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Wavelength Dependent Photochemistry of Expanded Chromophore and Asymmetric Dibenzothiophene *S*-Oxides Derivatives

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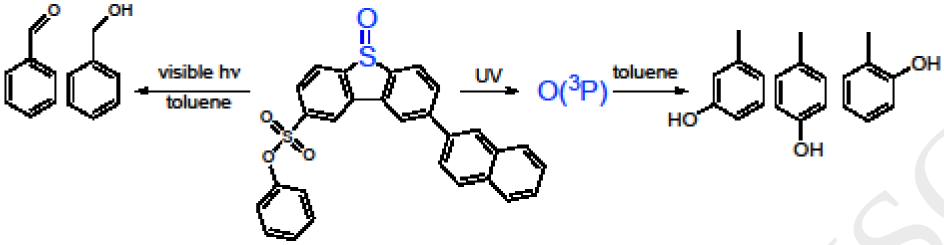
Graphical abstract



Highlights

- Irradiation of aryl and sulfonate ester substituted dibenzothiophene *S-oxides* exhibits wavelength dependent photochemistry.
- Upon irradiation with UV-light, photodeoxygenation yielding atomic oxygen was observed.
- The dibenzothiophene S-oxide derivatives when irradiated by visible light facilitated the oxidation of the benzylic position of toluene.

Abstract

Irradiation of dibenzothiophene *S*-oxide (DBTO) is believed to generate ground state atomic oxygen [$O(^3P)$]. The irradiation conditions and the efficiency of the deoxygenation event are not ideal when working with biological systems. Dinaphtho[2,1-b:1′,2′-d]thiophene S-oxide (DNTO) and several other analogs were shown to allow visible light to drive deoxygenation due to red-shifted absorbance of the DBTO derivatives. Additionally, DNTO and its analogs did not substantially improved quantum yield of deoxygenation ($\Phi_{deox.}$). To improve both $\Phi_{deox.}$ and absorbance, changes were made to the DBTO scaffold. The first change was an addition of an electron withdrawing group (EWG) to weaken the S–O bond strength of the sulfoxide to improve $\Phi_{deox.}$. The second change was the addition of an aromatic substituent to enhance and red-shift the absorbance. Common intermediate experiments were performed in toluene to examine if these new DBTO analogs produced a common oxidant under both UV and visible light