

# UC San Diego

## UC San Diego Previously Published Works

### Title

A Wearable Colorimetric Dosimeter to Monitor Sunlight Exposure

### Permalink

<https://escholarship.org/uc/item/0f01s9dj>

### Journal

Advanced Materials Technologies, 3(6)

### ISSN

2365-709X

### Authors

Wang, Junxin  
Jeevarathinam, Ananthakrishnan Soundaram  
Jhunjhunwala, Anamik  
[et al.](#)

### Publication Date

2018-06-01

### DOI

10.1002/admt.201800037

Peer reviewed



# HHS Public Access

Author manuscript

*Adv Mater Technol.* Author manuscript; available in PMC 2021 April 28.

Published in final edited form as:

*Adv Mater Technol.* 2018 June ; 3(6): . doi:10.1002/admt.201800037.

## A Wearable Colorimetric Dosimeter to Monitor Sunlight Exposure

**Junxin Wang,**

Department of NanoEngineering, University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093, USA, jjokerst@ucsd.edu

**Dr. Ananthakrishnan Soundaram Jeevarathinam,**

Department of NanoEngineering, University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093, USA, jjokerst@ucsd.edu

**Anamik Jhunjhunwala,**

Department of Bioengineering, University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093, USA

**Haowen Ren,**

Center for Memory and Recording Research University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093, USA

**Jeanne Lemaster,**

Department of NanoEngineering, University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093, USA, jjokerst@ucsd.edu

**Yanqi Luo,**

Department of NanoEngineering, University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093, USA, jjokerst@ucsd.edu

**Prof. David P. Fenning,**

Department of NanoEngineering, University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093, USA, jjokerst@ucsd.edu

**Prof. Eric E. Fullerton,**

Center for Memory and Recording Research University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093, USA

**Prof. Jesse V. Jokerst**

Department of NanoEngineering, University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093, USA, jjokerst@ucsd.edu

### Abstract

---

Conflict of Interest

The authors declare no conflict of interest.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

The personal ultraviolet (UV) dosimeter is a useful measurement tool to prevent UV induced dermal damages; however, conventional digital dosimeters are either bulky or require external power sources. Here, a wearable, colorimetric UV film dosimeter that provides color transition, from purple to transparent, is reported to indicate the UV dose. The film dosimeter is made of a purple photodegradable dye ((2Z,6Z)-2,6-bis(2-(2,6-diphenyl-4H-thiopyran-4-ylidene)ethylidene)cyclohexanone or DTEC) blended in low density polyethylene film. The DTEC film discolored 3.3 times more under the exposure of UV light (302 nm) than visible light (543 nm), and a UV bandpass filter is developed to increase this selectivity to UV light. The DTEC film completely discolors to transparency in 2 h under an AM 1.5 solar simulator, suggesting the potential as an indicator for individuals with types I–VI skin to predict interventions to avoid sunburn. Finally, the DTEC film is integrated with the UV bandpass filter on a wristband to function as a wearable dosimeter for low cost and convenient monitoring of sunlight exposure.

## Keywords

colorimetric sensors; UV dosimeters; wearable sensors; wristbands

## 1. Introduction

Sun exposure can damage the skin due to ultraviolet (UV) light. Previous studies found that UVA (400–320 nm) and UVB (320–290 nm) light can cause photoaging, sunburn, and skin cancers.<sup>[1]</sup> Photoaging results from the breakdown of collagen and other proteins.<sup>[2]</sup> Sunburn occurs as a result of enhancing epidermal expression of the transient receptor potential channel member 4 which increases dermal sensitivity to thermal and mechanical irritation.<sup>[3]</sup> UVB light can also cause squamous cell carcinoma or melanoma because of p53 DNA mutations or stimulation of melano-genesis.<sup>[4]</sup> Conversely, UV exposure can kill bacteria, viruses, and can facilitate Vitamin D metabolism.<sup>[5]</sup> Therefore, exposure to UV radiation should be moderate, but this is difficult because the UV intensity varies depending on weather, altitude, and ozone depletion level.<sup>[6]</sup>

UV sensitivity changes with skin type. People with fair skin color are more sensitive to UV light than people with dark skin. Multiple studies have indicated that the minimum erythema UVB dose is 20–30, 25–35, 30–50, 45–60, 60–100, and 100–200 mJ cm<sup>-2</sup> for skin types I–VI, respectively.<sup>[7]</sup> This requires personalized tools to monitor sunlight exposure.

Wearable dosimeters can address this issue by measuring an individual's UV dose. Polysulfone films are wearable dosimeters that increase the absorbance at 330 nm upon receiving cumulative UV radiation.<sup>[8]</sup> However, this wavelength requires spectroscopic instruments to read the results, which can be cumbersome for the end user. Colorimetric dosimeters are simpler—here, the UV dose is indicated by a color transition in the UV sensing material. Lee and Armani recently demonstrated a colorimetric film dosimeter composed of the UV-sensitive polymer, *ortho*-nitrobenzyl modified poly(methyl acrylate).<sup>[9]</sup> Under UV radiation, this colorless polymer decomposed to nitrosobenzaldehyde followed by the formation of yellow azolinked dimers in which the yellowness index determined UV dose.<sup>[9]</sup> In addition to this plastic sensor, Khiabani et al. printed titanium oxide and brilliant

blue FCF together on paper followed by sealing with polyvinylpyrrolidone.<sup>[10]</sup> The titanium oxide absorbed UV light and then decolorized brilliant blue FCF resulting in a color degradation that indicated the exposed UV dose.<sup>[11]</sup> Versus digital dosimeters, these colorimetric dosimeters measure UV dose more conveniently, yet might be limited by a relatively low color change as a function of UV dose or aqueous-soluble dyes that can be dissolved in water or sweat. More recently, Shi et al. published a wearable patch containing a photodegradable dye and stretchable electronics for measuring UV dose.<sup>[12]</sup> This dosimeter reveals a distinct color change upon exposure to UV, and the UV dose can be electronically quantitated. Similarly, Araki et al. described a laminated UV dosimeter made of crystal violet lactone and Congo red to measure UV dose with a more significant color switch. The dyes offer strong color change activated by (4-phenoxyphenyl)diphenylsulfonium triflate upon UV light radiation, and the exposed UV dose could be read via smartphones.<sup>[13]</sup> These dosimeters provide multiple approaches for measuring UV dose and have excellent sensitivity and selectivity to UV.

Here, inspired by fluorescence quenching and wearable sensors,<sup>[14]</sup> we present a simpler yet easily interpretable wristband-based colorimetric dosimeter. The wristband consists of a customized UV bandpass filter and a strong colored film made of low-density polyethylene (LDPE) and photodegradable dye, (2Z,6Z)-2,6-bis(2-(2,6-diphenyl-4H-thiopyran-4-ylidene)ethylidene)cyclohexanone (DTEC). The result of UV dose can be easily read by comparing the color of the DTEC film with a reference color band that was calibrated to reveal the exposed UV dose.

## 2. Results and Discussion

### 2.1. Synthesis and Characterization of DTEC

We first synthesized DTEC from IR 1061—a well-known near infrared fluorescent imaging agent that has a photodegradable polymethine carbon skeleton.<sup>[15]</sup> The chloride group of IR1061 was substituted with keto functionality via  $S_N2$  reaction conditions as shown in Figure 1A. The chemical structure of the synthesized product was verified using liquid chromatography-electrospray ionization mass spectrometry and proton nuclear magnetic resonance spectroscopy ( $^1\text{H}$  NMR). The measured  $m/z$  value was 643.23, in close agreement with the calculated molecular mass of DTEC (i.e., 643.21).  $^1\text{H}$  NMR further confirmed the structure (Figure S1, Supporting Information).

DTEC exhibits interesting optical properties including a high solvatochromism in nature and linear discoloration under UV radiation. DTEC prepared in toluene, chloroform, or ethanol displayed absorbance peaks at 544, 570, and 580 nm (Figure 1B), respectively. This observation indicated the positive solvatochromism of DTEC because the absorbance peak of DTEC red shifted with increased polarity of the solvents. In addition, DTEC became transparent upon UV light exposure. After exposure to a 302 nm UV lamp, DTEC prepared in tetrahydrofuran (UV cut-off at 220 nm<sup>[16]</sup>) had a linearly decreased magnitude ( $R^2 > 0.97$ ) at its absorbance peak (i.e., 536 nm or  $A_{536}$ ) within the visible spectrum (Figure 1C). This discoloration was more sensitive with more blue-shifted UV light: under constant exposure time, the  $A_{536}$  of DTEC decreased more at 254 nm (2.28 mW  $\text{cm}^{-2}$ ) than at 302 nm (2.94 mW  $\text{cm}^{-2}$ ) or 365 nm (1.98 mW  $\text{cm}^{-2}$ ) (Figure 1C). The strong, linear, and

irreversible color degradation of DTEC upon UV radiation indicates the potential to detect UV dose in a colorimetric scale.

To control the discoloration of DTEC, we investigated the mechanism underlying the discoloration using the free radical scavenger diethylhydroxylamine (DEHA). Free radicals generated from the dissolved gas in the DTEC solvent likely mediate the DTEC discoloration because DTEC has a poly methine structure similar to cyanine dyes. Cyanine dyes exhibit free radical-mediated degradation where singlet oxygen breaks the double bonds in the polymethine moiety.<sup>[17]</sup> To validate this hypothesis, we studied the influence of DEHA on DTEC's  $A_{536}$  at constant UV dose. Exposing DTEC to 254 nm UV lamp for 5 min resulted in an 94% decrease in the  $A_{536}$ . In contrast, adding increasing DEHA slower the discoloration. The decrease of  $A_{536}$  ( $A_{536}$ ) was reduced to 20% with 0.1% DEHA (Figure 1D). However, degassing DTEC solution with nitrogen ( $N_2$ ) prior to UV irradiation did not affect the discoloration (Figure 1D, inset). Therefore, the discoloration of DTEC was due to nonoxygenated free radicals. Regardless of the mechanism, the selective discoloration of DTEC indicated its potential as a colorimetric UV dosimeter.

## 2.2. Fabrication and Characterization of DTEC Film

To fashion DTEC into a wearable dosimeter, we blended DTEC with a LDPE film. LDPE is an ideal substrate material because of its low cost, flexibility, and high UV transparency.<sup>[18]</sup> Using the polymer solution casting technique, DTEC and LDPE powder were dissolved in toluene and cast into a 140  $\mu\text{m}$  thick purple film (Figure 2A). The color density of the film was adjustable by tuning the DTEC/LDPE weight ratios. This could be used to customize the device for individuals with different personal tolerance to UV exposure (Figure 2B,C). The DTEC film was very thermally stable. Spectroscopic data showed no significant decrease ( $p > 0.20$ ) in the  $A_{536}$  even after being heated to 50  $^{\circ}\text{C}$  for 120 min (Figure 2D) or at room temperature for 30 d ( $p > 0.37$ ) (Figure 2E and Figure S3, Supporting Information).

The DTEC film remained its discoloration property under UV exposure. At 302 nm, the  $A_{536}$  of DTEC decreased over time ( $R^2 > 0.98$ ) (Figure 2F). Additionally, the DTEC film had 20% more sensitivity (based on absorbance change) than a recently reported film dosimeter (Figure S4, Supporting Information).<sup>[11]</sup> However, unlike the previously described transparent colorimetric film dosimeter that was only sensitive to UV,<sup>[9]</sup> the DTEC film also degraded in visible light radiation (Figure 2C). To further quantitate this change, we measured the discoloration rate of the DTEC film when it was exposed to 543 nm HeNe laser at the same radiation intensity as 302 nm UV lamp (2.94  $\text{mW cm}^{-2}$ ). The DTEC film exposed to this 543 nm light revealed a 3.3-fold slower decrease in the  $A_{536}$  (Figure 2F).

## 2.3. Development of UV Bandpass Filter and the Characterization Using Solar Simulator

To increase the selectivity of the color change to UV light, we developed a UV bandpass filter by depositing alternating silver and aluminum oxide layers on a LDPE film (Figure 3A) similar to the UV-transparent metal structures as UV bandpass filters<sup>[19]</sup> (the LDPE film has high transmission (over 89%) in the UV (red line in Figure 3B)). The UV bandpass filter selected 53% of 328 nm light with limited transmission beyond 500 nm (<10%) (Figure 3B).

The colorimetric response of DTEC film to solar radiation was characterized using an AM1.5 solar simulator. The solar simulator was calibrated to provide illumination equal to one sun. The DTEC film became brown after 30 min of exposure to the simulator, and spectroscopic measurements indicated a decrease of 58.5% in the  $A_{536}$  ( $2.0\% \text{ min}^{-1}$ ) (Figure 3C,D, film only). The decrease rate of  $A_{536}$  was reduced to only  $0.6\% \text{ min}^{-1}$  with the UV bandpass filter (Figure 3C,D, filter). After 120 min of exposure, both the bare DTEC film (76% decrease in  $A_{536}$ ) as well as the DTEC film covered by the UV bandpass filter (44% decrease in  $A_{536}$ ) had nearly complete discoloration. We also included a negative control with aluminum foil to account for variables other than light, e.g., humidity. The  $A_{536}$  of DTEC film decreased by 10% after a 120 min exposure with only minimal discoloration (Figure 3C,D, Al foil).

To further test whether the DTEC film can respond to various sunlight intensities differently, we covered the DTEC films with neutral-density filters of increasing optical density (OD) (Figure 3E) to simulate strong and weak sunlight. After 40 min of exposure, the  $A_{536}$  of the DTEC film decreased 57%, and the DTEC film became colorless (Figure 3F). In contrast, the neutral-density filters exponentially ( $R^2 > 0.89$ ) reduced the  $A_{536}$  and retained the color (Figure 3F). These results suggested that the bandpass filter reduced UV transmission to the DTEC film, but the device still maintained a UV dose-dependence and strong color change with a UVB dose detection limit of  $0.03 \text{ mJ cm}^{-2}$  (Figure S5, Supporting Information).

To functionalize the DTEC film as a wearable sensor, we next integrated the DTEC film and the UV bandpass filter on a 3D-printed wristband (Figure 4A,B). The wristband was also equipped with a reference band to avoid relying on digital devices for reading. The four colors (purple to white) in the reference band are the color of the DTEC films that were exposed to a solar simulator for 10, 20, 30, and 120 min, respectively. Therefore, each color corresponds to a certain UV dose because the UV intensity of the solar simulator is constant. Individuals can easily estimate their UV dose by comparing the remaining color of the DTEC film with the color bars on the wristband. We tested the dosimeter on a sunny day with an average UV index of 6.6, and the DTEC film displayed a significant discoloration from purple to colorless after 120 min exposure (Figure 4C). As a control, the film exposed on a cloudy day revealed a smaller degree of color discoloration (Figure 4D,E).

### 3. Conclusion

In conclusion, we developed a wearable colorimetric dosimeter that degrades from purple to colorless upon cumulative UV exposure. The photosensitive film was fabricated by synthesizing DTEC from IR 1061 followed by film casting using LDPE. The stable DTEC film had 3.3-fold faster discoloration under exposure to UV light than visible light. A UV bandpass filter was developed to enhance the selectivity of color change for UV light. The final discoloration rate was  $0.6\% \text{ min}^{-1}$  when the DTEC film was integrated with the bandpass filter and then exposed to the AM1.5 solar simulator. The DTEC film and UV bandpass filter were combined on a 3D printed wristband for personal quantification of sunlight exposure.

## 4. Experimental Section

### Materials and Instruments:

Sodium hydride was purchased from Fisher scientific. Tetrahydrofuran, chloroform, ethanol, acetone, *N*-hydroxysuccinimide, dimethylformamide, *tert*-butyl-methyl-ether, and IR1061 were purchased from Sigma Aldrich. LDPE (particle size < 400  $\mu\text{m}$ ) was purchased from Alfa Aesar. Toluene was purchased from Macron Fine Chemicals. The plastic wrap (Total Home) was purchased from CVS Pharmacy. Light control black aluminum wrap was purchased from Cinefoil.

An 8 W 38 UV lamp (3UV) was used as the UV light source to characterize the decolorization of DTEC film. The UV lamp housing has three UV wavelengths: 254, 302, and 356 nm. The solar simulator test used a temperature-controlled Class A solar simulator (Newport) equipped with an AM 1.5 filter. Absorbance data was collected via a SpectraMax M5 spectrophotometer. LDPE film casting used a Fisher scientific Isotemp hot-plate. The illuminance meter (Dr.meter) and UV index meter (Solar Light Company, Inc) were purchased from Amazon. The HeNe laser (Research Electro-Optics Inc., LHGR-0200, 5 mW, 543 nm), biconvex lens (Newport, SBX022), and digital power meter (Newport, model 1918-C) were used for comparing the decolorization rate between UV light and visible light.

### Synthesis and Verification of DTEC:

The protocol of DTEC synthesis was optimized based on a previous publication.<sup>[20]</sup> First, sodium hydride (0.38 mmol, 2.9 eq.) was dissolved in anhydrous dimethylformamide (1.0 mL) with *N*-hydroxysuccinimide (0.38 mmol, 2.9 eq.) under nitrogen purging. Subsequently, IR1061 (0.334 mmol, 1.0 eq.) was dissolved in anhydrous dimethylformamide (1.3 mL) under nitrogen purging and transferred dropwise to the first solution. The above reaction was conducted for 3 h. The reaction status was monitored by comparing the migration of IR1061 and the synthesized dye on a thinlayer chromatography (TLC) plate in methanol. The dye was added in *tert*-butyl-methyl-ether dropwise for purification. The precipitates were collected and filtered using 0.22  $\mu\text{m}$  filter paper and dried under vacuum for 3–4 hours. The chemical structure of dye was confirmed using mass spectroscopy and 1H nuclear magnetic resonance. 1H NMR ( $\text{CDCl}_3$ )  $\delta$  1.86 (m, 2H), 2.70 (m, 4H), 2.89 (d, 1H), 6.07 (d, 2H), 6.88 (s, 2H), 7.43 (m, 12H), 7.58 (m, 8H), 7.99 (d, Hz, 2H).

### Discoloration Characterization of DTEC Dissolved in Tetrahydrofuran:

First, DTEC was dissolved in tetrahydrofuran (0.01  $\text{mg mL}^{-1}$ ) in quartz cuvettes. The solutions were exposed to a 302 nm UV lamp for 14 min for the UV dose curve experiment. DEHA was diluted to 10%, 1%, 0.1% in tetrahydrofuran. Then, 2  $\mu\text{L}$  of DEHA, 10% DEHA, 1% DEHA, and 0.1% DEHA were added into 2 mL DTEC solution. The solutions were exposed to 365 nm UV light for 10 min for the characterization of wavelength selectivity.

### LDPE Film Casting Method:

DTEC was first dissolved in toluene at 0.1  $\text{mg mL}^{-1}$ . The DTEC film was fabricated by mixing DTEC solution (2 mL) with LDPE powder (0.25 g) in toluene (13 mL) with stirring

in a scintillation vial at 100 °C for 10 min. The solution was poured into a glass petri dish (diameter = 50 mm), and the petri dish was put on a larger petri dish (diameter = 60 mm) with silicon oil to ensure uniform heat distribution. The solvent was evaporated at 70 °C and covered the petri dish with a funnel to prevent superheating between the top and bottom of the DTEC solution. The funnel was also purged with nitrogen to drive out solvent vapor. The evaporation process took 50 min, and the petri dish was transported to room temperature. The temperature and evaporation time are critical to cast a smooth film with uniform color. After cooling, the film was extracted from the petri dish using tweezers. The thickness of one DTEC film was determined by averaging the thickness of 6 DTEC films measured with a caliper.

#### Design and Fabrication of UV Bandpass Filter:

Openfilters<sup>[21]</sup> was first used to design the structures of silver and aluminum oxide thin film layers. Then, based on the designed layers, 30 nm silver and 40 nm aluminum oxide were alternatively deposited on plastic wrap substrate using DC and RF magnetron sputtering. The transmission spectrum of the fabricated filter was measured using the spectrophotometer.

#### Measurement of DTEC Film Decolorization Using Solar Simulator, 302 nm UV Lamp, and Real Sun:

DTEC films were first trimmed into pieces that fit the measurement chamber size of the spectrophotometer, and the absorbance of film was measured three times to make sure that the same spot of the film was measured in every measurement. The absorbance of DTEC films was measured from 510 to 550 nm. A LDPE film was fabricated without adding DTEC and its absorbance was measured for baseline. Then, images of the films were taken using a DSLR camera (Nikon D500) that was set on a tripod in a basement with constant control over illumination. The films were fixed on a white paper for images. After each exposure, the absorbance was measured and images of each film were collected. The relative decrease of absorbance was calculated using the following equation

$$\text{REL decrease} = \frac{\text{Absorbance after exposure} - \text{Absorbance of plain film}}{\text{Absorbance before exposure} - \text{Absorbance of plain film}} \quad (1)$$

A 302 nm UV lamp and HeNe laser (543 nm) were used to compare the response of DTEC film to UV light and visible light. The power of the UV lamp was first measured at the position where DTEC film was exposed (2.94 mW cm<sup>-2</sup>). To achieve the same energy density of laser light, the biconvex lens was put right in front of the laser to expand the laser beam. By adjusting the position of power meter, a distance was found where the power of laser exposed on DTEC film was also 1.47 mW. A black cover board was fixed at the location of the power meter with screws and the DTEC was taped on the cover board for exposure. The absorbance was measured and photos of the DTEC films ( $n = 3$ ) exposed by UV lamp or HeNe were taken every 30 min for 2 h, and then the decrease of absorbance and change of color were compared.



In the solar simulator test, the DTEC films were wrapped with black aluminum foil to avoid secondary exposure from reflection. Three films from different fabrications were exposed directly to the solar simulator, and three films were covered with UV bandpass filter and aluminum foil, respectively. The absorbance of each film was measured and images of each film were taken after exposure to 10, 20, 30, and 120 min. To simulate attenuated sun brightness, 3 replicate DTEC films were covered with neutral-density filters of increasing attenuations (OD value is 0.3, 1.5, 2.0, and 2.5), respectively. The filter-covered DTEC film was exposed to solar simulator for 40 min followed by absorbance measurements. The dose of UVB was estimated based on the ASTM G173–03 reference spectral data.

To measure the UV dose detection limit of the dosimeter, the change of absorbance was also measured at 536 nm of the DTEC/LDPE film that was wrapped with black aluminum foil (i.e.,  $0 \text{ mJ cm}^{-2}$ ). Then, the change of absorbance of the blended film versus the exposed UVB dose was plotted. The correlation between the UVB dose and change of absorbance was calculated using Origin's linear fitting function. The fitted equation and  $R^2$  value is  $y = 6.87461x + 0.01412$  and 0.956, respectively. The detection limit of the device was calculated at 3 standard deviations above the mean of the value at  $0 \text{ mJ cm}^{-2}$ .

To test the wristband sensor, the sensor was placed under sunlight at noon and the illuminance and UV Index were recorded every 10 min using an illuminance meter and a UV index meter. Photos of the wristband sensor were taken every 30 min. This was repeated until the film turned transparent.

### Design and Fabrication of 3D-Printed Wristband Sensor:

The design of the wristband was done in SolidWorks Professional 2015. The wristband was 13 mm long with 6 holds (diameter = 0.2 mm) on one side. The DTEC film and reference band were attached to the wristband with double sided tape. The color of the reference band was determined by copying the color of DTEC film after 10, 20, 30, and 120 min exposure to the solar simulator.

### Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

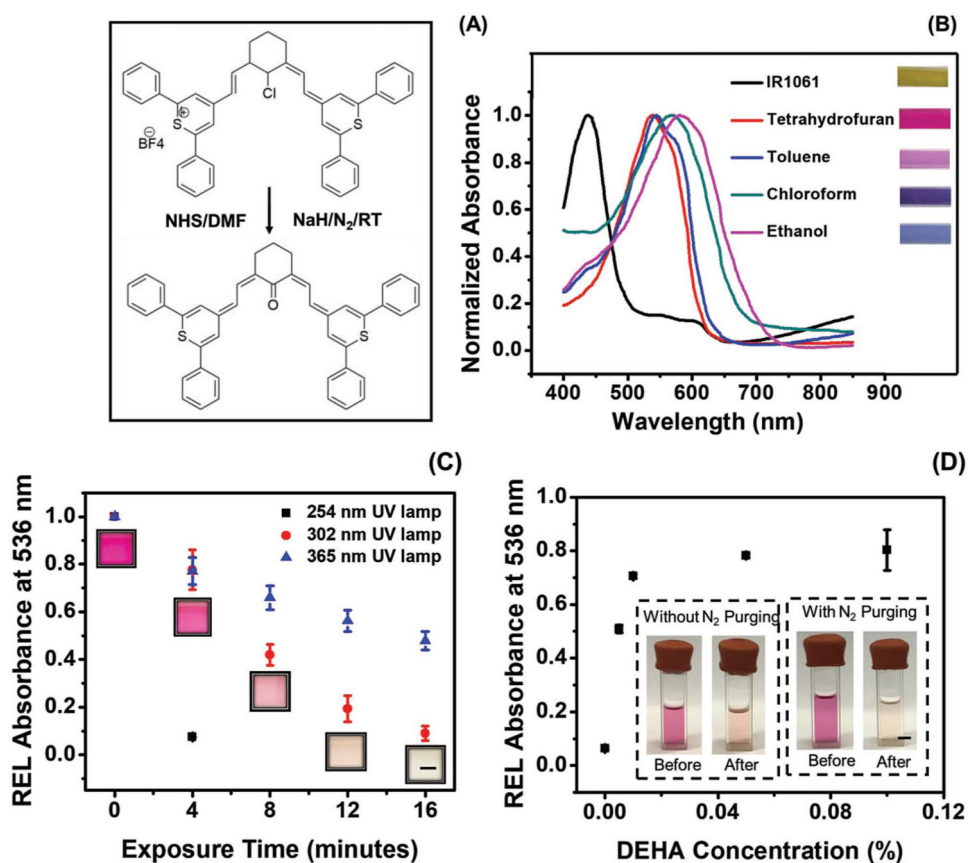
### Acknowledgements

J.W. and A.S.J. contributed equally to this work. The authors acknowledge funding from DP2 HL137187, R00 HL117048, and infrastructure from S10 OD021821. The authors also thank Dr. Donald Sirbully and Spencer Ward for providing the HeNe laser and other optical tools.

### References

- [1]. a) Wlaschek M, Tantcheva-Poór I, Naderi L, Ma W, Schneider LA, Razi-Wolf Z, Schüller J, Scharffetter-Kochanek K, J. Photochem. Photobiol., B 2001, 63, 41; [PubMed: 11684450] b) Svobodová AR, Galandáková A, Šianská J, Doležal D, Lichnovská R, Ulrichová J, Vostálová J, Arch. Dermatol. Res 2012, 304, 407; [PubMed: 22271212] c) Narayanan DL, Saladi RN, Fox JL, Int. J. Dermatol 2010, 49, 978; [PubMed: 20883261] d) Pfeifer GP, Besaratinia A, Photochem. Photobiol. Sci 2012, 11, 90. [PubMed: 21804977]

- [2]. Fisher GJ, Kang S, Varani J, Bata-Csorgo Z, Wan Y, Datta S, Voorhees JJ, Arch. Dermatol 2002, 138, 1462. [PubMed: 12437452]
- [3]. Moore C, Cevikbas F, Pasolli HA, Chen Y, Kong W, Kempkes C, Parekh P, Lee SH, Kontchou N-A, Yeh I, Jokerst NM, Fuchs E, Steinhoff M, Liedtke WB, Proc. Natl. Acad. Sci. USA 2013, 110, E3225. [PubMed: 23929777]
- [4]. a)Brash DE, Rudolph JA, Simon JA, Lin A, McKenna GJ, Baden HP, Halperin AJ, Pontén J, Proc. Natl. Acad. Sci. USA 1991, 88, 10124; [PubMed: 1946433] b)Atillasoy ES, Seykora JT, Soballe PW, Elenitsas R, Nesbit M, Elder DE, Montone KT, Sauter E, Herlyn M, Am. J. Pathol 1998, 152, 1179. [PubMed: 9588887]
- [5]. a)Grobner M, Grobner J, Hulsen G, Photochem. Photobiol. Sci 2015, 14, 352; [PubMed: 25410623] b)Bogh MKB, Schmedes AV, Philipsen PA, Thieden E, Wulf HC, J. Invest. Dermatol 2010, 130, 546. [PubMed: 19812604]
- [6]. Godar DE, Photochem. Photobiol 2005, 81, 736. [PubMed: 15819599]
- [7]. a)Dornelles S, Goldim J, Cestari T, Photochem. Photobiol 2004, 79, 540; [PubMed: 15291306] b)Fitzpatrick TB, Arch. Dermatol 1988, 124, 869 [PubMed: 3377516] c)Diffey BL, Jansén CT, Urbach F, Wulf HC, Photodermatol., Photoimmunol. Photomed 1997, 13, 64. [PubMed: 9361131]
- [8]. Parisi AV, Kimlin MG, Photochem. Photobiol 2004, 79, 411. [PubMed: 15191049]
- [9]. Lee ME, Armani AM, ACS Sens. 2016, 1, 1251.
- [10]. Khiabani PS, Soeriyadi AH, Reece PJ, Gooding JJ, ACS Sens. 2016, 1, 775.
- [11]. Mills A, Grosshans P, McFarlane M, J. Photochem. Photobiol. A: Chem 2009, 201, 136.
- [12]. Shi Y, Manco M, Moyal D, Huppert G, Araki H, Banks A, Joshi H, McKenzie R, Seewald A, Griffin G, Sen-Gupta E, Wright D, Bastien P, Valceschini F, Seité S, Wright JA, Ghaffari R, Rogers J, Balooch G, Pielak RM, PLoS One 2018, 13, e0190233. [PubMed: 29293664]
- [13]. Araki H, Kim J, Zhang S, Banks A, Crawford KE, Sheng X, Gutruf P, Shi Y, Pielak RM, Rogers JA, Adv. Funct. Mater 2017, 27, 1604465.
- [14]. a)Xie C, Upputuri PK, Zhen X, Pramanik M, Pu K, Biomaterials 2017, 119, 1; [PubMed: 27988405] b)Zhang N, Chu X, Fathalla M, Jayawickramarajah J, Langmuir 2013, 29, 10796; [PubMed: 23895408] c)Shen Y, Sun Y, Yan R, Chen E, Wang H, Ye D, Xu J-J, Chen H-Y, Biomaterials 2017, 148, 31; [PubMed: 28961533] d)Chang TM, Sinharay S, Astashkin AV, Tomat E, Inorg. Chem 2014, 53, 7518; [PubMed: 25008284] e)Hu X, Wang Q, Liu Y, Liu H, Qin C, Cheng K, Robinson W, Gray BD, Pak KY, Yu A, Cheng Z, Biomaterials 2014, 35, 7511; [PubMed: 24912814] f)Xu J, Wang S, Wang G-JN, Zhu C, Luo S, Jin L, Gu X, Chen S, Feig VR, To JWF, Rondeau-Gagné S, Park J, Schroeder BC, Lu C, Oh JY, Wang Y, Kim Y-H, Yan H, Sinclair R, Zhou D, Xue G, Murmann B, Linder C, Cai W, Tok JB-H, Chung JW, Bao Z, Science 2017, 355, 59. [PubMed: 28059762]
- [15]. a)Tao Z, Hong G, Shinji C, Chen C, Diao S, Antaris AL, Zhang B, Zou Y, Dai H, Angew. Chem., Int. Ed 2013, 52, 13002;b)Horiuchi H, Ishibashi S, Tobita S, Uchida M, Sato M, Toriba K.-i., Otaguro K, Hiratsuka H, J. Phys. Chem. B 2003, 107, 7739;c)Wagh A, Qian SY, Law B, Bioconjug. Chem 2012, 23, 981; [PubMed: 22482883] d)Ishihara M, Fujisawa S, In Vivo 2007, 21, 163. [PubMed: 17436564]
- [16]. Shukla V, Schiøtz Nielsen W, Batsberg W, Eur. J. Lipid Sci. Technol 1983, 85, 274.
- [17]. a)Gorka AP, Nani RR, Zhu J, Mackem S, Schnermann MJ, J. Am. Chem. Soc 2014, 136, 14153; [PubMed: 25211609] b)Nani RR, Kelley JA, Ivanic J, Schnermann MJ, Chem. Sci 2015, 6, 6556. [PubMed: 26508998]
- [18]. Briassoulis D, Aristopoulou A, Bonora M, Verlodt I, Biosyst. Eng 2004, 88, 131.
- [19]. Jakši Z, Maksimovi M, Sarajli M, J. Opt. A: Pure Appl. Opt 2004, 7, 51.
- [20]. Strekowski L, Mason JC, Say M, Lee H, Gupta R, Hojjat M, Heterocycl. Commun 2005, 11, 129.
- [21]. Larouche S, Martinu L, Appl. Opt 2008, 47, C219. [PubMed: 18449250]



**Figure 1.** Synthesis and characterization of DTEC. Panel (A) depicts the synthetic process of DTEC where the chloride moiety of IR 1061 was converted to a keto moiety by dimethylformamide (DMF), *N*-Hydroxysuccinimide (NHS), sodium hydride (NaH), and under N<sub>2</sub> purging at room temperature (RT). Panel (B) shows the absorbance spectra of IR1061 (black) and the DTEC dissolved in organic solvents with increasing polarity. A full spectrum from 200 to 1000 nm is included in Figure S2 (Supporting Information). The color of DTEC in tetrahydrofuran, toluene, chloroform, and ethanol is red, pink, violet, and blue, respectively, as shown in the inset. Data of absorbance change in panel (C) reveal that the DTEC degrades to transparent as a function of UV exposure (UV dose). Exposure to 302 nm UV lamp causes a linear decrease ( $R^2 > 0.97$ ) in the  $A_{536}$  of DTEC prepared in tetrahydrofuran (UV cutoff 220 nm<sup>[16]</sup>), and the discoloration rate increases with deeper UV light. The inset shows the corresponding images of DTEC and a complete discoloration after 16 min exposure. Comparatively, exposure to 254 nm UV lamp ( $2.28 \text{ mJ cm}^{-2}$ ) completely decolorizes DTEC in 4 min, and the irradiation of 302 nm ( $2.94 \text{ mJ cm}^{-2}$ ) for 4 min only caused 20% decrease of the absorbance. The discoloration rate can be reduced by adding DEHA (a free radical scavenger) as shown in panel (D). The relative absorbance of DTEC at 536 nm increased with increasing DEHA dose, which indicates that free radicals mediate this color change. The inset shows that degassing using N<sub>2</sub> had little effect on DTEC color change under 254 nm irradiation (6 min) suggesting nonoxygenated free radicals were involved. The error bars

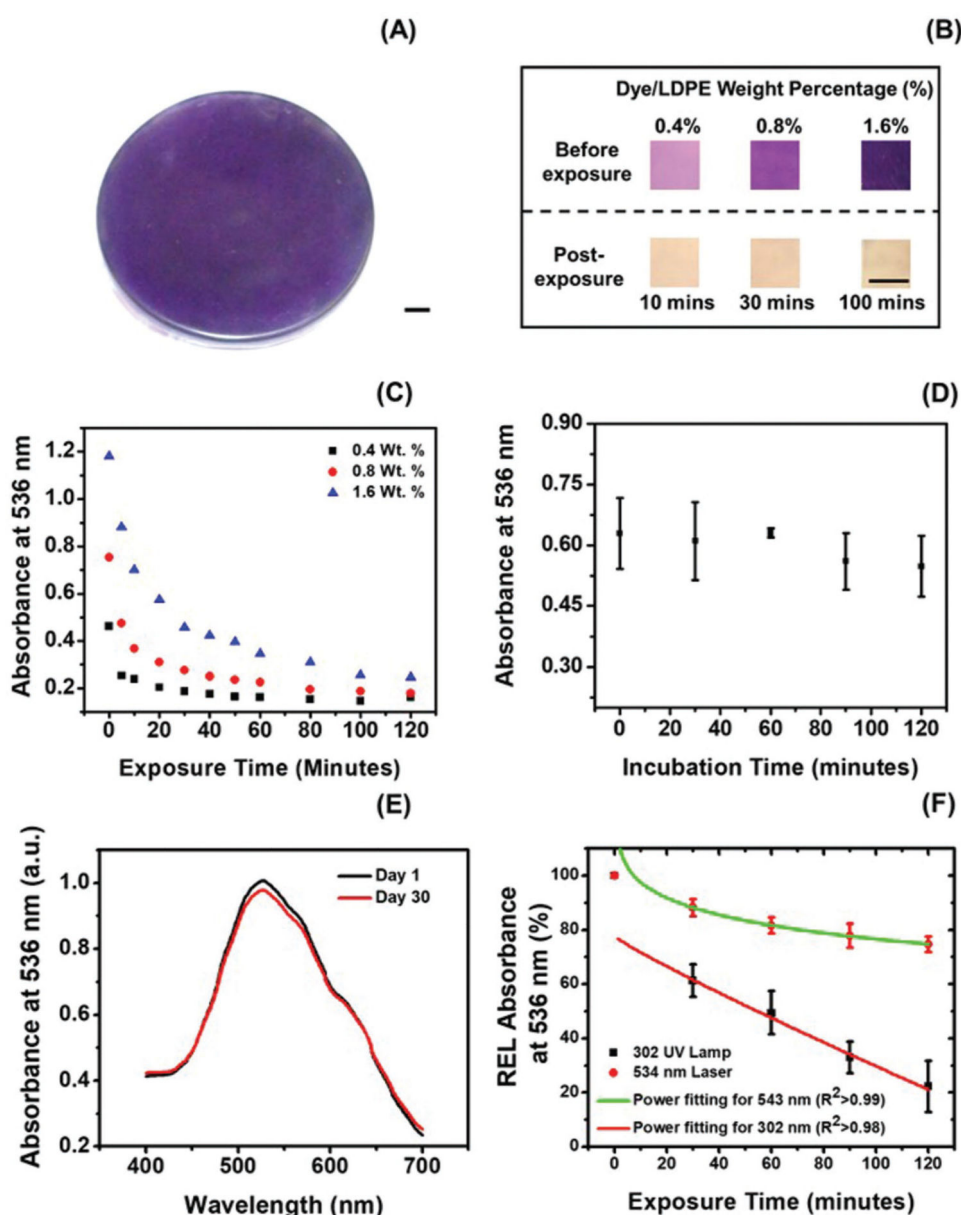
in panels (C) and (D) represent the standard deviation of 3 replicate samples. Scale bars in panel (C) and panel (D) represent 5 mm.

Author Manuscript

Author Manuscript

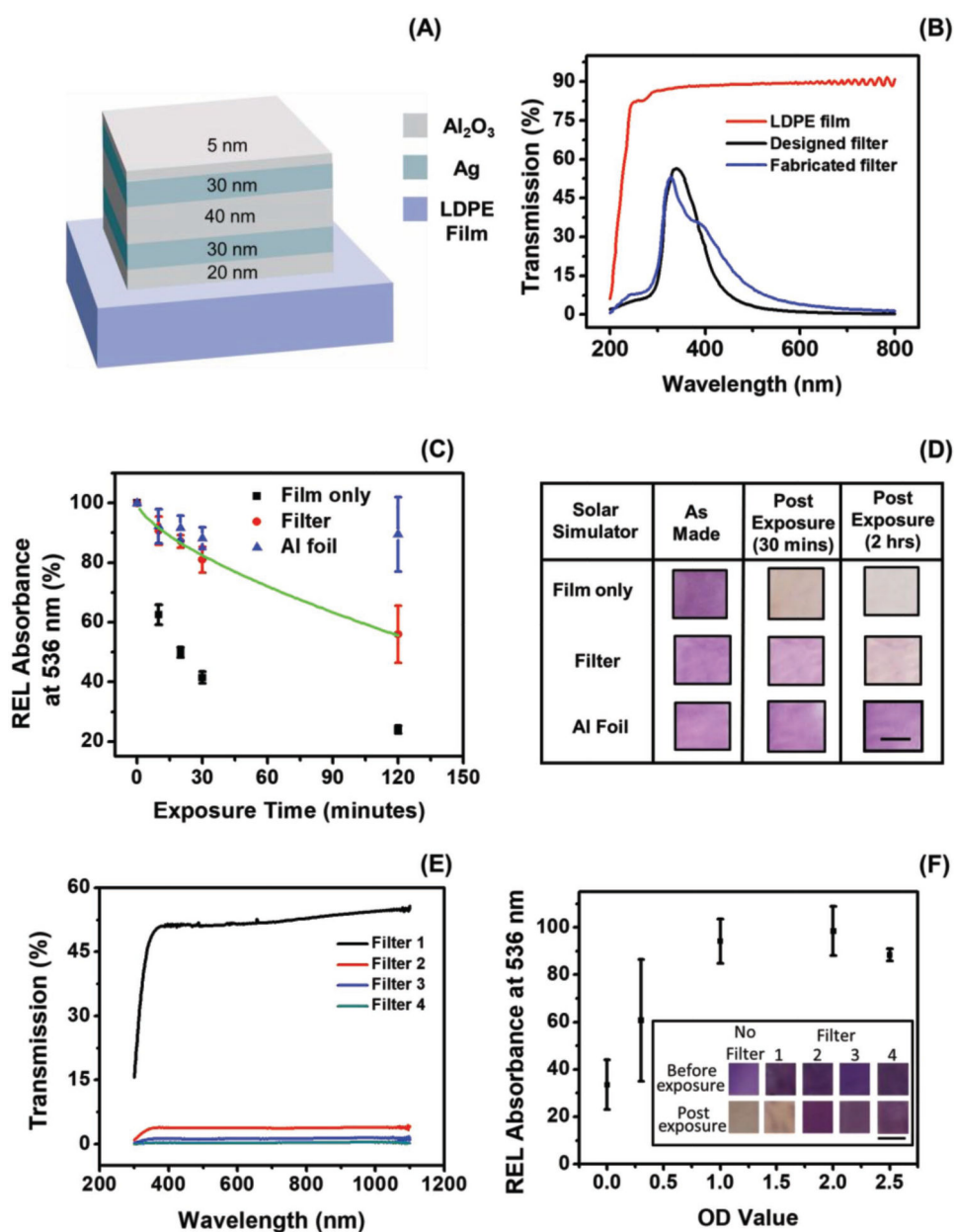
Author Manuscript

Author Manuscript



**Figure 2.** Fabrication and characterization of DTEC/LDPE film. Panel (A) shows the uniformity of color of the LDPE film cast with DTEC. Figure S2 (Supporting Information) presents the full spectrum of DTEC film from 200 to 1000 nm. Panel (B) shows the original state and decolorized state of film made of DTEC/LDPE film ratio at 0.4%, 0.8%, and 1.6%. It takes 10, 30, and 80 min for 0.4%, 0.8%, and 1.6% DTEC (wt%) LDPE film to achieve a similar transparent state (see colors in panel (B) and absorbance in panel (C)). These exposure times are equivalent to 28, 85, and 282 mJ cm<sup>-2</sup> UVB, respectively. This indicates that the DTEC/LDPE weight ratios of 0.4%, 0.8%, and 1.6% are suitable for skin types I, V, and VI.<sup>[7b]</sup> Panel (D) shows an insignificant difference ( $p > 0.20$  between 0 and 120 min) in the  $A_{536}$  of DTEC film over time when it is treated on a 50 °C hot plate in the dark. Panel (E) compares the absorbance spectrum of DTEC film between day 1 and day 30 suggesting the long-term

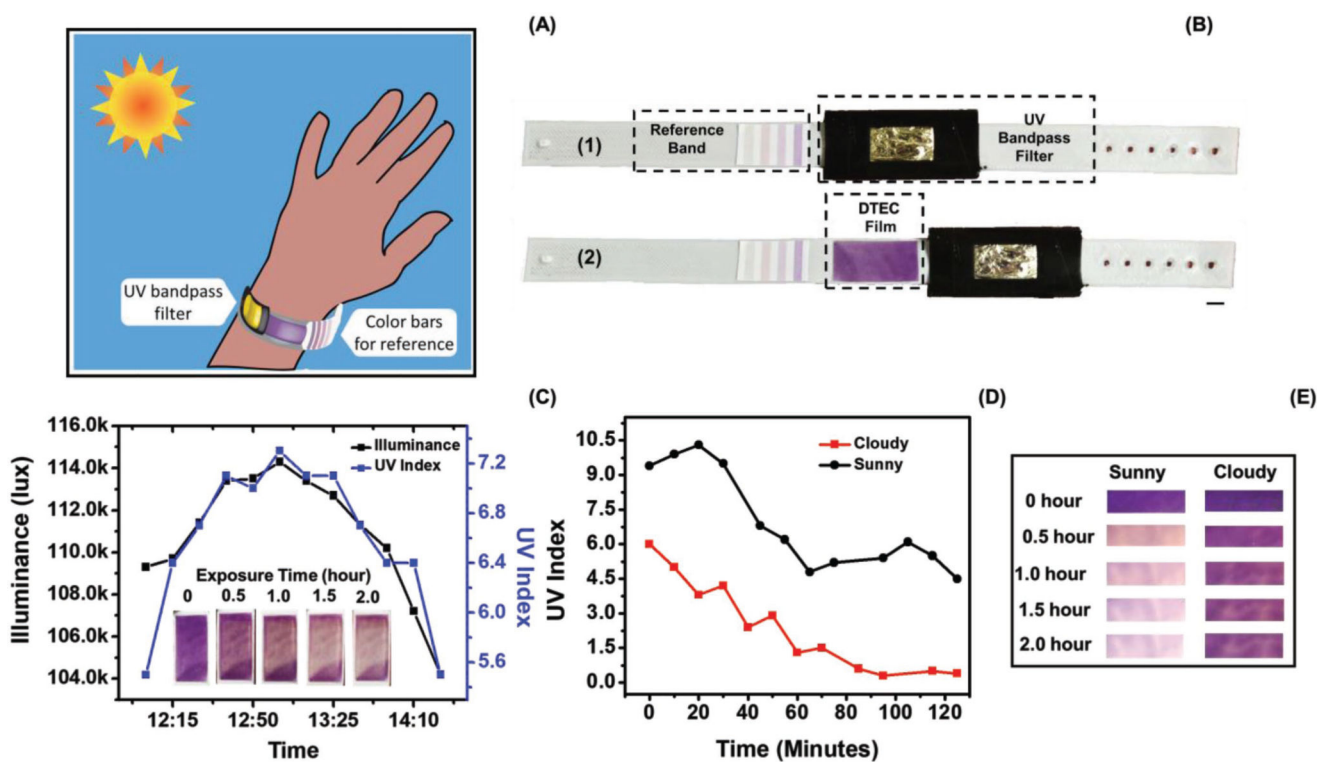
stability of DTEC film. The film was kept in dark and ambient environment. Panel (F) compares the absorbance decrease of the film exposed to the 302 nm UV lamp and 534 nm laser at constant irradiation density, respectively. Power regression shows a strong correlation ( $R^2 > 0.98$ ) between the relative absorbance and the exposure time at 302 nm. The  $A_{536}$  decreased 3.3-fold faster with 302 nm light perturbation than 534 nm perturbation (2 h exposure time). The scale bars in panel A and B represent 5 mm. The error bars in panels (D) and (F) represent the standard deviation of 3 films.



**Figure 3.** Characterization of decolorization using solar simulator. Panel (A) shows the layered structure of the customized UV bandpass filter. Alternative aluminum oxide ( $\text{Al}_2\text{O}_3$ ) and silver (Ag) thin films were deposited on a LDPE film. Panel (B) shows the transmission spectra of the substrate (LDPE film) and the simulated (design filter) and fabricated (actual filter) UV bandpass filter. The fabricated UV bandpass filter resulted in 53% transmission at 328 nm and 10% transmission at 500 nm, which agree nicely with simulated values. Panel (C) quantitates the discoloration of DTEC film after exposure to the AM 1.5 solar simulator. After a 2 h exposure, there was a 86% decrease in the  $A_{536}$  of DETC film corresponding to complete discoloration from purple to transparent (panel (D)). Conversely, the UV bandpass filter decreases  $A_{536}$  to 44% ( $0.6\% \text{ min}^{-1}$ ; green line fitting represents power regression  $R^2$

> 0.94). The decrease in  $A_{536}$  was further reduced to 10% with minimal discoloration when the DTEC film was covered with aluminum foil as a negative control. Panel (E) shows that transmission spectra of the neutral-density filter used to simulate dim sunlight. The neutral-density filters with increasing optical density (OD) decreased the light striking the DTEC film, and the corresponding attenuations in the discoloration of DTEC films without the customized UV bandpass filter were characterized in panel (F). After exposure to a solar simulator, the neutral-density filters of increased optical density exponentially reduce the change of the DTEC film's  $A_{536}$  ( $R^2 > 0.89$ ). The inset in panel (F) compares the corresponding color change of the DTEC films. The error bars in panels (C) and (F) represent the standard deviation of 3 DTEC films; the scale bars in panels (D) and (F) are 5 mm.





**Figure 4.**

Prototype of the 3D-printed wristband UV sensor. Panel (A) depicts the concept of the wearable UV dosimeter. The DTEC film and the UV bandpass filter are integrated on a wearable wristband. The UV bandpass filter covers the DTEC film, and it can slide along the wristband to read the color change by eye. A reference band is also included. The colors reflect the UV dose that is calibrated using the solar simulator. The exposed UV dose can be easily estimated by comparing the color of DTEC film with the reference band. Panel (B) shows the fabricated wristband. Panel B (1) and B (2) shows the wristband when the UV bandpass filter is closed for measurements and open for reading, respectively. Panel (C) shows the discoloration of DTEC film under direct sunlight exposure (UV exposure was quantified via the UV index). The average illuminance and UV index during the exposure was 110 883 lx and 6.6, respectively. Panel (D) plots the UV index of the sunny and cloudy day for the comparison of discoloration on a sunny and cloudy day. The color of the DTEC film exposed on the sunny and cloudy day is shown in panel (E). The DTEC film had less color change on a cloudy day because there was less UV exposure. The scale bars in panels (B) represent 5 mm.