Supporting Information

Visible Light Induced Oxygenation of Benzene by the Triplet Excited State of 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone

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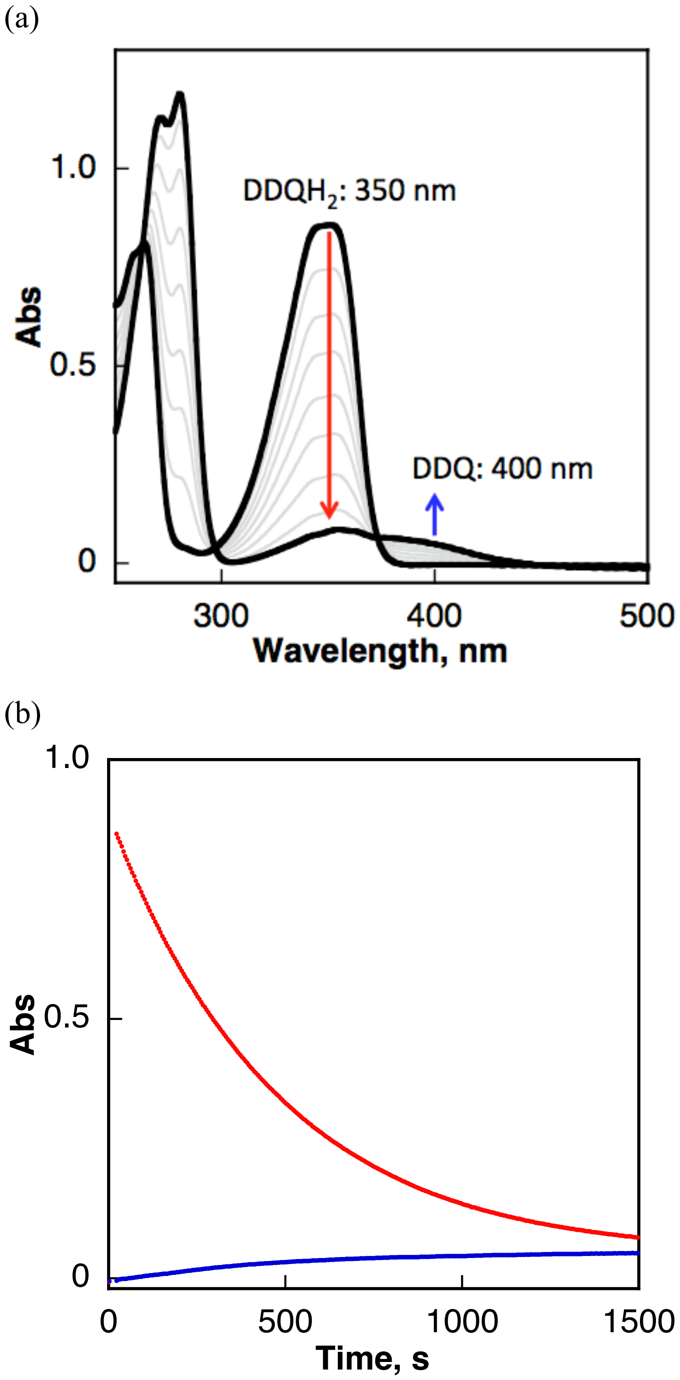
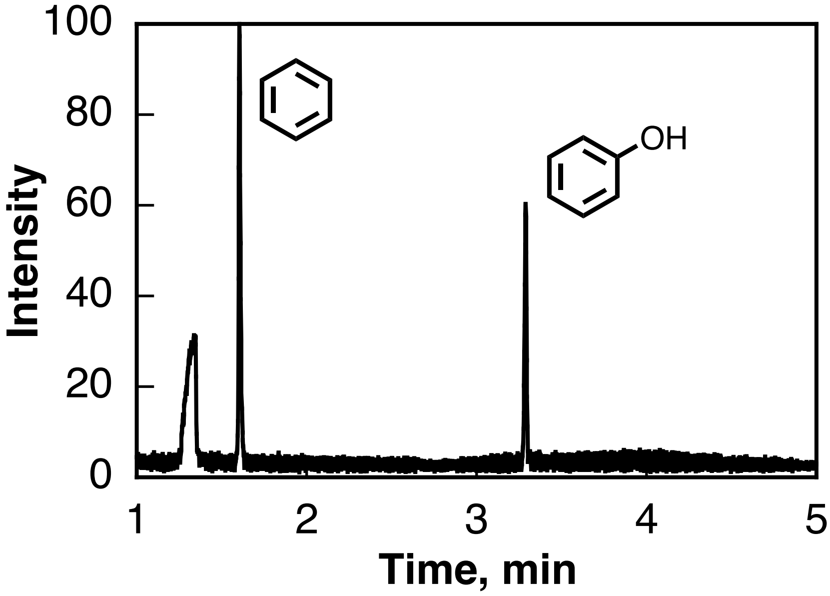


Figure S1. (a) UV-vis spectral change of DDQH$_2$ (0.10 mM) upon addition of TBN (1.5 mM) in O$_2$-saturated MeCN at 298 K. (b) Time profiles at 350 nm (red) and 400 nm (blue).

(a)



(b)

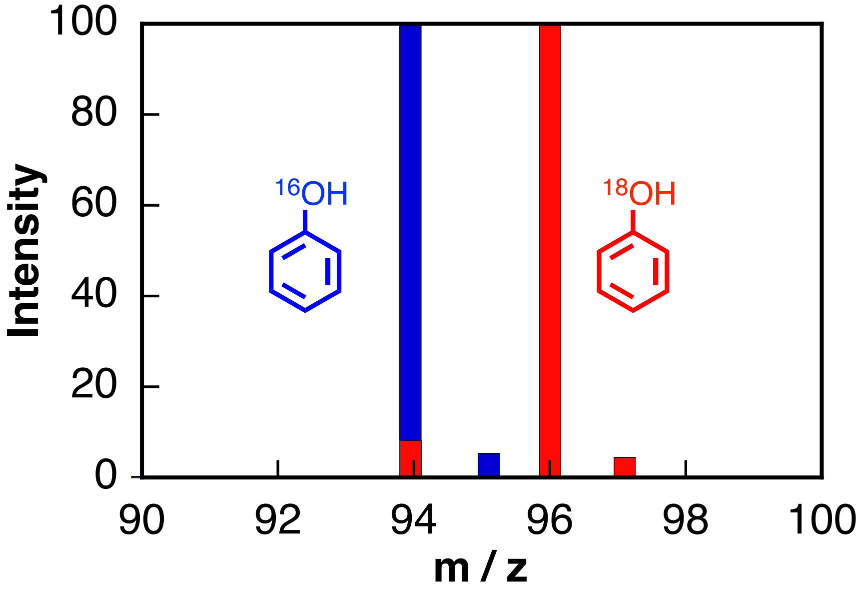


Figure S2. (a) GC-MS chart of reaction mixture after photoirradiation and (b) GC-MS spectra of phenol produced by photooxygenation of benzene with DDQ in nitrogen saturated MeCN at 298K: [benzene] = 10 mM; [DDQ] = 5.0 mM; [H_2O] = 1.0 M [(blue) $H_2{}^{16}O$; (b) $H_2{}^{18}O$ (98%, red)].

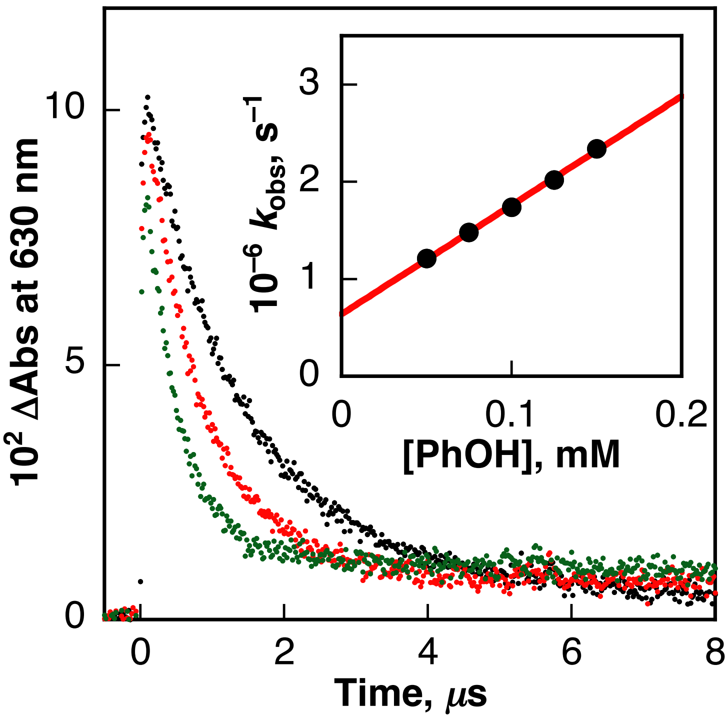


Figure S3. Decay time profiles of ^{3}DDQ* in the presence of various concentrations of phenol (0.50, 1.0 and 1.5 mM) after nanosecond laser excitation of an MeCN solution of DDQ (1.2 mM) with phenol. Inset: Plot of k_{obs} vs [PhOH].

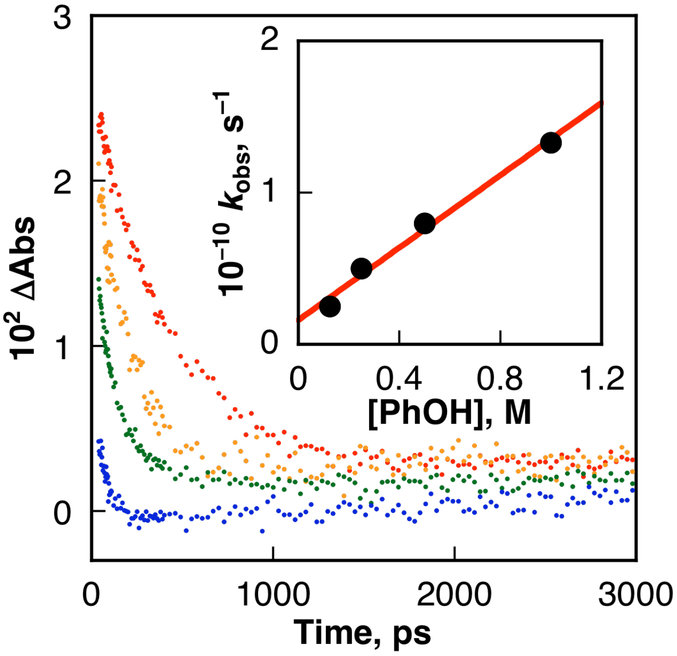


Figure S4. Decay time profiles of ^{3}DDQ* (λ = 630 nm) in the presence of various concentrations of phenol (red; 0.13 M, orange; 0.25, green; 0.50 and blue; 1.0 M) after femtosecond laser excitation of an MeCN solution of DDQ (5.0 mM) with phenol. Inset: Plot of k_{obs} vs [PhOH].

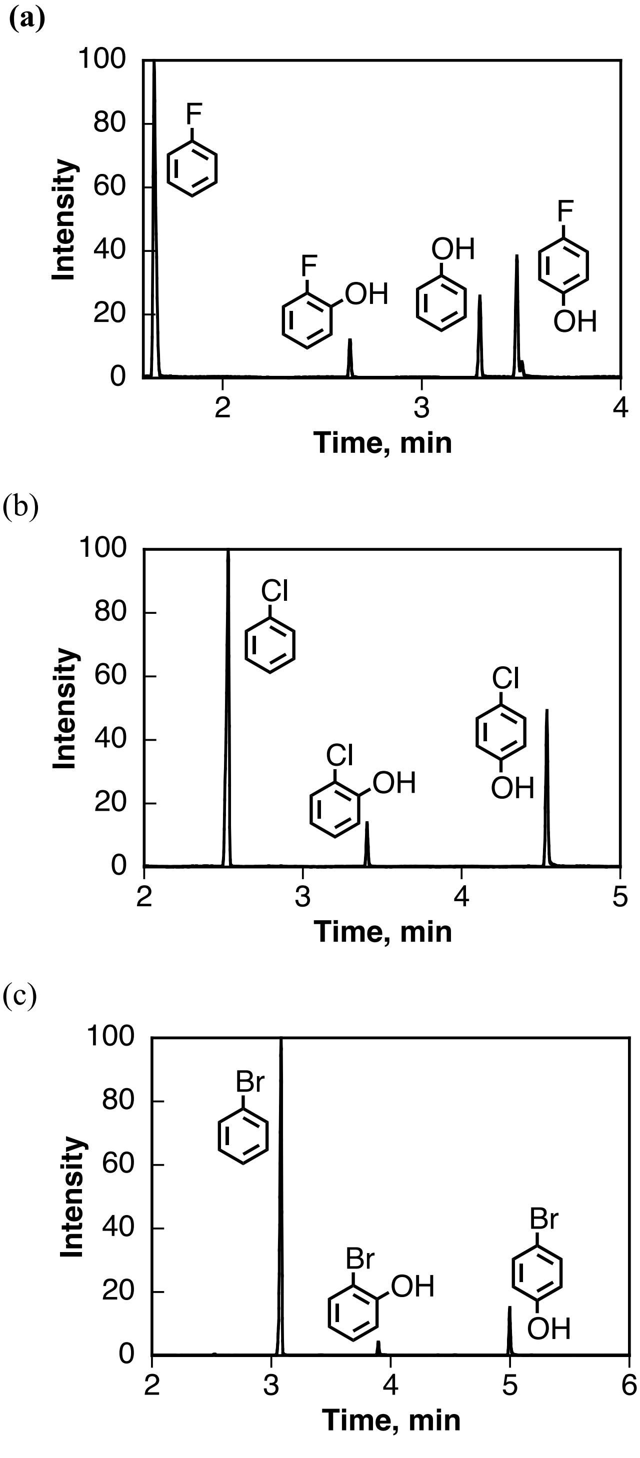


Figure S5. GC charts of reaction mixture obtained by photooxygenation of (a) fluoro- (b) chloro- (c) bromobenzene with DDQ in nitrogen saturated MeCN at 298K after photoirradiation.

Experimental Section

Materials. Chemicals were purchased from commercial source and used without purification, unless otherwise noted. 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) was obtained commercially and purified by recrystallization from hot dichloromethane.[S1] Potassium ferrioxalate used as an actinometer was prepared according to the literature and purified by recrystallization from hot water.[S2] Acetonitrile was of spectral grade, obtained commercially and used without further purification. Deuterated [$^2H_3$] acetonitrile (CD_3CN) was obtained from Euri SO-TOP, CEA, France, and used as received.

Reaction Procedure. The stoichiometric photoreaction carried out by the following procedure. A CD_3CN solution (0.60 cm^3) containing DDQ (40 mM) and D_2O (0.5 M) in an NMR tube sealed with a rubber septum was deaerated by bubbling with nitrogen through a stainless steel needle for 5 min. In the case of photocatalytic reaction, the DDQ solution (3.0 mM) with *tert*-butyl nitrite (TBN, 1.5 mM) and D_2O (0.5 M) in an NMR tube with rubber septum was saturated with oxygen by bubbling oxygen through a stainless steel needle for 5 min. After the bubbling, benzene (1.80 μmol; 30 mM) or halogenated benzene (1.80 μmol; 30 mM) was added to the solution. The solution was then irradiated with a 500 W xenon lamp (Ushio Optical Module X SX-UID 500XAMQ) through color glass filter transmitting $\lambda > 390$ nm at room temperature. After photoirradiation, the corresponding oxygenated product was identified and quantified by comparison of the ^1H NMR spectra with that of an authentic sample. The ^1H NMR measurements were performed on a Japan Electron Optics JMN-AL300 (300 MHz) NMR spectrometer.

Quantum Yield Determinations. A standard actinometer (potassium ferrioxalate) was used for the quantum yield determination of the DDQ photosensitized oxygenation of benzene with water. A square quartz cuvette (10 mm i.d.) that contained an MeCN solution (3.0 cm^3) of DDQ (2.0 mM) and benzene or halogenated benzene (50 mM) was irradiated with monochromatized light of λ = 420 nm from a Shimadzu RF-5300PC fluorescence spectrophotometer. Under the conditions of actinometry experiments, DDQ absorbed essentially 75% incident light of λ = 420 nm (Abs_{420} = 0.70). The light intensity of monochromatized light of λ = 420 nm was determined as 2.5×10^{-8} einstein s^{-1}. The photochemical reaction was monitored using a Shimadzu GC-17A gas chromatograph and Shimadzu MS-QP5000 mass spectrometer. The quantum yields were determined from increase of phenol derivatives.

Phosphorescence Measurements. Phosphorescence of DDQ (0.75 mM) in deaerated 2-methyltetrahydrofuran glass in a quartz tube (3 mm in diameter) was measured at 77 K using a HORIBA Fluoromax-4 florescence spectrophotometer by excitation at 400 nm.

Laser Flash Photolysis. The measurements of nanosecond transient absorption spectra in the photochemical reactions of DDQ with benzene and H_2O in MeCN were performed according to the following procedures. Typically, a nitrogen saturated MeCN solution containing benzene (1.0×10^{-2} – 1.0 M) and DDQ (1.2 mM) was excited by a Nd:YAG laser (Continuum, SLII-10, 4-6 ns fwhm) at λ = 430 nm with the power of 10 mJ/pulse. Photoinduced events were estimated by use of a continuous Xe lamp (150 W) and an InGaAs-PIN photodiode (Hamamatsu 2949) as a probe light and a detector, respectively. The output from the photodiodes and a photomultiplier tube was recorded with a digitizing oscilloscope (Tektronix, TDS3032, 300 MHz). The transient spectra were recorded for fresh solutions in each laser excitation. All experiments were performed at 298 K.

Femtosecond transient absorption spectroscopy experiments were conducted using an ultrafast source: Integra-C (Quantronix Corp.), an optical parametric amplifier: TOPAS (Light Conversion Ltd.) and a commercially available optical detection system: Helios provided by Ultrafast Systems LLC. The source for the pump and probe pulses were derived from the fundamental output of Integra-C (λ = 786 nm, 2 mJ/pulse and fwhm = 130 fs) at a repetition rate of 1 kHz. 75% of the fundamental output of the laser was introduced into a second harmonic generation (SHG) unit: Apollo (Ultrafast Systems) for excitation light generation at λ = 393 nm, while the rest of the output was used for white light generation. The laser pulse was focused on a sapphire plate of 3 mm thickness and then white light continuum covering the visible region from λ = 410 nm to 800 nm was generated via self-phase modulation. A variable neutral density filter, an optical aperture, and a pair of polarizer were inserted in the path in order to generate stable white light continuum. Prior to generating the probe continuum, the laser pulse was fed to a delay line that provides an experimental time window of 3.2 ns with a maximum step resolution of 7 fs. In our experiments, a wavelength at λ = 393 nm of SHG output was irradiated at the sample cell with a spot size of 1 mm diameter where it was merged with the white probe pulse in a close angle ($< 10^{\circ}$). The probe beam after passing through the 2 mm sample cell was focused on a fiber optic cable that was connected to a CMOS spectrograph for recording the time-resolved spectra (λ = 410 - 800 nm). Typically, 1500 excitation pulses were averaged for 3 seconds to obtain the transient spectrum at a set delay time. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. All measurements were conducted at room temperature, 295 K.

Theoretical Calculations. Density functional theory (DFT) calculations were performed with Gaussian09 (Revision C.02, Gaussian, Inc.).[S3] The calculations were performed on a 32-processor QuantumCube$^{\mathrm{TM}}$ at the B3LYP/6-31+G(d,p) level of theory. Graphical outputs of the computational results were generated with the GaussView software program (ver. 3.09) developed by Semichem, Inc.

References for SI

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