

Redox-Responsive Gels with Tunable Hydrophobicity for Controlled Solubilization and Release of Organics

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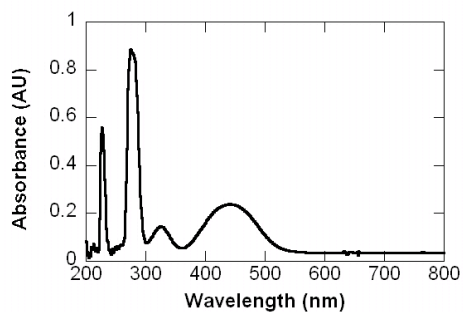
Confirmation of the ability of FeCl₃ to oxidize ferrocene

Solutions of both ferrocene and FeCl₃ in BuOH are yellow in color, as is evident from their UV-vis absorption spectra (Figure S1). Ferrocene shows an absorption peak at 227nm and 280nm corresponding to the $\pi \rightarrow \pi^*$ transition of the cyclopentadiene ring.¹ Ferrocene also gives a broad, relatively weaker peak at 450nm which is a result of the symmetry forbidden transitions of electrons from non-bonding a_{1g} to the antibonding e_{1g}^* level of the iron 3d-orbital.² FeCl₃ gives a very broad peak with an extended shoulder from 280nm to 450nm, consistent with literature reports.¹ It is important to note that neither ferrocene nor FeCl₃ solutions absorb light of wavelength 642nm.

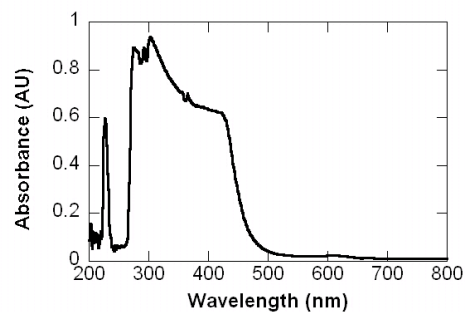
The color of the ferrocene solution was observed to change upon the sequential addition of drops of FeCl₃ solution from yellow to green to blue, as manifested by the changes in the absorption spectrum (Figure S2). A new peak was observed at 642nm, the height of which increased with increasing amounts of FeCl₃ solution added. The peak at 642nm characterizes the symmetry-allowed $^2E_{2g} \rightarrow ^2E_{1u}$ transition of the ferrocenium cations confirming the successful oxidation of the ferrocene by FeCl₃.

The confirmation of the ability of FeCl_3 to oxidize ferrocene dissolved in butanol was followed by experiments to ascertain if FeCl_3 could oxidize ferrocene moieties attached to polymeric gels. The chemical oxidation of ferrocene covalently attached to polymer backbone using chemical oxidizing agent $\text{Ce}(\text{SO}_4)_2$ has been shown by Kuramoto et al.³ When gels synthesized in this work containing ferrocene in the reduced state were allowed to equilibrate with a solvent containing dissolved FeCl_3 the color of the gel was observed to change from orange to blue. The final blue color of the gel was similar to the blue color of ferrocene solution in butanol after oxidation by FeCl_3 . The change in the color of the gel was used as evidence to conclude that ferrocene groups inside the gel had been oxidized. The color change results are shown in Figure S3 which compares the color of a gel piece in a reduced state and a gel piece after oxidation in a butanol solution containing FeCl_3 . Moreover, the color change took place throughout the bulk gel confirming the ability of FeCl_3 to diffuse inside the gel and react with ferrocene moieties throughout the gel.

The diffusion and the subsequent reaction of the ferric ions of FeCl_3 with the ferrocene groups was also evident in the observed decrease in concentration of FeCl_3 in the original solution as measured using UV-visible spectrophotometry. The results are shown in Figure S4 where the UV-visible absorbance peaks in the solution attributable to FeCl_3 at 280nm and 335nm show a decrease in height after reaction with the ferrocene containing gels.



(a)



(b)

Figure S1 UV-vis absorption spectra of solution of (a) ferrocene, and (b) FeCl_3 in butanol

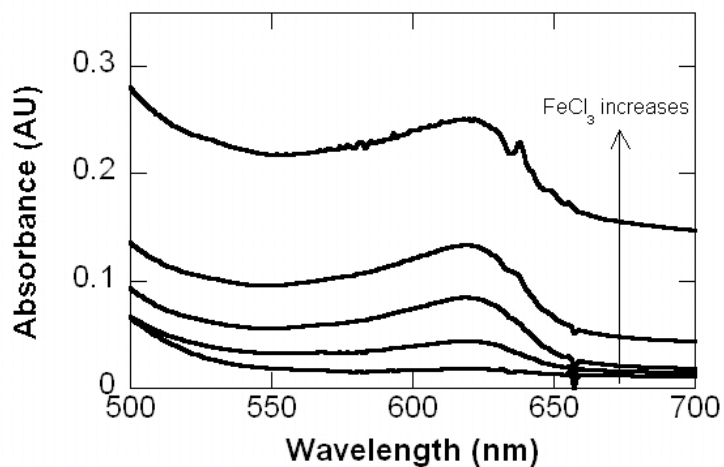


Figure S2 Series of UV-vis absorption spectra of ferrocene solution in butanol obtained after drop-wise addition of FeCl_3 to the solution

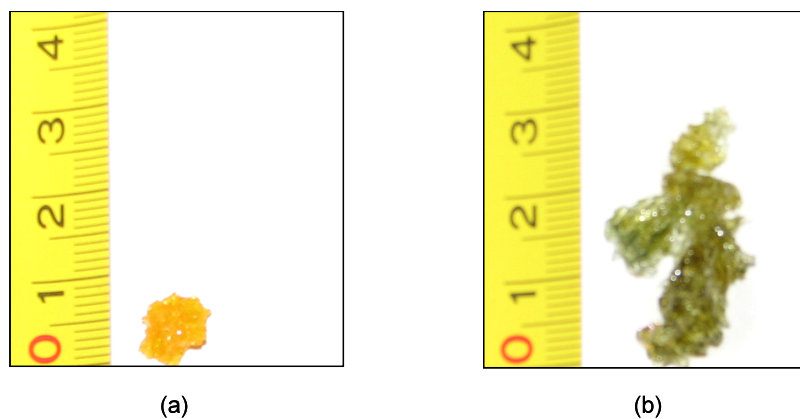


Figure S3 Image of a gel piece (a) in reduced state, (b) in swollen state after oxidation by FeCl₃ dissolved in butanol

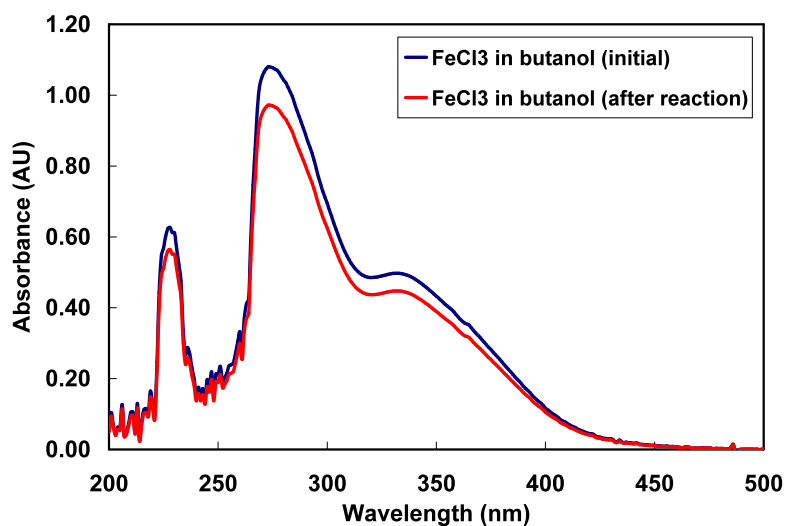


Figure S4 UV-visible spectrum of FeCl₃ containing butanol before (in blue) and after (in red) reaction with ferrocene containing methacrylate gel

References

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