CHAPTER 5

Electrochemical polymerization of iron(III) polypyridyl complexes through C–C coupling of redox non-innocent phenolato ligands

Electrochemical oxidation of a phenolato based μ-oxo-diiron(III) complex \([\{L^1\}Fe(\mu-O)Fe(L^1)\}^{2+} (1)\) results in formation of a phenoxy radical ligand rather than an iron(IV) species and undergoes rapid C–C coupling at the 4-positions of the phenoxy ligand to form tetra nuclear complexes upon deprotonation. Further oxidation leads to the formation of well-defined polymer films of \([\{-(L^1)Fe(\mu-O)Fe(L^1)-\}^\text{n+}\) on a range of electrodes in dichloromethane, which allows for spectroscopic characterization of the species formed by chemical oxidation in solution.

This chapter has been published:
Chapter 5

5.1 Introduction

The redox chemistry of transition metal complexes has seen rapid progress recently driven both by a desire to understand the inner workings of bioinorganic systems and the necessity to achieve sustainability in chemical processes, and especially catalysis.\textsuperscript{1,2} These efforts have provided insight into mechanisms for many homogeneous catalytic and enzymatic reactions.\textsuperscript{3} The role played by redox non-innocent ligands\textsuperscript{4} in biological systems\textsuperscript{1,5} has been recognized for many decades and such an approach is increasingly seeing application in homogeneous catalysis, not least because of the role of such ligands, \textit{e.g.}, tyrosine,\textsuperscript{6} in enabling two electron redox processes using first-row transition metals.\textsuperscript{4,7}

The phenolato moiety,\textsuperscript{8,9} in particular, imparts substantial redox flexibility to metal complexes due to the accessible redox chemistry of the phenolate unit itself. Phenols, such as tyrosine, undergo one and two electron oxidation readily, however, outside of the protective environment of an enzyme, they equally readily undergo bimolecular coupling reactions to form oligomeric and polymeric structures.\textsuperscript{10} Efforts to tame the redox chemistry of phenols has focused on their incorporation within metal complexes with the goal of balancing the redox chemistry of the metal center with that of the ligand. The one-electron oxidation of these metal-phenolato complexes leads to species described as either a higher valent metal species (M\textsuperscript{m+1}L\textsuperscript{−}) or ligand radicals (M\textsuperscript{m}L\textsuperscript{−}) that are essentially electronic isomers of each other.\textsuperscript{11,12}

The study of metal-bound phenoxy radicals is of special interest in the context of biological systems, not least the enzyme galactose oxidase (GO).\textsuperscript{13} The structure of the GO copper(II) binding site, in its inactive form, contains two imidazole rings (histidine residues), two phenol moieties (tyrosine residues), and an acetato ligand.\textsuperscript{11,14} In its active form, the formal oxidation state of GO has been assigned as copper(III), however, its spectroscopic properties suggest assignment of a copper(II)-phenoxy radical structure is more appropriate.\textsuperscript{6}

Inspired by phenolato based enzymes, phenolato based Fe(II) complexes have been applied in oxidation catalysis\textsuperscript{11} for example with O\textsubscript{2} for catechol C−C bond cleavage by Velesumay \textit{et al.},\textsuperscript{15,16} and in the μ-oxo-diiron(III) polypyridyl complex (1),\textsuperscript{17} based on the ligand 2-(((di(pyridin-2-yl)methyl)(pyridin-2-yl)methyl)amino)methyl)phenol, in which each of the Fe(III) centers are coordinated to a phenolato ligand (Figure 1), applied over a decade ago by Feringa \textit{et al.} to the selective oxidation of benzyl alcohols to aldehydes with H\textsubscript{2}O\textsubscript{2}.\textsuperscript{18} In the latter case, the activity of the complex was ascribed tentatively to the involvement of the phenolato moiety. However, the stability of phenol based ligands in oxidation reactions, outside of the confines of an active site of an enzyme, is uncertain and indeed coupling of oxidized phenolato ligands,\textsuperscript{12,19,20} as well as phenols,\textsuperscript{21} has been noted in the literature already. Indeed the oxidation of phenols catalyzed by transition metal complexes is a key mechanistic tool in oxidation chemistry.\textsuperscript{22}

The challenge faced in biomimetic oxidation catalyst systems is to balance the intrinsic reactivity of the oxidized ligand, specifically radical dimerization, with the stabilization of formally high metal oxidation states (Fe(IV)). In particular, it is essential to avoid the oxidatively driven dimerization of the phenol ligand.
In this chapter, we report that electrochemical oxidation of 1 results in sufficient phenoxy radical character for aryl C–C coupling of the phenol units to take place (Scheme 1). In dichloromethane, the coupling between phenoxy radical units occurs both at 200 and 293 K without compromising the integrity of the Fe(III)-O-Fe(III) bridge in the binuclear complex and thereby results in the formation of well-defined polymer films containing 4,4'-bisphenolato bridged diiron complexes (poly-1). The polymer formed undergoes highly reversible electrochemical oxidation to singly and doubly oxidized states, in which the oxidation is localized on the 4,4'-bisphenolato core and shows good stability under ambient conditions. Comparison of spectroscopic data obtained upon electrochemical and chemical oxidation of 1 in acetonitrile with data obtained from thin films of poly-1 confirms that a similar oxidative coupling occurs in acetonitrile also, however, the integrity of the Fe(III)-O-Fe(III) core of the C–C coupled complexes (3) is compromised. Hence, the formation of polymer films (poly-1) by further C–C coupling of 3 is precluded due to the instability of the oligomers formed initially. The oxidatively driven C–C coupling is blocked effectively by the incorporation of tert-butyl groups at the para- and ortho- positions of the phenol units (i.e. 2).

Scheme 1. Mechanism for oxidative dimerization of 1 to form a 4,4'-bis-phenolato bridged-bis-μ-oxo-diiron(III) polypyridyl complex (3) that subsequently undergoes coupling at the other phenolato units to form oligomers (i.e. poly-1).
5.2 Results and Discussion

5.2.1 Structure and spectroscopic characterization of \([(L^2)\text{Fe}(\mu-O)\text{Fe}(L^2)](\text{ClO}_4)_2\) (1) and \([(L^2)\text{Fe}(\mu-O)\text{Fe}(L^2)](\text{ClO}_4)_2\) (2).

The ligand HL\(^1\) and the complex \([(L^2)\text{Fe}(\mu-O)\text{Fe}(L^2)](\text{ClO}_4)_2\) (1) have been prepared previously together with single crystal X-ray structural determination of \([(L^2)\text{Fe}(\mu-O)\text{Fe}(L^2)](\text{PF}_6)_2\)\(^{15}\). HL\(^2\) and 2 were prepared by analogous methods to HL\(^1\) and 1, respectively. Synthesis and detailed FTIR and \(^1\)H NMR characterization of HL\(^2\), HL\(^2\), 1 and 2 are provided in Appendix A. The ESI mass spectrum of 1 shows a base peak at \(m/z\) 445 \([(L^2)\text{Fe}(\mu-O)\text{Fe}(L^2)]^{2-}(\text{ClO}_4)_2\) and of 2 at \(m/z\) 557 \([(L^2)\text{Fe}(\mu-O)\text{Fe}(L^2)]^{2+}(\text{ClO}_4)_2\). In both cases, ESI mass spectra show no evidence for the presence of mononuclear species. The \(^1\)H NMR spectra of both 1 and 2 show signals in the range of -5 to 40 ppm in CD\(_2\)CN which, together with broadening\(^{24}\) and the magnetic susceptibility, determined using Evans method\(^{16}\) of 2.78 BM and 2.76 BM for 1 and 2, respectively (see in ref 23 for details), and the absence of X-band EPR signals for both 1 and 2 at 77 K, is consistent with antiferromagnetically coupled dinuclear iron(III) complexes.

Non-resonant Raman spectra of 1 and 2 (\(\lambda_{\text{exc}}\) 785 nm and \(\lambda_{\text{exc}}\) 1064 nm) were recorded in solution (acetonitrile and acetone) and in the solid state, whose peak positions compare well with the computed IR spectra. Complex 1 shows bands at 1595, 1562, 1475, 1455, 1279, 1205, 1154, 1114, 1025, 890, 602, 559, 431, 292 and 217 cm\(^{-1}\), which compare closely with related complexes bearing pyridyl and phenolato ligands, e.g., \([\text{Fe}^{III}\text{Fe}^{II}(\text{bpbpmp})(\text{CH}_3\text{CO}_2)]\)\(\text{ClO}_4\) (1591, 1564, 1478, 1451, 1276, 1274, 1151, 1112, 890, 795, 636, 612, and 335 cm\(^{-1}\), where bpbpmp is 2-bis([(2-pyridylmethyl)-aminomethyl]-6-[(2-hydroxybenzyl)(2-pyridylmethyl)]-aminomethyl]-4 methylphenol)\(^{26}\). The bands at 1595 and 602 cm\(^{-1}\) (found with DFT at 1251 and 582 cm\(^{-1}\), see in ref 23 for details) are assigned to \(\nu(\text{CO})\)phenol mode and \(\nu(\text{Fe-O})\) phenol mode, respectively\(^{27}\), while the bands at 1595/1562 and 1475/1455 are largely in plane bending modes of the pyridyl and phenolato moieties, respectively. Complex 2 shows overall similar spectra, except for bands associated with Fe-O and phenol based modes. Raman spectra of complex 2 in the solid state at \(\lambda_{\text{exc}}\) 785 nm show the bands at 1601, 1469, 1442, 1413, 1314, 1269, 1131, 836, 740, 606, 537 nm, which compares closely with 1. The bands at 1268 cm\(^{-1}\) and 540 cm\(^{-1}\) are assigned to \(\nu(\text{CO})\)phenol mode and \(\nu(\text{Fe-O})\) phenol mode, respectively. The absence of change between the solid state spectrum and those obtained in acetonitrile and acetone indicate that the solid state structure is retained in solution with EPR and ESI mass data.

Both 1 and 2 show visible absorption (\(\varepsilon_{535}\) (1) \(4.1\times10^2\) M\(^{-1}\) cm\(^{-1}\), \(\varepsilon_{423}\) (2) \(4.7\times10^3\) M\(^{-1}\) cm\(^{-1}\)) in acetonitrile and more intense bands in the near-UV region (Figure 2). The absorption spectra are consistent with those reported for Fe(III)-phenolato complexes elsewhere\(^{28}\) and the longest wavelength absorption is assigned to a phenolato to Fe(III) charge-transfer transition (LMCT) based on resonance Raman spectroscopy and DFT (see in ref 23 for the details). The absorption band at 343 nm is assigned to a mixture of phenolato-to-Fe(III) and oxo-to-Fe(III) charge-transfer transitions. The absorption spectrum of 1 in acetonitrile is concentration independent (between 3.9 µM and 1 mM) indicating that dissociation of a mononuclear complex is highly unfavorable.
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Figure 2. UV-vis absorption spectra of 1 (black) and 2 (red), 0.075 mM in acetonitrile.

Raman spectra recorded at $\lambda_{\text{exc}}$ 532, 561 nm and 355 nm in dilute solution (0.25 to 0.5 mM) show resonance enhancement of some of the Raman bands of 1 and 2 (see in ref 23 for details). The spectrum obtained at $\lambda_{\text{exc}}$ 561 nm although resonant with an absorption assigned as a phenolato to Fe(III) charge transfer band, is similar to the Raman spectra obtained at 1064 nm and 785 nm. At $\lambda_{\text{exc}}$ 355 nm, in resonance with an absorption band assigned to an oxo-to-Fe(III) charge transfer, bands at 411 cm$^{-1}$ and 430 cm$^{-1}$ are enhanced strongly, which are ascribed, tentatively to Fe-O-Fe modes that observed typically between 380 and 540 cm$^{-1}$.27

5.2.2 Cyclic voltammetry of 1 and 2 in acetonitrile.

The cyclic voltammogram of 1 in acetonitrile at room temperature displays three irreversible oxidation processes at 1.22 V, 1.40 V and 1.57 V and one irreversible reduction at 0.37 V vs SCE on the return cycle (Figure 3). The irreversible redox waves are assigned to phenol centered processes by comparison with the voltammetry of HL$^1$ and HL$^2$ (see Figure S28 in ref 23), with the process at 0.37 V ascribed to the reduction of a product of a follow-up chemical reaction between the oxidized phenol units. In contrast, the voltammetry of 2 shows two are electrochemically reversible redox processes assigned to phenolato centered oxidations at 1.04 V and 1.23 V.

Figure 3. Cyclic voltammetry of 1 (black) and 2 (red, current axis is offset for clarity) (1.0 mM) in acetonitrile (0.1 M TBAPF$_6$) at a glassy carbon electrode ($d = 3$ mm) working electrode with Pt counter electrode and an SCE reference electrode at 0.1 V s$^{-1}$. The initial potential in each case (*) was the open circuit potential; initial scan directions are indicated by arrows.
5.2.3 Thin layer cyclic voltammetry and spectroelectrochemistry of 1 and 2 in acetonitrile.

In situ monitoring of the changes that occur during cyclic voltammetry of 1 and 2 was carried out using an optically transparent thin layer (OTTLE) cell, to characterize the products of the formed after electrochemical oxidation. Thin layer voltammetry of 2 shows that the first redox wave is reversible (chemically) but that the second redox process is chemically irreversible despite that the cyclic voltammetry at a GC (Figure 3) electrode shows that both redox waves are electrochemically reversible.29 A cyclic voltammogram from 0.3 V to between the 1st and 2nd redox waves (Figure 4a) shows the reversible formation of singly oxidized species with strong bands at 410 and 430 nm, weaker bands at 490 and 680 nm, and isosbestic points maintained at 553 and 723 nm (Figure 4, vide infra).

These bands are characteristic of a phenoxyl radical cation and are consistent with the coincidence of the redox waves of 2 with those of HL2. Upon returning the potential to 0.2 V a nearly complete recovery of the initial spectrum was obtained. Addition of [(NH4)2Ce(NO3)6](CAN) to 2 in acetonitrile resulted in similar spectral changes (Figure 6) consistent with one electron oxidation only, i.e. to 2+, with absorption bands in the near-UV and visible region similar to those observed by spectroelectrochemistry. The original spectrum of 2 recovered rapidly, except for a small decrease in the absorbance due to dilution.

![Figure 4](image)

**Figure 4.** Thin layer voltammetry of 2 (5 mM) (right) at 0.01 V s⁻¹ in an OTTLE cell in acetonitrile (0.1 M TBAPF₆) (Left) monitored in situ by vis-NIR spectroscopy. The inset shows the change in absorbance at selected wavelengths as a function of applied potential. The initial (black) and final (spectra) are shown as bold lines.

Substantial changes in the vis-NIR absorption spectrum of 1 were observed in acetonitrile during the first positive cycle after 1.31 and 1.72 V and on the return cycle, an irreversible reduction at 0.81 V vs Ag/AgCl (Figure 5). The electrochemical oxidation of 1 at 1.4 V (number 2, red line in Figure 5a/b) resulted in the appearance of the visible absorption band at 465 nm and NIR absorption at 850 nm. Oxidation at more positive potential (number 3, blue line, Figure 5a/b) resulted in a further increase in absorbance at 475 nm together with bands at ca. 740 and 900 nm. Subsequent reduction (number 4, green line, Figure 5a/b) resulted in a decrease in absorbance at 475 and 900 nm and appearance of the new bands at 404 and 478 nm. Reduction at 0.81 V (number 1, cyan line, Figure 5c/d) resulted in complete loss of the absorbance at 470 nm and an increase in absorbance at ca. 820 nm (Figure 5c/d). The new irreversible oxidation processes at 0.89 and 1.37 V vs Ag/AgCl appear in the second cycle.
The first oxidation (number 2, pink line, Figure 5c/d) resulted in the reappearance of the NIR absorption band and the bands at 404 and 456 nm. Oxidation at more positive potentials (number 3, navy line, Figure 5c/d) showed a decrease in NIR absorption and an increase in absorbance at 404 nm (vide supra). Overall, the oxidation of 1 in acetonitrile results in a permanent loss in the original visible absorption band, and the spectroelectrochemistry indicates that iron(III)-phenolato type complexes are no longer present in solution after the second cycle. It should be noted that the stability of the complex upon repeated cycles may be affected by the decrease in pH through concomitant water oxidation at the platinum working electrode.

**Figure 5.** Thin layer cyclic voltammetry of 1 (5.0 mM) in acetonitrile (0.1 M TBAPF$_6$ at 293 K) (a) first cycle, (c) second cycle and Vis-NIR absorption spectra recorded in situ during (b) first cycle (d) second cycle. The spectra were recorded at the points in the voltammogram indicated in (a) and (c).

### 5.2.4 Oxidation of 1 with ceric ammonium nitrate (CAN).

The loss in absorbance after several cyclic voltammetric cycles under thin layer conditions could indicate precipitation of the products from solution. Chemical oxidation of 1 with [(NH$_4$)$_2$Ce(NO$_3$)$_6$] (CAN) was followed by UV-vis-NIR absorption and resonance Raman spectroscopy. As observed by thin layer spectroelectrochemistry, addition of 1 equiv. of CAN to 1 in CH$_3$CN, resulted in an immediate appearance of an absorption band at 465 nm, which decayed over time concomitant with the appearance of new bands at 780 nm and 850 nm. Resonance Raman spectra recorded at 473 nm and 785 nm during the oxidation provide insight in the species responsible for these absorption bands (vide infra).
Figure 6. UV-vis absorption spectra of (a) 1 (0.25 mM) in acetonitrile with 1 equiv. of CAN, (c) 2 in acetonitrile (0.2 mM) with 1 equiv. of CAN. Time dependence of UV-vis absorption of (b) 1 at 465, 785 and 850 nm addition of 1 equiv. of CAN, (d) 2 at 425, 488 and 625 nm addition of 1 equiv. of CAN.

5.2.5 Cyclic voltammetry of 1 in dichloromethane.
In stark contrast to that observed in acetonitrile (vide supra), the cyclic voltammetry of 1 in dichloromethane shows a single irreversible oxidation at 0.81 V vs Ag/AgCl in the first sweep towards positive potentials, followed by two reduction waves at 0.55 V and 0.34 V on the reverse sweep (Figure 7a). The second cycle showed two new redox waves and a decrease in the current of the oxidation wave at 0.81 V.

Figure 7. (a) Cyclic voltammetry of 1 (0.5 mM) in dichloromethane containing 0.1 M TBAPF₆ at 293 K, (b) electrochemical position of poly-1 on a gold electrode by cyclic voltammetry (at 0.1 V s⁻¹ during repetitive cycles between 0.0-1.2 V vs Ag/AgCl).

Repeated cyclic voltammetry of 1 between 0.0 and 1.2 V (vs Ag/AgCl, Figure 7b) results in a steady increase in current for the redox waves assigned (vide infra) to poly-1/poly-1⁺ and poly-1⁺/poly-1²⁺
at ca. 0.34 and 0.55 V, respectively, i.e. one of phenolato units in 1 undergoes a one electron oxidation, after which coupling with another phenoxyl radical complex occurs in an overall four electron ECCE process. The current response at $> 0.81$ V decreased over multiple cycles along with an increase in current response of the redox waves at 0.34 and 0.55 V, consistent with a buildup of poly-1 at the electrode (vide supra). The decrease in current response at $> 1.0$ V is in part due to depletion of the diffusion layer, however, stirring between cycles to “refresh” the depleted diffusion layer resulted in only a slight recovery of the current response from 1. This indicates that film formation results in a reduction in conductivity$^{30}$ at the onset potential for oxidation of 1, although the film continues to grow in thickness with each cycle. Polymer film formation was observed in dichloromethane at room temperature and at 200 K on a range of electrodes, including platinum, gold, GC and ITO electrodes.

The electrochemical oxidation of 1 and 2 can be viewed, formally, as an Fe(III)-O-Fe(III) to Fe(III)-O-Fe(IV) and subsequently to Fe(IV)-O-Fe(IV) process. However, the close correspondence of the potentials for the first and second oxidation of the ligand $^{31}$H$^1$ with that of 1 and 2 indicates, together with the oxidative phenol – phenol coupling observed, that oxidation results primarily in a decrease in electron density on the phenolate units$^{32}$ and in particular the phenol C4 positions. Indeed, DFT calculations (see ref 23 for the details) indicate that the oxidation hardly affects the occupation of d-orbitals on the iron(III) centers (whose occupations remain constant at ca. 4.6 electrons) for both 1 and $^{1+}$1. Furthermore, in 1 the spin density was observed mainly on the iron and adjacent ligating atoms and (symmetrically) on the phenols (Figure 8a). After oxidation to the radical cation $1^{++}$, the spin density diminishes on one phenol and increases at the other phenol (Figure 8b), primarily at the C4 position as anticipated in Scheme 1.

**Figure 8.** Spin-density plots obtained at (COSMO+ZORA)S12g/TZ2P for (a) 1 and (b) $1^{++}$. See Table S1 in ref 23 for relative energies of spin states.$^{33}$

Hence the redox chemistry of 1 in dichloromethane can be rationalized as an ECCE mechanism, $^{21b,32}$ by analogy with dimethylaniline redox chemistry.$^{34}$ The irreversible oxidation at 0.81 V (vs Ag/AgCl) yields initially an iron bound phenoxyl radical cation $1^{++}$, which undergoes dimerization via ary1 C–C coupling at the *para* position of the phenol unit to form $H_23^{2+}$, followed by double deprotonation to form 3 (Scheme 1). The dimer 3 obtained is symmetrical and exhibits two reversible one-electron oxidation waves at 0.34 and 0.55 V, which generate the radical cation $3^{++}$ and symmetric dication $3^{2+}$, respectively (Scheme 2).
Scheme 2. Oxidation of para-bisphenoxy bridge in 3 and poly-1 to monocationic and dicationic states.

5.2.6 Cyclic voltammetry at poly-1 modified electrodes.
Poly-1 modified electrodes show two fully reversible oxidation waves at 0.34 and 0.55 V in monomer free solution. The cyclic voltammetry at the electrode modified with poly-1 shows a linear dependence (see Figure S33b in ref 23) on the scan rate between 0.1 and 1.0 V s⁻¹, and $E_{p,a} = E_{p,c}$ and $I_{p,a} = I_{p,c}$ for both redox waves, as expected for surface-confined redox process. The non-Faradaic current shows a linear dependence on the scan rate and is unaltered by repeated cyclic voltammetry, further indicating that the film is not altered significantly upon oxidation or reduction (vide infra). The absence of a significant redox wave at 0.81 V on a poly-1-modified electrode indicates that the degree of polymerization is high, as the polymer chain ends (i.e. non-dimerized phenolate units) would be expected to show a reversible redox wave at a potential similar to that of 2.

Poly-1 modified electrodes prepared from solutions of 1 in dichloromethane, show fully reversible redox waves at 0.34 and 0.55 V (see Figure S35 in ref 23) in monomer free acetonitrile. However, in contrast to dichloromethane, a steady decrease in current was observed indicating desorption poly-1 over repeated cycles due either to ligand decomposition or breakup of the μ-oxo bridging unit. Nevertheless, the relative robustness of poly-1 in monomer free acetonitrile indicates that the lack of polymer film formation from 1 in acetonitrile (vide supra) is due to the solubility and lack of stability of the oligomers formed initially upon oxidation and not due to lack of C-C bond formation.
5.2.7 Vis-NIR absorption spectrotelectrochemistry of poly-1.
The vis-NIR absorption spectrum of poly-1 shows a weak band in the visible region similar to that of 1 in solution (vide supra). Oxidation of a poly-1-modified ITO electrode was carried out by cyclic voltammetry with simultaneous acquisition of vis-NIR absorption spectra (Figure 9). The spectra obtained for the singly and doubly oxidized poly-1⁺ show some resemblance to the spectra obtained upon oxidation of 1 in acetonitrile (vide supra). Electrochemical oxidation of poly-1 at 0.5 V to form poly-1⁺ results in the appearance of absorption bands at 430, 471 and an intense band at 870 nm. Further oxidation at 1.0 V to form poly-1²⁺ resulted in the disappearance of the NIR absorption band at 870 nm and the appearance of a more intense visible band at 475 nm. Subsequent reduction at 0.5 V resulted in a recovery of the spectrum of poly-1⁺ and at 0.0 V of the initial spectrum.

![Figure 9](image-url)

**Figure 9.** Vis-NIR absorption spectroscopy and (inset) cyclic voltammetry of a poly-1 film on an ITO slide (in dichloromethane containing 0.1 M TBAPF₆). Initial spectrum (black) and absorption spectra recorded during the cyclic voltammetry at the potentials indicated by the red, blue and gray arrows (see inset).

5.2.8 Resonance Raman spectroscopy of poly-1.
The Raman spectrum recorded from a poly-1 modified gold or ITO electrode is devoid of signals from the complex due to the limited thickness of the polymer layer and lack of resonance enhancement. By contrast, polarization of the poly-1 modified electrode at 0.5 V vs SCE in monomer free dichloromethane to form poly-1⁺, which has a strong absorbance at 870 nm, results in the appearance of intense Raman scattering at λₑₓᶜ 785 nm. The bands at 1618, 1556, 1478, 1377 and 1131 cm⁻¹ observed are identical to the Raman spectrum of 1 obtained in acetonitrile with 1 equiv. of CAN (Figure 10). The intense band at 1618 cm⁻¹ is assigned, tentatively, to an aromatic C=C stretching mode (observed at 1592 cm⁻¹ in the computed IR spectrum) and at 1556 cm⁻¹ to a C-O stretching mode of the phenoxy unit (found at 1579 cm⁻¹ in the computed IR spectrum, Figure S19 in ref 23).¹¹,³³ Similarly, the polarization of the electrode at 0.85 V to form poly-1²⁺ (which shows strong absorbance at 475 nm) resulted in the appearance of intense Raman scattering at λₑₓᶜ 488 nm, with bands at 1608, 1523, 1349, 1343, 1263 and 1139 cm⁻¹. Again, these bands are virtually identical to those observed in the Raman spectrum (λₑₓᶜ 473 nm) of 1 with 1 equiv. of CAN (vide
The bands at 1608 and 1523 cm\(^{-1}\) are ascribed to C=C and C=O stretching mode, respectively.\(^{33}\)

![Resonance Raman spectra](image)

**Figure 10.** Resonance Raman spectra of (red line) a poly-\(^{1}\) modified gold electrode at \(\lambda_{\text{exc}}\) 785 nm, (black line) \(^{1}\) in CH\(_2\)CN with 1 equiv. of CAN at \(\lambda_{\text{exc}}\) 785 nm, (blue line) a poly-\(^{2}\) modified gold electrode at \(\lambda_{\text{exc}}\) 488 nm, (grey line) \(^{1}\) in CH\(_2\)CN with 1 equiv. of CAN at \(\lambda_{\text{exc}}\) 473 nm. Identical spectra were obtained for poly-\(^{1}\) on ITO.

In the case of oxidation with CAN, it is tempting, considering the time dependence of the changes in absorbance and the similarity of the initial absorbance to that of the one electron oxidized form of \(^{2}\) (Figure 4), to assign the absorption band at 465 nm to the one electron oxidized form of \(^{1}\). However, comparison of the Raman spectrum of \(^{1}\) with CAN recorded at 473 nm with that recorded at 488 nm for poly-\(^{1}\) (Figure 10), confirms that the formation of the two electrons oxidized 4,4'-bisphenolato species \(^{3}\) from \(^{1}\) is extremely rapid. The subsequent changes, i.e. the decrease in intensity and appearance of the NIR absorption bands are due to reduction of the primary oxidation product to the monocationic species \(^{3+}\).

### 5.3 Conclusions

In the present study, we show that the electrochemical oxidation of a phenol based Fe(III) complex, used earlier in alcohol oxidations,\(^{18}\) leads to surprisingly well-defined reactivity of the iron(III) bound phenoxy radical generated. Of relevance to catalysis is that in acetonitrile, despite the quite complex spectroelectrochemical changes observed, one electron oxidation with Ce(IV) leads to essentially instantaneous C–C bond formation followed by further oxidation (to form \(^{3}\), and related oligomers) and then slower reduction to the radical cation and then further reduction. The reduced C–C coupled tetra nuclear complex formed appears similar to the original complex spectroscopically. The introduction of tert-butyl groups at the para-position of the phenol moieties leads to a dramatic increase in stability and precludes phenol C–C bond formation. The data indicate that for complexes bearing phenol units, similar processes may occur and present challenges to interpretation of spectroscopic analyses under reaction conditions. Notwithstanding this, the formation of well-defined iron containing polymers on electrode surfaces presents an opportunity for controlling oxidative coupling of phenols using complexation with Fe(III). It should be noted that despite that it does not undergo C–C coupling, complex \(^{2}\) shows similar reactivity in the oxidation
of alcohols as is observed for complex 1. Future studies will explore the relevance of oxidative phenol-phenol coupling chemistry under conditions in which catalysis with H₂O₂ is carried out.

5.4. Acknowledgements

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5.5. References

(17) Under IUPAC recommended nomenclature µ-O-bridge should be referred to as oxido and not oxo; in the present study oxo is used in correspondence with the existing extensive body of literature on Fe(III)-µ-O-Fe(III) complexes
(25) The values are calculated per dinuclear iron complex.
(29) Oxidation at higher potentials leads to a red shift in the visible absorption followed by a complete loss of absorbance ascribed to acidification of the solution due to oxidation of adventitious water at the platinum working electrode.
(32) Where E is an electrochemical and C a chemical step.