

Supporting Information

**Photocatalytic Oxidation of Sulfur Mustard and Its Simulant on
BODIPY-Incorporated Polymer Coatings and Fabrics**

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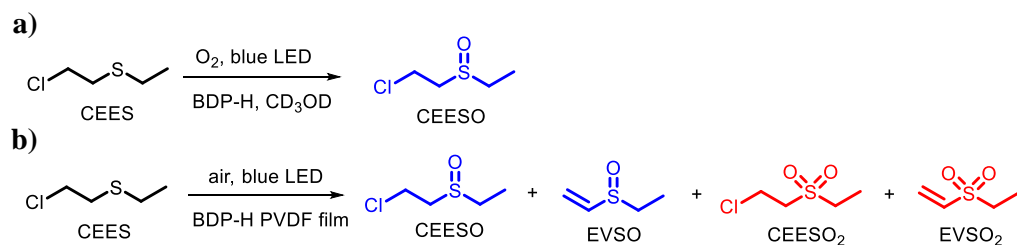
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1. Materials and Methods

All chemicals and reagents were purchased from commercial sources and used as received. BDP-I was purchased from Aces Pharma. BDP-SO₃ was purchased from TCI America. All other chemicals and reagents were purchased from Sigma-Aldrich. ¹H-NMR spectra were recorded on a 300 MHz Varian NMR spectrometer using the residual proton resonance of the solvent as the internal standard. ¹³C NMR spectra were proton decoupled and recorded on a 300 MHz Varian NMR spectrometer using the carbon signal of the deuterated solvent as the internal standard. GC-MS analysis was performed on an Agilent Technologies 6890N GC system equipped with a 5973N mass selective detector and a HP-5MS SemiVol column (30 m × 0.250 mm × 0.5 μm film thickness). UV-visible absorption spectra were collected using a Jasco V-750 spectrophotometer. SEM images were taken using a Phenom ProX desktop SEM. Samples were supported on double-sided carbon tape and sputter coated with gold prior to analysis. Fibers were prepared on a programmable floor-stand electrospinning unit (MTI Corporation MSK NFES-4). Confocal microscope Z-stack images were collected using a Zeiss LSM 700 confocal microscope and collapsed to two dimensions using a maximum intensity projection algorithm in Zen 2012. Light irradiation was performed using solderless LEDs purchased from RapidLED. Each light source setup (blue, white and red) contains two LEDs that are mounted ~3.5 cm apart on a piece of metal.

2. NMR and GC-MS Spectra

2.1 Decontamination of CEES in solution and on BDP-H/PVDF films



Scheme S1. Decontamination of CEES by BDP-H a) in solution (methanol-d₄) and b) on a piece of BDP-embedded PVDF film.

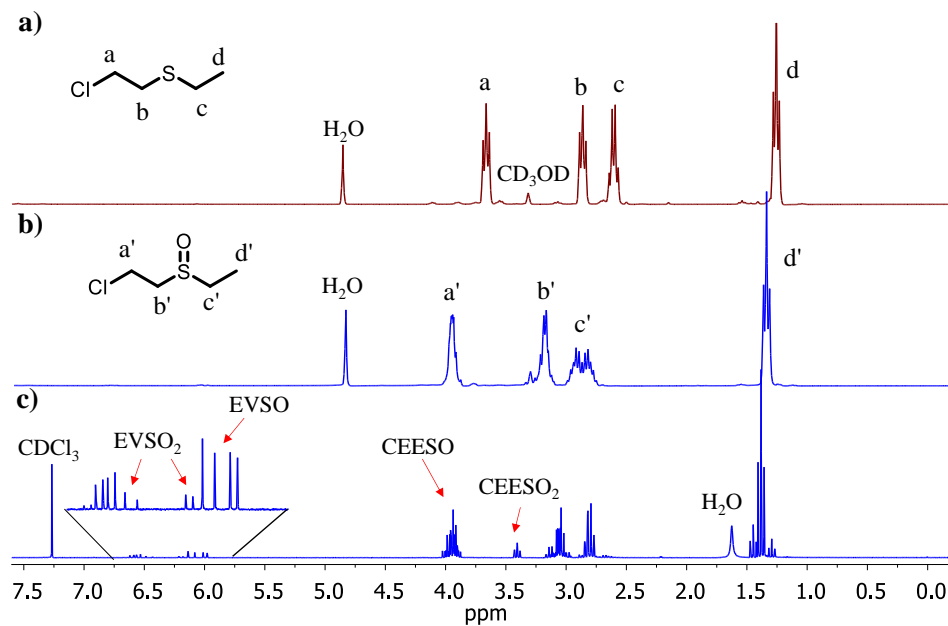


Figure S1. ^1H NMR spectra of a) pure CEES in CD_3OD , b) photooxidation product of CEES catalyzed by BDP-H in CD_3OD , and c) photooxidation products of CEES on BDP-H/PVDF film extracted with CDCl_3 . Reaction conditions: blue LED was used for both b) and c); irradiation time was 30 min for b) and 60 min for c).

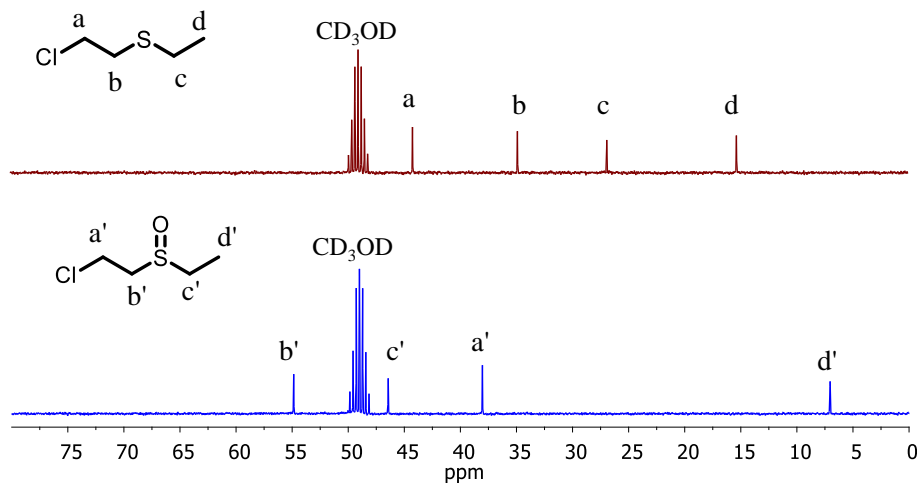


Figure S2. ^{13}C NMR spectra of BDP-H (1.5 mM) and CEES (172 mM) in methanol- d_4 before (top) and after (bottom) blue LED irradiation (30 min) under O_2 atmosphere. CEES was completely converted to CEESO.

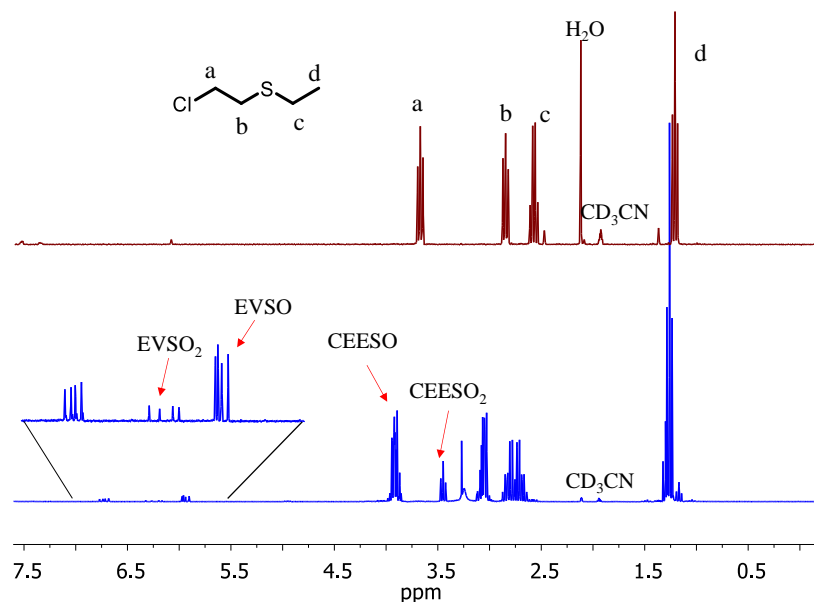


Figure S3. ^1H NMR spectra of BDP-H (1.5 mM) and CEES (172 mM) in acetonitrile- d_3 before (top) and after (bottom) blue LED irradiation (30 min) under O_2 atmosphere. CEES was completely gone after irradiation and multiple oxidation products, CEESO, CEESO $_2$, EVSO and EVSO $_2$, were formed.

2.2 Decontamination of HD in solution

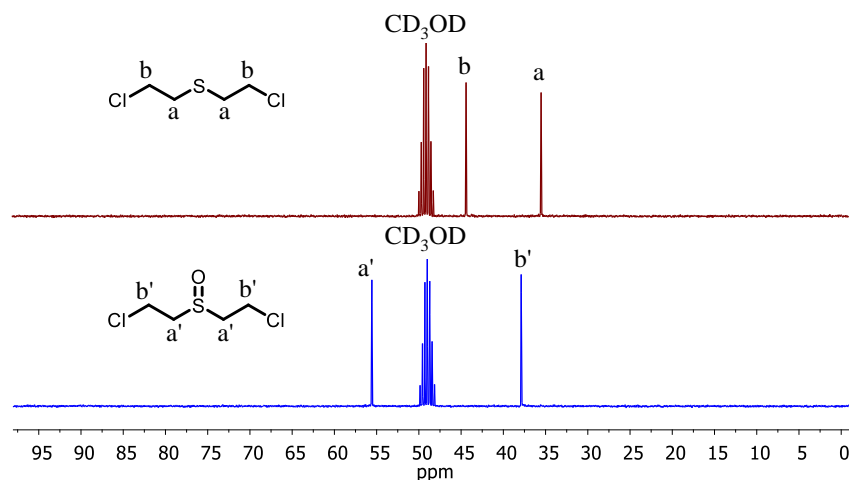


Figure S4. ^{13}C NMR spectra of BDP-H (1.5 mM) and HD (172 mM) in methanol- d_4 before (top) and after (bottom) blue LED irradiation (30 min) under O_2 atmosphere. HD was completely converted to HDO.

2.3 GC-MS Spectra of HD and CEES decontamination

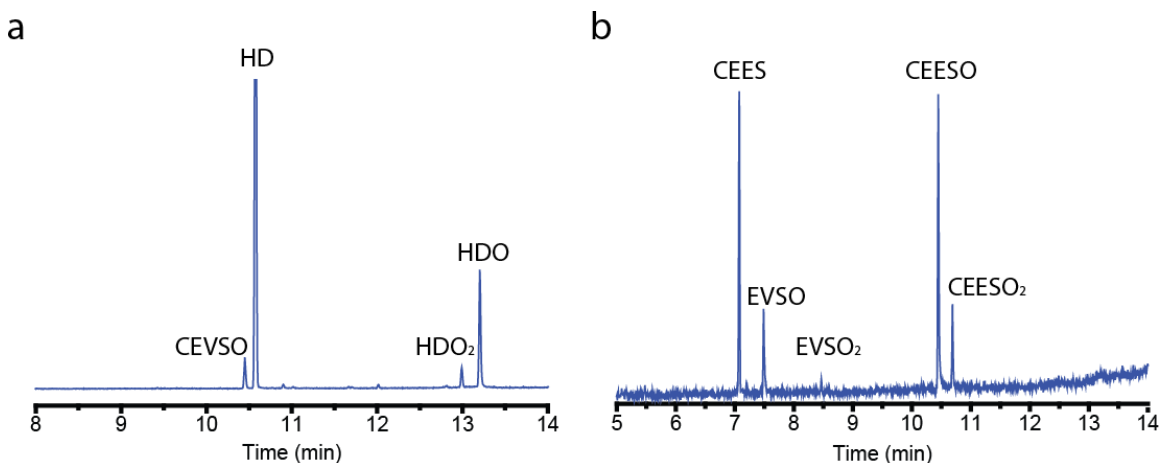


Figure S5. GC-MS spectra of photooxidation products of a) HD or CEES b) on a piece of BDP-SO₃/PVDF film irradiated by blue LED for 60 min under air atmosphere. Each peak was confirmed by MS analysis. Reaction didn't go to completion due to the slow kinetics of BDP-SO₃ photosensitizer. Photooxidation of HD is generally slower than CEES.

3. Photooxidation studies on Other BODIPY-Incorporated Materials

3.1 PVDF films containing different wt% of BDP-H

1 g PVDF (Mw 534,000) was mixed with 6 g DMF and heated at 50 °C for 2 hours. Appropriate amount of BDP-H was added to the solution and then dropped cast onto a Teflon plate to dry. For example, 10 mg BDP-H was added to the above solution to make a PVDF film with 1 wt% BDP-H.

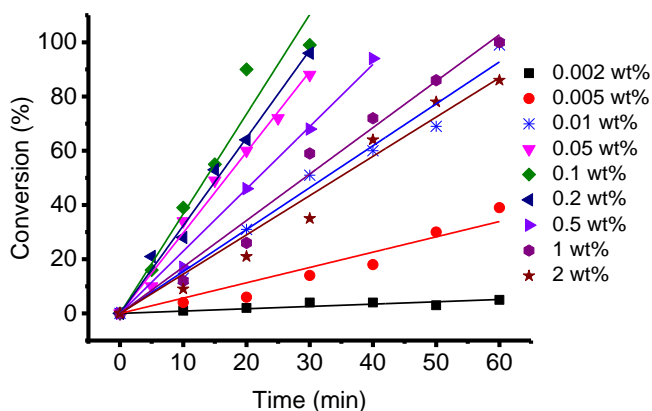


Figure S6. Oxidation of CEES over time on PVDF films (ca. 18 mg) containing different wt% of BDP-H under blue LED and air atmosphere.

3.2 Other Polymer Films doped with BODIPY photosensitizers

In addition to PVDF, various other types of polymer films were prepared to test their decontamination ability against CEES. Both PVA and 2-hydroxyethyl cellulose gave 0% reactivity toward CEES. This was probably due to the oxygen impermeability of these two polymer films. Both PS and PMMA gave partial decontamination. Out of all the films prepared, PVDF film gave the most prominent result, almost quantitative decontamination of CEES. It's still not clear to us why PVDF gave the most efficient decontamination result. Macro-size pores within the films (shown on SEM) probably help facilitate the mass transfer of CEES and $^1\text{O}_2$ throughout the films.

To prepare BODIPY-incorporated polymer films, appropriate amount of polymer (2 g PVA (M_w 89,000-98,000), 0.5 g 2-hydroxyethyl cellulose (M_w 250,000), 1.5 g PMMA (M_w 120,000), 2 g PS (M_w 350,000)) were dissolved (heating if necessary) in 10 mL of solvent (Table S1). 10 mg BODIPY photosensitizer was added to the polymer solution and then dropped cast onto a Teflon plate to dry.

Film	Solvent	Photosensitizer	CEES Conversion (%)
PVA	H ₂ O	BODIPY-SO ₃	0
2-hydroxyethyl cellulose	H ₂ O	BODIPY-SO ₃	0
PMMA	CH ₃ Cl	BODIPY-Ph	31
PMMA	DMF	BODIPY-Ph	52
PS	CH ₃ Cl	BODIPY-Ph	17
PS	DMF	BODIPY-Ph	60
PVDF	DMF	BODIPY-Ph	100

Table S1. Photooxidation of CEES on various BODIPY/polymer films under blue LED irradiation (60 min) and air atmosphere.

3.3 BODIPY-coated ACUs

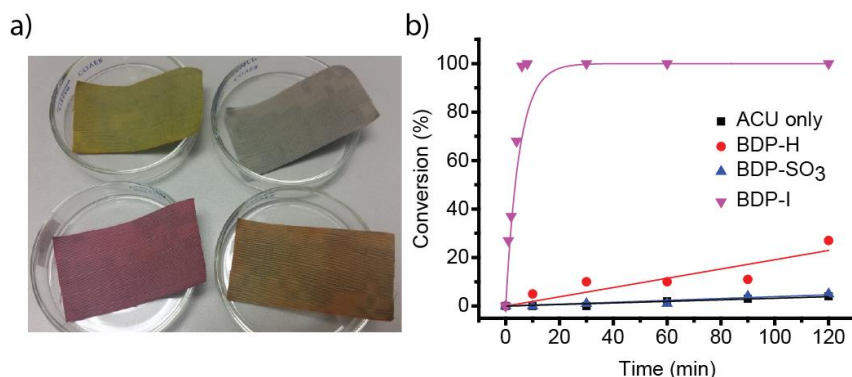
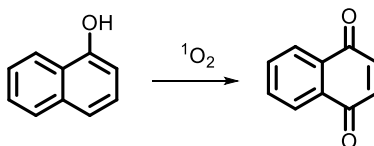


Figure S7. a) Photo images of BODIPY dip-coated ACUs: BDP-H ACU (top left), blank ACU (top right), BDP-I ACU (bottom left), and BDP-SO₃ ACU (bottom right). b) Oxidation of CEES over time on BODIPY dip-coated ACUs under blue LED irradiation and air atmosphere.

4. Detection of $^1\text{O}_2$ Generation



Scheme S2. Oxidation of 1-naphthol by singlet oxygen.

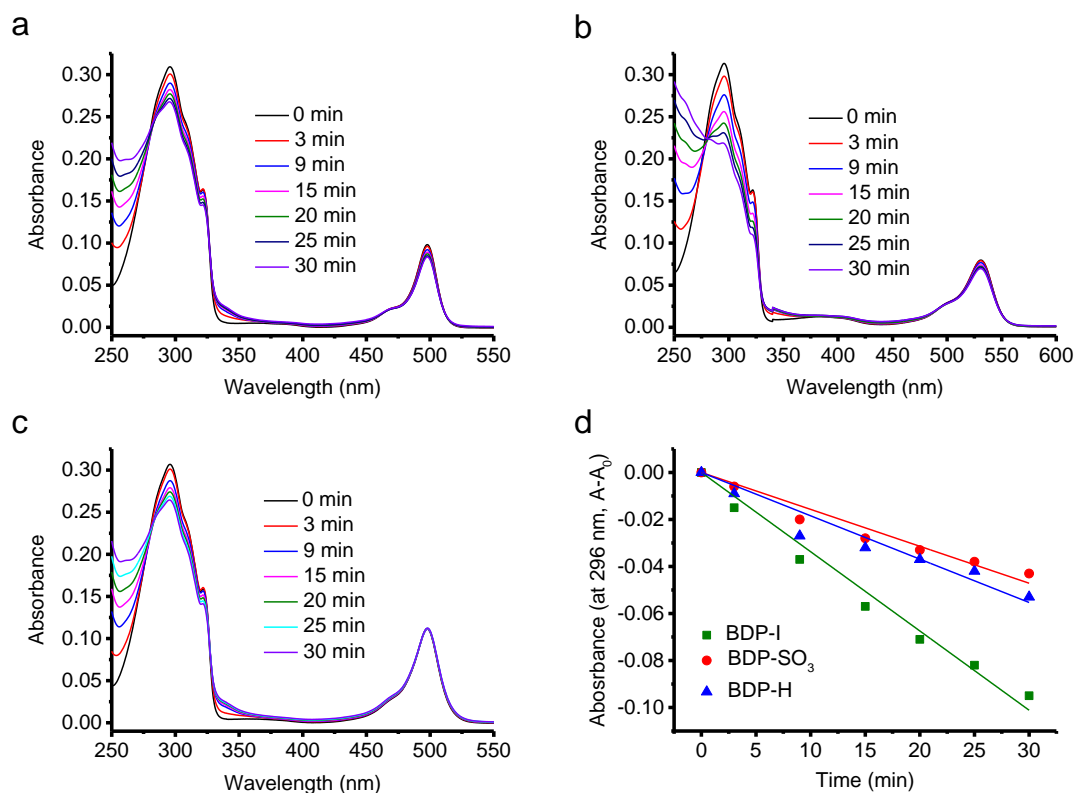


Figure S8. Absorption spectra of 100 μM 1-naphthol and 1 μM BODIPY in methanol irradiated with a blue LED over time a) BDP-H; b) BDP-I; c) BDP-SO₃. d) Oxidation of 1-naphthol (monitored at 296 nm) over time by BODIPY photosensitizers in methanol irradiated under blue LED and air atmosphere. Note that absorbance of BODIPY photosensitizers (around 500 nm) also slightly decreased over time due to quenching by $^1\text{O}_2$.

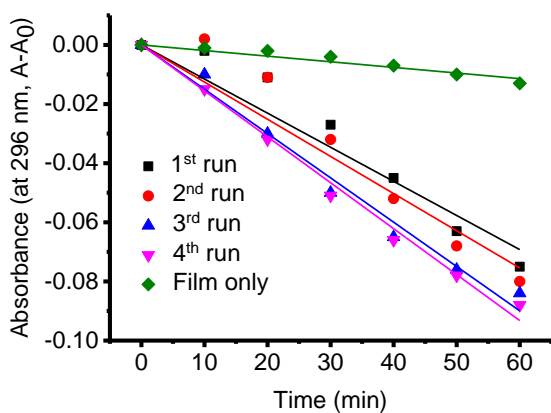
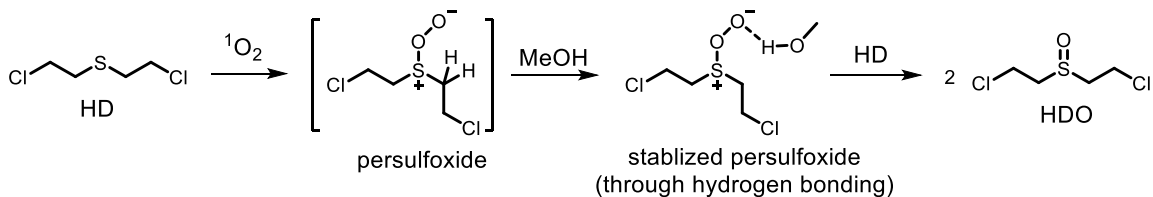


Figure S9. Oxidation of 1-naphthol by a piece of BDP-SO₃ PVDF film under blue LED light and air atmosphere over four consecutive runs. The film was washed with isopropanol after each cycle.

5. Oxidation Mechanism of HD by Singlet Oxygen



Scheme 3. Oxidation mechanism of HD by ¹O₂ in a protic solvent, such as methanol.

6. Confocal Microscope Images

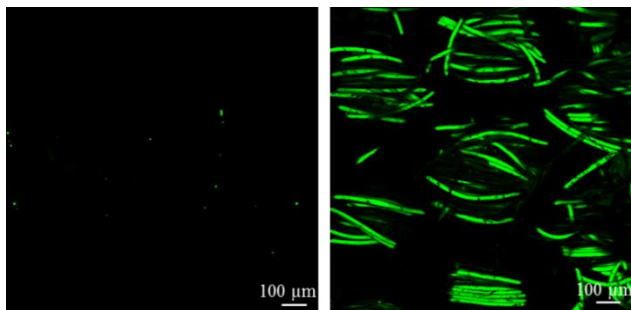


Figure S10. Confocal microscope images (20× magnifications) of blank ACU (left) and BDP-H ACU (right).

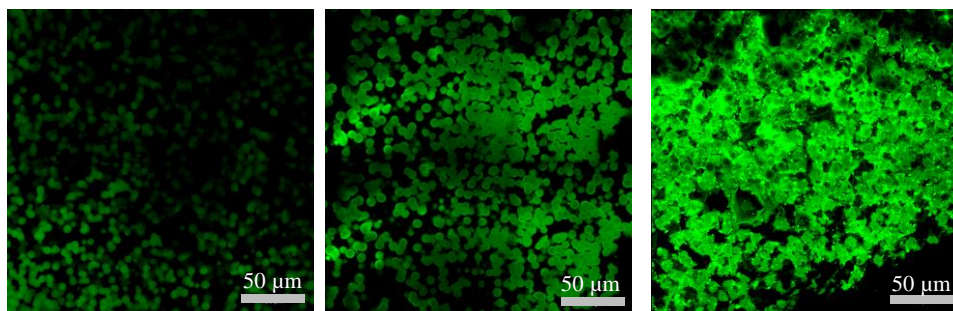


Figure S11. Confocal microscope images (100× magnifications) of 0.01 wt% (left), 0.2 wt% (middle), and 2 wt% (right) BDP-H/PVDF films.

7. Spectral Power Distribution of LEDs

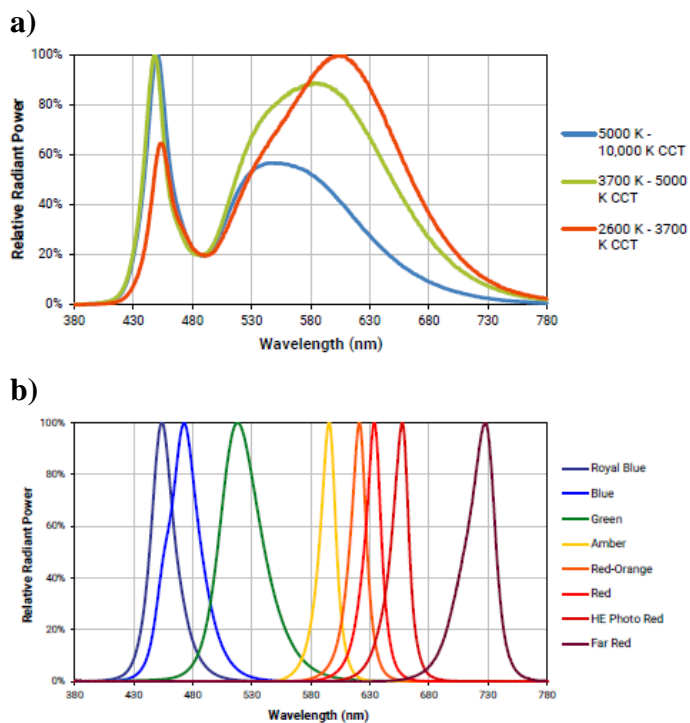


Figure S12. Relative spectral power distribution of a) white and b) color LEDs.¹ The blue LED used in our experiments has dominant emission wavelengths between 450-495 nm and the red LED has dominant wavelengths between 600-650 nm. Wavelengths of white LED span the whole visible spectrum and consist of little power distribution from the blue portion.

1. Cree Inc. Product Family Data Sheet.

<http://www.cree.com/ledcomponents/media/documents/XLampXPE.pdf>