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Decontamination of Chemical-Warfare Agent Simulants by Polymer Surfaces Doped with the Singlet Oxygen Generator Zinc Octaphenoxyphthalocyanine

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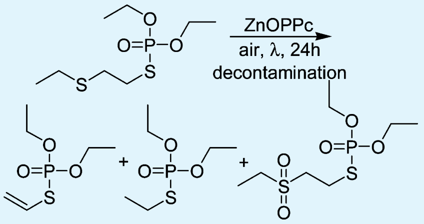
Ⓢ *Supporting Information*



ABSTRACT: Using reactive singlet oxygen ($^1O_2$), the oxidation of chemical-warfare agent (CWA) simulants has been demonstrated. The zinc octaphenoxyphthalocyanine (ZnOPPc) complex was demonstrated to be an efficient photosensitizer for converting molecular oxygen (O_2) to $^1O_2$ using broad-spectrum light (450−800 nm) from a 250 W halogen lamp. This photosensitization produces $^1O_2$ in solution as well as within polymer matrices. The oxidation of 1-naphthol to naphthoquinone was used to monitor the rate of $^1O_2$ generation in the commercially available polymer film Hydrothane that incorporates ZnOPPc. Using electrospinning, nanofibers of ZnOPPc in Hydrothane and polycarbonate were formed and analyzed for their ability to oxidize demeton-S, a CWA simulant, on the surface of the polymers and were found to have similar reactivity as their corresponding films. The Hydrothane films were then used to oxidize CWA simulants malathion, 2-chloroethyl phenyl sulfide (CEPS), and 2-chloroethyl ethyl sulfide (CEES). Through this oxidation process, the CWA simulants are converted into less toxic compounds, thus decontaminating the surface using only O_2 from the air and light.

KEYWORDS: *singlet oxygen, chemical-warfare agent simulants, zinc octaphenoxyphthalocyanine, decontamination, electrospinning, photooxidation*

■ INTRODUCTION

The potential danger of chemical-warfare attacks has led to an increased need for developing novel decontamination methods for the surfaces of buildings and vehicles that could be exposed to chemical-warfare agents (CWAs). Common methods for the neutralization of exposed surfaces include extensive washes with alkaline and/or hypochlorite solutions.[1,2] Although these solutions are extremely effective at minimizing the threats posed by CWAs through a variety of hydrolysis and/or oxidation reactions, they unfortunately also promote corrosion and accelerate the degradation of metals and other materials that are commonly found on military assets. Furthermore, the continued use of large amounts of traditional decontamination solutions has the potential to negatively impact the surrounding environment. Decontamination methods that are efficient, do not damage the surfaces they clean, and are environmentally friendly would be a benefit over currently used methods and have been an extensive area of interest for the military. A decontamination foam known as DF-200, composed of quaternary ammonium compounds, hydrogen peroxide, and diacetin, can quickly eliminate GD (soman), VX (*O*-ethyl *S*-[2-(diisopropylamino)ethyl] methylphosphonothioate), and HD (mustard gas) while being environmentally benign.[3,4] Unfortunately, this method requires the use of specialized foam-spraying equipment, making it less practical for general use than traditional methods. Decon Green is an environmentally friendly solution that can decontaminate most surfaces without damaging them, but it is less effective than previous methods and can damage aluminum airframes.[5]

Paints and other coatings are commonly applied to protect, seal, and preserve various metal, wooden, and concrete surfaces. Some contaminants can be absorbed into these coatings, leaving them unchanged by the cleaning processes. Any untreated contamination is a serious problem as even small amounts of some CWAs can be deadly.[6,7] For example, the dermal LD_{50} of VX is only 0.04 mg/kg.[6] Complete decontamination requires that the absorbed contaminants are either removed or destroyed in some type of reaction. A surface that can decontaminate itself from any absorbed agents that were not removed by the cleaning process would provide an extra layer of defense. A self-decontaminating surface is of interest because it could minimize the spread of CWAs and eliminate the need for postcontamination cleaning.[8−14] This ability for the surfaces of buildings and vehicles to destroy CWAs would help limit contamination by ensuring that the surface is constantly cleaning itself.

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Singlet oxygen ($^1O_2$) is a reactive, short-lived species with a lifetime of a few microseconds in solution[15,16] to tens of milliseconds in air[17] or CCl_4.[16] The generation of $^1O_2$ can occur through a variety of chemical reactions (such as reacting hydrogen peroxide with sodium hypochlorite),[18] microwave radiation, pulsed radiolysis, organic molecule charge transfer, low-yielding direct absorption of 600 nm light, and most commonly through energy transfer from photosensitizers.[15] The generation of $^1O_2$ through photosensitization is a process that occurs in nature in which a compound transfers energy absorbed from light to O_2 to excite it from its ground triplet state to its excited singlet state. The $^1O_2$ will react with numerous chemical species including olefins, dienes, aromatics, peptides, and sulfur atoms,[19−22] making $^1O_2$ a promising oxidant for CWAs to convert them into less harmful species. For example, 2-chloroethyl ethyl sulfide (CEES), a mustard simulant, is oxidized by $^1O_2$ to form 2-chloroethyl ethyl sulfoxide when in a solution with a constant stream of O_2 and exposed to a 600 W lamp.[23]

Metallophthalocyanines are well documented as photosensitizers that transfer energy from light to excite ground-state triplet oxygen (O_2 ($^3\Sigma_g$)) to singlet oxygen ($^1O_2$ ($^1\Delta_g$)).[24−26] Many metallophthalocyanines are being studied for photodynamic therapy (PDT) in an effort to combat cancer cells.[27−29] Complexes that generate $^1O_2$ also provide antibacterial character.[30−33] Zinc octaphenoxyphthalocyanine (ZnOPPc) has been previously studied for its photochemical properties and was proven to be efficient at generating $^1O_2$ with a quantum yield (Φ_Δ) of $^1O_2$ formation ranging from 0.45 to 0.60 in solution.[34−36] If it is incorporated into a polymeric matrix, then this complex should produce $^1O_2$ within the polymer,[37] which would promote the spontaneous oxidation of CWA and other chemicals. As a result of this property and the relative ease of synthesis and potential for modifications, this complex has been targeted as a potential self-decontaminating additive for a variety of materials in this study.

This article reports the singlet oxygen generation by the ZnOPPc complex in solution and incorporated into polycarbonate (PC) and Hydrothane (HT) matrices, and its ability to oxidize chemicals that are near the surface of polymer, resulting in self-decontamination. Of course, the use of $^1O_2$ as a decontaminating agent is a method that could result in degradation or oxidation of some polymer surfaces that are reactive toward $^1O_2$. Our focus is to show that ZnOPPc generates $^1O_2$ when incorporated into polymer films and to use these doped films to oxidize and degrade the CWA VX simulants demeton-S and malathion as well as HD simulants CEPS (2-chloroethyl phenyl sulfide) and CEES through activated oxygen from the air. The effect that $^1O_2$ has on the polymer surface will also be monitored. Electrospun fibers of ZnOPPc-doped PC and HT were also analyzed for decontamination ability because of their increased surface area that should result in larger amounts of $^1O_2$. Additionally, the fibers could be used for filtration to potentially trap and decontaminate larger amounts of CWAs.

■ EXPERIMENTAL SECTION

General Information. All chemicals were purchased from Aldrich or Acros and were used without further purification. Polycarbonate (PC) resin pellets had an average molecular weight (M_w) of 45 000 g/mol. Hydrothane pellets were obtained from CardioTech. All ^1H NMR spectra were taken in $CDCl_3$ (from Cambridge Isotope Laboratories, Inc.) at 300 MHz with TMS as an internal standard on a Bruker AVANCE 300 MHz spectrometer. GC/MS data were obtained from an Agilent 7890A GC connected to a 5975C inert XL MSD with triple-axis detector. FTIR spectra were acquired via diffuse reflectance using a Thermo Scientific Nicolet 6700 FTIR. An Agilent 8453 UV−vis spectrometer was used to obtain all UV−vis spectra. Electrospun fibers were analyzed using a Carl Zeiss SMT Supra55 scanning electron microscope (SEM) operated using an accelerating voltage of 3−5 kV. Both the polymer films and fibers were analyzed by confocal microscopy using an Olympus Lext 3D measuring laser microscope OLS4000. Polymer degradation was analyzed by data obtained from gel-permeation chromatography (GPC) using a Waters GPC system with RI detection. The samples were analyzed at 40 °C on two columns connected in series (Shodex KF-806 M and Waters Styragel HR 4E).

Synthesis. The synthesis of ZnOPPc followed previously reported methods outlined by Maree et al.[34] Following the procedure by Wöhrle et al.,[38] 4,5-dichlorophthalonitrile (1.00 g, 5.08 mmol), phenol (1.43 g, 15.2 mmol), and K_2CO_3 (11.2 g, 81.2 mmol) were heated while stirring in DMSO at 90 °C for 2 h. After cooling to room temperature, 4,5-diphenoxyphthalonitrile was isolated in ca. 80% yield by crystallization from ethanol (clean by ^1H NMR and GC/MS). A solution of 4,5-diphenoxyphthalonitrile (1.00 g, 3.20 mmol) in 1-pentanol was added to $ZnCl_2$ (207 mg, 1.52 mmol) and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) (308 mg, 2.03 mmol) and refluxed under a N_2 atmosphere overnight. After concentrating the solution, the product was precipitated by adding methanol and water. Thorough rinsing with water and methanol afforded a clean product (by IR, UV−vis, and NMR) in ca. 85% yield.

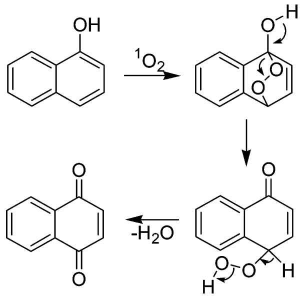
Film Generation. Films doped with ZnOPPc were formed by solution casting 3 mL of a 5 wt % polymer solution containing 0, 0.1, or 0.5% ZnOPPc by weight. Polycarbonate or Hydrothane (HT) were dissolved in dichloromethane (DCM) or DCM/DMF (dimethyl formamide) solutions (4:1 for polycarbonate and 3:1 for hydrothane). The drying of the films was mediated by loosely capping the scintillation vial to allow for slow evaporation, which generated a smooth even film without cracks and deformities. The resulting films were analyzed by confocal microscopy and tested for singlet oxygen ($^1O_2$) generation using 1-naphthol as the quencher.

Electrospun Fibers. In a typical electrospinning experiment, a solution of 5.0 g of PC and ZnOPPc (0, 0.1, or 0.5% by weight) in 20 mL of DCM or 4:1 DCM/DMF was added to a syringe with a 22 gauge flat-tip needle. The solution was dispensed from the syringe at a constant rate of 15 μL/min, controlled by a syringe pump. During this time, a constant current of 15 kV was applied using a Spellman CZE1000R high-voltage power supply. A grounded collection plate covered in aluminum foil was placed perpendicular to the polymer flow at a distance of 15 cm from the tip of the syringe needle. Electrospinning was performed at room temperature with a relative humidity between 10 and 20%. The same setup was used for the ZnOPPc-doped HT fibers, except that the solvent employed was 3:1 DCM/DMF and the concentration was 2.0 g in 20 mL. Fiber morphology and size were analyzed by SEM and confocal microscopy.

Singlet Oxygen Generation. Singlet oxygen generation by ZnOPPc has been previously reported in several solvents.[34−36] To verify that the complex made was capable of generating singlet oxygen, 1-naphthol was used as a singlet oxygen quencher. In the presence of $^1O_2$, 1-naphthol is converted to naphthoquinone (Scheme 1).[39,40] The mechanism of this process occurs through a 4 + 2 cycloaddition followed by a loss of H_2O. Additionally, a nonsensitized oxidation has been reported to proceed through a photoionization reaction that could compete in this system.[40]

In a UV−vis cuvette, a solution containing 5.0×10^{-4} M 1-naphthol and 5.0×10^{-6} M ZnOPPc in DMSO was irradiated with broad-spectrum light (450−800 nm) from a 250 W halogen light through the side of a UV−vis cuvette while air was bubbling through the solution to ensure that an adequate amount of O_2 is continuously available. UV−vis spectra were recorded every 30 s to monitor the reduction in the characteristic absorbance of 1-naphthol (299 nm) to verify the quenching of singlet oxygen. A new peak at 325 nm appears that corresponds to naphthoquinone formation, but this peak overlaps with

Scheme 1. Oxidation of 1-Naphthol by Singlet Oxygen



the shoulder of 1-naphthol and cannot be used for kinetic data. The experiment was repeated using zinc phthalocyanine (ZnPc) as the photosensitizer as a reference. Both reactions were then repeated using CCl_4 as the solvent.

Quantification of singlet oxygen generated by the ZnOPPc-doped polymers was accomplished by placing a small amount of the HT films (ca. 50 mg) at the bottom of the UV−vis cuvette filled with 3 mL of a 5×10^{-4} M 1-naphthol solution and irradiating with light while bubbling with air. There are many examples of singlet oxygen being generated from photosensitizers located within polymeric matrices that have laid the groundwork for this experiment.[37,41−46] The reaction was performed in acetonitrile, decane, ethylene glycol, and carbon tetrachloride for 0.1 and 0.5% ZnOPPc in HT (w/w). The dependence on the amount of catalyst on singlet oxygen production was analyzed in decane by repeating the reactions using 11.2, 26.2, 51.1, and 101.4 mg of film. The long-term $^1O_2$ production of the films was analyzed after the oxidation of 1-naphthol. The solution was decanted after the reaction was complete, and the film was rinsed thoroughly with hexanes. Excess solvent was removed by gentle heating (75 °C) for 15 min, and the recycled film was retested for $^1O_2$ generation by oxidizing 1-naphthol three more times. For consistency, the film was rinsed with hexanes and dried at 75 °C before the first run.

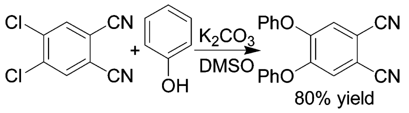
Because of its potential for nonspecific oxidation, $^1O_2$ species could lead to oxidation or degradation of the polymer films where it is being generated.[37] To analyze the effect of exposure to $^1O_2$, a small amount of the films cut into small squares (ca. 1 cm^2) from 0, 0.1, and 0.5% ZnOPPc in both PC and HT were exposed to light for 2 weeks in scintillation vials. After 1, 2, 4, 7, and 14 days, a small amount of each film (15−20 mg) was removed and dissolved in THF for GPC and IR analysis. Samples were compared with the commercially available polymer that was not exposed to light to determine the extent of degradation.

Surface Decontamination. Decontamination assessment of these materials was analyzed by placing the CWA simulant demeton-S on the film and irradiating with light for 24 h. In a 20 mL scintillation vial containing the various films or electrospun fibers, 0.8 μL (0.0035 mmol) of demeton-S was added, and the vial was closed tightly and sealed with parafilm. The samples were exposed to broad-spectrum light (450−800 nm) from a 250 W halogen lamp for 24 h. The samples were analyzed by GC/MS after adding 1 equiv of 1,2,3,4-tetrahydronaphthalene (700 μL of 0.0050 M solution in ACN) as an internal standard to allow for the quantification of demeton-S reduction using relative peak integrations (performed in triplicate and averaged). The same procedure was used to analyze the decontamination of the additional simulants CEPS (1.0 μL, 0.0068 mmol), CEES (0.8 μL, 0.0068 mmol), and malathion (1.0 μL, 0.0037 mmol). Using a thermocouple inserted and sealed through the cap of a scintillation vial, the internal temperature during these reactions was found to be above room temperature at 32−34 °C (room temperature during these measurements was 22−24 °C).

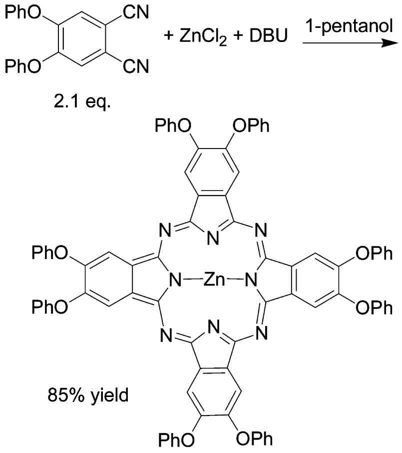
■ RESULTS AND DISCUSSION

Synthesis. Following previously reported syntheses of ZnOPPc,[38,47,48] 4,5-diphenoxyphthalonitrile was first isolated in 80% yield (Scheme 2) and verified by ^1H NMR and GC/MS. ZnOPPc was then isolated in 85% yield (Scheme 3), and the product was verified using IR (by the lack of a peak at 2300−2200 cm^{-1} from CN), UV−vis (λ_{max} = 680 in DMSO, single peak), and ^1H NMR (DMSO-d_6 δ: 8.47, s, 1H, Ar-*H*; 7.49, t, 2H, *m*-Ph-*H*; 7.34, d, 2H, *o*-Ph-*H*; 7.28 (overlaps with previous peak), t, 1H, *p*-Ph-*H*).

Scheme 2. Synthesis of 4,5-Diphenoxyphthalonitrile



Scheme 3. Synthesis of ZnOPPc



Film and Fiber Properties. SEM analysis of the electrospun fibers of PC with 0, 0.1, and 0.5% ZnOPPc revealed that the fibers were large with a very large variability in the size and shape when electrospun from DCM (Table 1). The fibers ranged in size from 3.4(2.9) to 9.2(2.9) μm, with the large fibers being flat ribbons and the smaller fibers appearing more round (see Figures S1−S6). When DMF was added to the solution to increase the dielectric constant, the size of the fibers decreased significantly. Although there is still a large variability in the fiber size, the range dropped to 0.9(6)−2.8(1.3) μm (Table 1), with the larger fibers again being flat ribbons and the

Table 1. Size of Electrospun Fibers of PC and HT from SEM Data

	average diameter (nm)	standard deviation (nm)
PC control DCM only (*n* = 78)	9224	2888
0.1% ZnOPPc/PC DCM only (*n* = 83)	4648	2585
0.5% ZnOPPc/PC DCM only (*n* = 94)	3437	2947
PC control DCM/DMF (*n* = 84)	1592	607
0.1% ZnOPPc/PC DCM/DMF (*n* = 81)	2803	1364
0.5% ZnOPPc/PC DCM/DMF (*n* = 83)	933	593
HT control (*n* = 80)	203	40
0.1%ZnOPPc/HT (*n* = 80)	304	86
0.5% ZnOPPc/HT (*n* = 87)	360	83

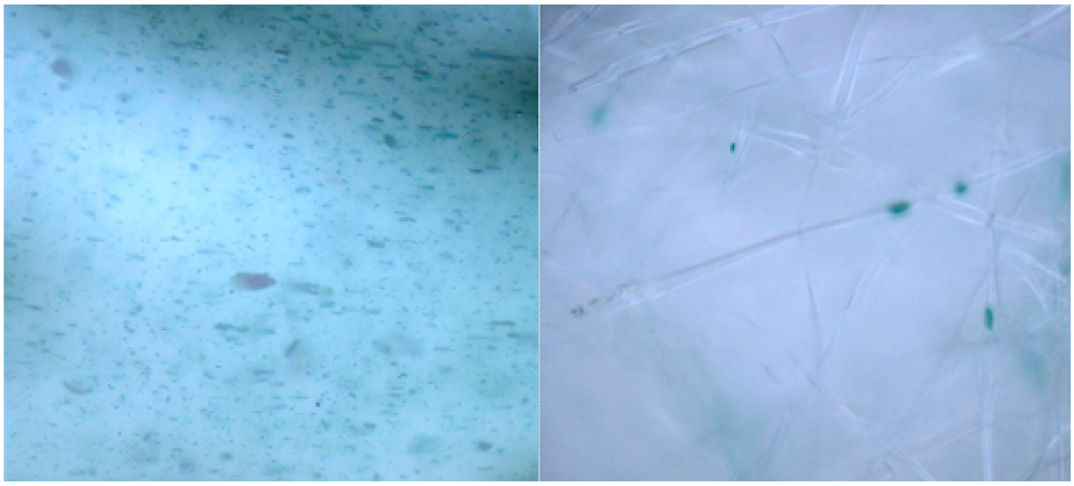


Figure 1. Confocal microscopy image of a 0.5% ZnOPPc/PC film cast from DCM (left) and fibers spun from 4:1 DCM/DMF (right) (2150× magnification).

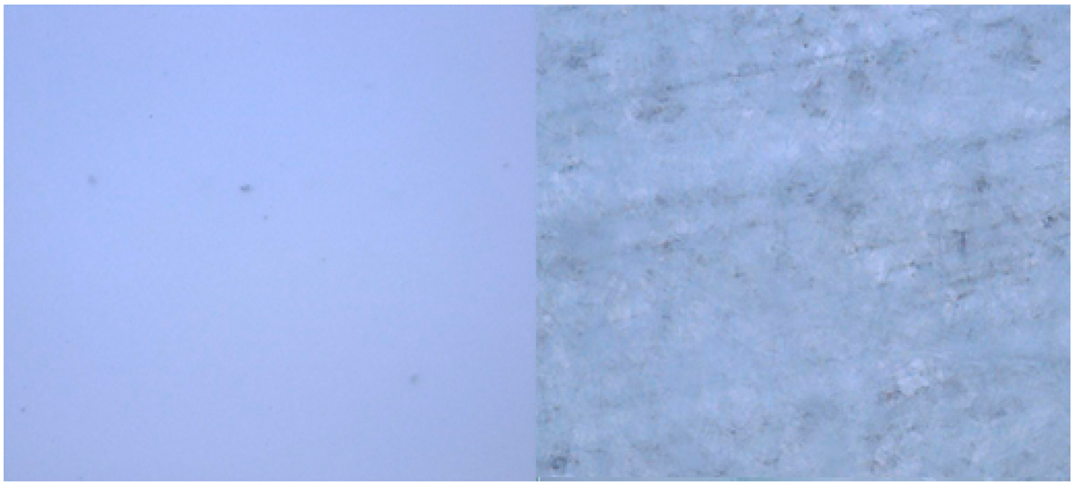


Figure 2. Confocal microscopy image of a 0.5% ZnOPPc/HT film (left) and fibers (right) from a 3:1 DCM/DMF solution (2150× magnification).

smaller fibers appearing more round (see Figures S1−S6). The HT fibers with 0, 0.1, and 0.5% ZnOPPc were much smaller than the PC fibers and exhibited much more uniformity in size and appearance (see Figures S7−S9) with a fiber size range of 200(40)−360(80) nm (Table 1) and all of the fibers appearing round.

Although the films appear to have a uniform color by a simple visual inspection, images obtained using laser confocal microscopy indicate aggregation of the ZnOPPc in the polycarbonate and hydrothane films with agglomerates ranging in size from 200 nm to 6 μm. Although electrospinning the PC does not remedy this aggregation within PC because the vivid coloring of the ZnOPPc agglomerates remain visible (Figure 1), the HT fibers do not show any signs of aggregation as evidenced by the lack of any notable color gradients throughout the fibrous mat (Figure 2). In this case, the ZnOPPc is either evenly distributed through the polymer matrix or the aggregates are so small that they are undetectable by confocal microscopy. It is expected that aggregation would limit the degradation of CWA simulants because it reduces the surface area of available ZnOPPc molecules as well as potentially self-quenching the $^1O_2$ generation.[49,50]

Singlet Oxygen Generation. Quantification of $^1O_2$ produced from ZnOPPc was performed by dissolving the complex in DMSO and irradiating with light in the presence of 1-naphthol, a $^1O_2$ quencher. When exposed to $^1O_2$, 1-naphthol is oxidized to naphthoquinone (Scheme 1).[39] This oxidation reaction can be monitored spectroscopically by observing the change in absorbance of 1-naphthol at 299 nm over the course of time. Although this reaction is quite slow, a distinct reduction of 1-naphthol is evident over time along with photobleaching of the ZnOPPc complex (Figure S17). Photobleaching is a reduction in the spectral peak associated with the photosensitizer without the growth of any new peaks.[35] When repeated in carbon tetrachloride (CCl_4), the kinetics of oxidation increase because of the increased $^1O_2$ lifetime compared to DMSO (0.026 s in CCl_4 and 3×10^{-5} s in DMSO).[51] Both the reduction of the 1-naphthol peak (Figure 3 and Table 2) and the photobleaching of ZnOPPc occur very quickly (Figure S18). The reactions were repeated using zinc phthalocyanine (ZnPc) as the photosensitizer with similar results. Using eq 1 and ZnPc as the standard (Φ_Δ = 0.67),[52] ZnOPPc is calculated to have a Φ_Δ of 0.78 and 0.60 in DMSO and CCl_4, respectively (the literature value is 0.60 in DMSO[35]). Because of the close agreement of these values to previous reports, there was no correction made to address the photobleaching effect. The results from the reactions in CCl_4 appear to be more reliable with more linear data, as shown in

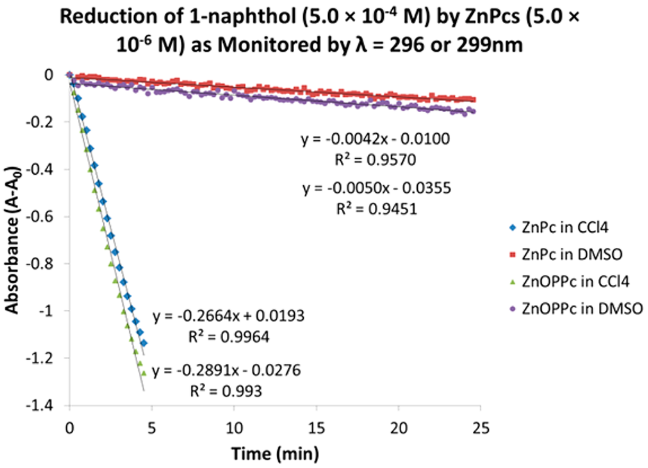


Figure 3. Reduction of 1-naphthol (5.0×10^{-4} M) by ZnOPPc and ZnPc (5.0×10^{-6} M) in DMSO and CCl_4 as monitored at $\lambda = 299$ nm (DMSO) or 296 nm (CCl_4) scanned every 30 s.

Table 2. Calculated 1-Naphthol Oxidation Rates for ZnPc and ZnOPPc in CCl_4 and DMSO

	k_{obs}	rate (k_{obs}/[Zn]) (M^{-1} s^{-1})
ZnPc in $CC1_4$	0.26	52 000
ZnPc in DMSO	0.0042	840
ZnOPPc in $CC1_4$	0.29	58 000
ZnOPPc in DMSO	0.0050	1000

Figure 3, and might be a result of potential aggregation that has been reported in DMSO at concentrations just above these experimental conditions (as dilute as 1×10^{-5} M).[34]

$$\Phi_\Delta = \Phi_\Delta^{std} \frac{R I_{abs}^{std}}{R^{std} I_{abs}} \qquad (1)$$

The ability of ZnOPPc to generate $^1O_2$ in solution has been confirmed; therefore, supporting the sensitizer in a polymer film should allow for singlet oxygen to be formed in the matrix of the polymer, as was previously reported with other photosensitizers.[37,41−46] Once generated, $^1O_2$ in the polymer should diffuse through the matrix and react with a $^1O_2$ quencher. Ogilby and co-workers report that $^1O_2$ can diffuse through cross-linked polymers at a rate of $2.5(5) \times 10^{-8}$ cm^2 s^{-1} that is independent of the degree of cross-linking.[46] The distance traveled by $^1O_2$ can be calculated using eq 2, where $t = 5\tau_\Delta$ and τ_Δ = $^1O_2$ lifetime.[37] On the basis of this equation, $^1O_2$ could travel as far as 10^{-4} cm through these polymers in air or CCl_4.

$$d = \sqrt{6tD} \qquad (2)$$

To test this, 0.1 and 0.5% ZnOPPc-doped HT films described above were used to produce $^1O_2$. The absorbance of 1-naphthol was monitored in a solvent that the HT film is insoluble in, such as ethylene glycol, acetonitrile (ACN), decane, and CCl_4 (the film was left as a solid at the bottom of the cuvette (or the top in the case of the dense CCl_4) and out of the path of the UV−vis light source). Because ZnOPPc is not soluble in these solvents, with exception of CCl_4, it was not surprising that there was no evidence of photosensitizer leaching into solution when examined using UV−vis. There is a possibility that the visually observed photobleaching of the film during the reaction in CCl_4 is the result of ZnOPPc leaching into solution and subsequently being photobleached before the concentration increases sufficiently to be detectable by UV−vis. When the sample is exposed to light, $^1O_2$ was formed, as confirmed by the oxidation of 1-naphthol shown in Figures 4 and 5.

As expected, the rate of 1-naphthol oxidation is dependent on the solvent that the reaction occurs in. For the reaction that proceeded in ACN, the solution from the completed reaction was analyzed by GC/MS to confirm the formation of 1,4-naphthoquinone. As shown in Table 3, there is a correlation between the lifetime that $^1O_2$ has in solution and the rate of oxidation of 1-naphthol. As would be expected, the longer $^1O_2$ can exist in a solution, the greater the chance it has to oxidize 1-naphthol before being quenched. In a solvent with a very long $^1O_2$ lifetime, such as CCl_4, the oxidation of 1-naphthol occurs very quickly because the $^1O_2$ species is not quenched by the solvent before it reaches the substrate. Because of the long lifetime of $^1O_2$ in solutions such as CCl_4, photobleaching of the ZnOPPc/HT film was visually observed. It should be noted

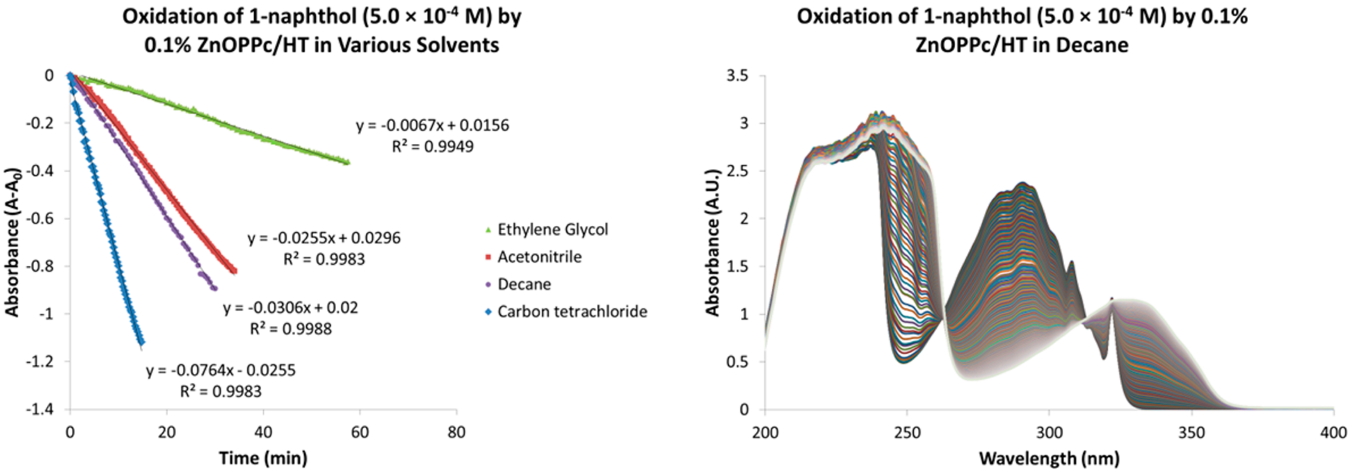


Figure 4. Oxidation of 1-naphthol (5.0×10^{-4} M) by 0.1% ZnOPPc/HT in multiple solvents (left). The reaction was monitored at 291 nm (ethylene glycol and decane) or 296 nm (ACN and CCl_4) scanned every 30 s. The plot on the right is the reaction in decane that shows the decrease in absorption at 291 nm and the growth of a new peak at 329 nm. Figure S21 shows that there is no absorption around 680 nm, indicating that ZnOPPc does not leach from the polymer matrix.

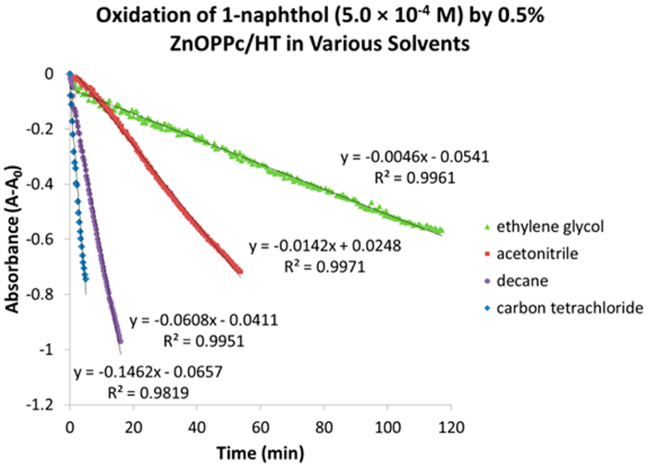


Figure 5. Oxidation of 1-naphthol (5.0×10^{-4} M) by 0.1% ZnOPPc/HT in multiple solvents. The reaction was monitored at 291 nm (ethylene glycol and decane) or 296 nm (ACN and CCl_4) scanned every 30 s.

Table 3. Rate of 1-Naphthol Oxidation by ZnOPPc/HT Films in Various Solvents

solvent	rate (k_{obs}/ZnOPPc]) (M^{-1} V^{-1}) 0.1% ZnOPPc	 0.5% ZnOPPc	$^1O_2$ lifetime (s)
ethylene glycol	516	355	7.5×10^{-6}
acetonitrile	1990	1040	5.5×10^{-5}
decane	2830	4730	2.8×10^{-5}
carbon tetrachloride	12 300	24 400	2.6×10^{-2}

that the reaction in CCl_4 occurred with half of the amount of the film than that used in the other reactions. The high rate of reaction with half of the amount of catalyst created the question about whether the reaction was dependent on the amount of catalyst film utilized. Although the reaction is significantly slower than the homogeneous reaction (58 000 M^{-1} s^{-1} for homogeneous reaction vs 24 400 M^{-1} s^{-1} for heterogeneous), this is the result of $^1O_2$ needing to diffuse through the polymer matrix to react with 1-naphthol.

The rate of oxidation of 1-naphthol was found to be dependent on the amount of ZnOPPc/HT film used (Figure 6), with the observed rate of oxidation increasing with increasing amount of film. There appears to be a saturation point, however; above 50 mg of 0.1% ZnOPPc/HT there may be competition between ZnOPPc and 1-naphthol for quenching the $^1O_2$. In the case where 101.4 mg of 0.1% ZnOPPc-hydrothane film was used, a 20-fold excess of 1-naphthol is in the reaction. Interestingly, as shown in the inset in Figure 6, as the amount of 0.1% ZnOPPc/HT film is increased from 51.1 mg to 101.4 mg, there is actually a decrease in the rate of 1-naphthol oxidation. This could be attributed to ZnOPPc self-quenching or the quenching of $^1O_2$ by interactions with the polymer matrix, though this has not been evaluated thus far and is the subject of future experiments.

During the oxidation of 1-naphthol, a CWA or simulant, it is important that the films themselves are not subject to accelerated degradation resulting from the presence of $^1O_2$ because this would result in decreased activity over time. To show that these films could be used over long periods of time without a loss of catalytic activity, a single sample of 0.1% ZnOPPc/HT film was used for four consecutive oxidation reactions. Before each use, the film was thoroughly rinsed with hexanes and gently heated in an oven at 75 °C for 15 min to ensure complete dryness. This rinsing was also used before the first run for consistency. The rate of 1-naphthol oxidation was consistent through all four reactions, showing that the films can be recycled and that $^1O_2$ can be continually generated without compromising the ability of the ZnOPPc-doped surface to generate more $^1O_2$ (Figure 7).

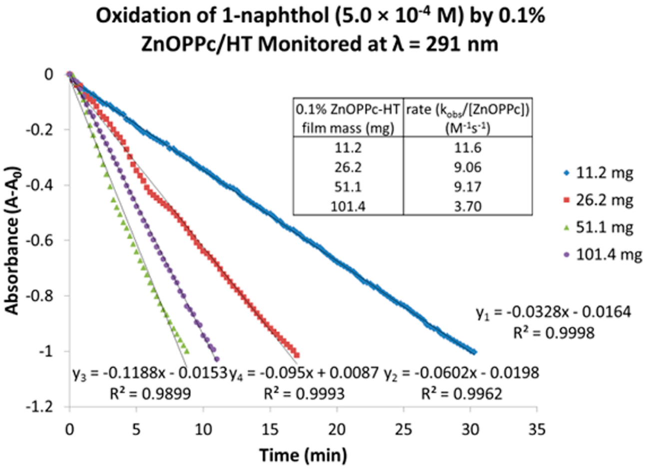


Figure 6. Oxidation of 1-naphthol (5.0×10^{-4} M) by varying amounts of 0.1% ZnOPPc/HT films in decane, monitored at λ = 291 nm, scanned every 30 s. The inset table shows the calculated rates for varying amounts of 0.1% ZnOPPc/HT films to oxidize 1-naphthol (5.0×10^{-4} M).

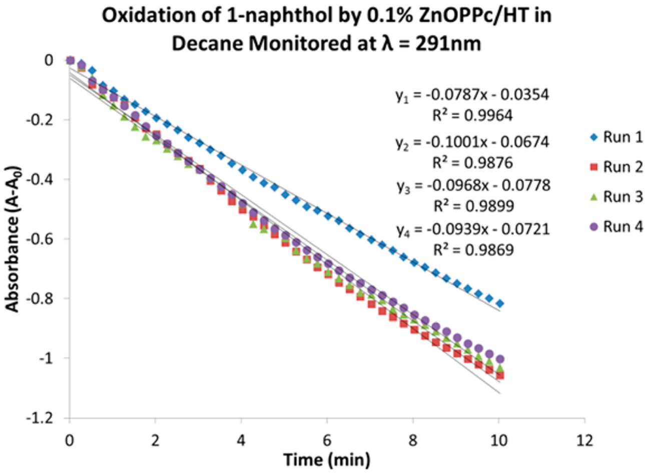
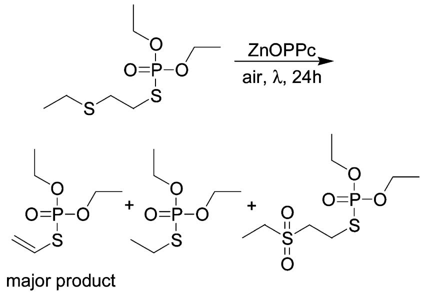


Figure 7. Oxidation of 1-naphthol (5.0×10^{-4} M) by 0.1% ZnOPPc/HT film, monitored at λ = 291 nm, scanned every 30 s, and recycled for three more identical trials.

Surface Decontamination. For the screening of the various films and fibers for the ability to decontaminate CWAs, demeton-S was chosen as a VX simulant.[53] After being exposed to $^1O_2$, demeton-S is oxidized to three main products (Scheme 4), namely, an S-vinyl phosphate (major product), an S-ethyl phosphate, generated via the cleavage of the S−C bond, and the double oxidation of the sulfur atom to form the sulfone. Sulfur oxidation resulting from the presence of $^1O_2$ has been extensively reported by the Clennan group,[54−62] including the oxidation of CWA simulants.[23] Additionally, the Clennan group has reported that this oxidative process can lead to the cleavage of S−C bonds, as observed in this research.[59−62]

Scheme 4. Proposed Oxidation of Demeton-S by $^1O_2$ on the Basis of the GC/MS Results



The initial screening with the ZnOPPc-doped PC surfaces showed good conversion of demeton-S to the S-vinyl phosphate degradation product previously reported for most samples with one exception being for the reaction on 0.1% ZnOPPc/PC fibers from the DCM/DMF mixture (Table 4). Significant amounts of sulfone occurred only for the reactions that had complete conversion. The electrospun fibers from a DCM only solution showed better reactivity than those from DCM/DMF. The reduction of demeton-S and the amount of oxidation products were both higher for the fibers that were electrospun from DCM alone versus the fibers that were electrospun from DCM/DMF. If there is a reaction occurring with the polymer, it will quench the $^1O_2$ before it can oxidize the CWA simulant. Interestingly, the PC fibers performed better than the corresponding films for the 0.5% ZnOPPc loading, but the PC films performed better than the corresponding fibers for the 0.1% ZnOPPc.

Table 4. Reduction of CWA Simulants on Various ZnOPPc-Doped Films and Fibers

surface	substrate	percent reduction
PC film[a]	demeton-S	30
0.1% ZnOPPc-PC film[a]	demeton-S	100
0.5% ZnOPPc-PC film[a]	demeton-S	78
PC film[b]	demeton-S	30
0.1% ZnOPPc-PC film[b]	demeton-S	96
0.5% ZnOPPc-PC film[b]	demeton-S	96
PC fibers[a]	demeton-S	0
0.1% ZnOPPc-PC fibers[a]	demeton-S	86
0.5% ZnOPPc-PC fibers[a]	demeton-S	96
PC fibers[b]	demeton-S	37
0.1% ZnOPPc-PC fibers[b]	demeton-S	34
0.5% ZnOPPc-PC fibers[b]	demeton-S	100
HT film	demeton-S	0
0.1% ZnOPPc-HT film	demeton-S	100
0.5% ZnOPPc-HT film	demeton-S	100
HT fibers	demeton-S	0
0.1% ZnOPPc-HT fibers	demeton-S	30
0.5% ZnOPPc-HT fibers	demeton-S	99
HT film	malathion	1
0.1% ZnOPPc-HT film	malathion	76
0.5% ZnOPPc-HT film	malathion	94
HT film	CEPS	42
0.1% ZnOPPc-HT film	CEPS	76
0.5% ZnOPPc-HT film	CEPS	85
HT film	CEES	59
0.1% ZnOPPc-HT film	CEES	99
0.5% ZnOPPc-HT film	CEES	99

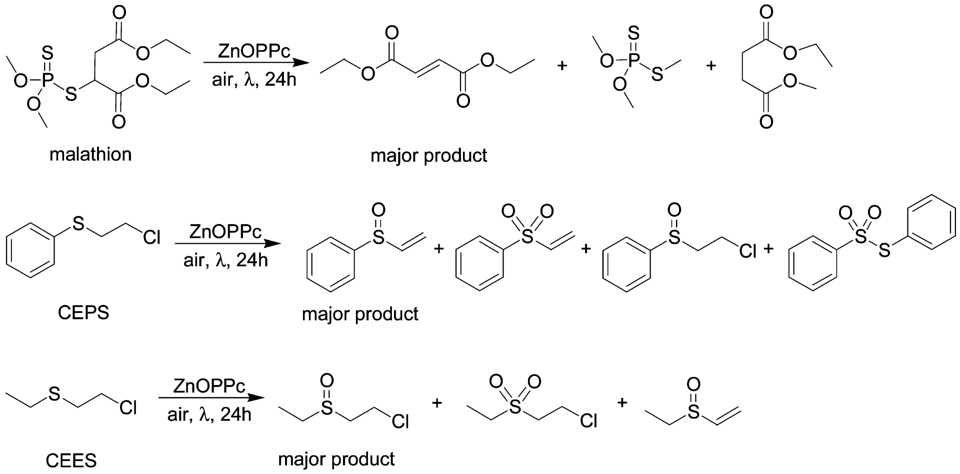
[a] Films and fibers were cast from DCM. [b] Films and fibers were cast from 4:1 DCM/DMF mixture.

The initial screening of the HT surfaces showed complete reaction of demeton-S with large amounts of both oxidation products for the ZnOPPc/HT films tested (Table 4). Unfortunately, the fibers of 0.1% ZnOPPc/HT that were electrospun did not exhibit the same high reactivity, showing only 30% reduction of demeton-S after 24 h of light exposure. The 0 and 0.5% ZnOPPc/HT fibers exhibited the same reactivity as the films. The trend between the fibers and films is the same here for HT as was observed for PC. Although the surface area is much higher for the fibers than the films, the lower activity might be related to an increased rate of photobleaching. The films did not exhibit noticeable photobleaching, whereas the fibers were much lighter in color after 24 h of light exposure. Because the 0.1% ZnOPPc/HT loading has such a small amount of ZnOPPc and the fibers are so small that they appear white initially, the high rate of photobleaching prevents complete oxidation of demeton-S. For the fibers with 0.5% ZnOPPc/HT, a faint green color is still visible after 24 h, and the reaction appears to have been fast enough that complete oxidation of demeton-S occurs before photobleaching becomes a problem.

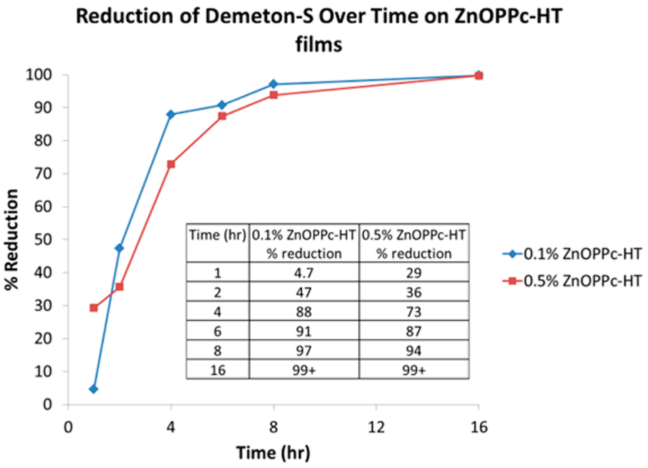
Because of the success of the ZnOPPc/HT films to decontaminate demeton-S, these films were also tested for their ability to decontaminate another VX simulant, malathion, as well as two HD simulants, CEPS (2-chloroethyl phenyl sulfide) and CEES (2-chloroethyl ethyl sulfide).[53] When exposed to $^1O_2$, these compounds are oxidized, as shown in Scheme 5. For malathion, the decontamination was rather efficient for both the 0.1 and 0.5% ZnOPPc/HT films, with 76 and 94% reduction, respectively. Some of this reduction can be attributed to possible trapping by the HT film because there is a reduction of 42% corresponding to the HT film without photosensitizer. All of the proposed oxidation products were also observed in the standard, as malathion purchased commercially contains small amounts of these contaminants. In these reactions, the amount of malathion was reduced, but there was not an increase in the amount of the degradation products compared to the standard. This could be the result of further oxidation of the products into molecules that are too volatile to be detected by solution GC/MS. When CEPS is exposed to $^1O_2$, the sulfur atom is oxidized along with cleavage of the C−Cl bond (Scheme 5). This simulant is less susceptible to oxidation than demeton-S based on the lower reduction of 76 and 85% on 0.1 and 0.5% ZnOPPc/HT films, respectively (Table 4). This compound is very different, chemically, than mustard gas because of the presence of the phenyl ring that reduces the reactivity of the sulfur atom. The simulant CEES is much more chemically similar to mustard gas; however, it is much more volatile (156−157 °C for CEES[63] vs 245−247 °C for CEPS[64]). Under the same conditions, there is 99% reduction for both 0.1 and 0.5% ZnOPPc/HT films (Scheme 5); however, some of this reduction may be due to a loss of simulant in the headspace of the vial. This is supported by the results obtained for HT film samples without any ZnOPPc that showed an apparent CEES reduction by 59%.

Although complete decontamination of demeton-S was observed within a 24 h time period for HT films containing ZnOPPc, the minimum time period required was sought. To elucidate the minimum time required for complete decontamination, a series of films were tested for their ability to oxidize

Scheme 5. Proposed Oxidation Products for CWA Simulants Malathion, CEPS, and CEES by $^1O_2$ on the Basis of the GC/MS Results



demeton-S over 1, 2, 4, 6, 8, and 16 h. Complete oxidation of demeton-S was observed after 16 h, with over 90% being oxidized after only 8 h (Figure 8). The two limiting factors for this reaction appear to be the finite amount of O_2 in the sealed vial (to prevent evaporation of demeton-S) that is being consumed and the continued oxidation of the products that consumes more O_2. Although there is a decrease in the amount of demeton-S when the light exposure is increased, a concomitant increase in the oxidation products was not observed. For the longer reaction times, two new products, vinyl ethyl sulfoxide and vinyl ethyl sulfone, begin to form. These two products result from both S−C bonds breaking and oxidation at the sulfur atom from demeton-S. There may also be other minor oxidation products that were not detected by GC/MS resulting from other bond breaking reactions because there is not a quantitative yield of reaction products. Complete decontamination of demeton-S, however, occurs between 8 and 16 h in this system.



Time (hr)	0.1% ZnOPPc-HT % reduction	0.5% ZnOPPc-HT % reduction
1	4.7	29
2	47	36
4	88	73
6	91	87
8	97	94
16	99+	99+

Figure 8. Reaction of demeton-S on 0.1 and 0.5% ZnOPPc/HT films monitored over time on the basis of the GC/MS results.

GPC and IR Results. To analyze the effect that $^1O_2$ has on the polymer over long exposure times, thin films of PC and HT loaded with 0, 0.1, and 0.5% ZnOPPc were exposed to light for an extended period of time. The films were sampled after 1, 2, 4, 7, and 14 days for analysis by GPC. As evidenced by the absence of any low molecular weight species observed in the chromatograms at extended time periods (see Figures S24−S36), the polymer films were not significantly degraded by exposure to $^1O_2$. Additionally, IR spectra for films before and after light exposure for 24 h showed no change in the absorbance profiles of the polymers (see Figures S37−38). Overall, this shows that using the spontaneous generation of $^1O_2$ from a photosensitizer embedded within a polymeric matrix may be used to decontaminate surfaces after CWA exposure without damaging the surface.

■ CONCLUSIONS

We have shown that the $^1O_2$ generator, ZnOPPc, can be incorporated into films and fibers composed of polycarbonate and Hydrothane and can retain the ability to generate $^1O_2$. Aggregation of the ZnOPPc molecules can be observed by confocal microscopy, although this does not prevent the films and fibers from generating sufficient $^1O_2$ to oxidize 1-naphthol and CWA simulants. Taking advantage of the photosensitizing nature of these films, the chemical decontamination of CWA simulants demeton-S, malathion, CEPS, and CEES was demonstrated through oxidation of these compounds by $^1O_2$. For demeton-S, oxidative decontamination is complete between 8 and 16 h, facilitated by a 250 W halogen lamp. Using $^1O_2$ to decontaminate CWA simulants is an unselective oxidation process that may lead to oxidation of many different substrates and could lead to the oxidation or degradation of the film that contains a photosensitizer. For the matrices studied in this investigation, namely, Hydrothane and polycarbonate coatings, there was no observable degradation or oxidation of the polymers. By converting molecular oxygen found in the air to $^1O_2$, surfaces of ZnOPPc-doped polycarbonate and Hydrothane can self-decontaminate against CWAs without damaging the polymer themselves.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

SEM and Confocal images of ZnOPPc-doped films and fibers of PC and HT, UV−vis spectra, and GPC results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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