SUPPORTING INFORMATION

Photo-mediated formation and evolution of free radicals on quinone aromatic compounds: effect of molecular structure

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Text S1 All electron paramagnetic resonance (EPR) measurements were performed at room temperature (25 ± 2°C) by a Bruker EMX-micro spectrometer (Karlsruhe, Germany) with the method reported previously (Jia et al., 2017). Before each measurement sequence, the EPR spectrometer was calibrated with a commercial 2,2-diphenyl-1-picrylhydrazyl (DPPH) standard sample (g = 2.0036). This calibration was used to ensure accurate g-factor determination and spin-concentration quantification. The DPPH standard and all quinone samples were loaded into identical quartz EPR tubes. Measurements were then performed under the same instrumental conditions: X-band microwave frequency, 9.7 GHz; microwave power, 2.02 mW; center field, 3470 G; modulation amplitude, 4.0 G; sweep width, 200 G; receiver gain, 3.54×10^4; time constant, 41.0 ms; and sweep time, 167.7 s. For spectral preprocessing, blank spectra from empty quartz tubes were collected and subtracted from the raw spectra of all samples to correct for instrumental background. Polynomial baseline fitting was applied to signal-free regions at both ends of each first-derivative EPR spectrum. The baseline-corrected spectra were then double-integrated to obtain total signal areas. Radical concentrations were calculated by comparing the signal peak area, as derived from $(\Delta Hp\text{-}p)^2$ multiplied by the relative intensity. The instrument self-calibration procedure and standard reference guarantee the reliability of quantitative results for PFRs. The g-factor and spin density were determined by comparison with the DPPH standard radical, as described previously (Yang et al., 2017; Kiruri et al., 2014; Nwosu et al., 2015). Each treatment group included three independently prepared replicate samples. All quantitative data are reported as mean ± standard deviation to reflect measurement uncertainty.

Text S2 To detect formation of ROS in the model quinones before and after irradiation for 2h, EPR instrument parameters were adjusted as follows: center field, 3500 G; microwave power, 20 mW; sweep width, 200 G; sweep time, 30 s; and scan time, 2 min.

Text S3 Briefly, 0.1 g of quinone sample was mixed with 0.5 mL of deionized water to prepare a sample-water suspension. An aliquot of this suspension, 300 μL, was combined with 300 μL of freshly prepared horseradish peroxidase solution. The mixture was incubated for 24 h in a thermostatic shaker at 28 °C and 300 rpm to allow the reaction to proceed. After incubation, the

mixture was filtered, and the supernatant was passed through a 0.45 μm polyethersulfone membrane. The filtrate was collected in a black 96-well microplate, and fluorescence intensity was measured using a microplate reader. The peroxidase solution was prepared by dissolving 8 mg of 4-hydroxyphenylacetic acid and 4 mg of horseradish peroxidase in 50 mL of 0.1 M Tris buffer, adjusted to pH 8.8. For fluorescence correction, 300 μL of the sample-water suspension was mixed with 300 μL of a solution containing 10 μmol L^{-1} H_2O_2 and horseradish peroxidase. This mixture was incubated for 24 h under the same conditions. The filtrate was then collected and measured, and the resulting values were used to correct fluorescence intensity and improve analytical accuracy.

Text S4 The FTIR spectra were recorded in the range of 4000-400 cm^{-1} with a 4 cm^{-1} resolution, and 64 scans were performed on each sample. To quantify the relative absorption intensity of each region of the carbon band, the spectra were baseline corrected and integrated with OMNIC 8.2 software. The XPS consisted monochromatic Al Kα radiation (180 W, 12 mA, 15 kV) and diameter beam spot of 500 mm. The pellets (2.0 mg of sample dispersed in 200 mg of KBr) were ground with an agate mortar before being pressed.

Table S1. The surface elemental contents of model quinones before and after irradiation for 2h by XPS analysis

	C (%)	O (%)	Cl (%)	O/C
1,4-benzoquinone-CK	73.47	26.53	—	0.36
1,4-benzoquinone-light-2h	72.67	27.33	—	0.38
2- chlor-p-benzoquinone-CK	66.99	27.78	5.23	0.41
2- chlor-p-benzoquinone- light-2h	69.05	24.85	6.09	0.36
2-methyl-p-benzoquinone-CK	77.12	22.88	—	0.30
2-methyl-p-benzoquinone -light 2h	76.9	23.1	—	0.30
1,4-naphthaquinone -CK	82.05	17.95	—	0.22
1,4-naphthaquinone-light-2h	82.91	17.09	—	0.21
anthraquinone-CK	86	14	—	0.16
anthraquinone- light-2h	87.47	12.53	—	0.14

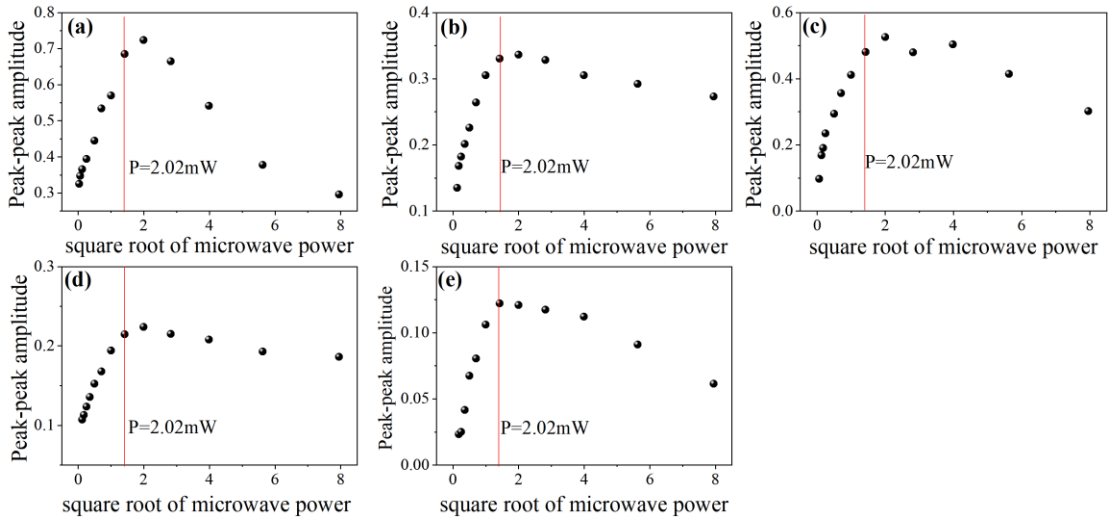

Fig.S1 Power saturation curve for the original model quinones. Panels (a)-(e) correspond to (a) 1,4-benzoquinone, (b) 2-chloro-p-benzoquinone, (c) 2-methyl-p-benzoquinone, (d) 1,4-naphthoquinone, and (e) anthraquinone, respectively. The red vertical line indicates the selected microwave power of 2.02 mW for all quantitative tests.

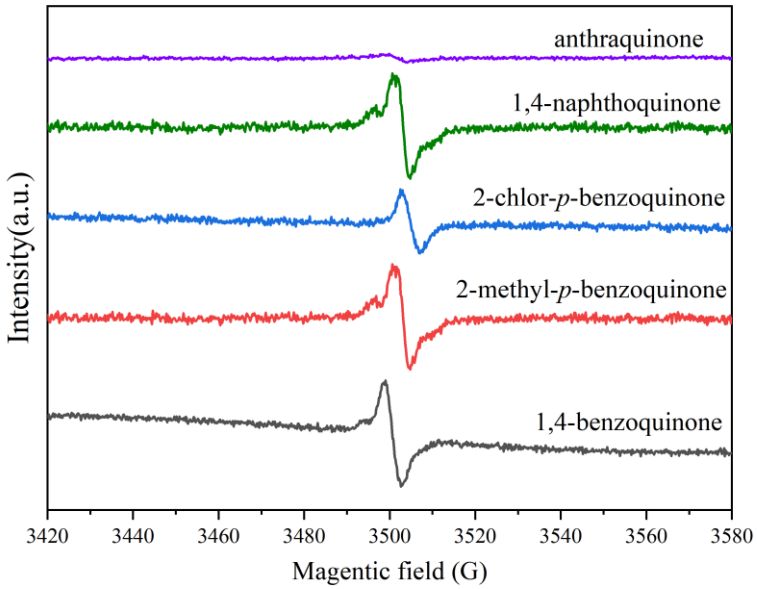

Fig.S2 Electron paramagnetic resonance (EPR) spectra obtained from original model quinones

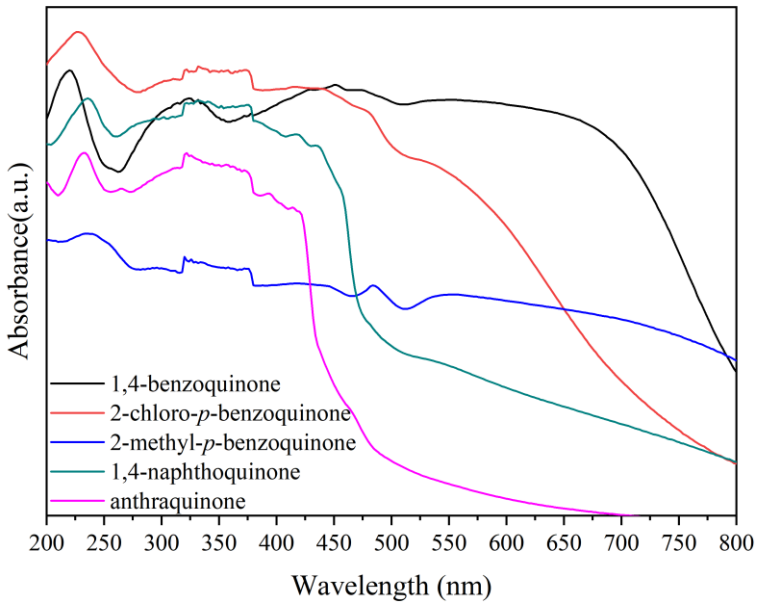

Fig.S3 UV-Vis diffuse reflectance spectra of original model quinones

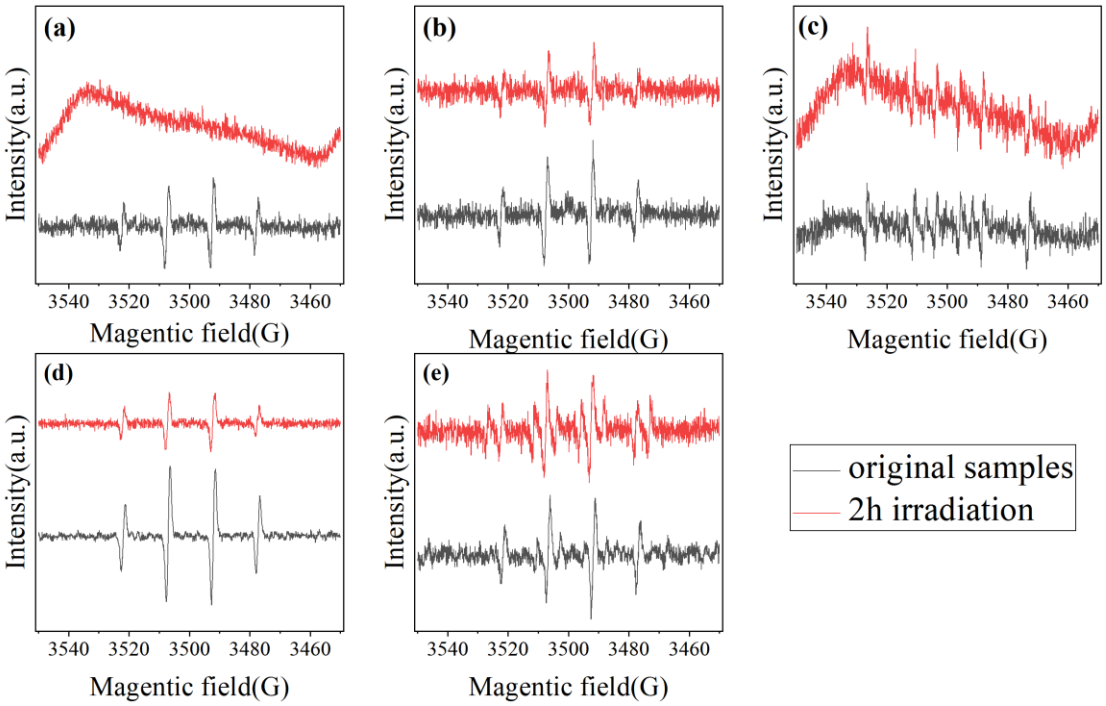

Fig.S4 Electron paramagnetic resonance (EPR) spectra obtained from model quinones after irradiation for 0h (black) and 2h (red) extracted by a mixture of H_2O with the spin-trapping agent of 5,5-dimethyl-1-pyrroline-N-oxide (DMPO). Panels (a) to (e) correspond to (a) 1,4-benzoquinone, (b) 2-chloro-p-benzoquinone, (c) 2-methyl-p-benzoquinone, (d) 1,4-naphthoquinone, and (e) anthraquinone.

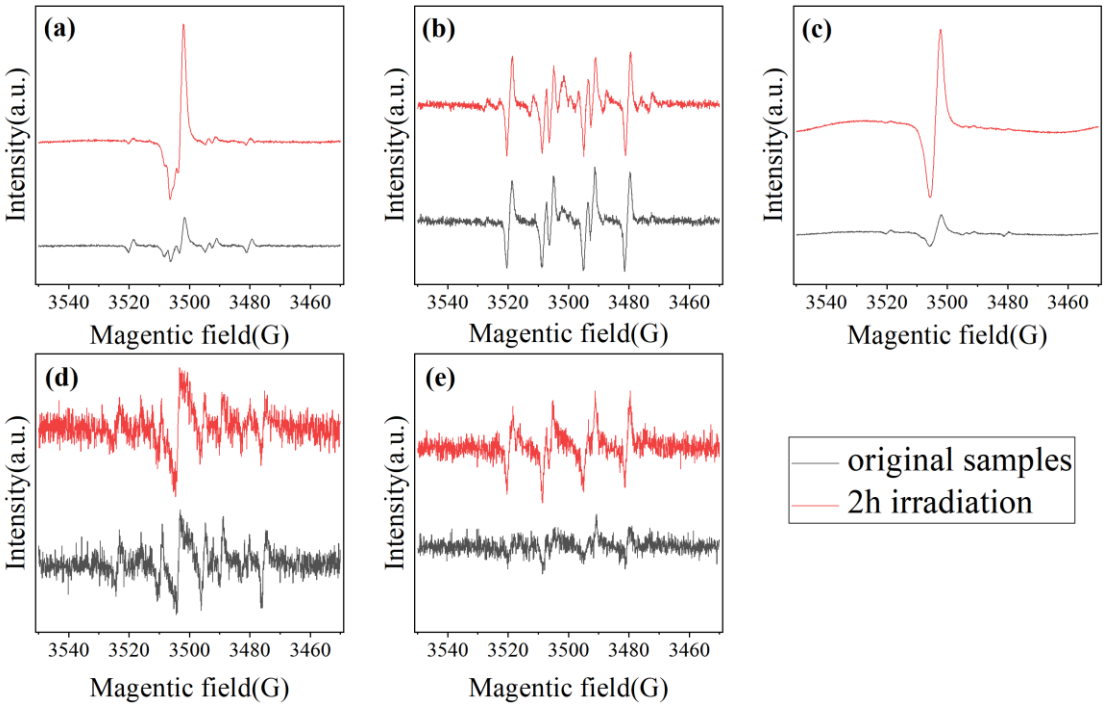

Fig.S5 Electron paramagnetic resonance (EPR) spectra obtained from model quinones after irradiation for 0h (black) and 2h (red) extracted by a mixture of dimethyl sulfoxide (DMSO) with the spin-trapping agent of 5,5-dimethyl-1-pyrroline-N-oxide (DMPO). Panels (a) to (e) correspond to (a) 1,4-benzoquinone, (b) 2-chloro-p-benzoquinone, (c) 2-methyl-p-benzoquinone, (d) 1,4-naphthoquinone, and (e) anthraquinone.

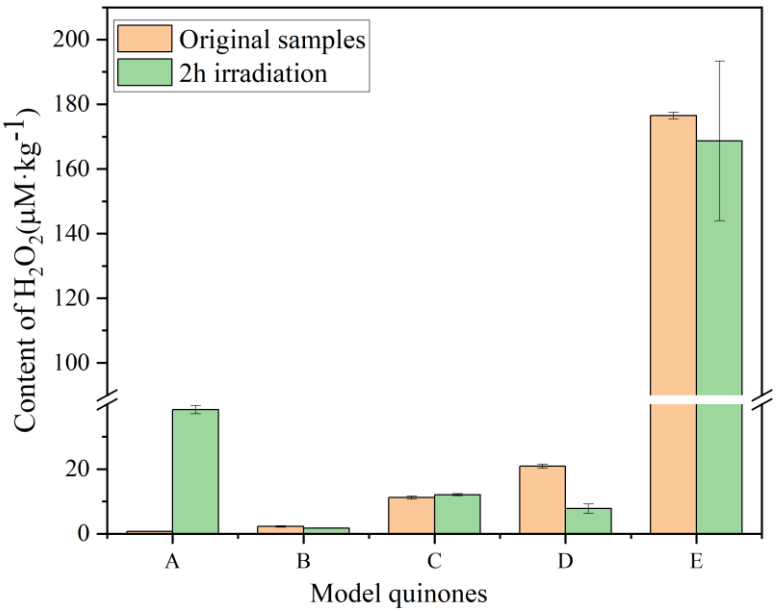

Fig.S6 Content of H_2O_2 in model quinones after irradiation for 0h (orange) and 2h (green). Panels A-E correspond to 1,4-benzoquinone, 2-chloro-p-benzoquinone, 2-methyl-p-benzoquinone, 1,4-naphthoquinone, and anthraquinone, respectively.

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