Supporting Information

Monohydroxylated Polybrominated Diphenyl Ethers (OH-PBDEs) and Dihydroxylated Polybrominated Biphenyls (di-OH-PBBs): Novel Photoproducts of 2,6-Dibromophenol

Hongxia Zhao,[1] Jingqiu Jiang,[1] Yanli Wang,[1] Hans-Joachim Lehmler,[2]*
Garry R. Buettner,[3] Xie Quan,[1] Jingwen Chen [1]

[1] Key Laboratory of Industrial Ecology and Environmental Engineering (Ministry of Education), School of Environmental Science and Technology, Dalian University of Technology Linggong Road 2; Dalian 116024, China

[2] Department of Occupational and Environmental Health, College of Public Health, The University of Iowa, IA 52242, USA

[3] Free Radical and Radiation Biology Program & ESR Facility, Carver College of Medicine, The University of Iowa, IA 52242, USA

Summary

Number of pages: 10

Text S1

9 Figures

1 Table

Text S1. Instrument Conditions

S1.1. HPLC-LTQ Orbitrap condition

The LTQ Orbitrap, a hybrid instrument with a linear ion trap (LIT) mass spectrometer linked to a high-resolution Fourier transform (FT) mass spectrometer, was exploited to perform high-resolution full-scan MS analysis.

Chromatographic separations were performed using an Accela HPLC system. The HPLC conditions were as follows: Column: Thermo C18, 150 × 2.1 mm, 5 μm particle size (Thermo Fisher Scientific, Bellefonte, PA). Mobile phase: (A) water, (B) acetonitrile. Flow rate: 0.2 mL/min. Injection volume: 5 μL. Gradient: Linear gradient of 35%-85% A over 20 minutes, 85%-85% A over 10 min, post time: 5 min.

The MS conditions were as follows: ion source: ESI; negative electrospray ion source voltage: 2.98 kV; full scan MS in the Orbitrap with a mass resolution of 30000, scan range: *m*/*z* 150-700, capillary voltage: 10 V, tube lens: 100 V, sheath gas flow: 30 arb, aux gas flow: 10 arb.

S1.2. GC-MS

The derivatized extracts were analyzed by an Agilent HP 6890 gas chromatograph coupled with a quadrupole mass selective detector HP 5975N operated in negative chemical ionization (NCI) mode. A DB-5MS column (15 m × 0.25 mm, 0.25 μm film thickness; J & W Scientific, Folsom, CA, USA) was used. The injector temperature was 280 °C. Auto injection of 1 μL of the samples was conducted in splitless mode and the split mode was turned on after 2 min. Methane was used as chemical ionization moderating gas and helium as carrier gas at a flow rate of 1.0 mL/min. The ion source and interface temperatures were set at

150 °C and 300 °C, respectively. The temperature of the GC oven was programmed as follows: the initial oven temperature was 90 °C held for 3 min, ramped to 210 °C at 30 °C /min with no hold time, then ramped to 236 °C at 2 °C/min with no hold time, then ramped to 300 °C at 20 °C/min. MS Quad: 150 °C, MS source: 150 °C, solvent delay: 4.00 min, scan scope: 70-540.

Figures S1-S9

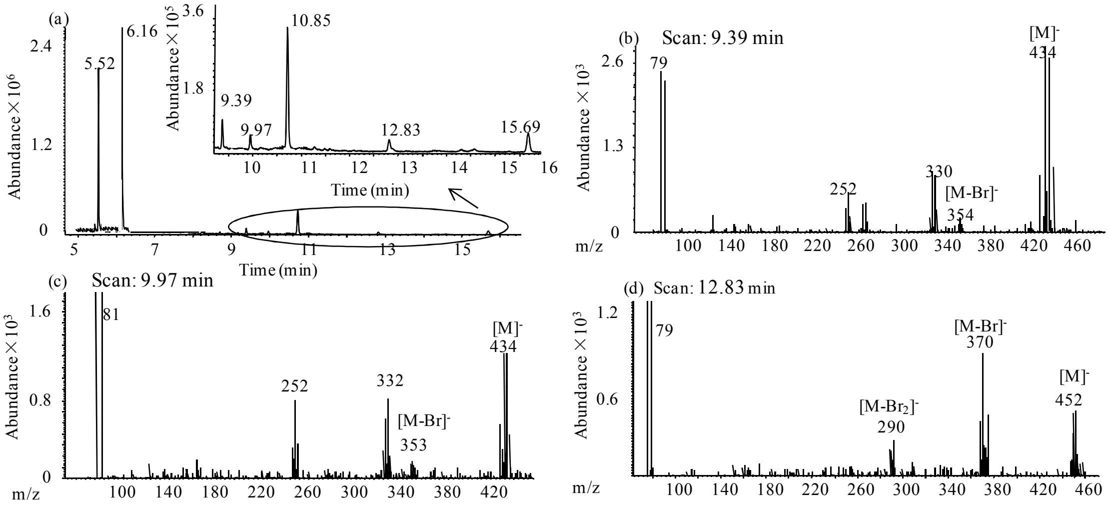


Figure S1. **(a)** The GC total ion chromatograph of 2,6-bromophenol(water solution, 80 μmol/L) and MS spectrum **(b-d)** of three tribrominated photoproducts with retention time of 9.39 min, 9.97 min, 12.83 min, respectively.

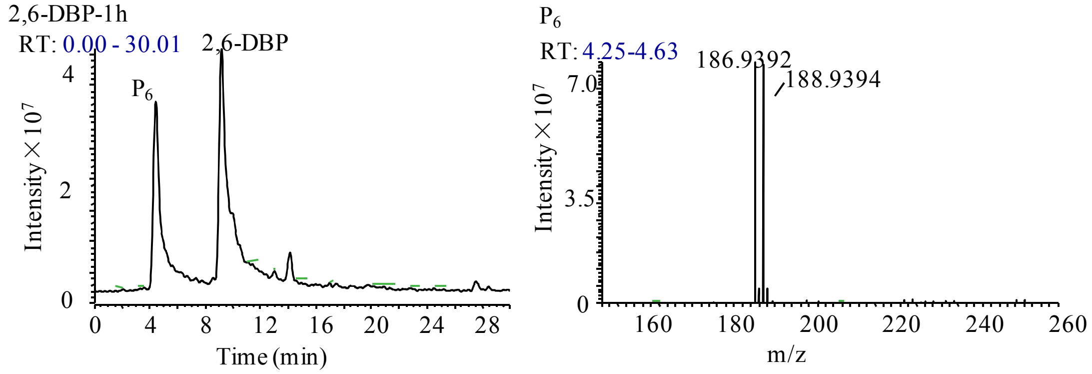


Figure S2. The total ion chromatograph of 2,6-bromophenol (aqueous solution, 80 μmol/L) and MS spectrum of monobromo-dihydroxybenzene with retention time of 4.43 min.

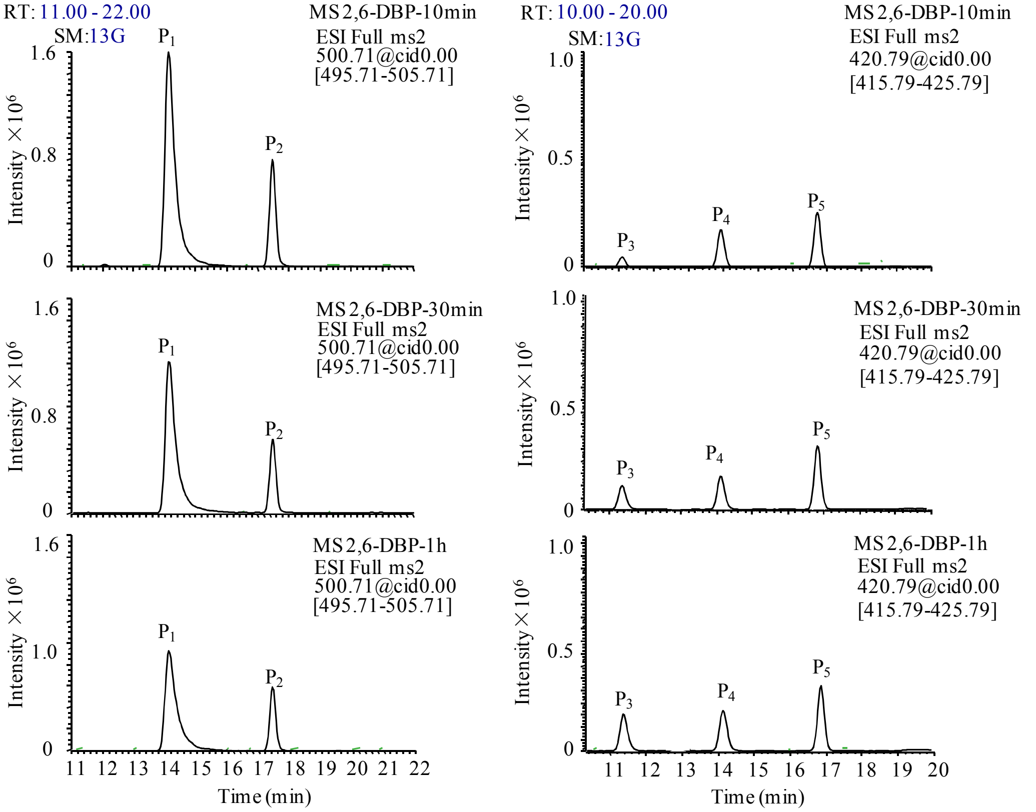


Figure S3. The LTQ-Orbitrap spectra of two tetrabrominated products P$_1$, P$_2$ and three tribrominated products P$_3$-P$_5$, which extract m/z = 495.71-505.71 and m/z = 415.79-425.79, respectively, with irradiation time of 10 min, 30 min and 1 h from 2,6-DBP.

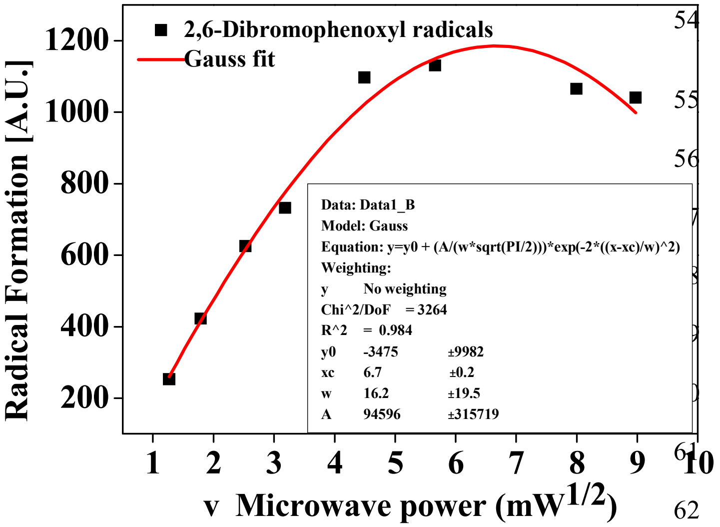


Figure S4. (Microwave power/mW)$^{1/2}$ dependence of the peak-to-peak intensity of radicals generated from irradiation of 2, 6-dibromophenol (phosphate buffer pH 7.4). (This plot is fitted using a Gaussian model.)

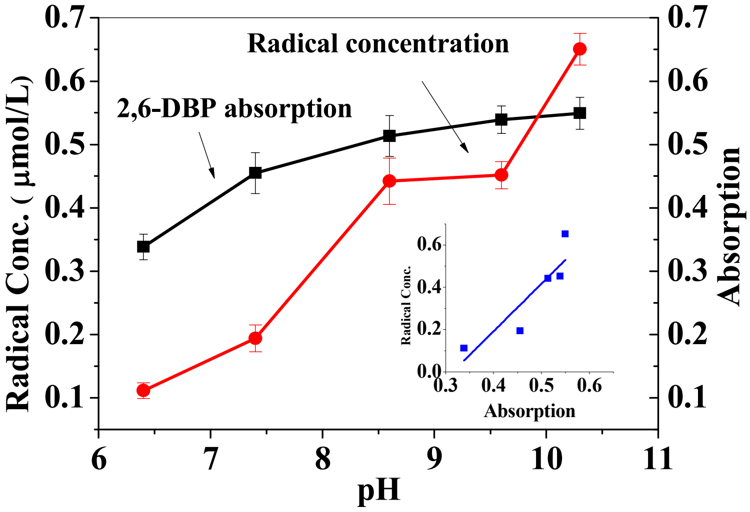


Figure S5. Effects of pH on the formation of radical and 2,6-DBP UV absorption, the inserted figure shows that the positive relationship of absorption and radical concentration. Error bars are standard deviations of triplicate measurements.

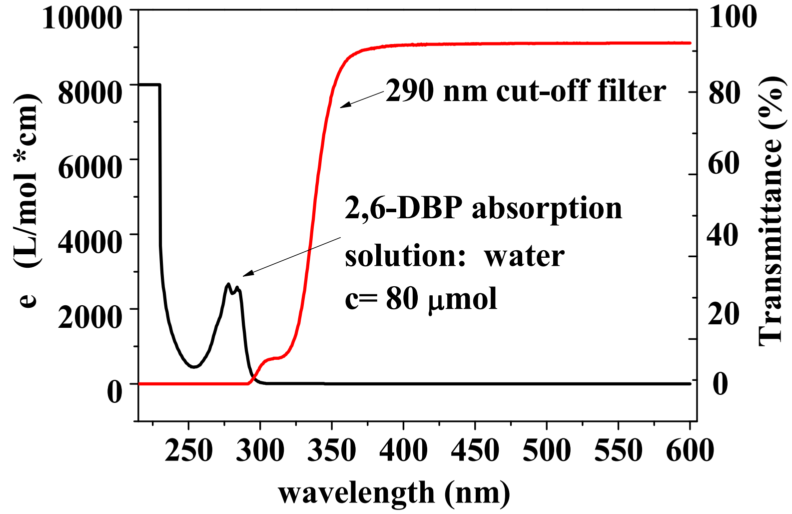


Figure S6. Absorption spectrum of 2,6-DBP in water (80 μmol/L); transmittance (%) of 290 nm cut-off filters.

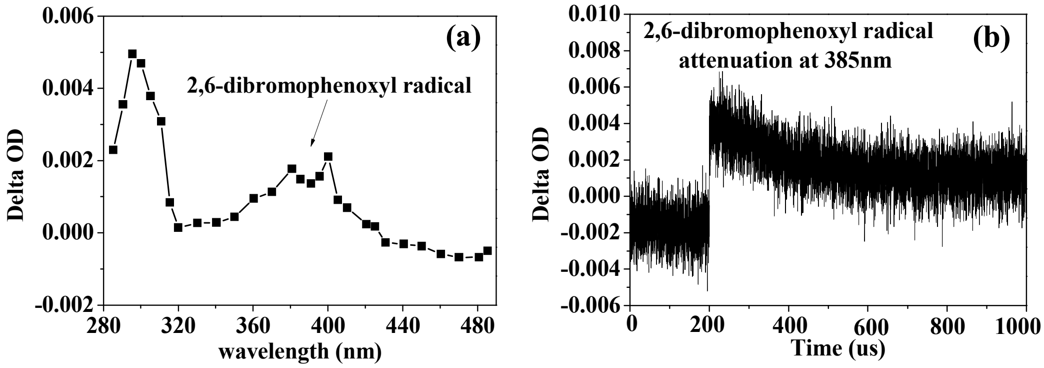
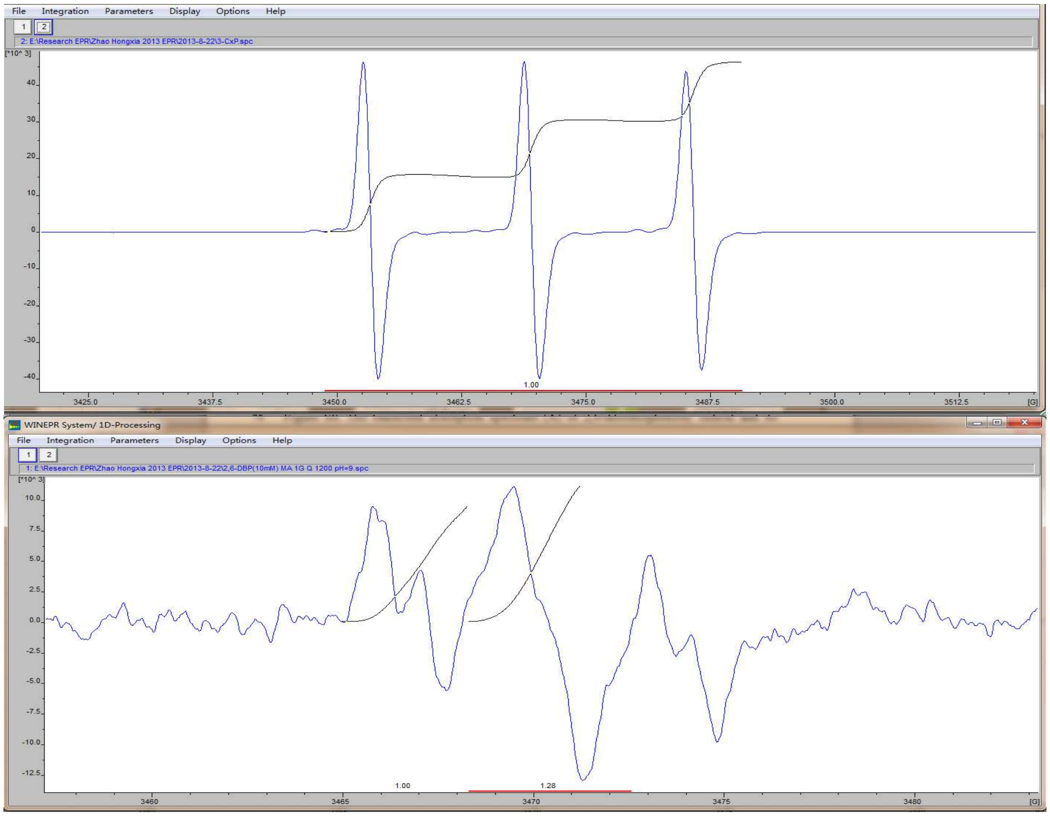


Figure S7. The transcient absorption spectra of 2,6-DBP in aqueous solution (1 mmol/L) bubbled with N_2. **(a)** The generated transient absorption spectrum of 2,6- dibromophenoxyl radical at laser pulse λ = 266 nm; **(b)** The decay curve of 2,6-dibromophenoxyl radical at 385nm (half-life time$_{\text{2,6-dibromophenoxyl radical}}$ was determined to be 122 μs).



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1: E:\Research EPR\Zhao Hongxia 2013 EPR\2013-8-22\2,6-DBP(10mM) MA 1G Q 1200 pH=9.spc

Figure S8. Quantification of the formed 2,6-dibromophenoxyl radical using 3-carboxy-PROXYL as a standard.
(a) Example double integration of a spectrum of the 3-carboxy-PROXYL standard solution;
(b) Example integration of a spectrum of 2,6-dibromophenoxyl radical.

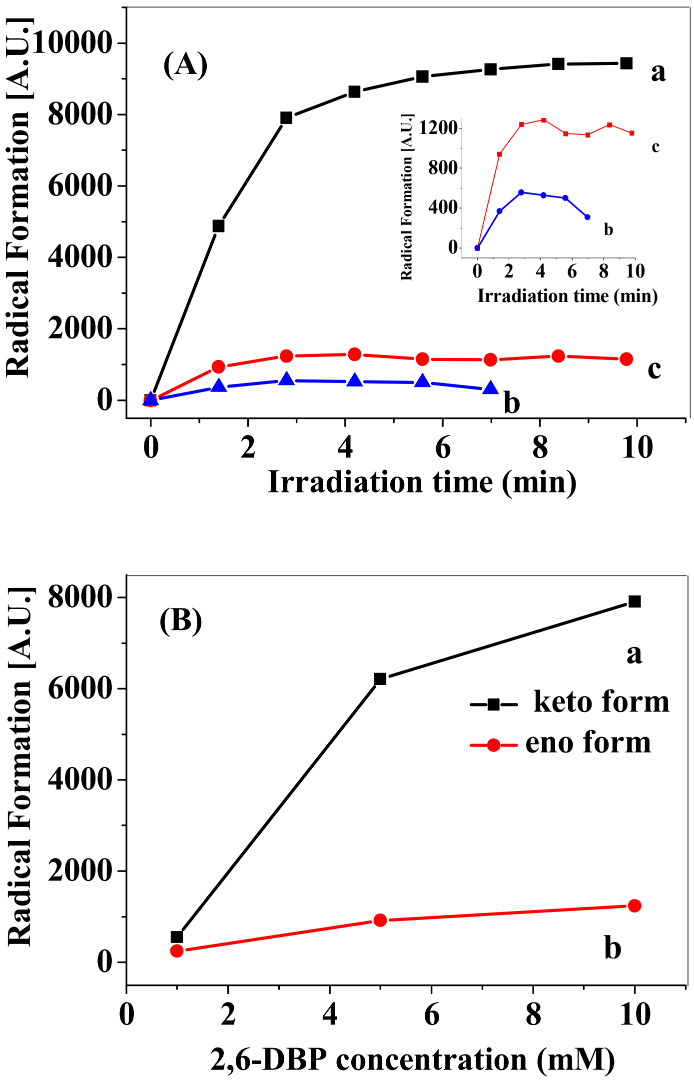

Figure S9. Free radical formation increases with time of light exposure and concentration of 2,6-DBP.

(A) Radical formation (A.U., derived from signal heights, peak-to-peak) correlated to irradiation time with: **(a)** 2,6-DBP (10 mM) + DMPO (50 mM) in water (pH = 7.4); **(b)** 2,6-DBP (1 mM) + DMPO (50 mM) in water (pH = 7.4); (c) 2,6-DBP (10 mM) in water (pH = 7.4).

(B) Concentration of 2,6-DBP in: **(a)** water (pH = 7.4) added DMPO (50 mM); **(b)** water (pH = 7.4) with 5.6 min irradiation time.

Table S1. The apparent yield (%) of six products from irradiation of 2,6-DBP with different times of UV-exposure.

Reaction Time (min)	tribrominated product 1	tribrominated product 2	tribrominated product 3	4'-OH-BDE73	4'4-di-OH-PBB80	1,2-di-OH-6-bromo-benzene
0	0	0	0	0	0	0
10	0.048	0.17	0.23	2.59	0.91	1.79
20	0.11	0.15	0.27	2.65	0.92	5.43
30	0.14	0.19	0.27	1.85	0.60	15
60	0.17	0.19	0.27	1.32	0.50	22
120	0.092	0.16[1]	0.26	0.49	0.19	29