

## Reduced Photobleaching of Conjugated Polymer Films through Small Molecule Additives

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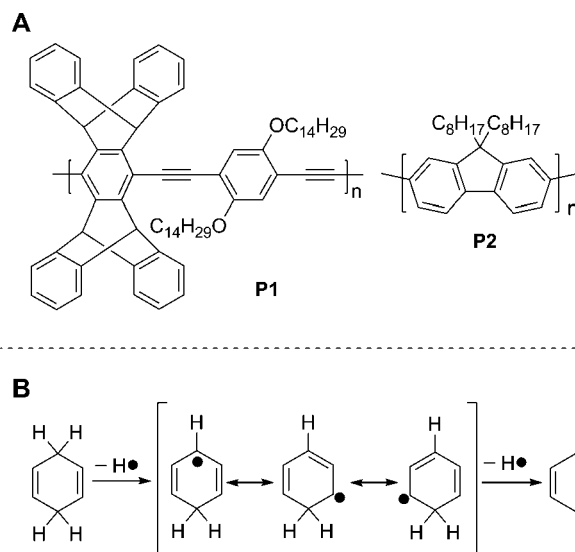
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**Introduction.** The photobleaching, or reduction in fluorescence quantum yield, of fluorescent dyes upon continuous excitation is a commonly encountered problem.<sup>1</sup> The mechanism of photobleaching in fluorescent dyes has been shown to be complex, sensitive to environmental and excitation conditions, and specific to each dye.<sup>2</sup> Nevertheless, two primary pathways are invoked to explain the photodegradation of fluorophores.<sup>3</sup> In the first pathway, fluorophores are degraded by reaction with singlet oxygen, which is produced by sensitization of ground-state triplet oxygen by a small population of triplet-state fluorophores.<sup>4</sup> The second pathway involves reactive radical intermediates formed by the photoionization of fluorophores upon excitation to the first or higher excited electronic states in a polar environment.<sup>5</sup>

Photobleaching is observed in most fluorescent conjugated polymers (CPs), such as poly(phenylene)s (PPs),<sup>6</sup> poly(*p*-phenylenevinylene)s (PPVs),<sup>7</sup> and poly(*p*-phenylene ethynylene)s (PPEs),<sup>8</sup> in both solution and the solid state. In such polymeric systems, photooxidation of a few repeat units can create nonemissive traps capable of quenching any excitons formed in the polymer and, thus, decreasing its fluorescence quantum yield over time. This effect is most important in thin films wherein energy migration to nonemissive traps is most efficient.

Approaches to retard the photobleaching of fluorophores usually entail the introduction of small molecule additives (via either an admixture or a covalent linkage) specifically designed to counter one or both of the degradation pathways mentioned earlier. For example, antioxidants, such as ascorbic acid,<sup>3d,9</sup> *n*-propyl gallate,<sup>10</sup>  $\beta$ -mercaptoethanol,<sup>3d,11</sup> and cysteine hydrochloride,<sup>12</sup> are employed to trap reactive radicals in fluorophore solutions. Triplet quenchers, such as cyclooctatetraene (COT),<sup>3a,13</sup> mercaptoethylamine,<sup>3a</sup> and *trans*-stilbene (TS),<sup>3b,14</sup> are used to rapidly deactivate the triplet excited-state of fluorophores, which can otherwise sensitize the formation of singlet oxygen by energy (or electron) transfer to triplet oxygen. Tertiary amines,<sup>15</sup> especially 1,4-diazabicyclo[2.2.2]octane (DABCO),<sup>16</sup> are employed as singlet oxygen quenchers in solution. In this case, singlet oxygen formation is not inhibited, but the added DABCO is proposed to regenerate unreactive triplet oxygen from singlet oxygen via reversible electron transfer.

Surprisingly, the utility of such additives in curbing the photobleaching of CPs has not been thoroughly investigated. Since CPs find application in a variety of devices, for example, organic light-emitting diodes,<sup>17</sup> solar cells,<sup>18</sup> and optically pumped lasers,<sup>19</sup> and as fluorescent sensors for a wide array of analytes,<sup>20</sup> retarding photooxidation processes in these polymers is a topic of significant interest. Herein we investigate the effect



**Figure 1.** (A) Structures of the fluorescent polymers used in this work. (B) General approach for the design of antioxidants.

of added antioxidants and triplet quenchers on the photostabilities of thin films of a pentiptycene-containing PPE, **P1**, and poly(9,9-dioctylfluorene), **P2** (Figure 1A). The rational design and synthesis of antioxidants and triplet quenchers that are compatible with conjugated polymer films are also presented.

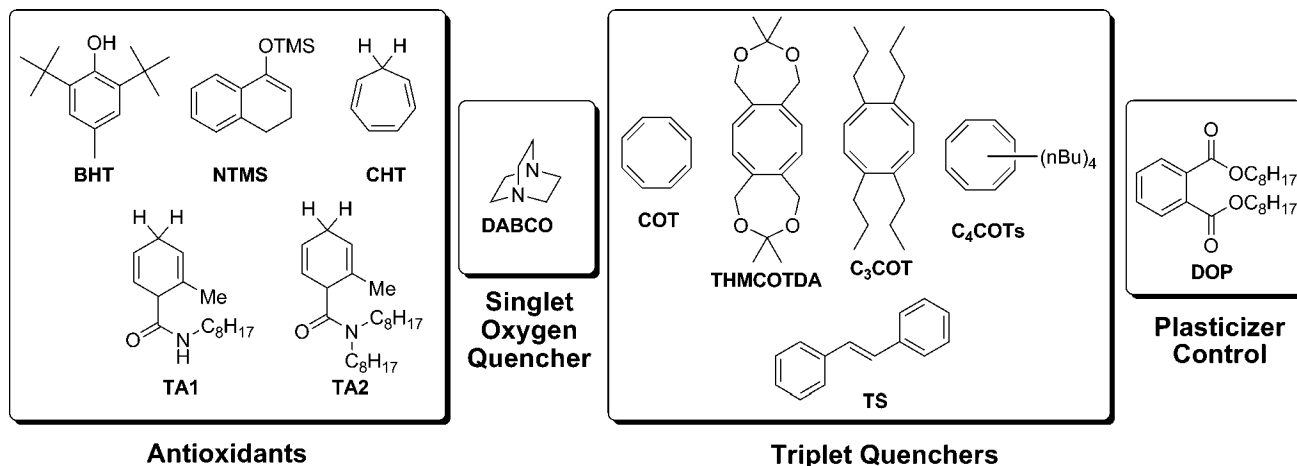
**Results and Discussion. Additive Design.** In choosing antioxidants to use with thin films of **P1** and **P2**, a major consideration is the solubility of the additives in the polymers, since phase separation of the additives will preclude any beneficial effects. Ascorbic acid and *n*-propyl gallate were not acceptable additives as they were insoluble in the PPE matrix; similarly, polar  $\beta$ -mercaptoethanol and ionic cysteine hydrochloride are not expected to be soluble in either **P1** or **P2**. Additionally, the oxidized form of the antioxidant, or the product of any reaction with reactive radicals, must not quench the fluorescence of **P1** or **P2**.

Adhering to these prescriptions, we proposed using a 1,4-dihydrobenzene moiety (Figure 1B) as the active component in antioxidants. 1,4-Dihydrobenzenes are predicted to quench any reactive radicals by liberating up to two hydrogen atoms (H<sup>•</sup>), and the benzene thus produced will not quench the fluorescence of a conjugated polymer film. In addition, 2,6-di-*tert*-butyl-*p*-cresol (**BHT**) and cycloheptatriene (**CHT**) were also investigated as antioxidant stabilizers. It was anticipated that both the aryloxy radical and the tropylium cation generated by oxidation of **BHT** and **CHT**, respectively, will not quench the fluorescence of the polymers investigated.

To minimize the detrimental effects of singlet oxygen, a variety of COTs, including COT itself, and *trans*-stilbene (**TS**) were investigated as potential triplet quenchers. Since COT is volatile and does not exhibit thermal stability, some alkylated derivatives were synthesized to counter the evaporation of COT from thin films of **P1** and **P2**. Furthermore, the use of **DABCO** as a singlet oxygen quencher was also investigated.

The effects of the aforementioned additives on the emission intensities of **P1** and **P2** were compared against those of dioctyl phthalate (**DOP**), a common plasticizer, to confirm that any observed photostability does not arise from simple plasticization.

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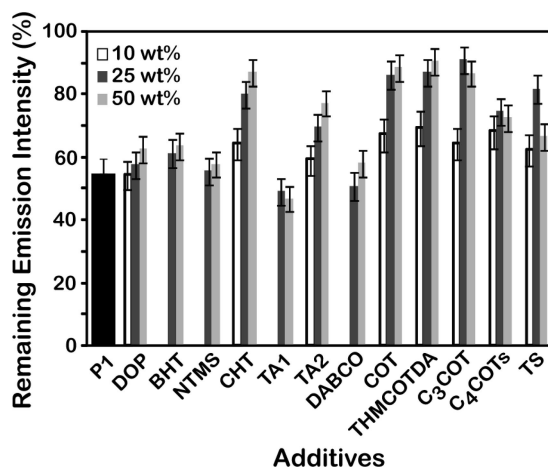


**Figure 2.** Structures of the small molecule additives investigated in this work.

**Synthesis.** Additives **BHT**, **NTMS**, **CHT**, **DABCO**, and **COT** and the dioctyl phthalate (**DOP**) plasticizer control (Figure 2) are commercially available. 1,4-Dihydro-*o*-toluamide additives **TA1** and **TA2** were synthesized in one-pot with 83% and 73% yields, respectively, from commercially available 1,4-dihydro-*o*-toluic acid via the acyl chloride (see Supporting Information). As previously reported, **THMCOTDA** was synthesized by a nickel(0)-catalyzed cyclo-tetramerization of propargyl alcohol and the isomer shown in Figure 2 isolated by formation of a diacetone.<sup>21</sup> **C<sub>3</sub>COT** was synthesized from **THMCOTDA** in three steps with 24% overall yield (see Supporting Information). Additionally, 1-hexyne was subjected to nickel(0)-catalyzed cyclization conditions to yield a mixture of four tetrabutyl-COT isomers (**C<sub>4</sub>COTs**, 82% by GC-MS analysis) and three tributylbenzene isomers (18%). The tetrabutyl-COT isomers could not be satisfactorily isolated from the cyclotrimers by column chromatography or separated by vacuum distillation without decomposition. Nevertheless, the mixture was investigated as an additive with the rationale that the tributylbenzene impurities will, at worst, serve as plasticizers for the polymer film.

**Polymer Thin Films.** Commercial **P2** was used without purification. Polymer **P1** was purified by multiple reprecipitations from methanol and washing with metal scavengers to exclude any impurities capable of giving rise to a false positive result. Thin films of **P1** and **P2** were spin-coated from chloroform solutions on 22 × 22 mm<sup>2</sup> glass substrates with either 25 or 50 wt % of each additive added to the spin-coating solutions. The uniformity of each thin film was confirmed by equivalent UV-vis absorption intensities from three different regions of the film. Photobleaching was accomplished by continuously irradiating ( $\lambda = 440$  nm for **P1**, 400 nm for **P2**) a 0.25 cm<sup>2</sup> area of the films with a 450 W Xe arc lamp under aerobic conditions with an average power density of 6.3 mW/cm<sup>2</sup>. The emission intensity at the emission maximum versus time was monitored for each polymer/additive combination over either 30 min (**P1**) or 60 min (**P2**) and the percent of photobleaching was calculated from the loss in fluorescence intensity at the maximum emission wavelength.

**Photobleaching.** Figure 3 shows a graph of the percent of the initial emission intensity that remains after the 30 min irradiation period for **P1**. Antioxidants **BHT**, **NTMS**, and **TA1** and the singlet oxygen quencher **DABCO** behaved similar to the plasticizer control **DOP** and therefore did not display a significant stabilization effect. However, antioxidants **CHT** and

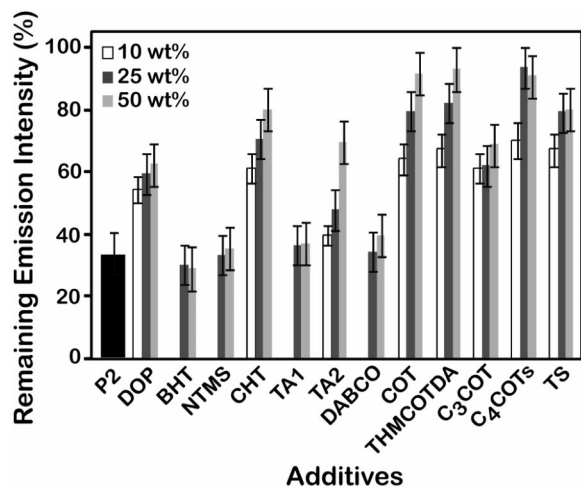


**Figure 3.** Percent remaining fluorescence intensity of thin films of **P1** mixed with either 10, 25, or 50 wt % stabilizers after irradiation for 30 min at 440 nm. The optical density of all the thin films was 0.1 ± 0.01.

**TA2** were effective at stabilizing **P1**, with up to 90 and 80% of the initial fluorescence retained after 30 min, respectively. The superior effectiveness of **TA2** over **TA1** is attributed to the improved miscibility of the *N,N*-dialkylamide moiety of **TA2** in the conjugated polymer matrix compared to the mono-*N*-alkylated amide of **TA1**. However, **TA2** was discovered to be significantly more susceptible to autoxidation than **TA1** and could not be stored for longer than approximately 1–2 months at –4 °C. Also, antioxidant **CHT** evaporated from spun-cast films with relative ease due to its volatility and therefore did not indefinitely impart photostability to thin films of **P1**.

Greater success was achieved with the use of triplet quenchers as stabilizing additives. Starting with **COT**, up to 90% of the initial emission intensity was conserved with 25 wt % of the additive. This result is echoed by both **C<sub>3</sub>COT** and **THMCOTDA**, the latter slightly surpassing **COT**. In comparison, the **C<sub>4</sub>COTs** underperformed with only 75% of the initial intensity remaining after 30 min; this is presumably due to the decreased COT content in the mixture and any counterproductive effects arising from the tributylbenzene impurities. Additionally, the presence of 25 wt % *trans*-stilbene displayed a moderately stabilizing effect on **P1**, although the effect was attenuated at a higher concentration.

Although the use of **COT** to stabilize thin films of **P1** suffered from the same evaporative loss encountered with **CHT**, tet-



**Figure 4.** Percent remaining fluorescence intensity of thin films of **P2** mixed with either 10, 25, or 50 wt % stabilizers after irradiation for 60 min at 400 nm. The optical density of all the thin films was  $0.1 \pm 0.01$ .

raalkylated **C<sub>3</sub>COT** and **THMCOTDA** proved effective solutions to this problem. Moreover, **THMCOTDA** exhibited remarkable thermal and chemical stability and did not noticeably phase separate from **P1** in thin films.

Concentration-dependent studies revealed that in all successful cases an additive concentration of at least 20 wt % was required to observe statistically significant stabilization. This observation is consistent with the practice of using high concentrations (ca.  $10^{-3}$  M) of similar additives to stabilize dilute solutions (ca.  $10^{-5}$  M) of fluorophores.<sup>9–16</sup> We hypothesize that since fluorescence stabilization by both triplet quenching and radical trapping is ultimately a diffusion-controlled process, a low additive concentration should not lead to significant suppression of photooxidation. Therefore, a small concentration of non-emissive traps will still be formed that are capable of quenching the excitons created in the thin film.

Figure 4 shows a graph of the percent of the initial emission intensity of **P2** that remains after 60 min of continuous irradiation. Similar to **P1**, a majority of the investigated antioxidants had a negligible effect on the photostability of **P2**, but **CHT** and **TA2** preserved 80% and 70% of the initial emission intensity, respectively. The stabilizing effects of **TA2** proved to be markedly dependent on concentration, with 50 wt % of the additive necessary to observe meaningful photostabilization.

Also in keeping with previous observations, the **COT** triplet quenchers—specifically **COT**, **THMCOTDA**, and **C<sub>4</sub>COTs**—proved most successful in stabilizing **P2**. Surprisingly, the **C<sub>4</sub>COTs** were reproducibly superior to **C<sub>3</sub>COT** in retarding photobleaching in **P2**; we are currently unsure as to the origin of this observation. Lastly, as with **P1**, the **COT** additives did not noticeably phase separate from thin films of **P2**, and at least 20 wt % of most additives was necessary to observe statistically significant stabilization.

**Conclusions.** Hydrogen atom donors, cycloheptatriene (**CHT**) and *N,N*-dioctyl-1,4-dihydro-*o*-toluamide (**TA2**), and a variety of cyclooctatetraene triplet quenchers effectively retarded the extent of photobleaching in thin films of a poly(*p*-phenylene ethynylene) and poly(fluorene). **CHT** and **TA2** preserved up to 80% of the initial emission intensities of both polymers after either 30 or 60 min of continuous irradiation. Tetraalkylated

**COTs**, **C<sub>3</sub>COT**, **C<sub>4</sub>COTs**, and **THMCOTDA**, proved most successful in photostabilizing polymer thin films, with up to 95% of the initial emission intensity retained at the end of the 30 or 60 min irradiation period. Moreover, these additives did not phase separate or evaporate from thin films, were thermally stable, and could be stored for extended periods without significant decomposition.

**Supporting Information Available:** Complete experimental procedures and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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