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 40ºC, followed by a temperature ramp at a rate of 10ºC min\(^{-1}\) up to 800ºC.

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\(^1\).
**Figure S1.** Difference spectra obtained by subtracting the absorbance of FeCl₃ 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 FeCl₃ solution shown in Figure 2.
Figure S2: Reported structures for polymers formed from (a) the reaction of aqueous phase FA with FeCl₃ as patented by Apblett,² (b) the reaction of aqueous phase FA with FeCl₃ at 85°C forming MOF MIL-88A,³ (c) the reaction of cis,cis-muconic acid with excess dialcohol in the presence of Ti(IV) butoxide,⁴ (this structure shows an example of metal-catalyzed polymerization of muconic acid),⁴ and (d) Fe(II) fumarate reported in references.⁵,⁶
**Figure S3.** Digital images of unfiltered solutions following 1 h and 24 h reaction times between maleic and succinic acids with FeCl$_3$ at pH 2.4, followed by filtration.
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.
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 FeCl$_3$·6H$_2$O) and Fe(II) fumarate in relation to Fe-polyfumarate and Fe-polymuconate.

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

<table>
<thead>
<tr>
<th>Reaction for thermal decomposition</th>
<th>% mass residual, (c1)</th>
<th>% Fe calculated from c1, (c2)</th>
<th>Calculated molar weight (g mol$^{-1}$) from c2</th>
<th>Molar weight based on chemical formula (g mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCl$_3$·6H$_2$O(s) → 0.5 Fe$_2$O$_3$ (s) + 4.5H$_2$O (g) + 3HCl (g) (see ref. 7)</td>
<td>29.7</td>
<td>20.7</td>
<td>270.5</td>
<td>270.5</td>
</tr>
<tr>
<td>Fe(II)C$_4$H$_2$O$_4$ → 0.5 Fe$_2$O$_3$ (s) + C$_2$H$_2$ (g) + 2 CO(g) + 0.25 O$_2$ (g) (see ref. 8)</td>
<td>46.9</td>
<td>32.8</td>
<td>170.7</td>
<td>169.9</td>
</tr>
<tr>
<td>Fe-fumarate (FeC$_x$O$_y$H$_z$)→ 0.5x Fe$_2$O$_3$ + gases</td>
<td>38.2</td>
<td>26.7</td>
<td>209.7</td>
<td>n.a.</td>
</tr>
<tr>
<td>Fe-muconate (FeC$_x$O$_y$H$_z$)→ 0.5x Fe$_2$O$_3$ + gases</td>
<td>35.4</td>
<td>24.8</td>
<td>225.8</td>
<td>n.a.</td>
</tr>
</tbody>
</table>
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. 1 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 FeCl₃ 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:


