature-responsive color change of these coatings by plotting the reflection band centers as a function of temperature (Figure 1a,b). In general, coatings containing 1−4 wt % of network show a continuous, reversible blue shift with increasing temperature within the Ch phase range due to the pre-transitional effect. For all coatings, the reflection wavelength reaches a minimum of ∼480 nm (greenish blue) at 54 °C, close to T_{i,A}. At 61 °C (above T_i), the reflection bands disappear. Dewetting in the isotropic phase was not observed in these samples. For 1 wt % of network, the reflection bands became unrecognizable when cooled from the isotropic phase due to strong scattering, and therefore, the data are not collected (Figure S8b). For the other concentrations, upon cooling through the Ch temperature range, the reflection centers red-shift to 870, 690, 670, and 630 nm for 2, 2.5, 3, and 4 wt % of network, respectively. Below T_{Sm-Ch}, the reflection wavelength does not shift further. We propose that below the transition point, the LC layer is stable in a “twisted-smectic A” structure (also known as the “twisted-grain-boundary” state), \(^{32,43,44}\) where the smectic A domains are twisted at the boundaries with their neighbors and maintain an overall helical structure. Based on this assumption, the decreased temperature response is most likely due to the suppressed pitch increase and Sm order formation by the network, the latter being further supported by the reduced intensity of the Sm-to-Ch transition peak on DSC with increasing network ratio (Figure S7).

Although high transparency reversibility is obtained with 4 wt % network, its thermochromic response is limited that obvious band shifts can only be observed above 45 °C. The coating with 2.5 wt % network has a similar thermochromic response to the one with 3 wt % (Figure 1c,d), but its transparency after the first temperature cycle is 10% less (Figure S10). Therefore, we consider 3 wt % of network as the optimal concentration for good transparency and thermochromic responsiveness. It shows a reversible, full-color band-shift from ∼480 nm (blue) to ∼700 nm (close to infrared) from 54 to 20 °C, while keeping a transparency of 80% (Figure 1c,d). Compared to the cooling round, the reflection band during the heating round in the cholesteric temperature range (particularly 37−49 °C) is broader, and its band center shift is steeper.

Figure 1. Thermochromic response of siloxane 2 coatings containing 1−4 wt % diacrylate 1 network. (a,b) Reflection band center wavelength during the first (a) heating and (b) cooling cycles between 22 °C (Sm) and 61 °C (isotropic). In (b), the data of the 1 wt % network coating are not shown due to strong scattering. (c,d) Transmission spectra of the fabricated coating with 3 wt % of network during the first (c) heating and (d) cooling cycles.
at higher temperatures. This hysteresis is observed in other polymer-stabilized systems using Sm−Ch liquid crystals,\textsuperscript{40} which we believe is generated from the network memory effect.

**Application of the Protective Topcoat.** On top of the network-stabilized coating layer of siloxane 2 with 3 wt % diacrylate 1 network, we added a protective topcoat (Scheme 2) using Sylgard 184, a commercial silicone elastomer. The topcoat is about 17 μm thick, as measured by interferometry. At room temperature (Sm phase), the resulting sandwiched coating presents a clear reflection band centered at ∼700 nm (Figure 2a). The reversible thermo-chromic response of the topcoat-protected coating is similar to the coating without a topcoat. Its transparency remains at 80% after the cycle (Figure 2b).

The reflection band center of the coating with and without a topcoat has a similar trend of color change between 22 and 53 °C (Figure 2c), but the center wavelength position of the sample with a topcoat appears slightly red-shifted (about 30 nm) compared to the sample without a topcoat. We believe that this observation is caused by diffraction of the spectrometer light by the Sylgard topcoat and the corresponding slight change in the incident angle. As a control experiment, we fabricated the siloxane-3 wt % network coating material in an alignment cell and studied its thermo-chromic response. Similar to the topcoat, the cell configuration does not

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**Figure 2.** (a,b) Transmission spectra of siloxane 2-3 wt % diacrylate 1 network coating with a Sylgard topcoat, during heating (a) and cooling (b) rounds between the room temperature and isotropic temperature. (c) Comparison of the reflection band shift of the 3 wt % network coating with and without a topcoat. Data collected during the cooling round of the cycle. (d,e) Photographic images of the 3 wt % network coating with a topcoat (d) in front of a pictured background at a distance, and (e) on a black background during a temperature cycle to the isotropic phase.
influence the temperature-response of the Ch−LC material (Figure S13), and the reflection band is also slightly red-shifted.

At room temperature, the coating shows a faded red color due to a combination of reduced red reflection (the band is partially infrared) and minor scattering (Figure 2e). During heating, the coating shows a gradual thermochromic response from 700 nm at room temperature (22 °C) to 480 nm (greenish-blue) at 53 °C, with various colors observed in-between. Upon entering the isotropic phase at 55 °C, the color disappears, and the coating becomes transparent (>95%, according to Figure 2a). In the cooling round, the color reappears below $T_i$ as greenish blue at 53 °C. The thermochromic response is reversed by cooling. Cooling back to 22 °C in the Sm phase, the faded red color reappeared. The coating still has good transparency at room temperature after the full cycle (Figure 2d). All spectra and photos were taken ~1 min after the target temperature was reached.

The consistency in transparency and thermochromic response of the coating is confirmed after 10 heat-and-cool thermal cycles from room temperature to isotropic while measuring transmission spectra (Figure 3). At room temperature (20 °C) during each cycle, the 500 nm transmission is at 80–85%. The consistency is seen in reflection band centers too, with small variations. The variation in the band center position among cycles is probably due to the minor change in the environmental temperature that could have impacted the actual sample temperature. Regardless of these variations, both transparencies and reflection centers under the same conditions fluctuate only slightly over cycles and without drifting, which prove the long-term steadiness in performance.

After touching the coating with a finger several times, the color and surface of the coating area with Sylgard protection are intact (Figure 4). In contrast, on the area where the topcoat was removed, visible fingerprints are observed, indicating a distorted surface (see Supporting Information Video 2 for the full video of the experiment). The Sylgard topcoat thus serves as a protective coating against surface damage.

**CONCLUSIONS**

We have developed a facile approach to fabricate reversible temperature-responsive Ch−LC photonic coatings with a protective topcoat. A Ch−LC oligosiloxane with a pre-transitional effect was successfully synthesized in one reaction step and blade-coated to obtain well-aligned Ch−LC coatings. By adding a small amount of crosslinked LC network, the alignment of the Ch−LC phase is stabilized across phase transitions, at the cost of a band-shift range reduction. Through a systematic study, we optimized the network concentration and found 3 wt % to be optimal for the thermochromic response. The optimized coating shows a reversible reflection color change from ~700 nm at room temperature to ~480 nm at 54 °C, and its color is also reversible from the isotropic phase. The transparency of the coating is maintained over the entire temperature variation from smectic to cholesteric to isotropic.

A layer of PDMS elastomer (Sylgard) can be directly blade-coated on top of the Ch−LC layer to obtain a protective topcoat. Due to this transparent PDMS topcoat, the coating
receives proper protection against mechanical force, without losing the device transparency. The thermochromic response of the LC layer is unaffected by this topcoat. We expect that other protective topcoats could also be applicable to this Ch–LC system for different protective functions. The reflective coatings combine easy processability, coating robustness, and a fully reversible temperature response, making them attractive for application as temperature indicator labels, aesthetics, and heat-regulating windows.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c19236.

- Oligomer synthesis and characterization and detailed spectral measurements of cells and coatings (PDF)
- Fast cooling test on the sample with a topcoat (AVI)
- Finger touching tests on the sample with/without a topcoat (AVI)

**AUTHOR INFORMATION**

Corresponding Authors
Guofu Zhou — SCNU-TUE Joint Lab of Device Integrated Responsive Materials (DIRM), National Center for International Research on Green Optoelectronics and Guangdong Provincial Key Laboratory of Optical Information Materials and Technology & Institute of Electronic Paper Displays, South China Academy of Advanced Optoelectronics, South China Normal University, Guangzhou 510006, China; Academy of Shenzhen Guohua Optoelectronics, Shenzhen 518110, China; ClimAd Technology B.V., Nijmegen 6538 TE, The Netherlands; orcid.org/0000-0003-1101-1947; Email: guofu.zhou@m.scnu.edu.cn

Laurens T. de Haan — SCNU-TUE Joint Lab of Device Integrated Responsive Materials (DIRM), National Center for International Research on Green Optoelectronics and Guangdong Provincial Key Laboratory of Optical Information Materials and Technology & Institute of Electronic Paper Displays, South China Academy of Advanced Optoelectronics, South China Normal University, Guangzhou 510006, China; orcid.org/0000-0003-4978-1808; Phone: +86-020-931-4813; Email: ldhaan@m.scnu.edu.cn

Authors
Weixin Zhang — SCNU-TUE Joint Lab of Device Integrated Responsive Materials (DIRM), National Center for International Research on Green Optoelectronics and Guangdong Provincial Key Laboratory of Optical Information Materials and Technology & Institute of Electronic Paper Displays, South China Academy of Advanced Optoelectronics, South China Normal University, Guangzhou 510006, China; Laboratory of Stimuli-responsive Functional Materials & Devices, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven 5600 MB, The Netherlands

Albert P. H. J. Schenning — SCNU-TUE Joint Lab of Device Integrated Responsive Materials (DIRM), National Center for International Research on Green Optoelectronics, South China Normal University, Guangzhou 510006, China; Laboratory of Stimuli-responsive Functional Materials & Devices, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven 5600 MB, The Netherlands; orcid.org/0000-0002-3485-1984

Augustinus J. J. Kragt — SCNU-TUE Joint Lab of Device Integrated Responsive Materials (DIRM), National Center for International Research on Green Optoelectronics, South China Normal University, Guangzhou 510006, China; Laboratory of Stimuli-responsive Functional Materials & Devices, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven 5600 MB, The Netherlands; ClimAd Technology B.V., Nijmegen 6538 TE, The Netherlands

Complete contact information is available at: https://pubs.acs.org/10.1021/acsami.0c19236

Author Contributions
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