

Supporting Information For

**On TAML-Peroxide Oxidation of Endocrine Disrupting
Bisphenol A Compounds: Green Synthetic Oligomerisation,
End Products, Toxicity and Mechanism**

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Standardisation of hydrogen peroxide stock solution

Hydrogen peroxide stock solution was made by diluting reagent grade ~30% w/v solution to approximately 2.5% v/v with deionised water and stored in a volumetric flask covered in aluminium foil to avoid photo-induced degradation. Solutions of hydrogen peroxide were standardized by (a) UV-Vis absorbance measurements and by (b) standard thiosulphate titration described below. The hydrogen peroxide stock solution was diluted in triplicate by pipetting 1.00 mL aliquots into 10.00 mL volumetric flasks and made up to the mark with deionised water. The absorbance at 230 nm in a quartz cuvette cell was measured using a UV-Visible spectrometer. The concentration used is the average of the three samples.

Standardisation of hydrogen peroxide with 0.0250 M sodium thiosulphate: Aqueous potassium iodide (10.00 mL, 0.0160 M) and sulfuric acid (5.00 mL, 2.0 M) solutions were added to deionised water (30.0 mL) in a conical flask (100 mL), followed by saturated ammonium molybdate solution (5 drops). Then hydrogen peroxide (2.00 mL, ~0.25% w/v) was added. After two minutes of stirring an orange-brown solution formed. This was then titrated against the standardised Hach sodium thiosulphate solution (0.0250 N) until the solution was very pale yellow. A microspatula of starch was then added, forming a blue-black solution. The sodium thiosulphate solution was carefully added drop-wise until the solution in the conical flask reached the colourless endpoint. This was repeated at least three times. The titration results were averaged and the accurate concentration of the hydrogen peroxide solution was calculated (approximately 75.0 mM).

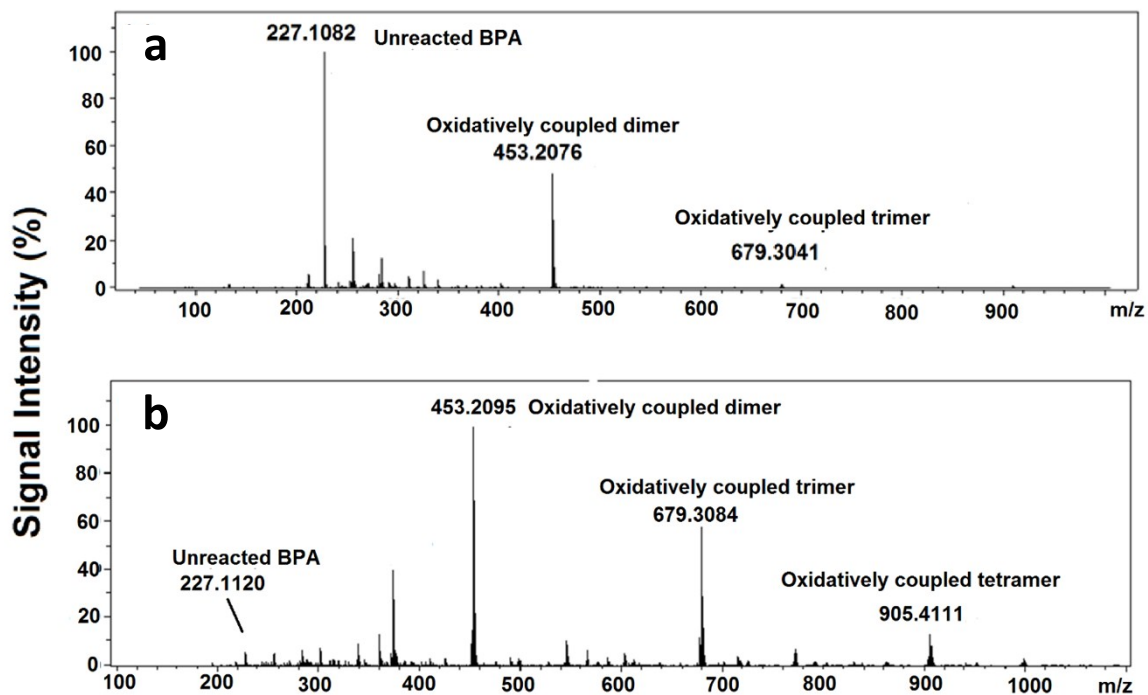


Fig. S1 High resolution ESI mass spectra (negative ion mode) of (a) the reaction products collected by SPE after treatment of BPA with the Fe^{III}-TAML (4 nM) oxidising system; (b) the reaction products collected by SPE after treatment of BPA with the Fe^{III}-TAML (40 nM) oxidising system. Conditions in both cases: BPA (43.8 μ M), H₂O₂ (4 mM), pH 8.5 (0.01 M, carbonate), 180 minutes, 25 °C).

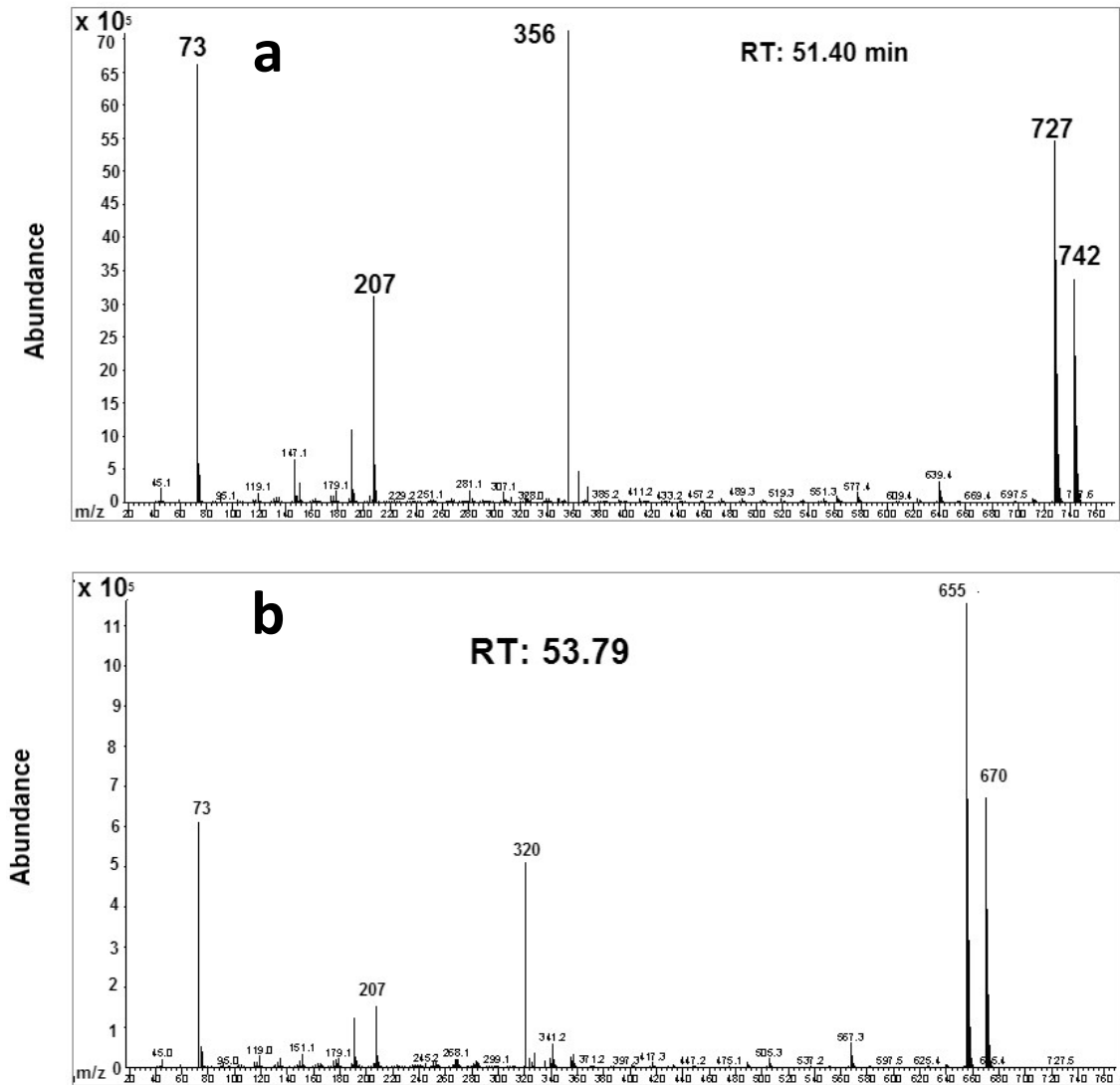


Fig. S2 GC-MS spectra of TMS derivatised sample of treated BPA (reaction conditions: BPA (43.8 μ M), H₂O₂ (4 mM), pH 8.5 (0.01 M, carbonate), and 25°C). (a) MS of GC peak with RT of 51.40 minutes and (b) MS of GC peak with RT of 53.79 minutes

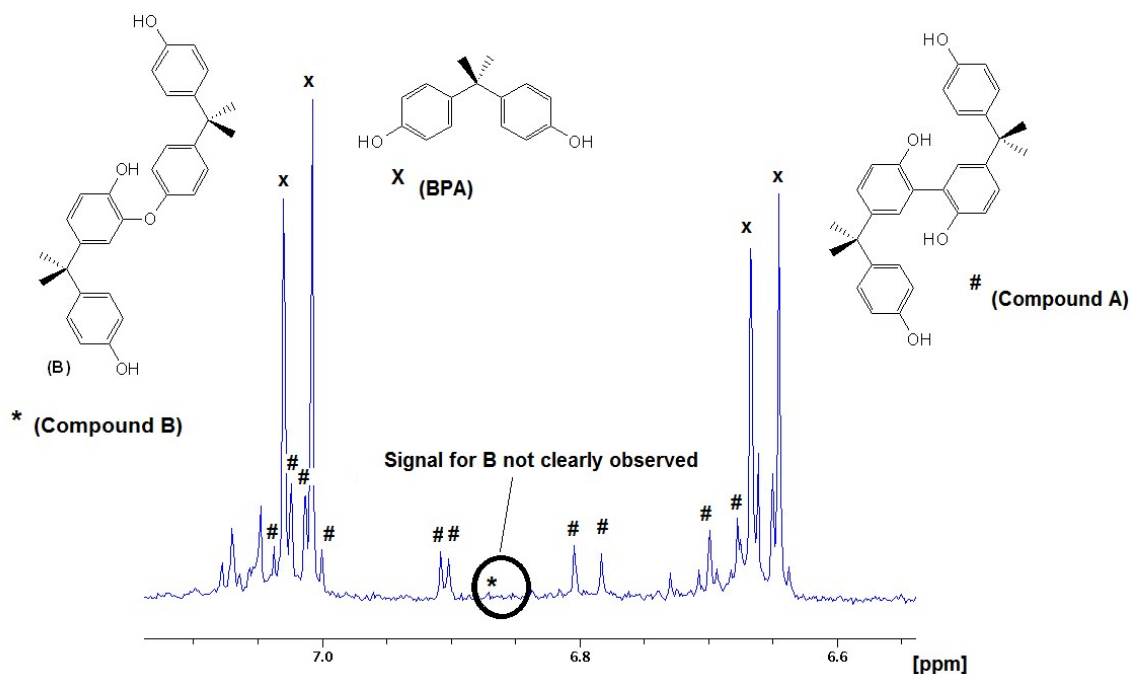


Fig. S3 ¹H NMR spectrum of BPA sample after catalytic oxidation for 180 minutes and isolation of products by SPE (reaction conditions: BPA (43.8 μ M), H₂O₂ (4 mM), pH 8.5 (0.01 M, carbonate), and 25°C).

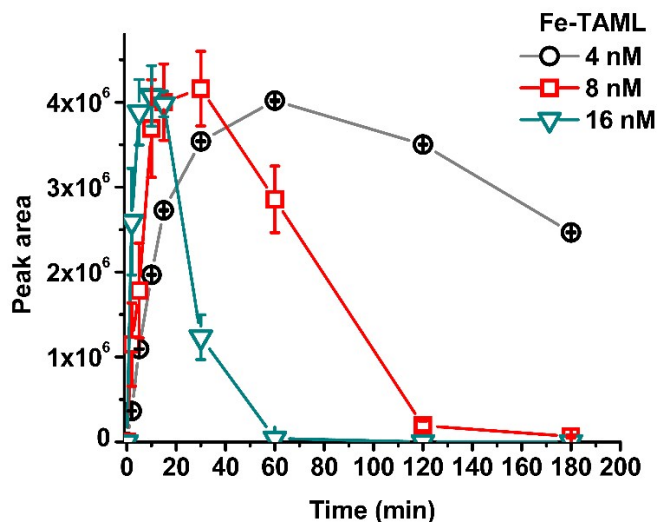
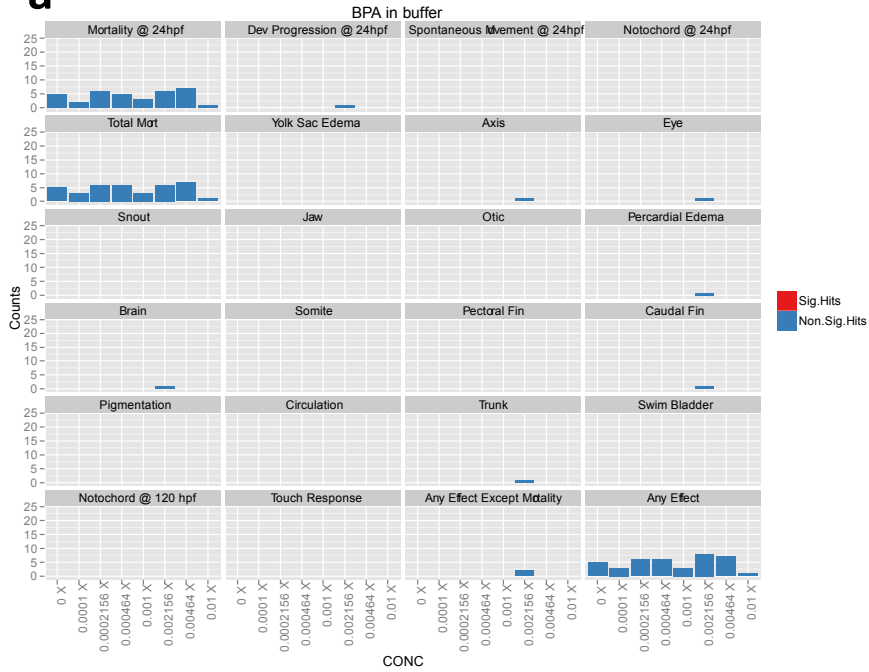
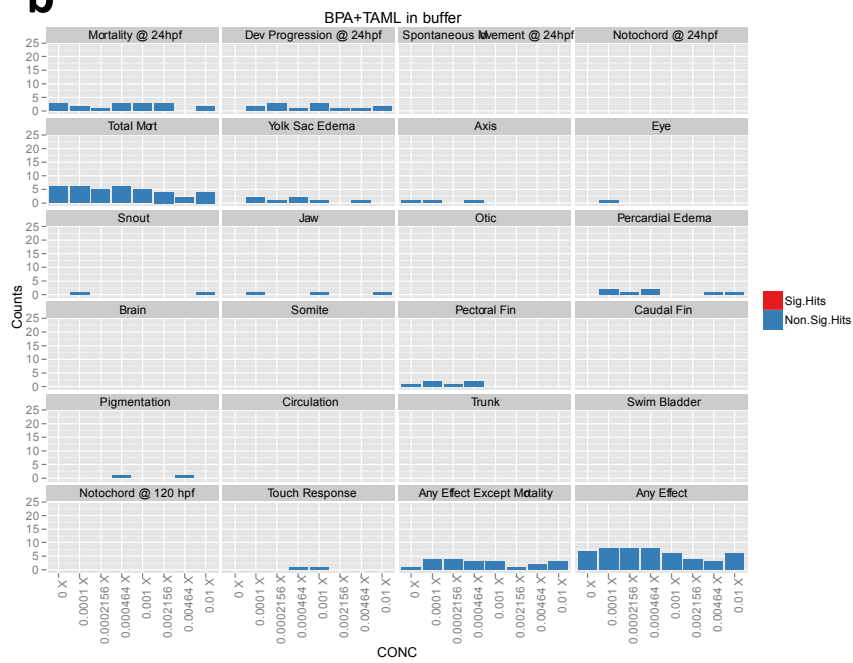


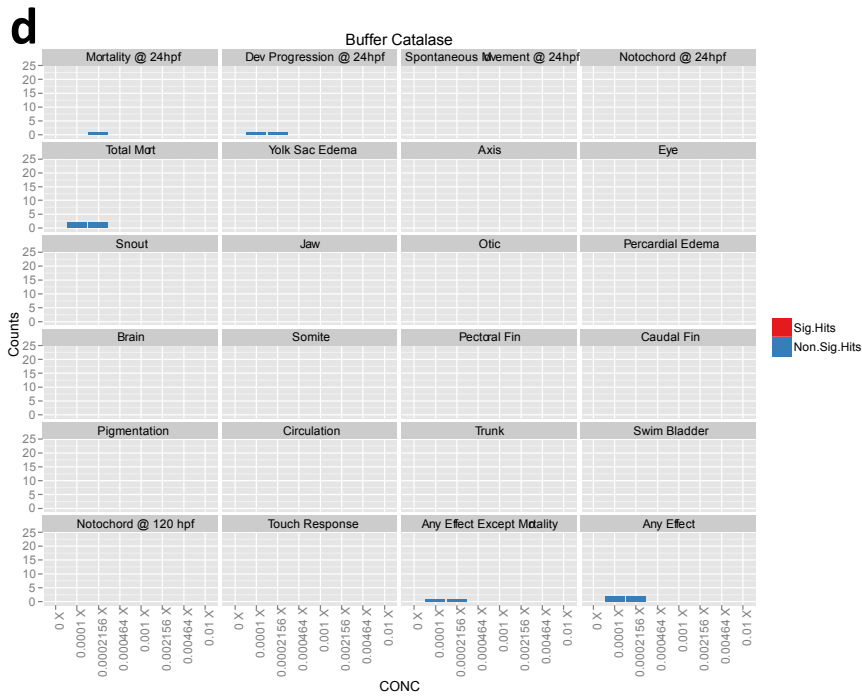
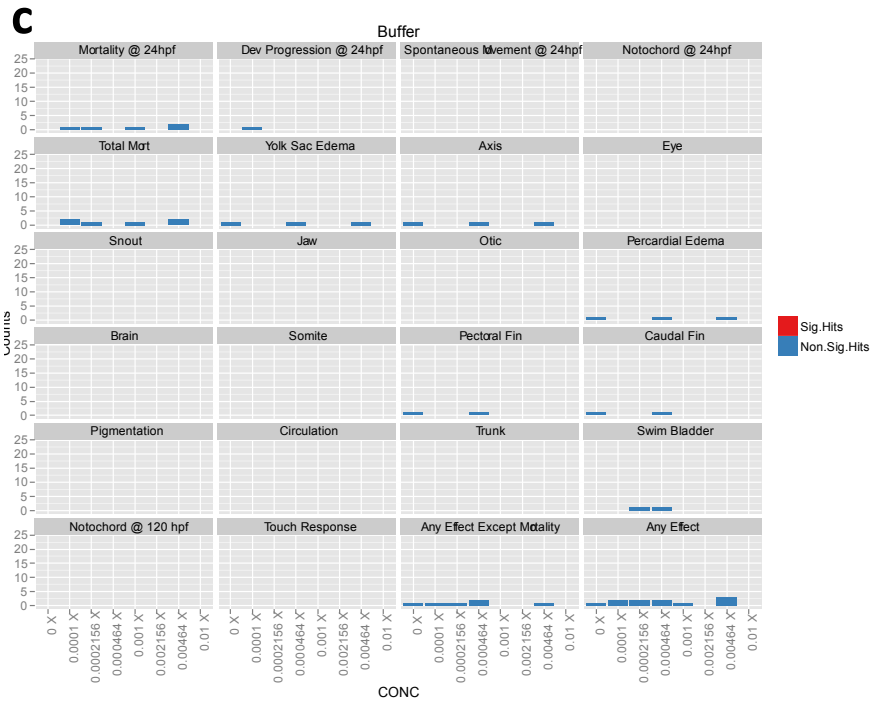
Fig. S4 Plots of the amount of the oxidatively coupled dimer of BPA detected in solution versus time when BPA is treated with the Fe^{III}-TAML/H₂O₂ oxidising system with the concentration of Fe^{III}-TAML set at 4, 8, or 16 nM (reaction conditions: BPA (43.8 μ M), H₂O₂ (4 mM), pH 8.5 (0.01 M, carbonate), 25 °C). Data points are each the mean of triplicate runs with estimated 3SD limits indicated.

a



b





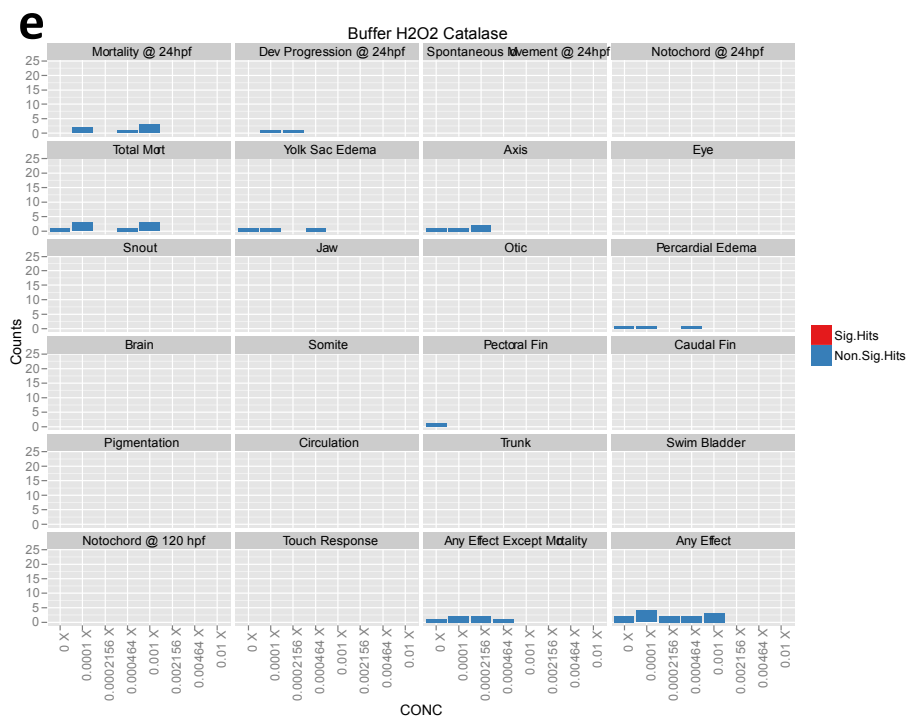


Fig. S5 Zebrafish developmental toxicity profiles of 10,000–100-fold diluted (0.0001–0.01), unfiltered, agitated, pH 7 (0.01 M, phosphate) solutions of (a) BPA (80 μ M), (b) BPA (80 μ M) with TAML (200 nM) (c) buffer only, (d) buffer treated with catalase, and (e) BPA (80 μ M) treated with TAML/H₂O₂ (200 nM/5 mM) for 12 hours and then treated with catalase.