

## Supporting Information

# Efficient formation of light-absorbing polymeric nanoparticles from the reaction of soluble Fe(III) with C4 and C6 dicarboxylic acids

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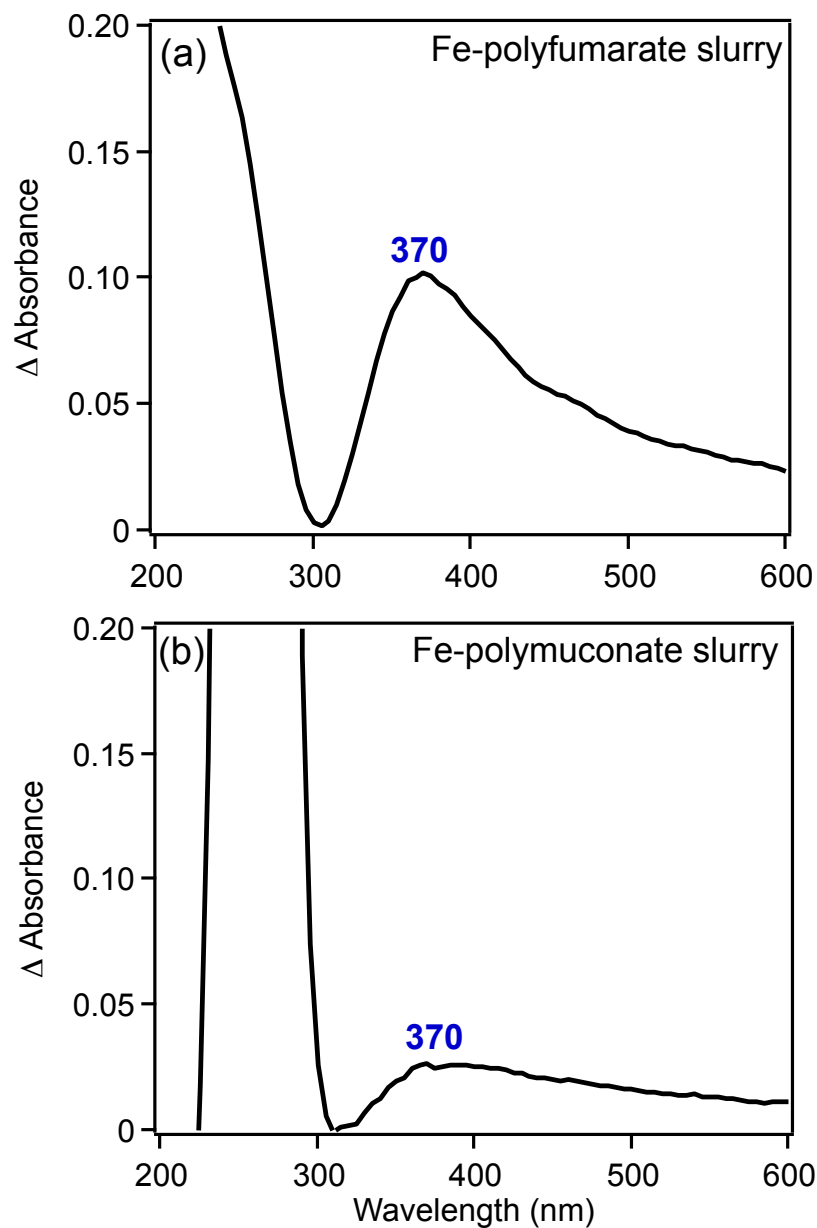
## **Additional Experimental Details**

For ATR-FTIR measurements, the particles were deposited onto a ZnSe crystal from a water/ethanol slurry followed by drying overnight. Absorption spectra of these particles were obtained by referencing to the clean and dry ZnSe crystal.

The TGA analysis was completed on a TGA Q50 V20.8 Build 34 instrument while flowing nitrogen gas at 40 and 60 mL/min for balance and samples, respectively. The sample was thermally equilibrated at 40°C, followed by a temperature ramp at a rate of 10°C min<sup>-1</sup> up to 800°C.

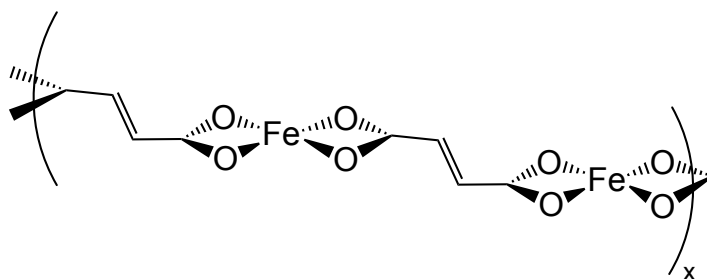
The TEM, SEM-EDS and EELS measurements were done at the Canadian Centre for Electron Microscopy, McMaster University. The samples were ground using a mortar and pestle. The powder was mixed with a solution of 50%/50% ethanol/DI water and sonicated for 10 min. TEM analysis was performed in a JEOL 2010F TEM/STEM operated at 200 kV. The electron microscope was equipped with a Gatan imaging filtering (GIF) system for the acquisition of the electron energy loss spectra (EELS).

The oxidation state composition of iron was analyzed by XPS in a Thermo-VG Scientific ESCALab 250 microprobe with a monochromatic Al K $\alpha$  X-ray source (1486.6 eV), operated with a typical energy resolution of 0.4 - 0.5 eV full width at half-maximum. To correct for extra charging, the binding energy curve in the Fe 2p region for each compound was calibrated against the C 1s peak in the survey spectrum, which has a value of 284.8 eV per reference<sup>1</sup>.

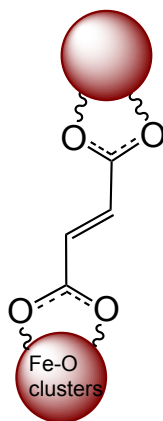


**Figure S1.** Difference spectra obtained by subtracting the absorbance of  $\text{FeCl}_3$  reactant standard solution (after accounting for dilution) from that collected for the unfiltered reaction solution after 120 min of reaction, as shown in Figure 2 in the main manuscript. The subtraction factor,  $s$ , was 1.1 for (a) and 1.2 for (b) according to this formula:  $\Delta$  Absorbance = Absorbance of mixture  $- s \cdot$  Absorbance of control  $\text{FeCl}_3$  solution shown in Figure 2.

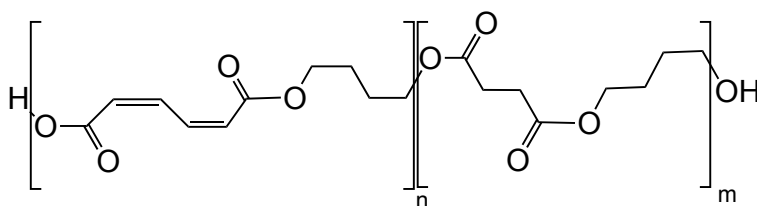
(a)



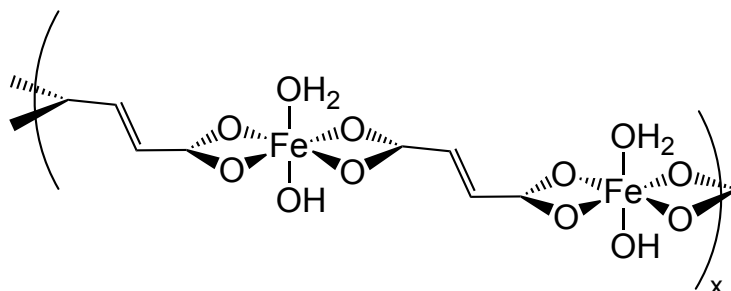
(b)



(c)

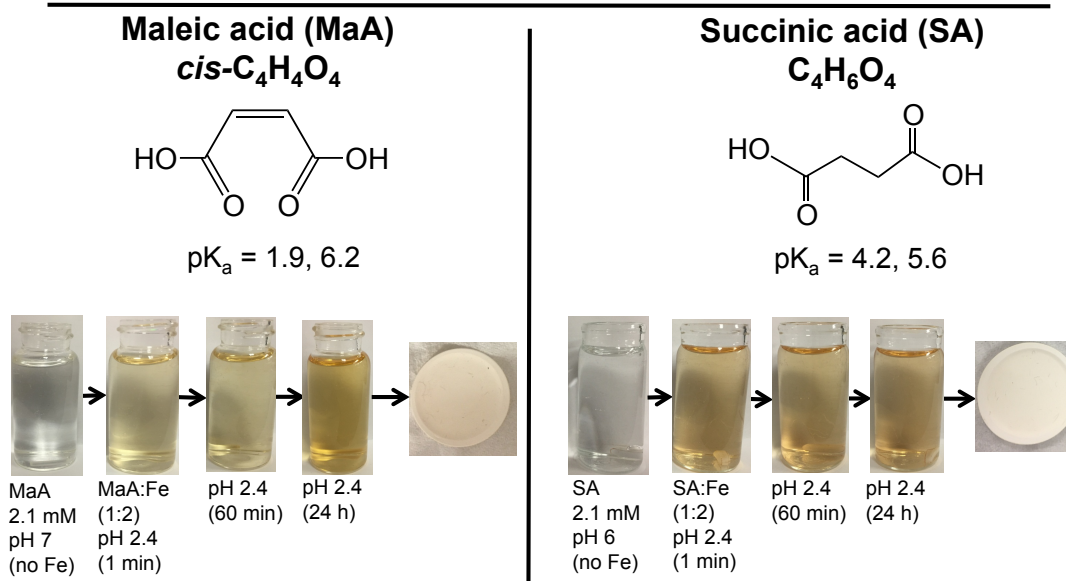


(d)

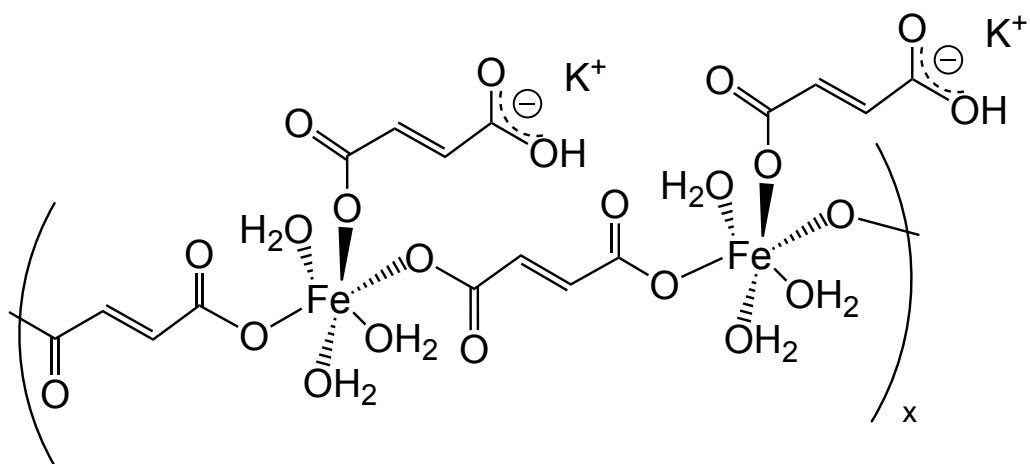


**Figure S2:** Reported structures for polymers formed from (a) the reaction of aqueous phase FA with  $\text{FeCl}_3$  as patented by Apblett,<sup>2</sup> (b) the reaction of aqueous phase FA with  $\text{FeCl}_3$  at  $85^\circ\text{C}$  forming MOF MIL-88A,<sup>3</sup> (c) the reaction of *cis,cis*-muconic acid with excess dialcohol in the presence of Ti(IV) butoxide,<sup>4</sup> (this structure shows an example of metal-catalyzed polymerization of muconic acid),<sup>4</sup> and (d) Fe(II) fumarate reported in references.<sup>5,6</sup>

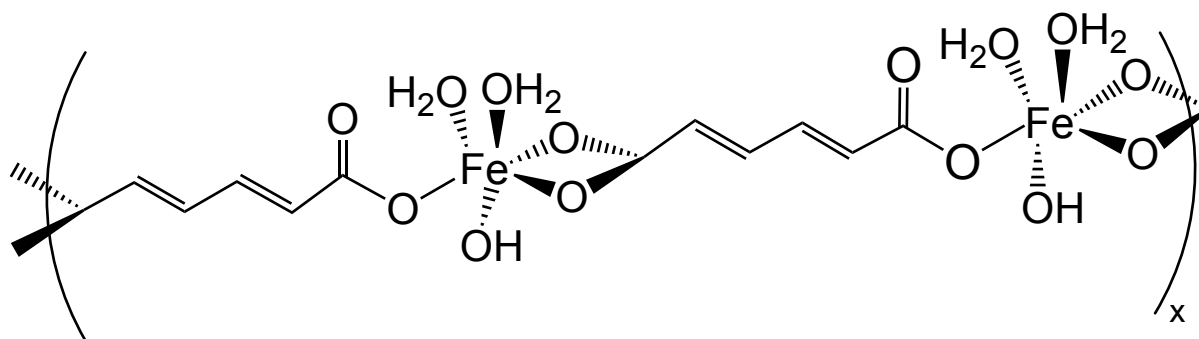
## Control Experiments



**Figure S3.** Digital images of unfiltered solutions following 1 h and 24 h reaction times between maleic and succinic acids with FeCl<sub>3</sub> at pH 2.4, followed by filtration.



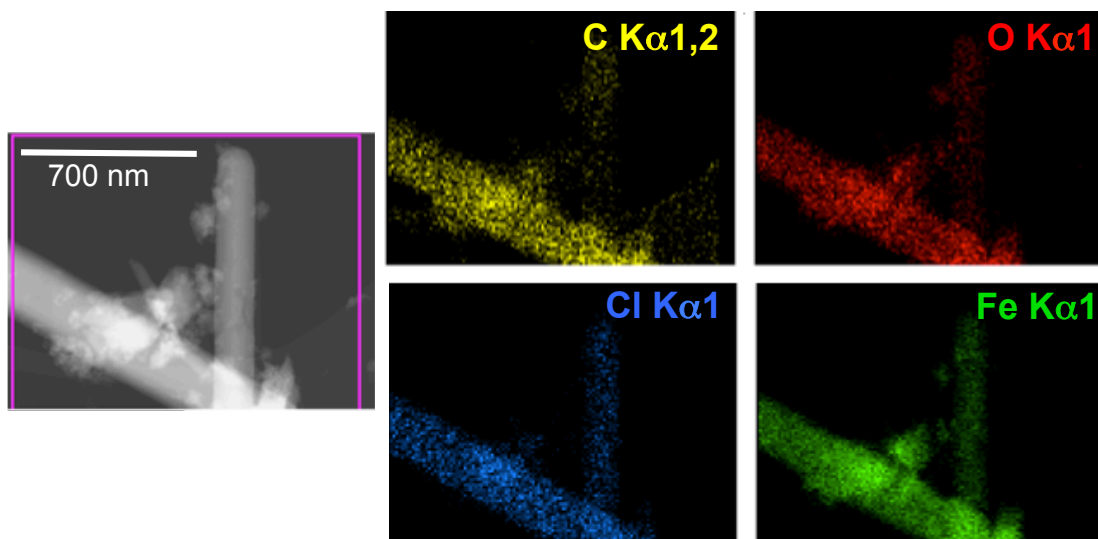
(a) Fe-polyfumarate



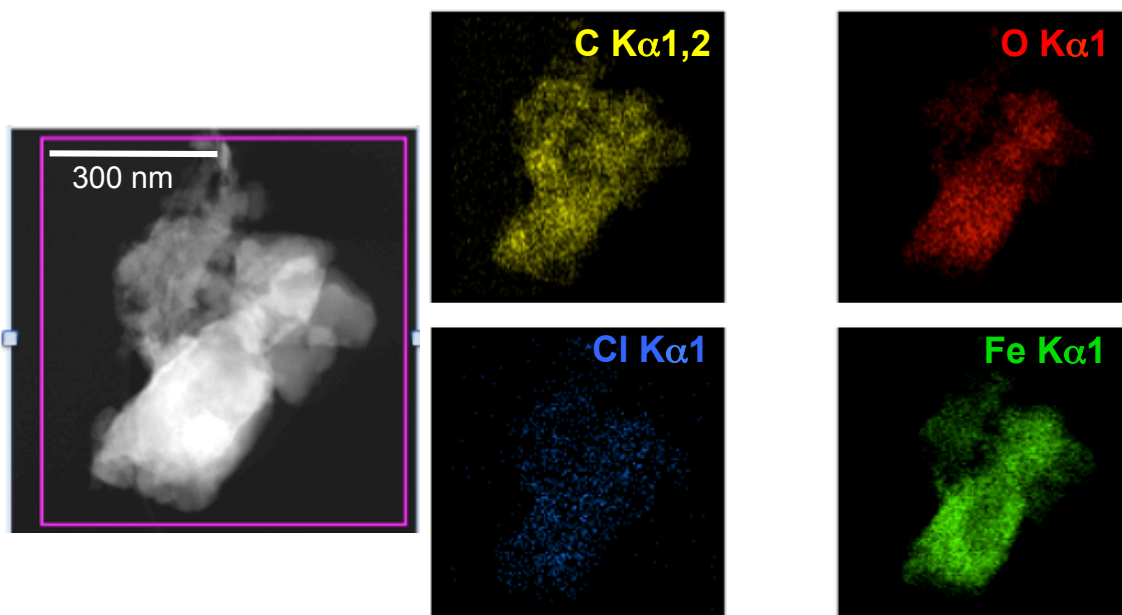
(b) Fe-polymuconate

**Figure S4.** Proposed chemical structure of (a) Fe-polyfumarate and (b) polymuconate formed in our studies based on the results of dry particle characterization detailed in the main text.

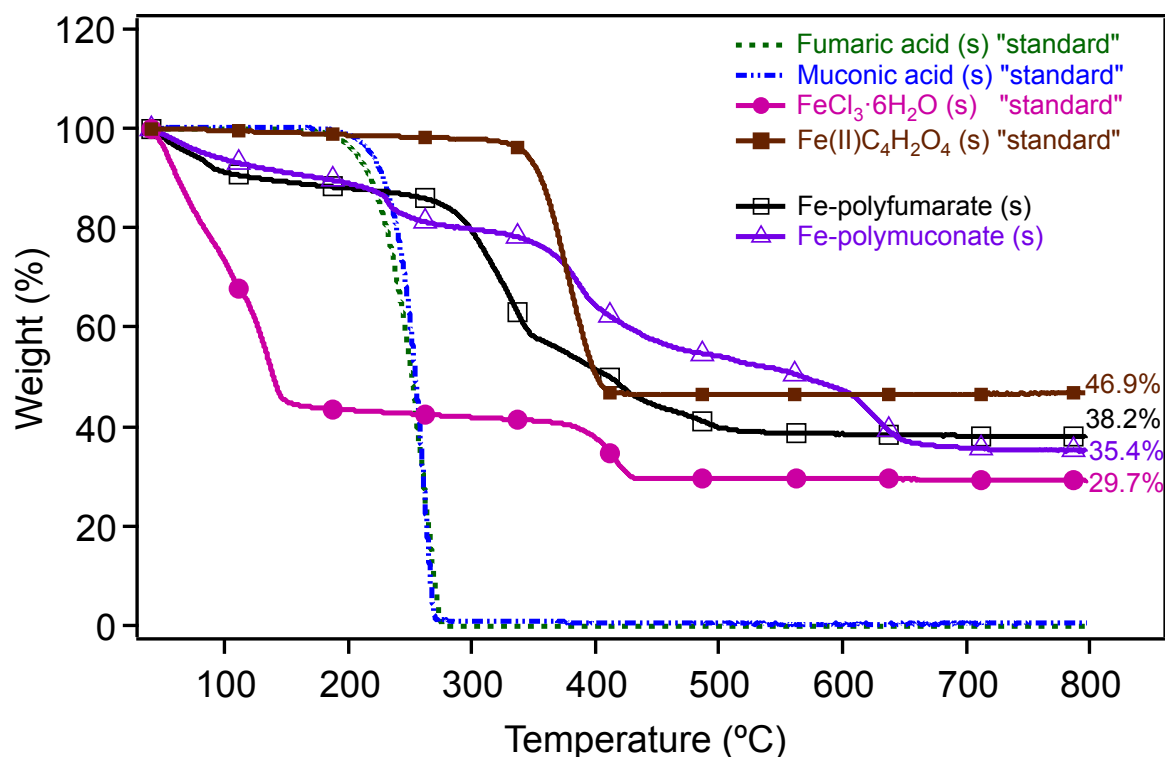
**(a) Fe-polyfumarate**



**(b) Fe-polymuconate**



**Figure S5.** Representative STEM-EDS images and elemental mapping (C, O, Cl, and Fe) of (a) Fe-polyfumarate, and (b) Fe-polymuconate particles.

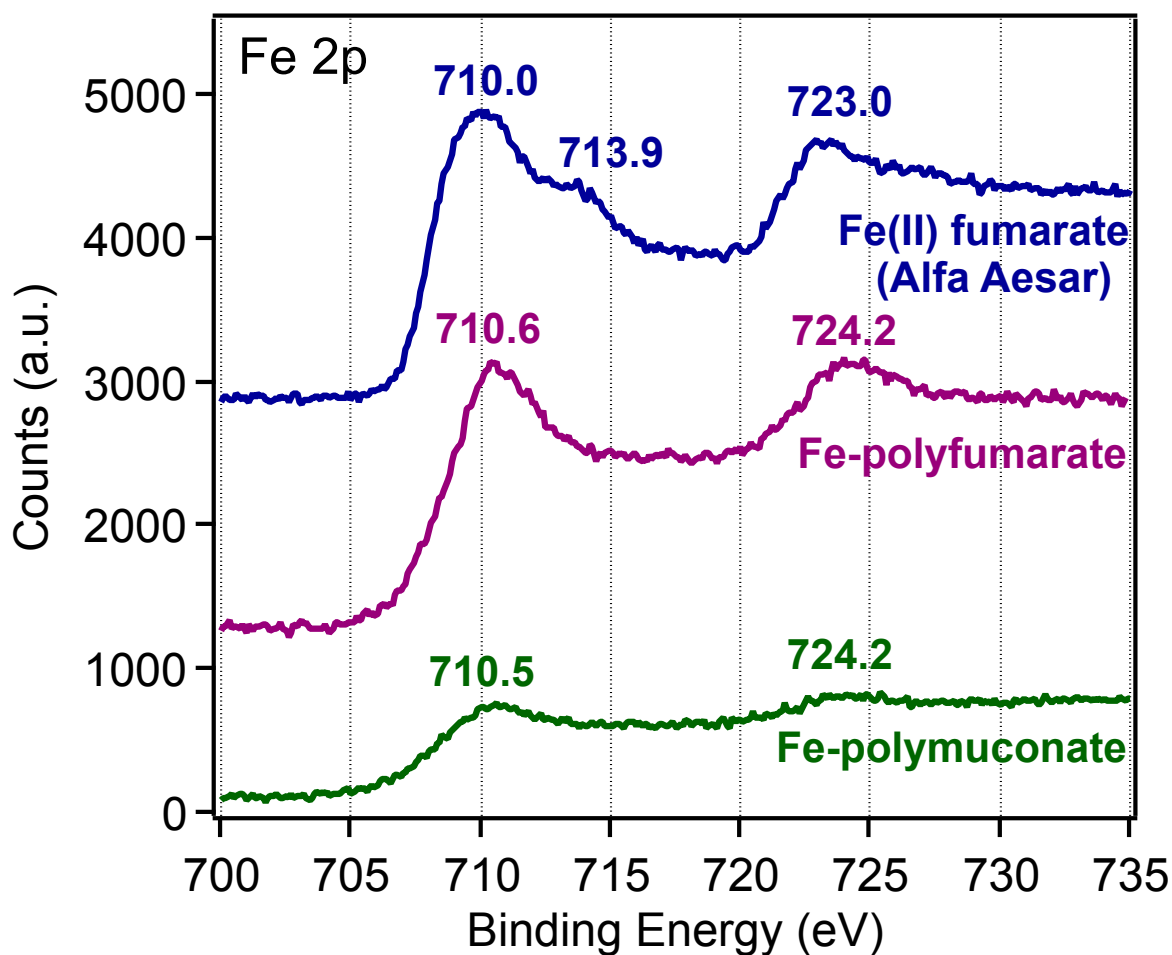


**Figure S6.** TGA curves showing % weight loss due to thermal decomposition of standard reactant compounds (FA, MA, and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) and Fe(II) fumarate in relation to Fe-polyfumarate and Fe-polymuconate.

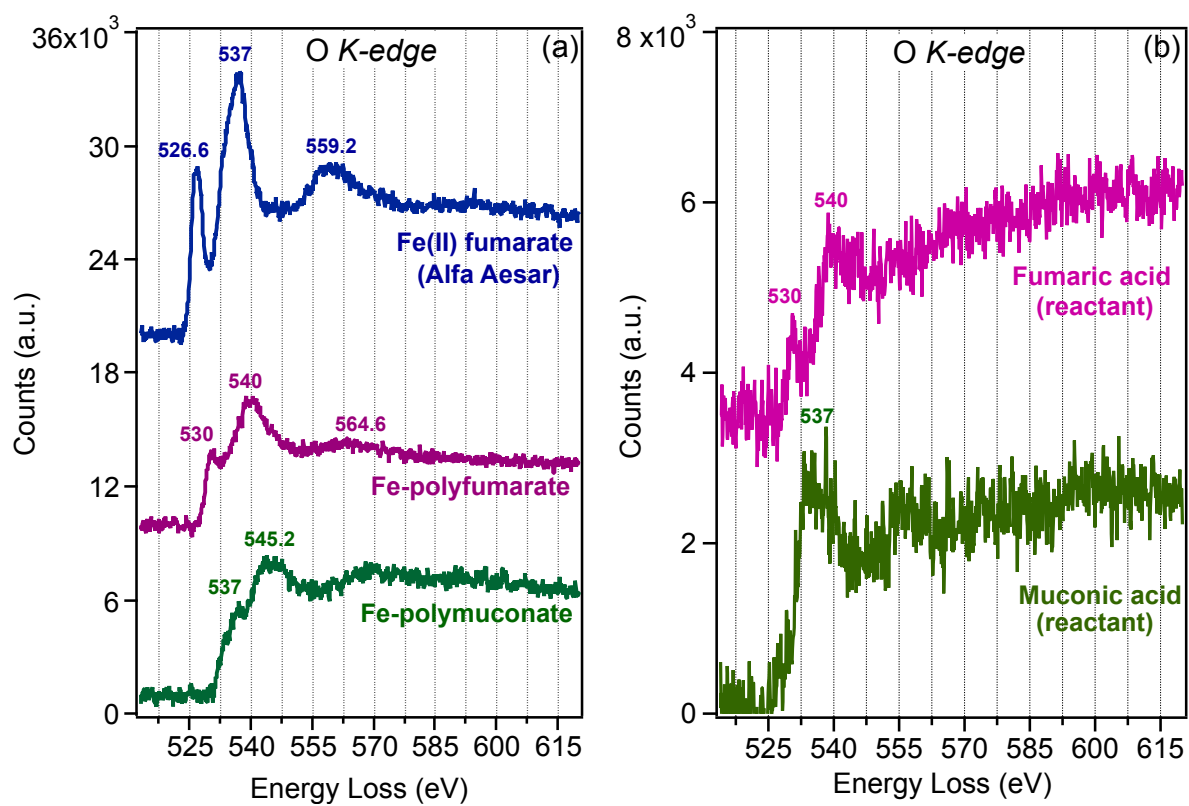
**Table S1:** Analysis of the TGA data (n.a. = not available)

Reaction for thermal decomposition	% mass residual, (c1)	% Fe calculated from c1, (c2)	Calculated molar weight ( $\text{g mol}^{-1}$ ) from c2	Molar weight based on chemical formula ( $\text{g mol}^{-1}$ )
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}(\text{s}) \rightarrow 0.5 \text{Fe}_2\text{O}_3(\text{s}) + 4.5\text{H}_2\text{O}(\text{g}) + 3\text{HCl}(\text{g})$ (see ref. <sup>7</sup> )	29.7	20.7	270.5	270.5
$\text{Fe}(\text{II})\text{C}_4\text{H}_2\text{O}_4 \rightarrow 0.5 \text{Fe}_2\text{O}_3(\text{s}) + \text{C}_2\text{H}_2(\text{g}) + 2 \text{CO}(\text{g}) + 0.25 \text{O}_2(\text{g})$ (see ref. <sup>8</sup> )	46.9	32.8	170.7	169.9
Fe-fumarate ( $\text{FeC}_x\text{O}_y\text{H}_z$ ) $\rightarrow 0.5x \text{Fe}_2\text{O}_3$ + gases	38.2	26.7	209.7	n.a.
Fe-muconate ( $\text{FeC}_x\text{O}_y\text{H}_z$ ) $\rightarrow 0.5x \text{Fe}_2\text{O}_3$ + gases	35.4	24.8	225.8	n.a.

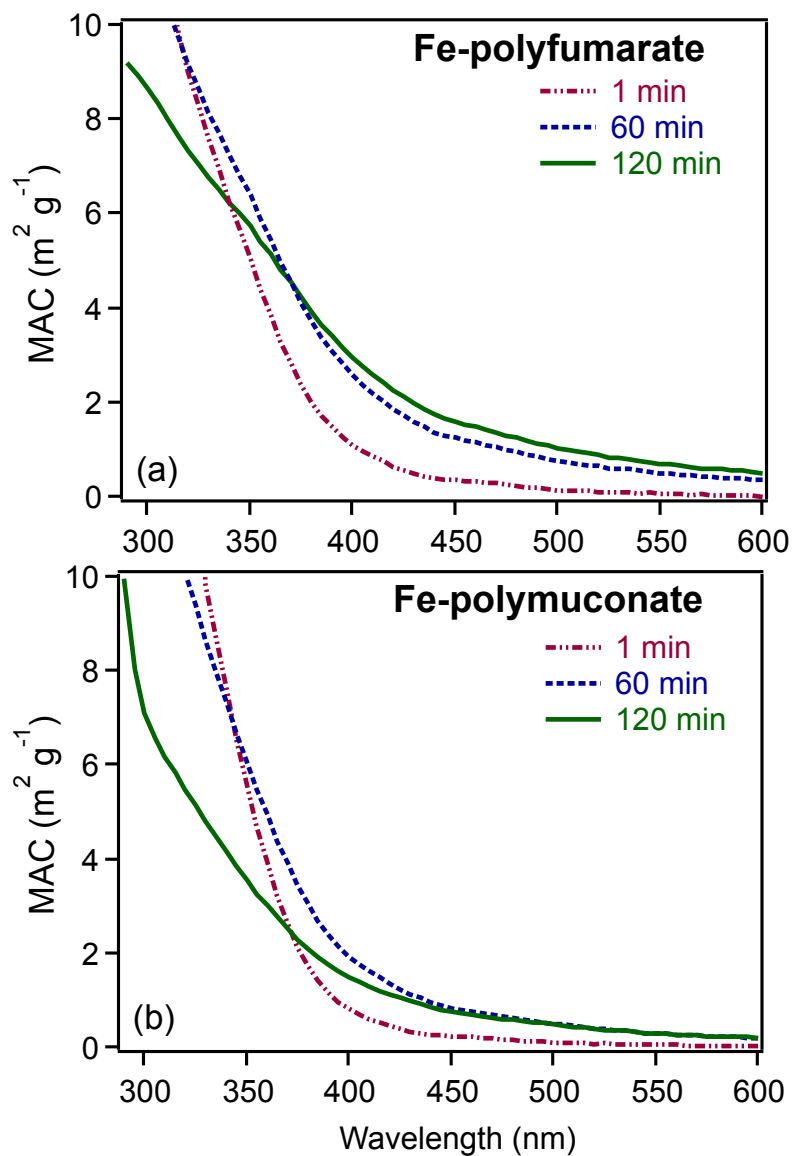




**Figure S7.** XPS spectra of the Fe 2p region for Fe-polyfumarate and Fe-polymuconate particles in relation to the standard compound, Fe(II) fumarate. Each binding energy curve was calibrated against the C 1s peak which has a fixed value of 284.8 eV per Ref. <sup>1</sup> to correct for charging. Spectra are offset for clarity.



**Figure S8.** Representative EELS spectra (Background subtracted) for the oxygen K-edge of (a) standard Fe(II) fumarate, Fe-polyfumarate and Fe-polymuconate particles, and (b) standard fumaric and muconic acids particles.



**Figure S9:** Mass-normalized absorption coefficient (MAC) plot for the reaction of 0.1 mM of (a) fumaric acid (FA), and (b) muconic acid (MA) with  $\text{FeCl}_3$  after 1, 60 and 120 min dark reaction at pH 3 (unfiltered solution). The final reaction mixture contain 1:2 molar ratio organic reactant:Fe. MAC values were calculated from Eq. (1) and were not corrected for the contribution from scattering by particles in solution.

## References:

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