Supplementary Information

Formation of Light Absorbing Soluble Secondary Organics and Insoluble Polymeric Particles from the Dark Reaction of Catechol and Guaiacol with Fe(III)

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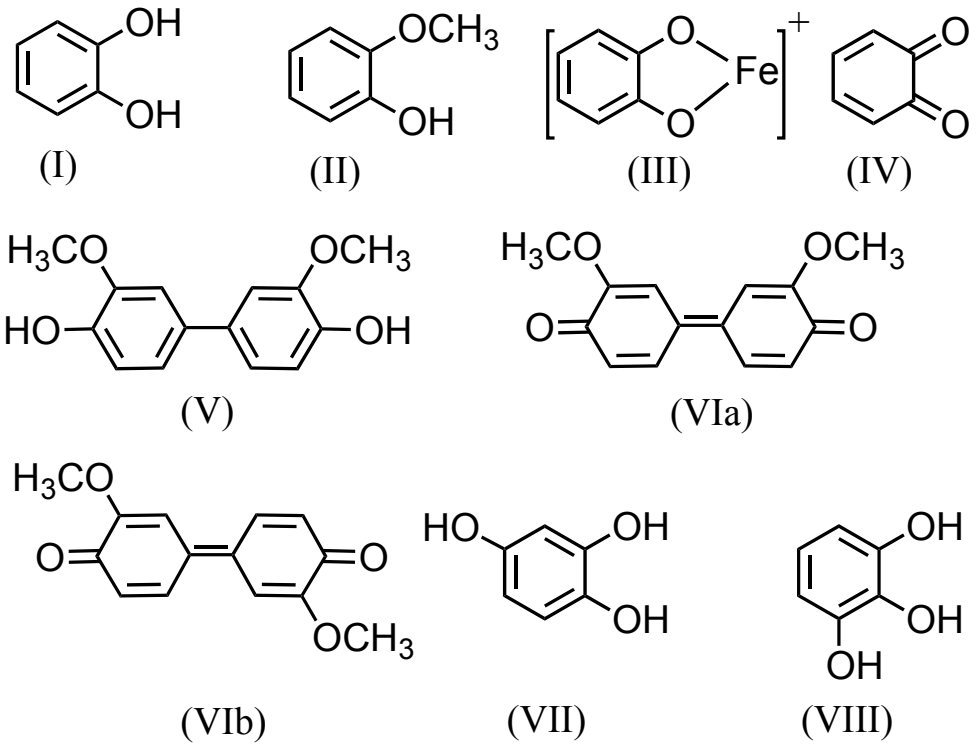
Supplementary Data (18 pages)

1.



Scheme S1: Chemical structures of (I) catechol, (II) guaiacol, (III) catechol-Fe complex, (IV) o-quinone, (V) 3,3'-dimethoxy-4,4'-biphenyldiol, (VIa) 3,3'-dimethoxy-4,4'-biphenoquinone, (VIb) 3,5'-dimethoxy-4,4'-biphenoquinone, (VII) 1,2,4-benzentriol, and (VIII) pyrogallol.

2. Additional experimental details

2a. Chemicals. Pyrogallol (1,2,3-trihydroxybenzene, ≥99%, CAS 87-66-1, Sigma-Aldrich) and 1,2,4-benzentriol (99%, CAS 533-73-3, Sigma-Aldrich) were used as reference compounds in the mass spectrometry experiments. The following chemicals were used in the hematite dissolution experiments: hematite nanoparticles (α-Fe_2O_3, >99.9%, Nanostructured and Amorphous Materials, 19 m^2/g surface area, 67 nm average diameter, 8.6 isoelectric point), sodium chloride (NaCl powder, 99%, ACS grade, BDH), acetic acid (CH_3COOH, 99.7%, ACS grade, glacial, Macron), ammonium acetate ($CH_3CO_2NH_4$, BioXtra, ≥98%, Sigma-Aldrich), hydroxylamine hydrochloride (NH_2OH•HCl, 99%, Sigma-Aldrich), 1,10-phenanthroline ($C_{12}H_8N_2$, ≥99%, Sigma-Aldrich), and ammonium iron(II) sulfate hexahydrate ($(NH_4)_2Fe(SO_4)_2$•$6H_2O$, 99% ACS reagent, Sigma-Aldrich).

2b. UV-visible spectroscopy and HPLC experiments. The following solvents were used in the preparation of mobile phase in the HPLC experiments: acetonitrile (HPLC grade, 99.9%, BDH), water (HPLC grade) and trifluoroacetic acid (TFA, HPLC grade, 99.9%, EMD). In a typical UV-vis experiments, 20 mL of either catechol (1 mM) or guaiacol (0.5 mM) were mixed with 0.4 mL $FeCl_3$ at a concentration that would yield the desired organic reactant:Fe molar ratio. The vial was wrapped with Al-foil to avoid photochemical reactions. After a given reaction time, a 3 mL aliquot was taken using a syringe, and the solution was filtered before collecting the UV-vis spectrum. In a typical HPLC experiment, 10 mL of a 1 mM catechol solution was placed in a vial wrapped in aluminum foil and placed on a stir plate. Then, 0.2 mL of either 25, 50, or 102 mM $FeCl_3$ solution was added to the catechol solution with continuous reaction to obtain a 2:1, 1:1 or 1:2 organic reactant:Fe molar ratio. The timer was started as soon as the $FeCl_3$ was added. Solutions were injected into the HPLC after a given reaction time as described in figures.

2c. Mass spectrometric experiments. Typical operating conditions were: spray voltage 2.8kV, mass resolving power 70,000 at *m/z* 200, capillary temperature 275°C, heater temperature 300°C, sheath gas 25 arbitrary units and auxiliary gas 4 arbitrary units. The operating conditions for the MS/MS part of the experiments were: N_2 collision partner and normalized collision energy (NCE = 120 arbitrary units). The sample injection volume was 10 μL. Accurate mass determinations were made with internal lock mass *m/z* 91.00368 and typical errors were better than 1 mmu. A Dionex Ultimate 3000 UHPLC was employed with a C18, 2.1x150 mm column (Waters, X-Bridge) operated at 0.2 mL/min. Xcalibur software was used for data collection, processing, and analysis.

2d. Sample preparation for scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) experiments. Particles from reaction of $FeCl_3$ with either catechol or guaiacol solutions were collected on nylon membrane filters after 1.5 hrs, washed multiple times with water, and re-suspended in water, aerosolized with a nebulizer (Salter Labs #8900-7), sent through a diffusion dryer, and collected on carbon type-B 400 mesh copper grids (Ted Pella, Inc. #01814-F) with an SKC Sioutas Cascade Impactor. Particles collected on stage "D" (>0.25 μm) of the impactor were analyzed with an FEI Magellan XHR SEM. Images of particles were taken at 10 kV and 25 pA and EDS analysis was done at 20 kV and 0.8 nA.

2e. Simulating acid-driven dissolution of iron (oxyhydr)oxides in mineral dust aerosols. Five vials containing 0.008 g of hematite were mixed with 1.75 mL of 0.01 M KCl at pH 1 (BKG 1). For determining total iron concentration according to the procedure described by Lanzl *et al.*[1], another 1 vial containing 0.008 g of hematite were mixed with 1.75 mL background solutions prepared by mixing 5 mL NaCl (25 mM) and 1 mL buffer (1 mL acetic acid+0.1 g ammonium acetate) at pH 1 (BKG 2). The slurries were allowed to mix for 10 days on a

medium speed vortex in the dark. Then, all vials were filtered using a 0.2 μm nylon membrane filters. The pH of the filtrate was about 0.2 higher from the initial value of 1. All filtrates were wrapped with Al-foil.

To determine the total dissolved iron concentration in these filtrates using UV-vis spectroscopy, a linear calibration was constructed from the absorbance at 510 nm of the complexes of standard solutions of $(NH_4)_2Fe(SO_4)_2 \bullet 6H_2O$ and 1,10-phenanthroline according to a modified procedure described by Stucki and Anderson.[2,3] Briefly, the concentrations of the standard solutions were in the range 0.0025-0.025 mM ($2.5 - 25 \times 10^{-6}$ M) using a background solution from a 100 mL NaCl (25 mM), 0.04 mL $NH_2OH \bullet HCl$ (1.3 mM) and 0.4 mL buffer (0.5 g $CH_3CO_2NH_4$ (s) + 5 mL CH_3COOH). The purpose of the addition of $NH_2OH \bullet HCl$ was to reduce Fe(III) to Fe(II). A 10 mL aliquot from each standard solution was mixed with 0.2 mL 1,10-phenanthroline (1 g/L) and allowed to sit in the dark for 30 min. All of the above was done under red light illumination in the lab to minimize the possible effects of photochemistry. A UV-vis spectrum was then recorded for each standard solution after zeroing the spectrometer with 3 mL of a background solution from a 10 mL NaCl (25 mM), 0.01 mL $NH_2OH \bullet HCl$ (1.3 mM), 0.04 mL buffer, and 0.04 mL 1,10-phenanthroline. Figure S1 shows the UV-vis spectra of the complexes and calibration curve, respectively. In order to use this calibration curve, the filtrates from hematite dissolution had to be diluted. To do that, 0.05 mL of filtrate with BKG 2 was diluted by the addition of 27 mL BKG 2. Then, 2 mL of this diluted solution was mixed with 0.2 mL $NH_2OH \bullet HCl$ (1.3 mM) and 2 mL 1,10-phenanthroline (1 g/L) followed by sitting for 30 min. A UV-vis spectrum taken for this solution showed a peak similar to the one in Figure S1(a), with an absorbance of 0.17 at 510 nm. From the calibration curve in Figure S1b,

the dissolved $[Fe]_{tot}$ = 0.00994 mM in the diluted solution. After taking into account the dilution factor, the $[Fe]_{tot}$ in the original 1 mL filtrate is calculated to be 5.4 mM.

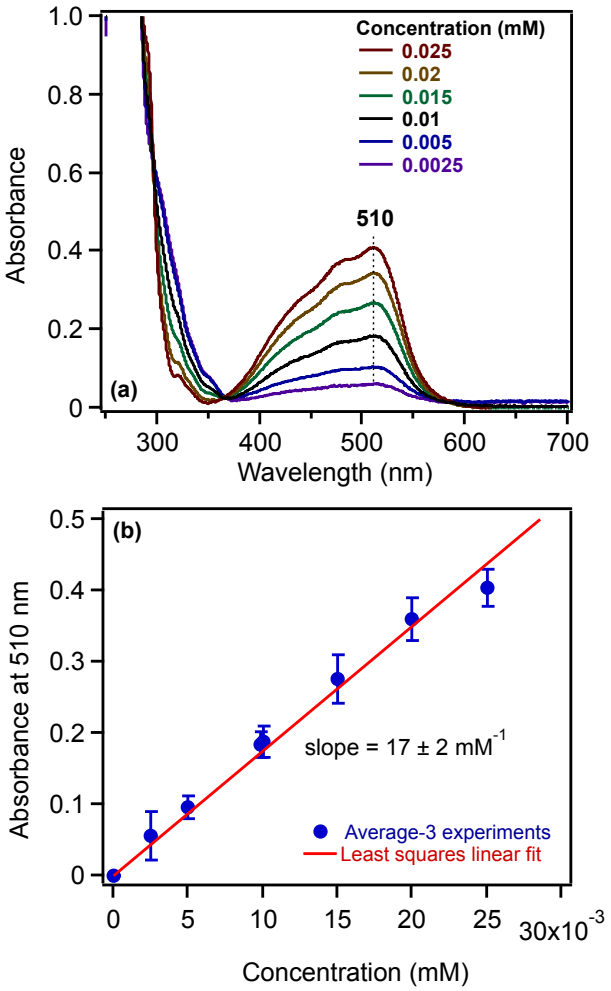


Figure S1: (a) Representative UV-vis absorbance spectra of the complexes between standard solutions of $(NH_4)_2Fe(SO_4)_2 \bullet 6H_2O$ and 1,10-phenanthroline. (b) Calibration curve constructed from the absorbance at 510 nm from spectra shown in panel (a).

For the experiments with standard solutions of catechol and guaiacol, the pH of the filtrates prepared in BKG 1 was raised to 3 by adding NaOH solution. After accounting for dilution by the base, the concentration of the organic solutions was calculated such that a 1:2 organic reactant:Fe molar ratio would be obtained in the final solution after reaction. Digital images of solution mixture were taken after 3 min and 1 hr of reaction, and then filtered.

3.

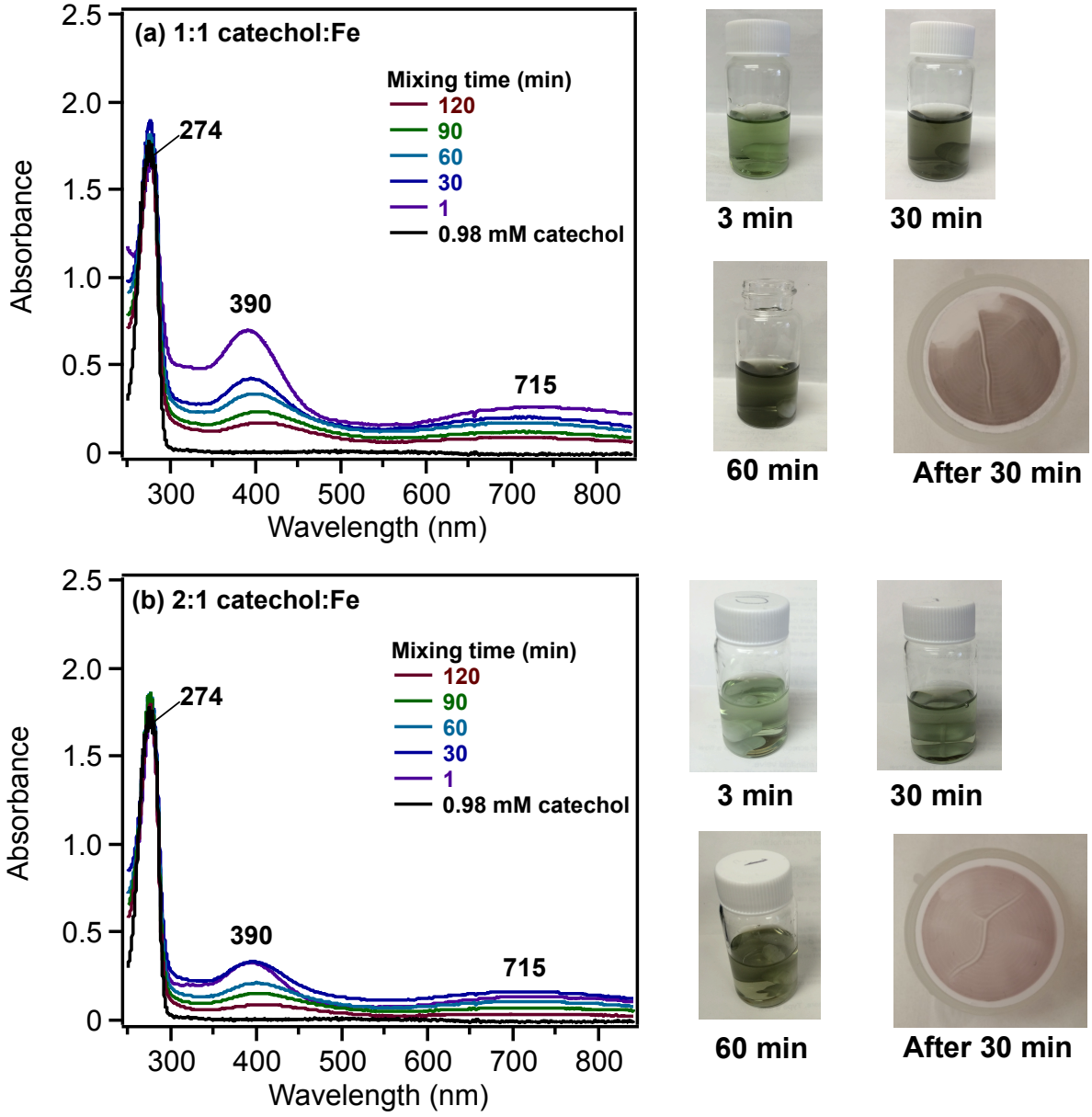


Figure S2: UV-vis spectra of unfiltered solutions after dark reaction and filtration of catechol (0.98 mM) with $FeCl_3$ at pH 3 at different ratios a function of time. Digital images of the corresponding unfiltered solutions and particles on filter after 30 min are shown on the right.

4.

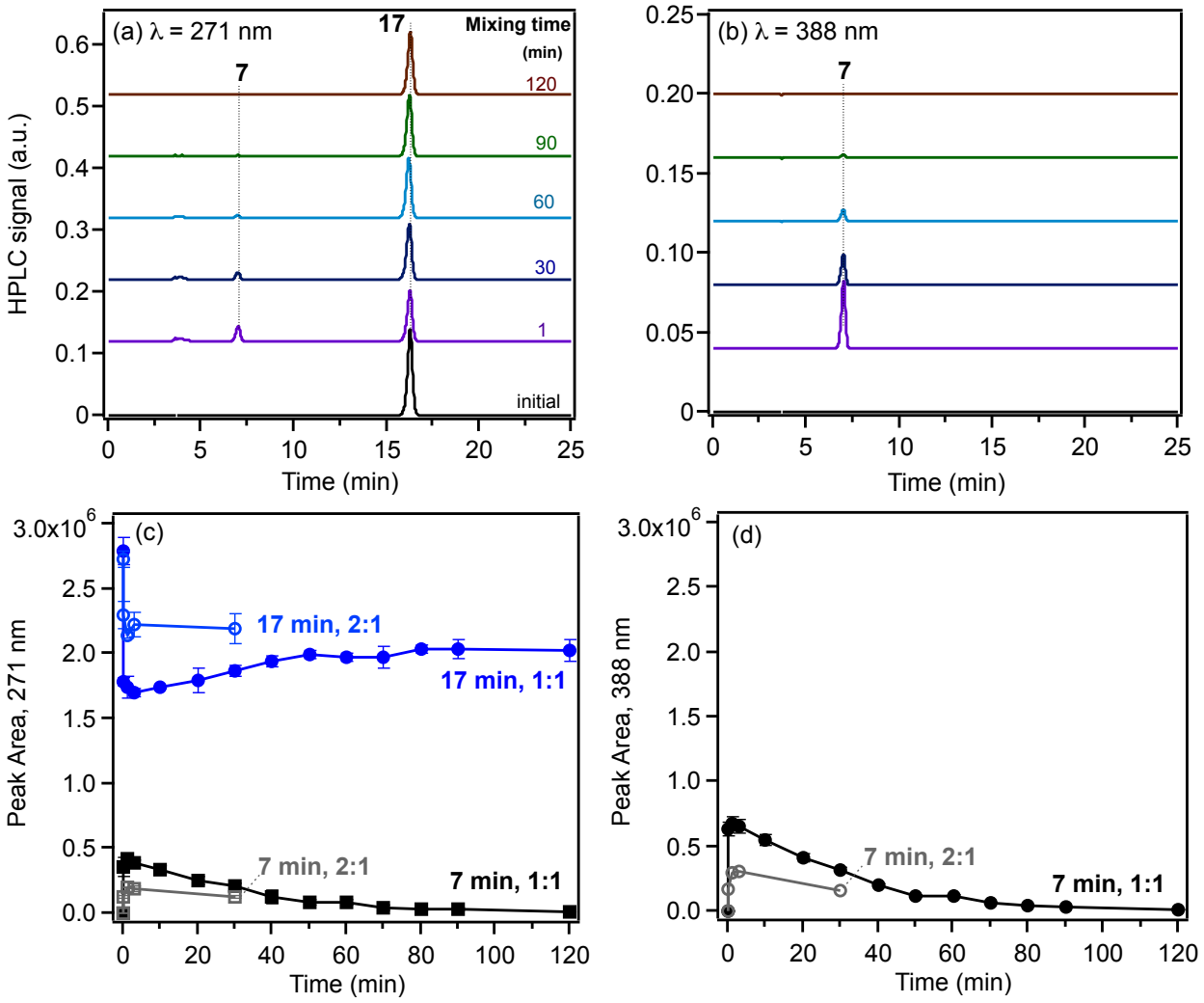


Figure S3: (a) and (b) HPLC chromatograms collected for initial catechol solutions (0.98 mM) and after reaction with $FeCl_3$ at pH 3 as a function of reaction time with a final molar ratio of 1:1. (c) and (d) The resultant kinetic curves from the integrated areas of the peaks at 7 and 17 min for solution mixtures containing 1:1 and 2:1 molar ratio of catechol:Fe.

5.

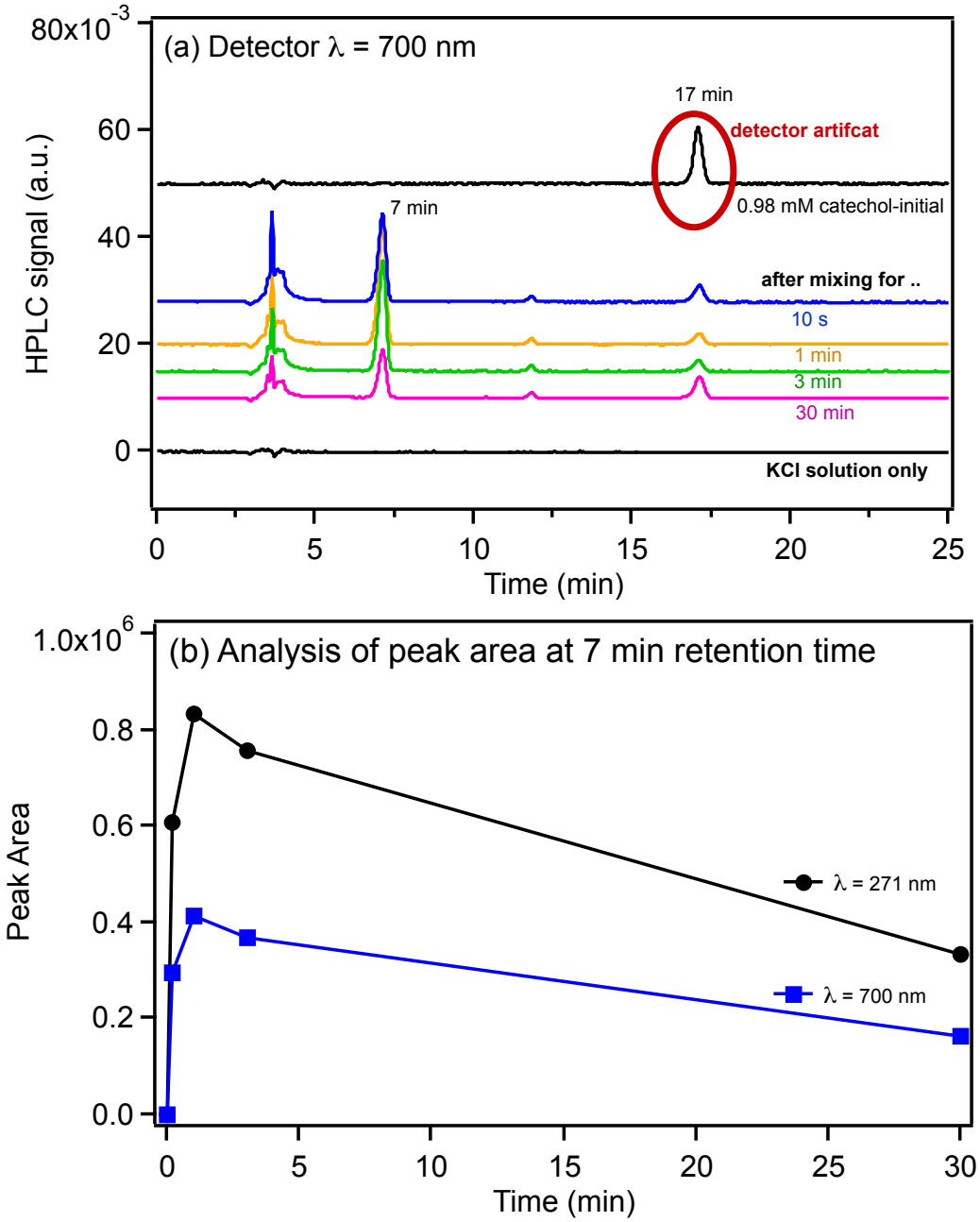
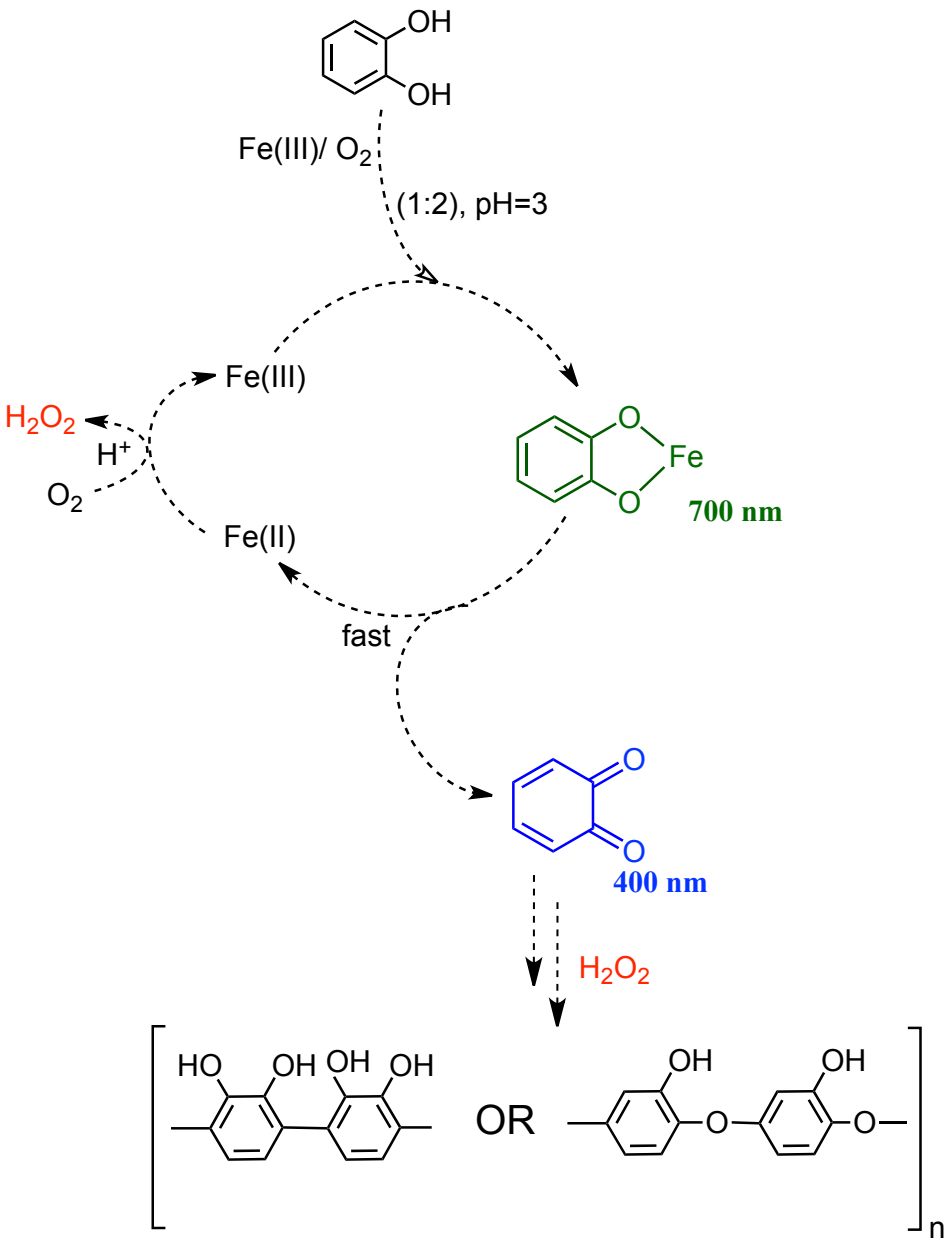


Figure S4: (a) HPLC chromatograms collected for initial catechol solutions (0.98 mM) and after reaction with $FeCl_3$ at pH 3 as a function of reaction time with a final molar ratio of 1:2, and (b) kinetic curves for the product peak at 7 min as a function of detector wavelength. The phrase "detector artifcat" refers to the signal at 700 nm for the 17 min peak that does not originate from the catechol standard solution in the absence of iron.

6.



Scheme S2: Suggested mechanism for catechol oxidation and polycatechol formation in the presence of excess Fe(III) in the dark under acidic conditions.

7.

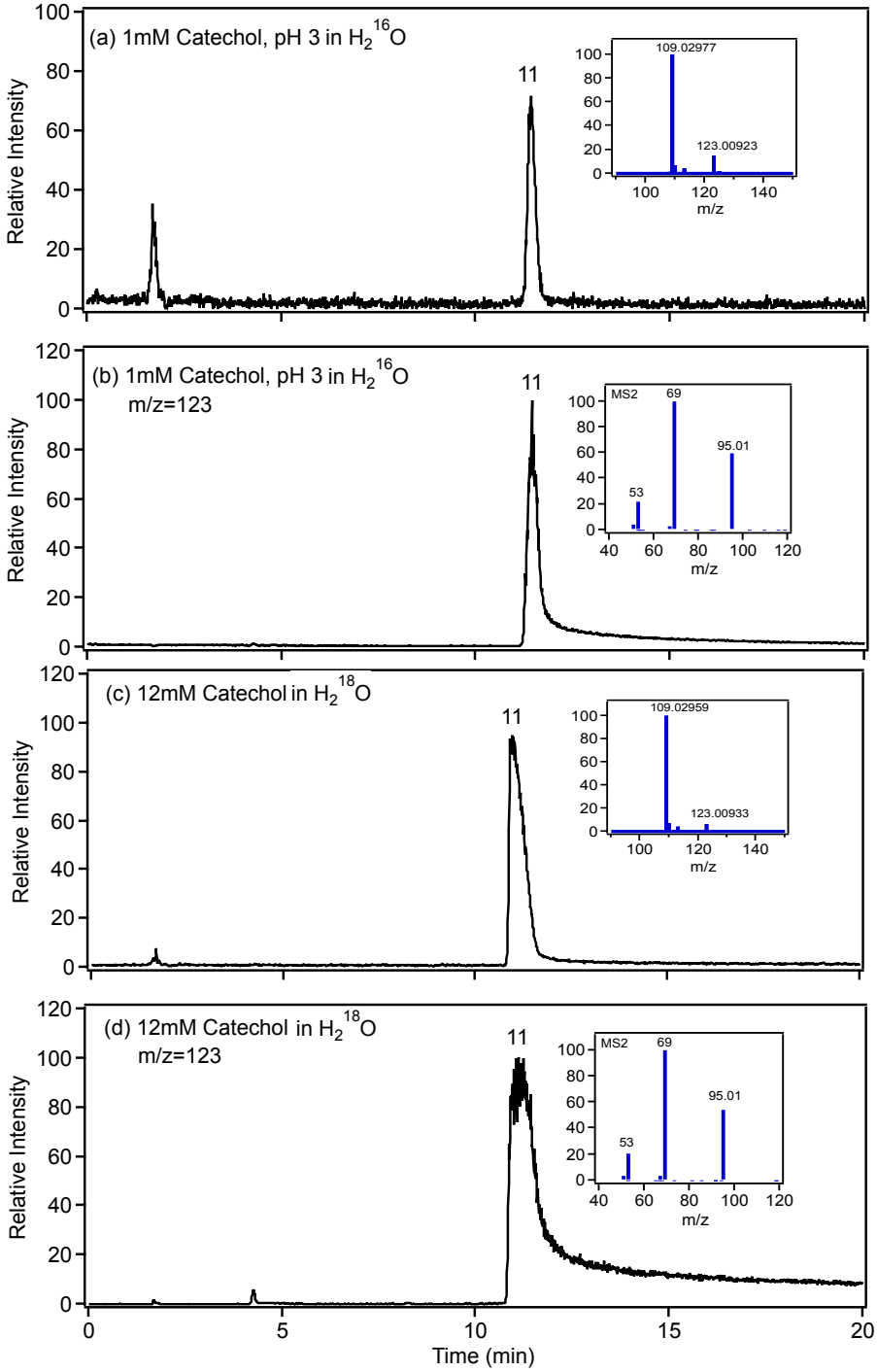
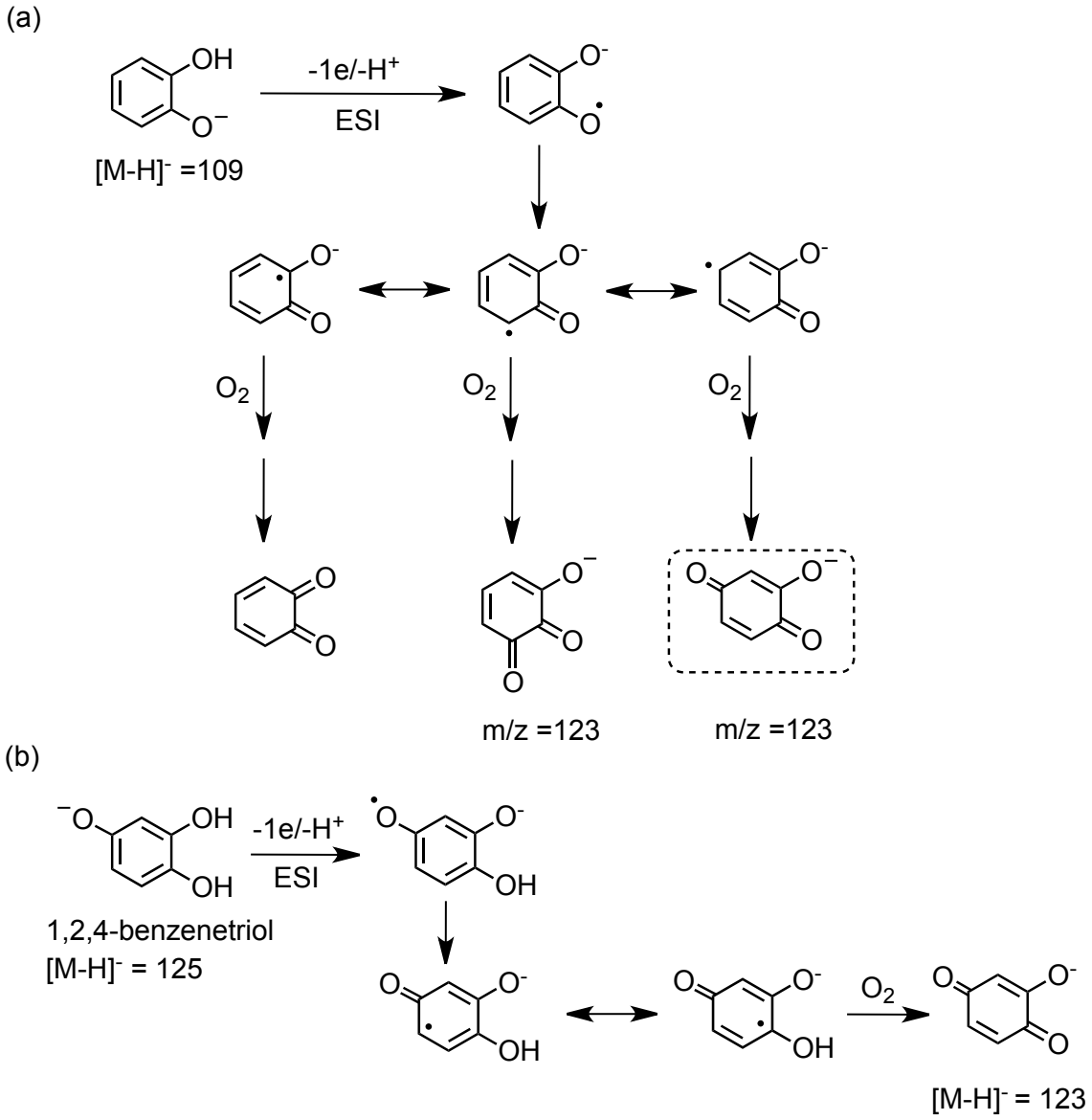


Figure S5: Total ion and *m/z* 123 LC-ESI-MS/MS negative ion mode chromatograms for catechol standard solutions under acidic conditions in normal water ($H_2{}^{16}O$, (a)-(b)) and in water-^{18}O ($H_2{}^{18}O$, (c)-(d)). The insets in (a) and (c) show the mass spectra for the major peaks, and those in (b) and (d) show the MS/MS spectra for the *m/z* 123 ion.

8.



Scheme S3: Suggested mechanism for the oxidation of (a) catechol and (b) 1,2,4-benzenetriol induced in the ESI chamber by O_2(aq) explaining the origin of the *m/z* 123 with the same fragmentation pattern for both chemicals.

9.

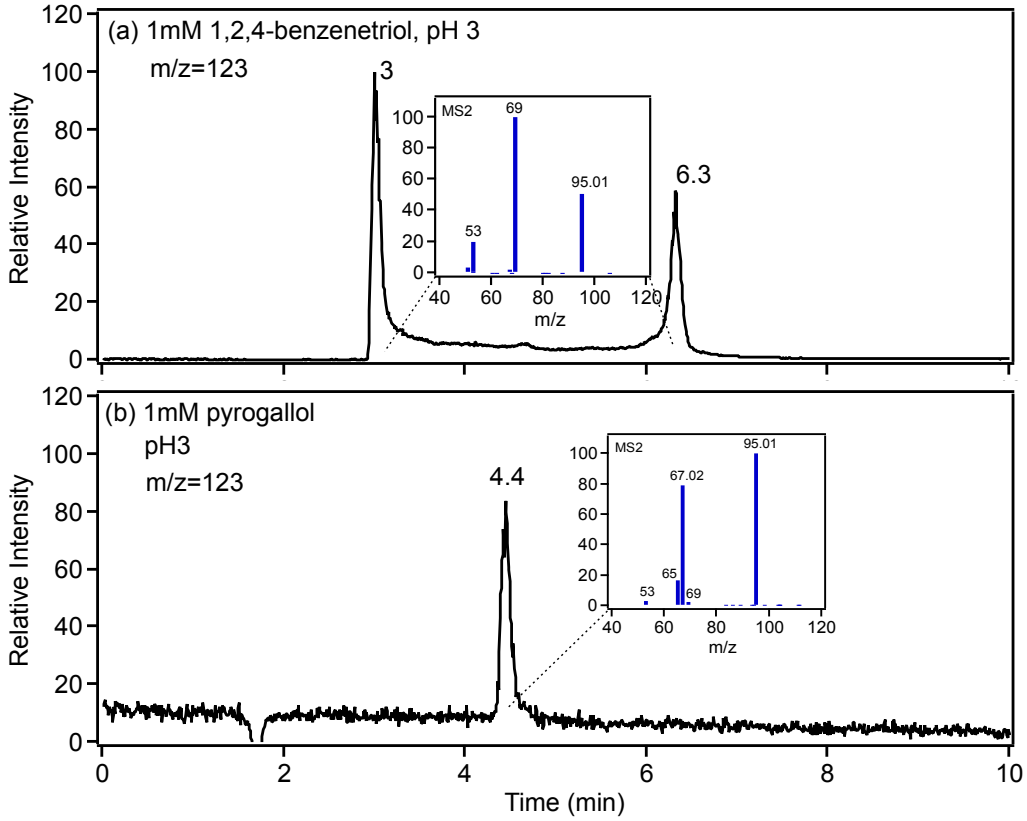


Figure S6: Chromatograms for *m/z* 123 of reference compounds 1,2,4-benzentriol and pyrogallol under acidic conditions in normal water ($H_2{}^{16}O$). The insets show the MS/MS spectra for the *m/z* 123 fragment.

10.

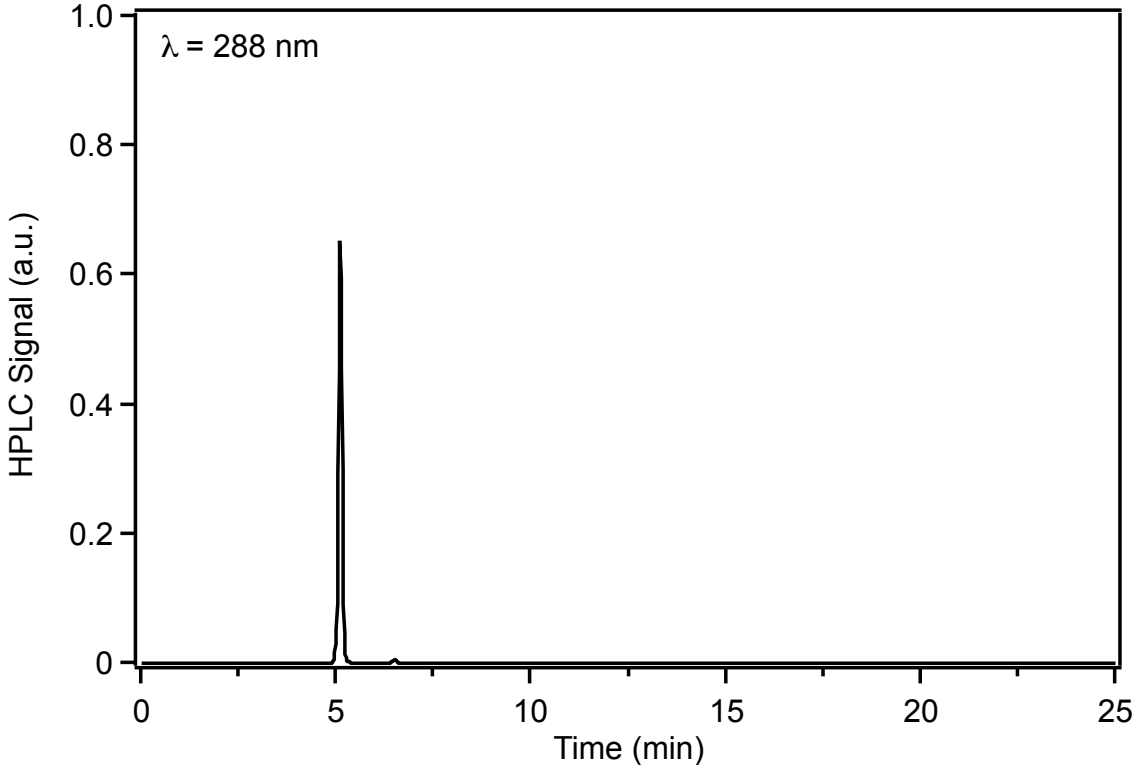


Figure S7: HPLC chromatograms collected for 1 mM standard solution of 1,2,4-benzentriol at pH 3.

11. Table S1: Intensity ratios of major peaks observed in the mass spectra of catechol and iron chloride solution with different ratios at pH 3 at a given different retention times

Solution	Retention time (RT)	% Intensity ratios of *m/z* 123/109 peaks
1 mM catechol standard solution in $H_2{}^{16}O$	11	14.9
12 mM catechol standard solution in **$H_2{}^{18}O$**	11	6.2
1 mM catechol: 2 mM $FeCl_3$ in $H_2{}^{16}O$ after 3 min reaction	4.5	79.4
	11	20.2
6 mM catechol: 12 mM $FeCl_3$ in **$H_2{}^{18}O$** after 3 min reaction	4.5	78.3
	11	7.99
1 mM catechol: 1 mM $FeCl_3$ in $H_2{}^{16}O$ after 3 min reaction	4.5	71.8
	11	16.8
1 mM catechol: 0.5 mM $FeCl_3$ in $H_2{}^{16}O$ after 3 min reaction	4.5	78.2
	11	13.7
1 mM catechol: 0.33 mM $FeCl_3$ in $H_2{}^{16}O$ after 3 min reaction	4.5	81.9
	11	16.1

12.

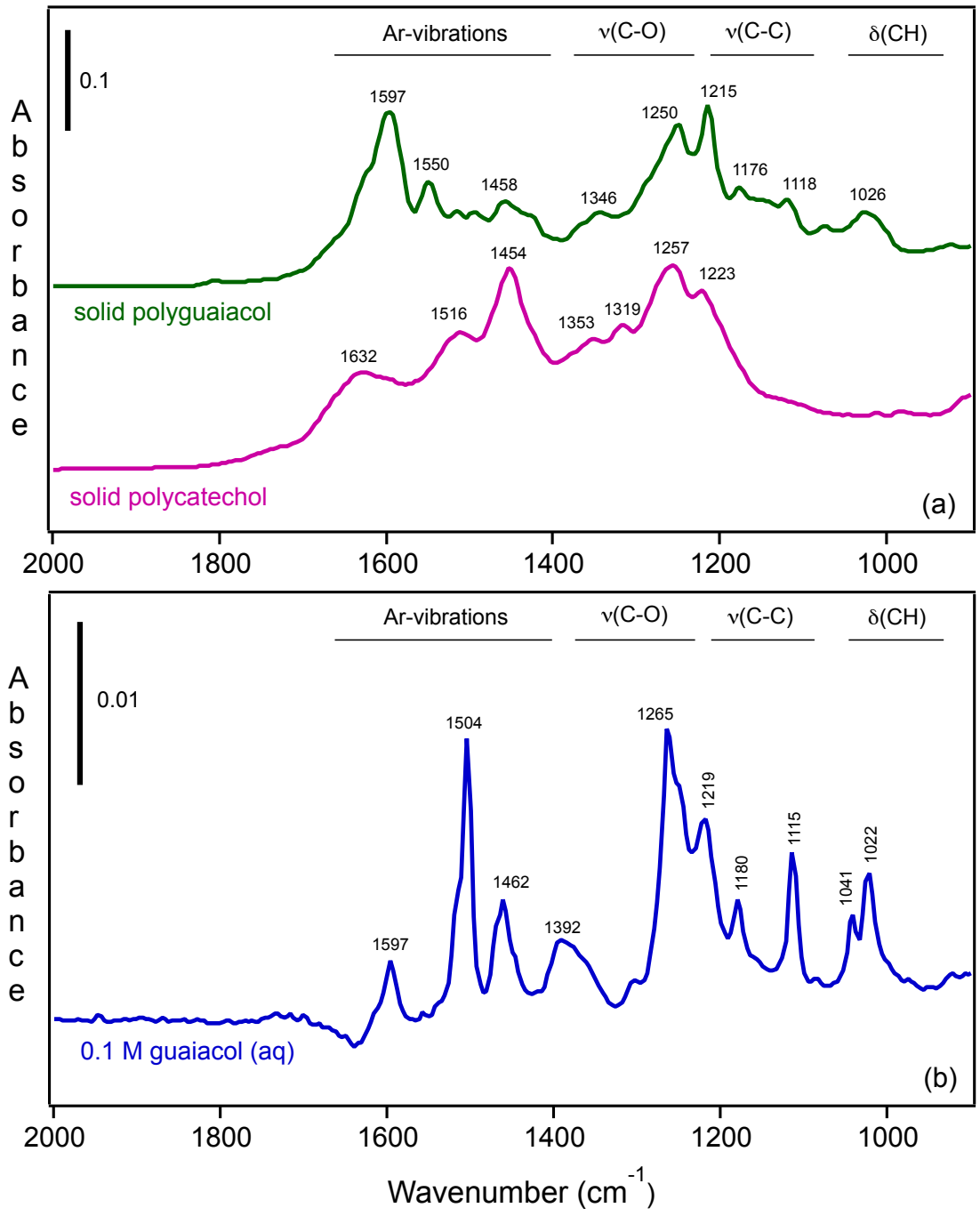


Figure S8: ATR-FTIR absorbance spectra of (a) solid polycatechol (bottom) and polyguaiacol (top) deposited on a ZnSe ATR crystal from a water/ethanol slurry followed by drying overnight, and (b) 0.1 M aqueous solution, and Similar spectra of catechol monomers were reported earlier.[4]

13.

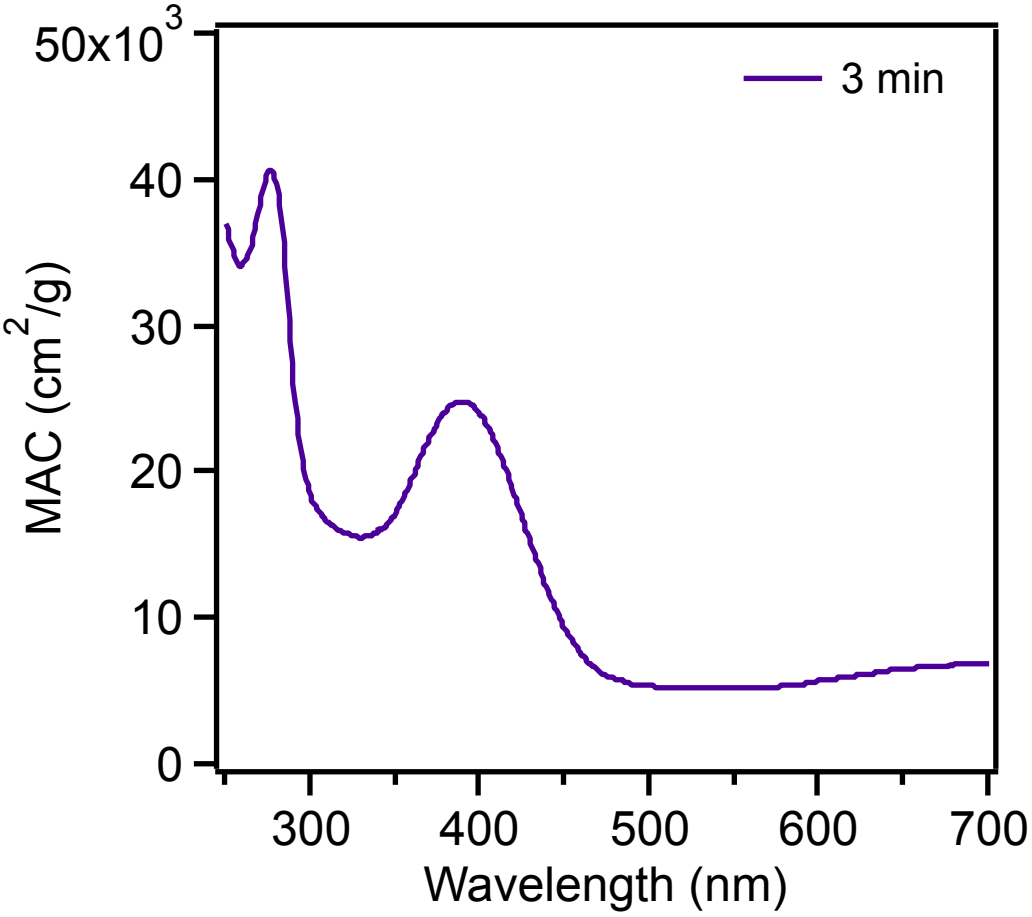


Figure S9: Mass-normalized absorption coefficient (MAC) plot for the reaction of 1 mM catechol with $FeCl_3$ after 3 min dark reaction at pH 3 (unfiltered solution). The final reaction mixture contain 1:2 molar ratio catechol:Fe. MAC was calculated from Eq. (1) and it was not corrected for the contribution from scattering by particles in solution.

14. References

(1) Lanzl, C.A.; Baltrusaitis, J.; Cwiertny, D.M., Dissolution of hematite nanoparticle aggregates: Influence of primary particle size, dissolution mechanism, and solution pH. *Langmuir* **2012**, *28*, 15797-15808.

(2) Stucki, J.W.; Anderson, W.L., The quantitative assay of minerals for Fe^{2+} and Fe^{3+} using 1,10-phenanthroline: I. Sources of variability. *Soil Sci. Soc. Am. J.* **1981**, *45*, 633-637.

(3) Stucki, J.W., The quantitative assay of minerals for Fe^{2+} and Fe^{3+} using 1,10-phenanthroline: II. A photochemical method. *Soil Sci. Soc. Am. J.* **1981**, *45*, 638-641.

(4) Tofan-Lazar, J.; Situm, A.; Al-Abadleh, H.A., DRIFTS studies on the role of surface water in stabilizing catechol-iron(III) complexes at the gas/solid interface. *J. Phys. Chem. A* **2013**, *117*, 10368-10380.