Supporting Information

Reaction of Phenol with Singlet Oxygen

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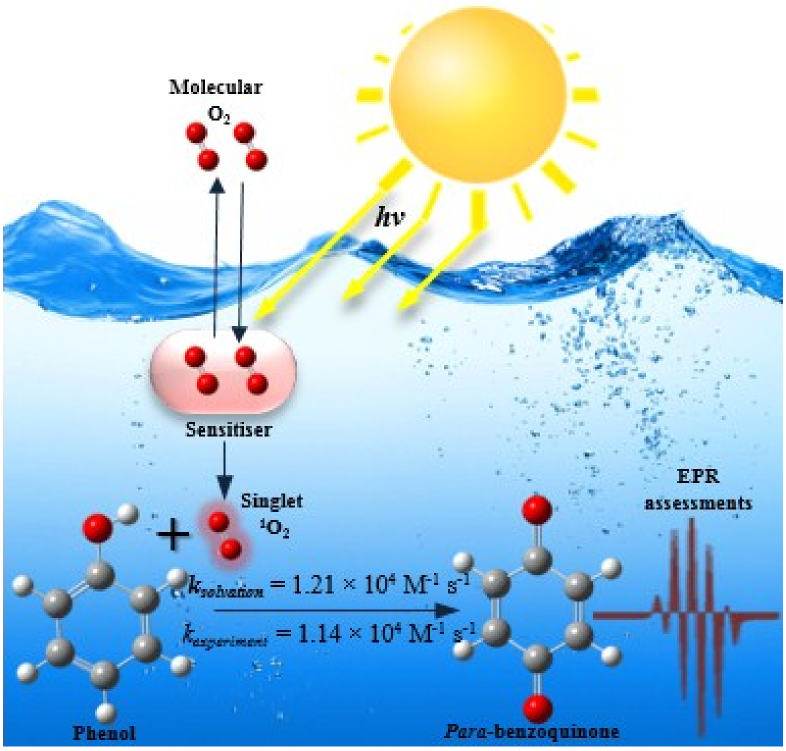
This document contains 11 pages, 5 Figures, and 2 Table

TOC graphic



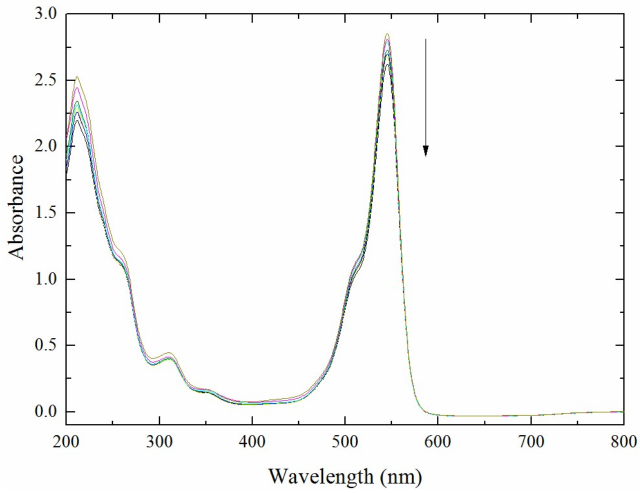


Figure S1: The time-course absorbance decay of rose bengal bleaching after illuminating for 0 - 24 h. Note that the results show minor bleaching of rose bengal over 24-h experiments.

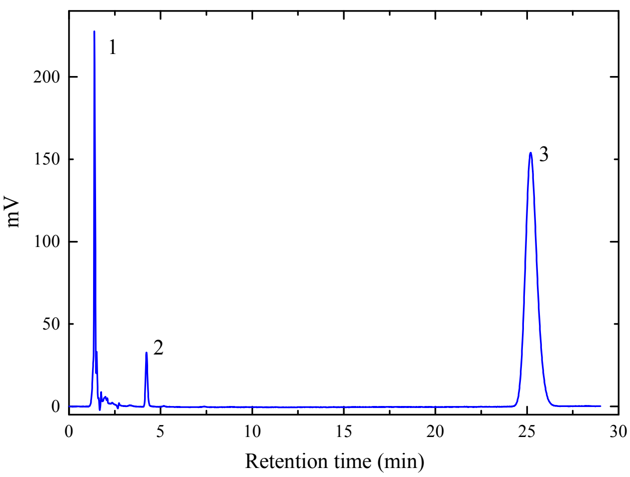


Figure S2: HPLC spectrum of (35 µM RB, 1 mM phenol) illuminated sample in buffered solution (pH 6.2); 1: rose bengal, 2: *para*-benzoquinone, 3: phenol.

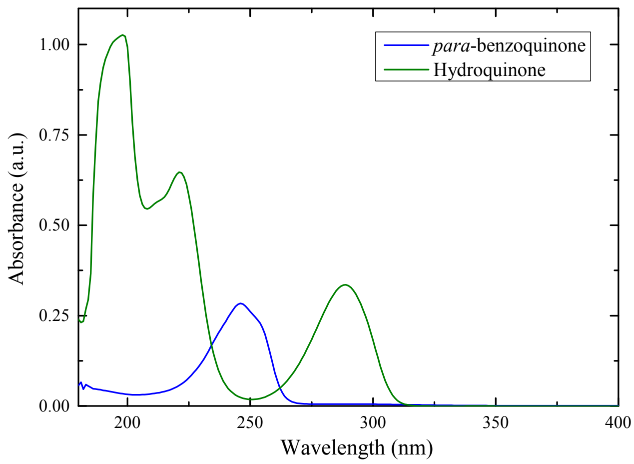


Figure S3: *para*-Benzoquinone (50 µM) and hydroquinone (50 µM) in 10 mM phosphate buffer solution (blank).

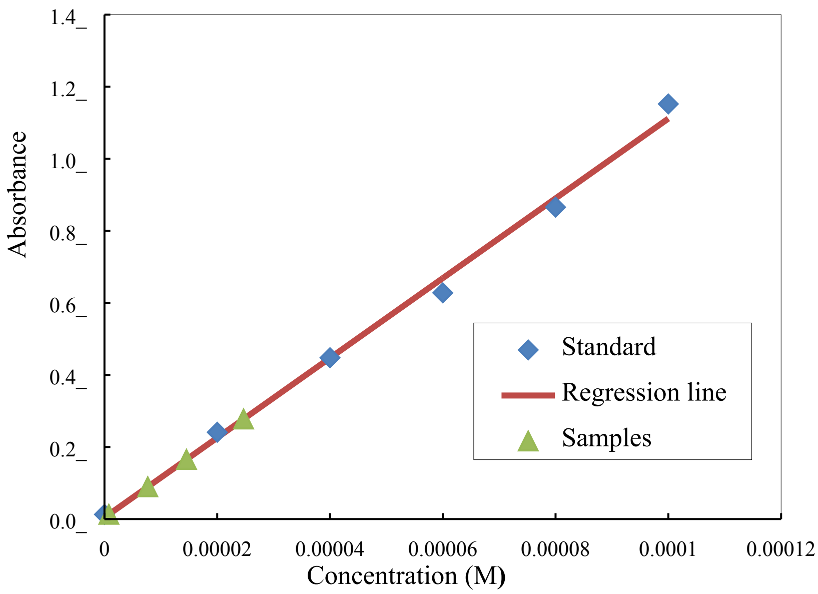


Figure S4: The absorbance values at 510 nm for complex of ferrous iron and 1,10-phenanthroline standards (*y*-axis) at different concentrations (*x*-axis).

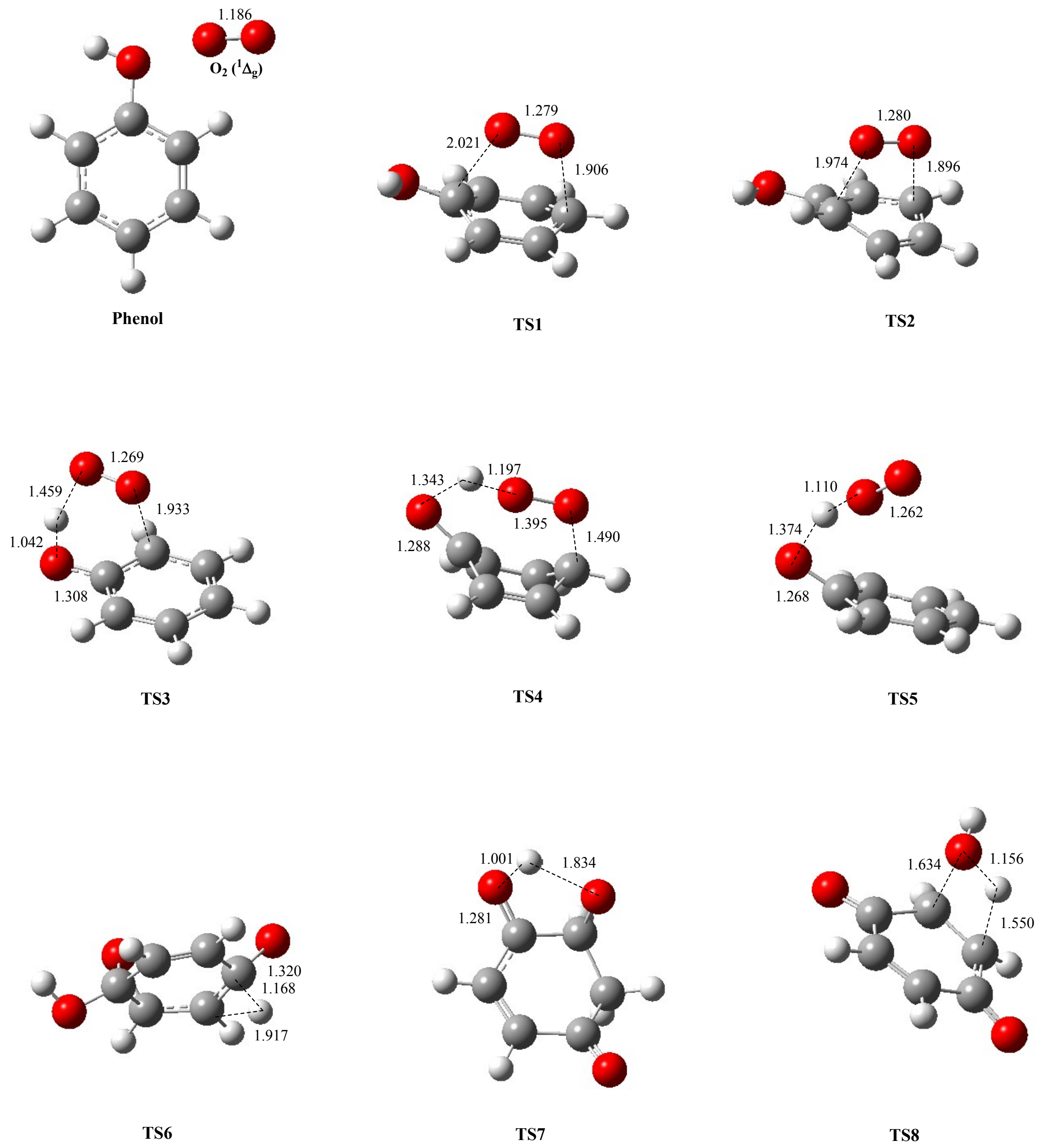


Figure S5: Optimised structures of transition states of phenol oxidation by singlet oxygen with M062X (distances are in Å).

Table S1: Ordinary differential equations (ODEs) and parameters for the estimated singlet oxygen concentration profile at 298.15 K, as coded in the POLYMATH software.[1]

	Variable	**Polymath Equation**
Explicit Equations (M^{-1} s^{-1}/ L E^{-1} or s^{-1})	k_v	$k_v = 1 \times 10^{10}$
	k_b	$k_b = 0.856$
	k°	$k^{\circ} = 6.5 \times 10^3$
	k_t	$k_t = 1.2 \times 10^9$
	k_d	$k_d = 5 \times 10^5$
	k_{isc}	$k_{isc} = 1 \times 10^9$
Integration Variables (M/ L E^{-1} s^{-1})	^{1}RB	^{1}RB(0) = 3.5×10^{-5}
	hv (0)	hv (0) = 32.75×10^{-5}
	Oxygen	Oxygen(0) = 3.9×10^{-5}
	^{1}RB*	^{1}RB*(0) = 0
	^{3}RB*	^{3}RB*(0) = 0
	RB_b	RB_b(0) = 0
	Singlet oxygen	Singlet oxygen(0) = 0
ODE Equations	d(^{1}RB)/d(t)	d(^{1}RB)/d(t) = - $kv \times {}^1$RB $\times hv$ - $k_b \times {}^1$RB $\times hv + k_t \times {}^3$RB* × Oxygen + $k^{\circ} \times {}^3$RB*
	d(SingletOxygen)/d(t)	d(SingletOxygen)/d(t) = $k_t \times {}^3$RB* × Oxygen - k_d × SingletOxygen
	d(hv)/d(t)	d(hv)/d(t) = 0
	d(RB_b)/d(t)	d(RB_b)/d(t) = $k_b \times {}^1$RB $\times hv$
	d(Oxygen)/d(t)	d(Oxygen)/d(t) = 0
	d(^{1}RB*)/d(t)	d(^{1}RB*)/d(t) = $k_v \times {}^1$RB $\times hv$ - $k_{isc} \times {}^1$RB*
	d(^{3}RB*)/d(t)	d(^{3}RB*)/d(t) = $k_{isc} \times {}^1$RB* - $k^{\circ} \times {}^3$RB* - $k_t \times {}^3$RB* × Oxygen
Independent Variable (s)	t	$t(0) = 0$; $t(f) = 10800$

1 Shacham, M.; Cutlip, M. B; Elly M. POLYMATH, http://www.polymath-software.com/, date of access: 23/2/2016.

Table S2: POLYMATH[1] ordinary differential equations (ODEs) and parameters for the solvation model at 298.15 K. The rate constants $k1$ to $k8$ come from Table 1 in the paper.

	Variable	**Polymath Equation**
Explicit Equations ($M^{-1}\,s^{-1}$/ $L\,E^{-1}$ or s^{-1})	k_v	$k_v = 1 \times 10^{10}$
	k_b	$k_b = 0.856$
	k°	$k^{\circ} = 6.5 \times 10^{3}$
	k_t	$k_t = 1.2 \times 10^{9}$
	k_d	$k_d = 5 \times 10^{5}$
	k_{isc}	$k_{isc} = 1 \times 10^{9}$
	$k1$	$k1 = 1.21 \times 10^{4}$
	$k6$	$k6 = 1.62 \times 10^{-2}$
	$k7$	$k7 = 2.91 \times 10^{-3}$
	$k8$	$k8 = 3.47 \times 10^{-2}$
Integration Variables (M/ $L\,E^{-1}\,s^{-1}$)	^{1}RB	^{1}RB(0) = 3.5×10^{-5}
	hv (0)	hv (0) = 1.157×10^{-9}
	Oxygen	Oxygen(0) = 3.9×10^{-5}
	^{1}RB*	^{1}RB*(0) = 0
	^{3}RB*	^{3}RB*(0) = 0
	RB_b	$RB_b(0) = 0$
	Singlet oxygen	Singlet oxygen(0) = 0
	Phenol	Phenol(0) = 1×10^{-3}
	$M6$	$M6(0) = 0$
	$M7$	$M7(0) = 0$
	$M8$	$M8(0) = 0$
	$M9$	$M9(0) = 0$
ODE Equations	d(^{1}RB)/d(t)	d(^{1}RB)/d(t) = - kv × ^{1}RB × hv - k_b × ^{1}RB × hv + k_t × ^{3}RB* × Oxygen + k° × ^{3}RB*
	d(SingletOxygen)/d(t)	d(SingletOxygen)/d(t) = k_t × ^{3}RB* × Oxygen - k_d × SingletOxygen - $k1$ × Phenol ×Oxygen - k_q × Phenol ×Oxygen
	d(hv)/d(t)	d(hv)/d(t) = 0
	d(RB_b)/d(t)	d(RB_b)/d(t) = k_b × ^{1}RB × hv

	d(Oxygen)/d(t)	d(Oxygen)/d(t) = 0
	d(^{1}RB*)/d(t)	d(^{1}RB*)/d(t) = kv × ^{1}RB × hv - k_{isc} × ^{1}RB*
	d(^{3}RB*)/d(t)	d(^{3}RB*)/d(t) = k_{isc} × ^{1}RB* - $k°$ × ^{3}RB* - k_t × ^{3}RB* × Oxygen
	d(Phenol)/d(t)	d(Phenol)/d(t) = -k1 × Phenol ×Oxygen
	d(M6)/d(t)	d(M6)/d(t) = k1 × Phenol × SingletOxygen- k6 × M6
	d(M7)/d(t)	d(M7)/d(t) = k6 × M6- k7 × M7
	d(M8)/d(t)	d(M8)/d(t) = k7 × M7- k8 × M8
	d(M9)/d(t)	d(M9)/d(t) = k8 × M8
Independent Variable (s)	t	t(0) = 0 ; t(f) = 3000

1 Shacham, M.; Cutlip, M. B; Elly M. POLYMATH, http://www.polymath-software.com/, date of access: 23/2/2016.

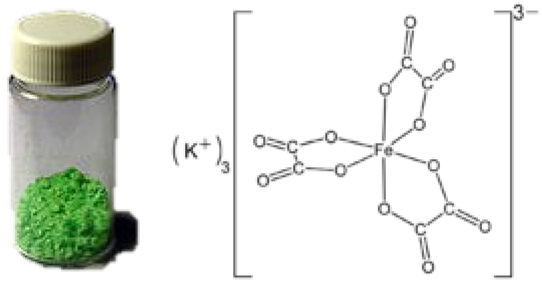
Actinometry Experiment

Materials:

1. Ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$)
2. 1,10-phenanthroline monohydrate
3. Sulfuric acid-98% (H_2SO_4)
4. Ferric chloride ($FeCl_3$)
5. Potassium oxalate ($K_2C_2O_4 \cdot H_2O$)
6. Sodium acetate (CH_3COONa)
7. DI water
8. Heat gun
9. Thermometer
10. Vacuum filtration system

Procedure:

- Phase 1: Preparation of ferrioxalate crystals.



Ferrioxalate ferrioxalate ($K_3Fe(C_2O_4)_3{\cdot}3H_2O$) was prepared in the dark room by mixing three volumes of 1.5 M potassium oxalate ($K_2C_2O_4$) with one volume of 1.5 M ferric chloride ($FeCl_3$) in a 2L beaker. Solution of 1.5 M $K_2C_2O_4$ was made by introducing 139.58 g $K_2C_2O_4{\cdot}H_2O$ in a 500 mL flask and filling the flask up to the mark with DI-water. Solution of 1.5 M $FeCl_3$ was prepared by the same way except for adding 101.37 g $FeCl_3$. The solution was mixed under magnetic stirring in a stream of warm air by a heat gun. The solution temperature was monitored by a thermometer and controlled to be around 45^o C by adjusting the wind speed and the distance between the heat gun and the beaker. The solution recrystallised three times in an ice bath. Between each recrystallisation, we washed the crystals with 600 mL water and then separated them using a vacuum filtration system. The resulting $K_3Fe(C_2O_4)_3{\cdot}3H_2O$ crystals appeared neon green in colour and were stored in an amber vial.

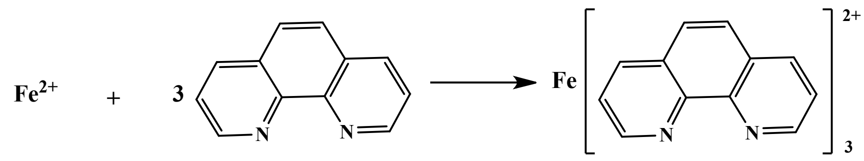
- Phase 2: Photoreaction of potassium ferrioxalate.

Exposure of potassium ferrioxalate ($K_3Fe(C_2O_4)_3{\cdot}3H_2O$) to green LEDs light results in the following reactions:

$$[Fe^{III}(C_2O_4)_3]^{3-} + h\nu \rightarrow [Fe^{II}(C_2O_4)_2]^{2-} + C_2O_4^{-\cdot} \qquad (1)$$

$$[Fe^{III}(C_2O_4)_3]^{3-} + C_2O_4^{-\cdot} \rightarrow [Fe^{III}(C_2O_4)_3]^{2-} + C_2O_4^{2-} \qquad (2)$$

$$[Fe^{III}(C_2O_4)_3]^{2-} \rightarrow [Fe^{II}(C_2O_4)_2]^{2-} + 2CO_2 \qquad (3)$$



Fe(II) analyte   1,10-phenanthroline   Fe(II)-1,10-phenanthroline   (4)

To prepare 0.15 M ferrioxalate solution for photolysis, we dissolved 7.368 g of the potassium ferrioxalate crystals in around 400 mL of DI-water in a 500mL flask. A volume of 50 mL 1N sulfuric acid is added and then diluted by DI-water by filling the beaker to the mark. For photolysis, in a photochemical reactor, 5 mL (V_1) solution was exposed to light generated by 24 LEDs. Dark control sample (blank) was processed exactly as the irradiated samples except covering it with aluminium foil. To produce sufficient ferrous iron, we irradiated the solution for 50 min.

For analysis, 2 mL (V_2) solution was taken from the reactor tube and mixed with buffer solution equal to $V_B = (V_2/2)$ to prevent solid precipitation, then 2 mL 0.1 wt % 1,10-phenanthroline was added in 50 mL (V_3) volumetric flasks and made up to the mark by adding DI-water. After around 30 min, the complex of ferrous iron and 1,10-phenanthroline was fully developed and ready for analysis. The complex concentration was determined on a UV-visible spectrophotometer at 510 nm using the calibration curve prepared in phase 3 below, see Figure S4.

- Phase 3: Calibration curve

Three solutions are needed to prepare the necessary standards for the calibration curve.

1. A buffer solution was made by mixing 600 mL 1 N Sodium acetate (CH_3COONa) (48.01 g) and 360 mL 1 N H_2SO_4 in a 1 L volumetric flask and diluted by DI-water until the level reaches the L-liter mark. Solution of 1 N H_2SO_4 was made by diluting 27.17 mL pure (98 %) sulfuric acid to 1 L by water.
2. Solution of 0.1 wt % 1,10-phenanthroline was prepared by adding 109.987 mg of 1,10-phenanthroline monohydrate to 100 mL by DI-water and stored in the dark.
3. Solution of 0.4 mM ferrous iron in 0.1 N H_2SO_4 was made freshly by diluting 0.1 M $FeSO_4$ in 0.1 N H_2SO_4. For this, 2 mL 0.1 M $FeSO_4$ in 0.1 N H_2SO_4 was mixed with 50 mL 1 N H_2SO_4 and diluted to 500 mL by DI-water. Solution of 0.1 M $FeSO_4$ in 0.1 N H_2SO_4 was prepared by mixing 13.901 g $FeSO_4 \cdot 7H_2O$ and 50 mL 1 N H_2SO_4 in a 500 mL volumetric flask and filling the flask with DI-water to the mark.

Volume (X) 0, 1.25, 2.5, 3.75, 5, 6.25 mL of 0.4 mM $FeSO_4$ were added to a series of 25 mL volumetric flasks and mixed with (12.5-X) mL 0.1 N H_2SO_4 and 6.25 mL buffer solution. The resulting concentrations of ferrous iron ranged from 0 to 0.1 mM. We added 2.5 mL 0.1 wt % 1,10-phenanthroline monohydrate to the volumetric flasks and left the solution to sit for a least 30 min to let the complex of ferrous iron and 1,10-phenanthroline develop fully. Standard solutions were analysed on a UV-Vis spectrophotometer at 510 nm and the standard curve was prepared by plotting the absorbance at 510 nm of each solution against the concentration; see Figure 3 in the article.

Cartesian Coordinates of Figure S5 structures (M06/6-311+G(d,p), (solvation)

Phenol

0 1

C	0.88628766	0.23411371	0.00000000
C	-0.49825534	0.19871571	0.00005100
C	-1.21339734	1.39037471	0.00002500
C	-0.54350034	2.60791071	-0.00003500
C	0.84404266	2.62858571	0.00001000
C	1.56736666	1.44535171	0.00001000
H	1.43892466	-0.69615129	-0.00000100
H	-1.04147134	-0.73612829	0.00013600
H	-1.10733534	3.53369471	-0.00016600
H	1.35942166	3.57991771	0.00001900
H	2.64795066	1.46560871	0.00001300
O	-2.57061234	1.30561671	-0.00018200
H	-2.95388034	2.18554671	0.00129000

Oxygen (singlet)

0 1

O	0.00000000	0.00000000	0.59573200
O	0.00000000	0.00000000	-0.59573200

Oxygen (triplet)

0 3

O	0.00000000	0.00000000	0.59770900

O	0.00000000	0.00000000	-0.59770900

Oxygen (singlet-mix HOMO and LOMO orbitals)

0 1

O	0.00000000	0.00000000	0.59605300
O	0.00000000	0.00000000	-0.59605300

TS1

0 1

C	-1.45484956	0.98662206	0.00000000
C	-2.09378956	-0.26719894	0.23471200
C	-1.48166656	-1.47698894	-0.20627000
C	-0.13389056	-1.48007594	-0.30280300
C	0.54771944	-0.27675594	0.05374200
C	-0.10899456	0.97733606	-0.11413800
H	-2.04760056	1.88720806	0.06870600
H	-2.07976056	-2.37427994	-0.30009600
H	0.42457444	-2.38771894	-0.47825400
H	1.62706544	-0.29371994	0.10767100
H	0.46602944	1.89088306	-0.14648500
O	0.09077044	-0.47328794	1.89419600
O	-1.17838456	-0.40013494	2.03185000
H	-3.71957256	-1.09788894	0.75616800
O	-3.39446056	-0.21846794	0.54252200

TS2

0 1

C	1.77257532	0.68561872	0.00000000
C	2.53521132	-0.53599728	-0.02442300
C	3.78340932	-0.56568228	-0.69899800
C	4.48988332	0.58524772	-0.64983900
C	3.86245732	1.72298872	-0.03085900
C	2.45940032	1.85649472	-0.03282500
H	4.21632432	-1.50440728	-1.01002200
H	5.52952732	0.63866072	-0.93817100
H	4.46575332	2.60412272	0.13864700
H	1.97281432	2.79714272	0.17478300
O	4.08304832	0.73863572	1.66405700
O	3.14464632	-0.12928428	1.72465200
H	1.99894832	-1.46405828	0.13840800
O	0.44347932	0.66873872	0.21458000
H	0.11091332	-0.23172028	0.22136500

TS3

0 1

H	-2.09277500	0.71122200	0.19344900
O	-2.38636800	-0.51988300	-0.53244400
O	-1.21477600	-0.94352200	-0.77600800
C	-0.22515400	0.72469500	0.41051500
C	0.83491100	1.38564800	-0.25732000
C	-0.09136100	-0.64635200	0.76830200

C	1.99158200	0.71085200	-0.50196100
H	0.69150200	2.41683900	-0.54666500
C	1.14457900	-1.30525200	0.52366500
H	-0.81996000	-1.07900800	1.43826900
C	2.14692600	-0.65160900	-0.12072800
H	2.81003700	1.21258500	-1.00106700
H	1.26373800	-2.33149500	0.84141400
H	3.08012800	-1.15507500	-0.33199400
O	-1.36655300	1.32803500	0.61742300

TS4

0 1

C	-2.20735795	0.68561872	0.00000000
C	-2.87708995	1.88492772	-0.59178300
C	-2.20473195	3.17215972	-0.22587400
C	-0.88547195	3.11507272	-0.39428600
C	-0.33673095	1.80131972	-0.90740900
C	-0.88948595	0.64561472	-0.12546400
H	-2.84068295	-0.10935428	0.36787500
H	-2.77392895	4.05195772	0.03740500
H	-0.22872695	3.96314672	-0.26735600
H	0.74231705	1.79372172	-1.02096600
H	-0.26946295	-0.19779228	0.14320500
O	-0.82687795	1.54940972	-2.29122700
O	-2.18167595	1.87845972	-2.25153100

H	-3.23159395	1.31949272	-2.11446400
O	-4.04032895	1.71175272	-1.11696400

TS5

0 1

C	-2.44147167	0.98662206	0.00000000
C	-2.59093467	2.23633806	-0.72325000
C	-1.51957767	2.66769906	-1.56380400
C	-0.52638367	1.78664206	-1.84255000
C	-0.45766867	0.49495206	-1.22453200
C	-1.34773267	0.14300206	-0.25551200
H	-3.11959367	0.80487106	0.82191700
H	-1.60817667	3.62216106	-2.06266800
H	0.23466333	2.05109506	-2.56552900
H	0.35156433	-0.16893494	-1.49513900
H	-1.25752967	-0.79755394	0.26954900
O	-3.61786267	0.13892006	-2.48675500
O	-3.99020067	0.39111906	-1.30787600
H	-4.18357267	1.47437806	-1.16045500
O	-3.75857767	2.72725006	-0.78866400

TS6

0 1

C	-1.10367898	0.28428093	0.00000000
C	-0.38580998	1.60335693	0.24041200

C	-1.12793098	2.88869893	0.20728300
C	-2.45611298	2.89423793	0.18466100
C	-3.25024198	1.64014193	-0.06310200
C	-2.50104698	0.43223593	-0.31776100
H	-0.52686298	-0.56096007	-0.35176700
H	-0.53649798	3.79520793	0.25455700
H	-3.02666198	3.81147593	0.24937900
H	-3.49210998	1.82402693	-1.18868300
H	-3.06842798	-0.37753407	-0.76048500
O	-4.29768998	1.32311293	0.67526700
O	-0.71615698	0.75995493	1.29073100
H	1.44268002	2.11866093	0.48550500
O	0.92504902	1.60770993	-0.14602200

TS7

0 1

C	-1.25418065	0.25083612	0.00000000
C	-1.65896065	1.67862212	-0.20882600
C	-0.76979765	2.81160812	-0.27929800
C	0.53941435	2.56829012	-0.40047900
C	1.09963235	1.17509012	-0.41724700
C	0.26248635	0.09983212	0.21558900
H	-1.76384465	-0.13894088	0.90562900
H	-1.19939165	3.80153612	-0.36605300
H	1.25192735	3.36278812	-0.58603600

H	0.49235435	0.14287012	1.28622700
H	0.57633835	-0.87049388	-0.16245100
O	2.19236235	1.00248112	-0.88766700
O	-1.74940665	-0.21359088	-1.17420800
H	-3.13907565	0.92633912	-0.80736400
O	-2.88567665	1.86078812	-0.52875300

TS8

0 1

C	-0.68561876	0.83612039	0.00000000
C	-1.63471776	1.79557939	-0.59034300
C	-1.11635676	3.20320539	-0.84395500
C	0.31683324	3.44765739	-0.84855900
C	1.22109424	2.38311339	-0.47144800
C	0.61478224	1.11719539	0.06819400
H	-1.10427376	-0.10562361	0.33086100
H	-1.73749076	3.72086639	-1.56839300
H	0.71471724	4.21447639	-1.49939000
H	-0.31629976	4.10463939	0.40487500
H	1.33111124	0.41233839	0.47264700
O	2.43224124	2.44528339	-0.55562100
O	-2.77297076	1.51713939	-0.86655400
H	-2.00658176	4.73668839	0.47013700
O	-1.44980176	3.94983039	0.57080200