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# **Post-Synthetically Elaborated BODIPY-based Porous Organic Polymers (POPs) for Photochemical Detoxification of a Sulfur**

## **Mustard Simulant**

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**ABSTRACT:** Designing new materials for effective detoxification of chemical warfare agents (CWAs) is of current interest given the recent use of CWAs. Although halogenated boron-dipyrromethene derivatives (4,4-difluoro-4-bora-3a,4a-diaza-s-indacene or BDP or BODIPY) at the 2 and 6 positions have been extensively explored as efficient photosensitizers for generating singlet oxygen  $({}^{1}O_{2})$  in homogenous media, their utilization in the design of porous organic polymers (POPs) has remained elusive due to the difficulty of controlling polymerization processes through cross-coupling synthetic pathways. Our approach to overcome these difficulties and prepare halogenated BODIPY-based porous organic polymers (**X-BDP-POP** where X = Br or I) represents an attractive alternative through post-synthetic modification (PSM) of the parent hydrogenated-polymer. Upon synthesis of both the parent polymer, H-BDP-POP, and its post-synthetically modified derivatives, **Br-BDP-POP** and **I-BDP-POP**, the BET surface areas of all POPs have been measured and found to be 640, 430, and 400 m<sup>2</sup>·g<sup>-1</sup>, respectively. In addition, the insertion of heavy halogen atoms at the 2 and 6 positions of the BODIPY unit leads to quenching of fluorescence (both polymer and solution-phase monomer forms) and enhancement of phosphorescence (detectable for polymer form only), as a result of efficient intersystem crossing. The heterogeneous photocatalytic activities of both the parent POP and its derivative for the detoxification of the sulfur mustard simulant, 2-chloroethyl ethyl sulfide (CEES), have been examined; the results show significant enhancement in the generation of the singlet oxygen (<sup>1</sup>O<sub>2</sub>). Both bromination and iodination of **H-BDP-POP** served to shorten by five-fold the Page 3 of 39

time needed for selective and catalytic photo-oxidation of CEES to 2-chloroethyl ethyl sulfoxide (CEESO).

#### INTRODUCTION

Despite bans by the Chemical Weapons Convention (CWC) endorsed in 1993 by the vast majority of the members of the United Nations, the stockpiling and use of chemical warfare agents (CWAs) constitute ongoing global concerns.<sup>1,2</sup> Bis(2-chloroethyl)sulfide, also known as sulfur mustard (HD) was one of the earliest CWAs to be deployed in war-time conflicts. That it is still used by rogue elements is likely a consequence of its low cost and facile production.<sup>1,3,4</sup> Remarkably, and unfortunately, a century after its invention, devising superior methods, materials, and protective equipment for the detoxification of HD is of contemporary relevance. Among the known methods for HD degradation are hydrolysis,<sup>5,6</sup> dehydrohalogenation,<sup>7</sup> and oxidation.<sup>8-12</sup> Two of these methods, hydrolysis and dehydrohalogenation, typically proceed slowly because of the low solubility of HD in water – a problem as well for its less toxic derivative, the CWA simulant 2-chloroethyl ethyl sulfide (CEES).<sup>7,13-17</sup> Stoichiometric and/or catalytic oxidative degradation of HD (or CEES), has been explored using polyoxometalates (POMs).<sup>18,19</sup> peroxides,<sup>20</sup> metal oxides,<sup>11</sup> and enzymes.<sup>21</sup> These oxidants, however, are reportedly non-selective, yielding, in part, doubly-oxygenated sulfone derivatives of HD or CEES. While not as acutely dangerous as HD, the sulfone derivative – unlike the sulfoxide – is highly toxic.<sup>11,21</sup> In contrast, oxidative degradation of HD or CEES via photo-generated singlet oxygen  $({}^{1}O_{2})$  has been shown to proceed with generally faster kinetics and with good to excellent selectivity for the sulfoxide over the sulfone derivative.<sup>22</sup>

Effective heterogenous photocatalysis using  ${}^{1}O_{2}$  is predicated on satisfying two main criteria: (i) efficient photosensitization, and (ii) presentation of sufficient porosity to attain high catalyst surface area (high catalyst exposure to reactants), and to enable rapid diffusive transport of reactants and products to and from catalyst active-sites. In principle, heterogenizing a photocatalyst may allow for ready separation of the catalyst from a reaction mixture while also facilitating reuse and allowing flexibility in solvent selection. Several metal-organic frameworks (MOFs)<sup>23,24</sup> based on various photosensitizers<sup>22,25-29</sup> have been employed to achieve fast and selective detoxification of HD or its simulant CEES; however, these microcrystalline powder materials could present processing challenges for some implementations. Complementary to crystalline MOFs are non-crystalline porous organic polymers (POPs).<sup>30-32</sup> Similar to MOFs, they offer high surface areas and chemical tunability, as well as high chemical and thermal stability. POPs have been explored for myriad applications, ranging from gas adsorption<sup>32</sup> and separation<sup>33</sup> to catalysis.<sup>34,35</sup> The versatile designs,<sup>36</sup> high porosity, and chemical stabilities<sup>37</sup> of these materials are based on the functionalization of their respective building-blocks. In this context, the design of a suitable POP requires the utilization of a building-block that is an efficient singlet-oxygen photosensitizer or is a precursor to one.

The BODIPY core (Figure 1) and its derivatives, with their tunable chemical structures and remarkable photophysical properties,<sup>38</sup> have been examined for candidate applications such as molecular imaging, photocatalysis, and photodynamic therapy (PDT).<sup>39-41</sup> Application of BODIPY as a fluorescent probe requires enhancement of the radiative relaxation pathways from the singlet state. In contrast, the application of BODIPY in photodynamic therapy requires favorable relaxation pathways through

intersystem crossing (ISC) to enhance yields of the triplet excited state, *i.e.* very much the same as required for effective photocatalytic oxidative degradation of CWAs. Thus, lessons learned from the design of BODIPY-based chromophores for PDT can be co-opted. Chromophore functionalization with heavier halogens engenders ISC via the enhanced spin-orbit coupling.<sup>42</sup> Given suitable energy-matching, the triplet excited state of BODIPY can sensitize the otherwise forbidden conversion of ground-state triplet oxygen (<sup>3</sup>O<sub>2</sub>) to electronically excited and chemically reactive <sup>1</sup>O<sub>2</sub>.<sup>42,43</sup> Although halogenated versions of BODIPY have been used in homogenous media as photochemical sensitizers for <sup>1</sup>O<sub>2</sub> formation, their application as heterogenized sensitizers remains relatively unexplored.

The development of versatile chemical structures of BODIPY requires molecular engineering at the different ring positions to access BODIPY-based polymers. Notably, numerous syntheses of non-porous 2D linear polymers via functionalization of the (2,6), (3,5) or 8 (*meso*) positions (Figure 1) of BODIPY have been described.<sup>44-58</sup> Among these studies, Chujo *et al.* showed that highly emissive nonporous BODIPY-based polymers can be obtained by replacing the boron's fluorine atoms with phenylethynyl groups using chemistry elaborated by Ziessel *et al.*<sup>59,60</sup> In contrast, examples of BODIPY-based porous organic polymers (POPs) are comparatively scarce. Among the examples are BODIPY POPs designed for iodine capture,<sup>61</sup> lithium-ion storage,<sup>62</sup> and photocatalysis.<sup>63-65</sup> Both polymerization of tridentate aryl co-monomers and of BODIPY core (Figure 1) functionalized at its 2 and 6 positions are reported to have been carried out via Sonogashira<sup>63,64</sup> or Suziki<sup>65</sup> coupling to generate conjugated porous polymers as candidate photocatalysts. Studies of the photocatalytic performance of BODIPY-based POPs, in

particular, showed that full conversion of thioanisole to methylphenyl sulfoxide is comparatively slow, evidently due to aggregation of the chromophores.

An important consideration from an in-field application perspective is the rate of photocatalytic degradation of the chemical threat. To enhance photodegradation rates, iodo-BODIPY, in molecular form, has previously been noncovalently doped<sup>26</sup> into non-porous polymeric matrices to yield a photosensitizer for oxidative degradation of HD and CEES by <sup>1</sup>O<sub>2</sub>. While the doped material yielded reasonably fast reaction rates, problems attributable to dopant (sensitizer) aggregation and leaching were evident. A redesign of BODIPY-based POPs ideally would: a) make use of halogenated-BODIPY chromophores to enhance intersystem crossing yields oxygen, b) employ a polymerization scheme capable of yielding good porosity and, therefore, good reactant accessibility, and c) employ a polymerization scheme that disfavors chromophore aggregation. Unfortunately, the preparation of halogenated-BODIPY POPs from prehalogenated-BODIPY monomers, using carbon-carbon coupling reactions, such as Sonogashira,<sup>66</sup> Yamamoto,<sup>67</sup> and Suzuki,<sup>68</sup> may induce uncontrolled polymerization and dehalogenation of the BODIPY center. We reasoned, however, that post-synthetic modification (PSM) – which has recently drawn attention with respect to evolving pristine polymers into more functional materials for specific applications, such as metal removal,  $^{69,70}$  energy conversion,  $^{71,72}$  and gas adsorption  $^{73-75}$  – might be an excellent tool for the insertion of needed halogen atoms on pre-formed BODIPY-containing POPs. In the present article, we report a new BODIPY-based monomer (H-BDP-M) featuring multiple polymerizing groups (two extending from the boron, and one from the meso position of the BODIPY core

(Scheme 1), leaving the 2 and 6 positions of BODIPY accessible for post-synthetic halogenation. The

polymerization of this new monomer produces the parent POP (**H-BDP-POP**), which is only subsequently halogenated to produce desired daughter POPs (**Br-** and **I-BDP-POPs**). Gas adsorption studies have been undertaken to unravel the porosity characteristics of each POP, while the activity and selectivity of both the parent and daughter materials as heterogeneous photocatalysts for the detoxification of a sulfur mustard simulant have been investigated. Furthermore, optical absorption and luminescence studies have been undertaken to establish/confirm the basis for the high activity of the halogenated-BODIPY POPs.

#### RESULTS AND DISCUSSION

**Molecular Design, Synthesis, and Structural Characterization.** The novel and stable conjugated porous organic polymers (**H-**, **Br-**, and **I-BDP-POPs**) and their respective monomers (**H-**, **Br-**, and **I-BDP-M**s) were synthesized via a multistep synthetic pathway. See Supporting Information, Section B and Scheme S1. The general synthetic routes and chemical structures of monomers and polymers are shown in Schemes 1 and 2, respectively. To access the porous organic polymers (POPs), we employed a BODIPY-based monomer (**H-BDP-M**) elaborated with three brominated phenyl units, one connected to the *meso*-carbon, and the other two to the boron atom through ethynyl units. Once **Br-Ph-BODIPY** was available, the parent monomer **H-BDP-M** was prepared according to a previous literature procedure<sup>76</sup> with slight modifications (84% isolated yield). See Supporting Information. The other two monomers, **Br-** and **I-BDP-M**, were synthesized<sup>77-79</sup> (Scheme 2) by bromination and iodination of **H-BDP-M** with *N*-bromosuccinimide (NBS) and *N*-iodosuccinimide (NIS), respectively. The molecular structural characterization of all three monomers was confirmed

(Figures S1–S8) by <sup>1</sup>H and <sup>13</sup>C (decoupled mode) nuclear magnetic resonance (NMR) spectroscopy. The structures of **H-**, **Br-**, and **I-BDP-M**s were determined (Table S1, Figures S9-11) by singlecrystal X-ray analysis. According to the crystal structures of the monomers, the BODIPY moieties are distant from each other, indicating that the three substituents connected to the chromophore through the boron atom and the *meso* position of BODIPY are sufficiently bulky to prevent chromophore [ $\pi$ ... $\pi$ ] stacking.

Sonagoshira coupling was used to convert the monomer, **H-BDP-M**, to the parent BODIPY-based POP, **H-BDP-POP**. Optimization of the reaction temperature (~90 °C) and the solvent (dimethylformamide (DMF)) led to an isolated yield of 90%. The polymer was then modified by either bromination or iodination creating the daughter polymers, **Br-** and **I-BDP-POP**s.

Polymer formation was confirmed, in part, by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The stacked spectra (Figure 2) demonstrate the emergence of a carbon-carbon triple bond (C–C=C–C) between **H-BDP-M** and 1,4-bis(ethynyl)benzene, with a stretching frequency (Figure S20) of ~2211 cm<sup>-1</sup>. This value is in good agreement with reported stretching frequencies<sup>62,64</sup> for C=C bonds in similar chemical environments. Polymer structures were further confirmed by solid-state <sup>13</sup>C NMR (Figure S21). The signals at 81.5 and 85.9 ppm arising from the carbons (H–C= and =C–C, respectively) of 1,4-diehynylbenzene were shifted downfield from their original places after the carbon-coupling reaction with **H-BDP-M** monomer.

With the aims of further corroborating (or not) the formation of polymers and of confirming their indicated that **H-**, **Br-**, and **I-BDP-POP**s are stable toward mass loss up to 300, 245, 215 °C,

respectively. Powder X-ray diffraction (PXRD) measurements (Figure S22) confirmed that the polymers are amorphous. The post-synthetic halogenations of **H-BDP-POP** to form **Br-** and **I-BDP-POPs** were confirmed by X-ray photoelectron spectroscopy (XPS), percentages of bromine and iodine atoms in **Br-BDP-POP** and **I-BDP-POP**s, respectively, were approximately equal to atomic % of nitrogen (Table S3) in each polymer. This indicates two halogen atoms were inserted on a BODIPY core. Scanning electron microscopy (SEM) images (Figure 3) showed that the parent polymer forms aggregates of micron and sub-micron size particles, and neither bromination nor iodination changes the polymer particle/aggregate morphology. According to energy dispersive spectroscopy (EDS), the post-modification of the pristine polymer led to homogeneous distributions of bromine and iodine atoms over the desired polymers (Figure S24). Dynamic light scattering studies showed the average colloidal particle diameters of polymers to be approximately 600, 1000, and 2000 nm (Figure S28) for H, Br, and I-BDP-POPs, respectively. Zeta-potential distributions of polymers (Figure S27) show that the pristine polymer particles have nearly neutral zeta-potential, while zeta-potentials of **Br**- and **I-BDP-POPs** are +38 and +43 mV, respectively. These results imply that post-synthetic halogenation of H-BDP-POP improves the dispersity of resultant polymers, which provides better sedimentation stability and solid loading capacity for halogenated POPs compared to H-BDP-POP.

**Gas Sorption and Surface Area Measurements.** The obtained nitrogen sorption measurements at 77 K (Figure 4A) yield Type I isotherms with hysteresis, as defined by the International Union of Pure and Applied Chemistry (IUPAC).<sup>80</sup> The steep uptake at low pressures indicates the presence of

micropores while the subsequent more gradual increase points to the presence of larger pores in all polymers. The hysteresis in the isotherms is tentatively ascribed to the swelling of polymer with increasing pressure as commonly observed in POPs, and to slow kinetics for N<sub>2</sub> uptake at 90 K.<sup>81</sup> The Brunauer-Emmett-Teller (BET) surface areas of **H**-, **Br**-, and **I-BDP-POP**s are 640, 430, and 400 m<sup>2</sup>·g<sup>-1</sup>, respectively. The decreases with halogenation are consequences of the mass contributed by the halogen atoms, and perhaps also blocking of small apertures by these larger atoms. Non-local density functional theory (NLDFT)-based pore size distributions (Figure 4B) indicate that post-synthetic halogenation diminishes the pore widths of the resulting polymers.

**Optical Studies.** UV-Vis absorption and fluorescence spectroscopies of all monomers were carried out to investigate the effect of the halogen substituents at the 2 and 6 positions of the BODIPY unit, and all obtained data are summarized in Table 1. The solutions of **H**-, **Br**-, and **I-BDP-M**s, all at 2.5 x 10<sup>-6</sup> M in CH<sub>2</sub>Cl<sub>2</sub>, were prepared. The UV-Vis absorption spectrum for **H-BDP-M** (Figure 5) displays a maximum at 502 nm, which is slightly red-shifted for **Br-BDP-M** (526 nm) and **I-BDP-M** (532 nm). These data imply that substituents at the 2 and 6 positions directly influence the energies of the frontier orbitals of the BODIPY moiety. The parent monomer, **H-BDP-M**, fluoresces strongly (40% quantum yield (QY) in glassy MeTHF under Ar atmosphere) with a spectral maximum at 513 nm in CH<sub>2</sub>Cl<sub>2</sub>. As illustrated in Figure 5 (right) and Table 1, the halogenated-monomers, **Br-** and **I-BDP-M**s, are much less efficient fluorophores. See Supporting Information, Figure S15 for emission/excitation spectra of BODIPY monomers in glassy MeTHF at 77 and 298 K. The decreased fluorescence QYs are consequences of halogen-induced enhancement (spin-orbit

coupling induced enhancement) of intersystem crossing from the initially formed singlet

photoexcited state to the lowest triplet excited state. (Recall that the strength of spin-orbit coupling within a given atom scales as the fourth power of the effective nuclear charge.<sup>82</sup>) Figure 6 (left) shows the combined UV-Vis diffuse reflectance spectra. The reflectance spectrum maxima for H- (489 nm), Br- (507 nm), and I-BDP-POPs (520 nm) are reasonably similar to the absorption maxima of the corresponding monomers. The room-temperature fluorescence behaviors (*i.e.*, emission maximum, QY, and singlet excited-state lifetime) of the series of polymers (Table 1) are parallel to those of the monomeric model chromophores and match expectations based on changes in intersystem crossing yield. Furthermore, no excimer formation was observed in the fluorescence spectra of polymers. This implies the absence of aggregation among the BODIPY units of the polymers. The excitation spectra (Figure S16) establish that energy can be transferred from photoexcited phenyl-alkyne units to the emissive singlet excited state of the BODIPY unit. Lowering the temperature to 77 K unveils detectable phosphorescence from **Br**- and **I-BDP-POP**s (and the corresponding monomers in glassy MeTHF) with phosphorescence being more prominent for the iodo versions. Figure 7 shows the excitation and emission spectra of **I-BDP-M** and **I-BDP**-**POPs** at 77 K. See Supporting Information for further details. Both the monomer and polymer emission spectra show far-red peaks attributable to phosphorescence. The phosphorescence intensity maximum is at  $\lambda = 759$  nm (E<sub>em(phos)</sub> = 13,120 cm<sup>-1</sup>). This, within the experimental uncertainty, is nearly an exact match for the energy of the forbidden  ${}^{3}\Sigma_{g}^{-}$  ground-state to  ${}^{1}\Sigma_{g}^{+}$  excited-state transition in the absorption spectrum of ground-state triplet oxygen, *i.e.* the transition that imparts to liquid  $O_2$  its characteristic pale blue color. Taken into consideration together with the evidence for high intersystem crossing yield, the energy match by **I-BDP-POP** points to the likelihood of unusually efficient sensitized singlet oxygen formation.

Density Functional Theory (DFT) Calculations. The DFT calculations (Figure 8 and Table 2) on geometry-optimized molecular structures of all monomers qualitatively reproduced experimental variations in HOMO–LUMO energy gaps ( $\Delta E$ ). The structures of H-, Br-, and I-BDP-Ms were geometry-optimized at the B3LYP/3–21G<sup>\*+</sup> energy level using Jaguar software.<sup>83</sup> The gas-phase DFT calculations (Figure 8 and Table 2) on these geometry-optimized molecular structures showed that both the HOMO and the LUMO are localized on BODIPY unit with no significant participation of the alkyne substituent, whereas the HOMO–1 and LUMO+1 are exclusively based on the alkyne substituents (Figure S26) at the *meso* and 4 positions of BODIPY core. Therefore, the HOMO-LUMO energy gap should be comparatively insensitive to chromophore polymerization via Scheme 2. Although halogenation at the 2 and 6 positions leads to stabilization of the HOMO and LUMO orbitals, the HOMO-LUMO energy gap ( $\Delta E$ ) differs only very slightly as a function of derivatization. For all compounds the energy gap between the HOMO-1 and LUMO+1 is substantially greater (> 4.5 eV) than the HOMO–LUMO gap between ( $\leq$ 3.0 eV), implying that the visible-region photosensitization entails electronic excitation exclusively for the BODIPY units, with no significant participation by the alkyne substituents.

The absorption spectra (Figure S14a) of the **H-**, **Br-** and **I-BDP-M**s revealed major bands at ~500 nm and ~250 nm associated with  $\pi \rightarrow \pi^*$  transitions in the BODIPY and alkyne moieties,

respectively. Therefore, the optical band gaps are estimated to be approximately 2.36, 2.23, and 2.21 eV for the BODIPY moieties of the H-, Br-, and I-BDP-Ms, while the alkyne substituents for three monomers have approximately 4.2 eV of the optical bandgap. These results are consistent with the gas phase DFT calculations which have shown that the HOMO $\rightarrow$ LUMO gap is associated with the BODIPY moiety and is ~3 eV, while the HOMO–1  $\rightarrow$ LUMO+1 gap of > 4 eV is associated to the alkyne moieties. Therefore, for excitation approximately at 2.36 eV (525 nm), the photosensitizing properties arise exclusively from the BDP moiety while the alkyne substituents have a structural role.

**Photosensitized Catalysis.** Figure 9A presents reaction rate data (in the form of plots of conversion vs. time) for photosensitized degradation of CEES by <sup>1</sup>O<sub>2</sub>, where the degradation yields exclusively CEESO (confirmed by <sup>1</sup>H and <sup>13</sup>C NMR data, see Supporting Information, Figures S31 and S32). A schematic representation of a plausible mechanism<sup>29,84</sup> for the formation of CEESO (the desired sulfoxide product) in preference to CEESO<sub>2</sub> (the much less desirable sulfone product) is presented in Figure 9B. **Br-BDP-POP** and **I-BDP-POP** behave essentially performed identical, yielding conversion half-lives of about 3 min. In contrast, the conversion half-life with **H-BDP-POP** as the photocatalyst is 17 min. Similar, but slightly faster catalysis, was observed with the model monomer catalysts, *i.e.* reaction half-lives of 2 min with **Br-** or **I-BDP-M**s as the photocatalyst and ~9 min with **H-BDP-M**.

Catalyst reusability (Figure 9C) was examined over four reaction cycles. During each cycle, samples were irradiated for 11 min, and then the same amount of fresh CEES was added to each reaction

vessel (without removal of the product from the previous cycle(s)). For neither halogenated polymer was a significant decrease in catalytic efficacy detected. When the reaction time was extended to 55 min, the photooxidation of CEES showed an accumulation of monooxygenated-sulfoxide (CEESO) product; no detectable over-oxidation to the toxic sulfone (CEESO<sub>2</sub>) was observed (Figure S34) in the NMR spectra.

The halogenated-POPs were further investigated by solution screening (using UV-Vis absorption spectroscopy) for chromophore leaching (Figure S37); none was detected. The combined results are consistent with efficient excited-state intersystem crossing for the halogenated-photocatalysts, and efficient sensitization of singlet oxygen formation by these catalysts in their lowest-lying triplet excited states.

Thioanisole is one of the most common model compounds used to gauge and compare the photoactivity of catalysts.<sup>85</sup> Results for photooxidation of thioanisole under various conditions are shown in Table S4. Little conversion of thioanisole was observed in the absence of irradiation or catalyst (**I-BDP-POP**). The addition of candidate scavengers for reactive oxygen species (ROS) such as NaN<sub>3</sub> (as <sup>1</sup>O<sub>2</sub> scavenger) and benzoquinone (as superoxide scavenger) led to significant decreases in the conversion yield of thioanisole under irradiation. However, no benzoquinone conversion was observed, implying that superoxide is not generated. Furthermore, direct quenching of photo-excited **I-BDP-POP** by azide can't be ruled out. The addition of NaI (as a hole scavenger) diminishes conversion, but by less than other scavengers. These results suggest that the candidate ROS scavengers used here primarily function not by scavenging, but instead by quenching photo-

excited **I-BDP-POP** and thereby suppressing ROS generation.<sup>86</sup> We turned, therefore, to the wellknown singlet oxygen probe 1,3-diphenylisobenzofuran<sup>87</sup> (DPBF), which decomposes to its peroxo derivative upon reaction with singlet oxygen.<sup>88</sup> Monitoring the electronic absorption of the probe molecule (Figure S29), revealed that irradiation of the catalysts **Br**- and **I-BDP-POP**s generates singlet oxygen. See Supporting Information for further details and discussion.

Full conversion of thioanisole to methyl phenyl sulfoxide (under 1 bar of air) by four representative BODIPY-containing porous photocatalysts from the extant literature (Table 3, Entries 2–5) reportedly requires 15 h or more. In contrast with **I-BDP-POP** as the photocatalyst under identical conditions to those for the conversion of CEES to CEESO, the half-life was found to be about 9 min. Complete conversion to methyl phenyl sulfoxide (Figure S36) was observed to occur in ~20 min. When the same reaction was examined under air, the half-life for thioanisole oxidation (Table 3) was approximately 16 min; full conversion was achieved in *ca.* 30 min.<sup>89</sup>

#### CONCLUSION

A BODIPY-based porous organic polymer (**H-BDP-POP**), having a substantial BET surface area  $(640 \text{ m}^2 \cdot \text{g}^{-1})$ , can be obtained in *ca*. 90% yield via Sonogashira coupling, and bromine loss from a derivative of BODIPY (**H-BDP-M**) featuring a pair of bromophenyl ethynyl substituents on boron and a single bromophenyl substituent at the *meso*-carbon of **H-BDP-M**. Notably, coupling at these sites is remote enough from the HOMO and LUMO to leave both orbitals largely unchanged by polymerization while the linkage scheme serves to prevent stacking/aggregating of the POPs' component chromophores. Post-synthetic bromination or iodination at the 2 and 6 positions of the

BODIPY core of **H-BDP-POP** yields polymers that display the signatures of efficient photo-excitedstate singlet to excited-state triplet intersystem crossing, including greatly attenuated fluorescence quantum yields, abbreviated singlet excited-state lifetimes, and low-temperature phosphorescence based on indirect photo-excitation, *i.e.*, initial excitation to singlet states. From measurements at 77 K, we find the energy for phosphorescence by **I-BDP-POP** (13,120 cm<sup>-1</sup>) is essentially a perfect match for the energy gap between ground-state triplet O<sub>2</sub> and the higher of two singlet O<sub>2</sub> excitedstates.

When illuminated under an  $O_2$  atmosphere, the POPs catalyze the oxidation of CEES to CEESO in MeOH. Consistent with enhanced intersystem crossing and photochemical sensitization of the otherwise forbidden conversion of  ${}^{3}O_{2}$  to  ${}^{1}O_{2}$ , the bromine- and iodine-elaborated derivatives of BODIPY-based POPs (**Br**- and **I-BDP-POPs**) accomplish the conversion *ca*. 5x faster than does the unelaborated polymer. The three new BODIPY-based POPs are quantitatively selective for the conversion of the sulfur mustard simulant to the sulfoxide, and not to the toxic sulfone. Given the ease and synthetic simplicity with which these promising photocatalytic polymers can be synthetically accessed, we suggest that they merit further investigation at higher technology readiness levels (TRLs).

#### EXPERIMENTAL

All materials, methods, and instrumentation as well as experimental details, including synthesis, NMR data, and supportive figures have been described in the Supporting Information.

#### ASSOCIATED CONTENT

## **Supporting Information**

Materials / General Methods / Instrumentation, Synthetic Protocols, NMR Spectroscopy, Crystallographic Characterization, N<sub>2</sub> Adsorption, and Desorption Isotherms, Photophysical Characterization, Diffuse Reflectance for Infrared Fourier Transform Spectroscopy (DRIFTS), Powder X-Ray Diffraction (PXRD), Thermogravimetric Analysis (TGA), X-Ray Photoelectron Spectroscopy (XPS), Density Functional Theory (DFT) Calculations, Photocatalytic Studies. This material is available free of charge through the Internet at <u>http://pubs.acs.org</u>.

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## Notes

The authors declare no competing financial interest.

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## **Captions to Schemes and Figures**

**Scheme 1.** Structure and design of **H-BDP-POP** using tritopic BODIPY monomer (**H-BDP-M**), and its halogenation through post-synthetic modification (PSM).

Scheme 2. Synthetic routes for the halogenation of H-BDP-M to Br- and I-BDP-Ms, polymerization of H-BDP-M to H-BDP-POP, and post-synthetic halogenation of H-BDP-POP to Br- and I-BDP-POPs.

**Figure 1.** Reported polymerization of BODIPY core at different positions for the synthesis of BODIPY-based polymers

**Figure 2.** Diffuse reflectance for infrared Fourier transform spectroscopy (DRIFTS) absorption spectra of the parent monomer and all the POPs.

Figure 3. Scanning electron microscopy (SEM) images of all the POPs.

**Figure 4.** Nitrogen sorption isotherms (a) of BDP-POPs at 77 K (filled shapes for adsorption, and hollow shapes for desorption). Estimated pore-size distribution profiles (b) using the 2D–NLDFT (N2–carbon finite pores, As = 6) method.

**Figure 5.** UV-Vis absorbance and fluorescence emission spectra of H-, Br-, and I-BDP-Ms (2.5  $\mu$ M) in CH<sub>2</sub>Cl<sub>2</sub> at RT under air.

**Figure 6.** UV-Vis diffuse-reflectance (left) and emission spectra (right) for H-, Br-, and I-BDP-POPs at 298 K.

Figure 7. Excitation and emission spectra of I-BDP-M (left) and I-BDP-POP (right) at 77 K.

**Figure 8.** Frontier molecular orbital distribution and energy levels of **H**- (in white), **Br**- (in red), and **I**- (in pink) **BDP-POP**s from density functional theory (DFT) calculations.

**Figure 9.** (a) Comparison of CEES oxidation over time with equimolar BODIPY-based monomers and porous organic polymers. (b) A plausible schematic representation of sulfur mustard simulant oxidation by singlet oxygen. (c) Reusability of the **Br-** and **I-BDP-POP** catalysts for four cycles, 11 min each. All experiments above were performed in 1mL of anhydrous MeOH under 1 atm  $O_2$ by using 1mol% catalyst irradiated with two green LEDs (total power of 450 mW·cm<sup>-2</sup>).









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Figure 3

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Figure 7





**Table 1.** Comparison of photophysical properties of BDP monomers and polymers in glassy MeTHF under Ar atmosphere.

Sample	Abs. λ <sub>max</sub> (nm)	Emission λ <sub>max</sub> (nm)	Abs. Coeff. (ε) (x10 <sup>5</sup> M•cm <sup>-1</sup> )	S1 Lifetime at RT (ns) [Amplitude]	λ <sub>ex</sub> (nm)	Total QY (%)	BDP Centered (485-700 nm) S <sub>1</sub> QY (%)	S1 (%) / Total (%)
H-BDP-M	502*	513*, 522	1.54*	5.3 [~100%]	490	-	40	-
Br-BDP-M	526*	538*, 546	1.97*	1.2 [96.5%]	515	-	7.7	-
I-BDP-M	532*	540*, 560	1.44*	0.2 [100%]	490	-	1.5	-
H-BDP POP	490	514	-	2.4 [100%]	340	3.4	1.2	35.7%
<b>Br-BDP POP</b>	505	542	-	1.2 [100%]	340	1.5	0.37	25.3%
I-BDP POP	520	552	-	0.2 [84.6%] 2.0 [15.4%]	350	0.52	0.08	15.4%

\*in CH<sub>2</sub>Cl<sub>2</sub> and at ambient condition.

Table 2. HOMO-LUMO energy levels of H-, Br-, and I-BDP-Ms calculated by dens	sity
functional theory (DFT).	

	Е <sub>номо</sub>	E <sub>HOMO-1</sub>	E <sub>lumo</sub>	E <sub>lumo+1</sub>	$\Delta E_{HOMO-LUMO}$
H-BDP-M	-5.79	-6.14	-2.78	-1.35	-3.01
Br-BDP-M	-5.99	-6.29	-3.10	-1.49	-2.90
I-BDP-M	-5.96	-6.27	-3.08	-1.47	-2.88

**Table 3.** Comparison of porous polymer catalysts with respect to the full conversion of<br/>thioanisole to methylphenyl sulfoxide.



Entry	Catalyst <sup>a</sup>	Solvent	Cat. mol%	Radiant Power	Conv. (%)	Time	
1	I-BDP-POP	MeOH	1	450 mW	99	0.5 h	
264	BDT1b	MeCN	1 (w %)	150 W	96	24 h	
358	PHP-5	МеОН	0.5	24 W	50	24 h	
465	CMPBDP	2-EE	0.1	100 W	99	24 h	
5 <sup>46</sup>	Iodic-BODIPY- PolyHIPE	МеОН	0.5	24 W	99	15 h	

<sup>a</sup>Catalysts 2, 3, 4 and 5 were listed as their given names in the references.

## **Table of Contents Graphic**

