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Electrochemical Polymerization of Iron(III) Polypyridyl Complexes through C–C Coupling of Redox Non-innocent Phenolato Ligands

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Supporting Information

ABSTRACT: Phenolato moieties impart redox flexibility to metal complexes due to their accessible (oxidative) redox chemistry and have been proposed as functional ligand moieties in redox non-innocent ligand based transition metal catalysis. Here, the electro- and spectroelectrochemistry of phenolato based μ -oxo-diiron(III) complexes $[(L^1)Fe(\mu-O)Fe(L^1)]^{2+}$ (**1**) and $[(L^2)Fe(\mu-O)Fe(L^2)]^{2+}$ (**2**), where $L^1 = 2-(((di(pyridin-2-yl)methyl)-(pyridin-2-ylmethyl)amino)methyl)phenol$ and $L^2 = 3,5-di-tert-butyl-2-(((di(pyridin-2-yl)methyl)-(pyridin-2-ylmethyl)amino)-methyl)phenol$, is described. The electrochemical oxidation of **1** in dichloromethane results in aryl C–C coupling of phenoxyl radical ligand moieties to form *tetra* nuclear complexes, which undergo subsequent oxidation to form iron(III) phenolato based polymers (poly-**1**). The coupling is blocked by placing *tert*-butyl groups at *para* and *ortho* positions of phenol units (i.e., **2**). Poly-**1** shows two fully reversible redox processes in monomer free solution. Assignment of species observed during the electrochemical and chemical $\{(NH_4)_2[Ce^{IV}(NO_3)_6]\}$ oxidation of **1** in acetonitrile is made by comparison with the UV–vis–NIR absorption and resonance micro-Raman spectroelectrochemistry of poly-**1**, and by DFT calculations, which confirms that oxidative coupling occurs in acetonitrile also. However, in contrast to that observed in dichloromethane, in acetonitrile, the oligomers formed are degraded in terms of a loss of the Fe(III)–O–Fe(III) bridge by protonation. The oxidative redox behavior of **1** and **2** is, therefore, dominated by the formation and reactivity of Fe(III) bound phenoxyl radicals, which considerably holds implications in regard to the design of phenolato based complexes for oxidation catalysis.

INTRODUCTION

The redox chemistry of transition metal complexes has seen rapid progress recently driven by both a desire to understand the inner workings of bioinorganic systems and the necessity to achieve sustainability in chemical processes, and especially catalysis.^{1,2} These efforts have provided insight into mechanisms for many homogeneous catalytic and enzymatic reactions.³ The role played by redox non-innocent ligands⁴ in biological systems^{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, e.g., tyrosine,⁶ in enabling two-electron redox processes using first-row transition metals.^{3,7}

The phenolato moiety,^{8,9} in particular, imparts substantial redox flexibility to metal complexes due to the accessible redox chemistry of the phenolato unit itself. Phenols, such as tyrosine, undergo one- and two-electron oxidations readily; however, outside of the protective environment of an enzyme, they equally readily undergo bimolecular coupling reactions to form oligomeric and polymeric structures.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 ($M^{n+1}L^-$) or ligand radicals ($M^nL^\bullet$) that are essentially electronic isomers of each other.^{11,12}

The study of metal-bound phenoxyl radicals is of special interest in the context of biological systems, not least the enzyme galactose oxidase (GO).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.^{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)-phenoxyl radical structure is more appropriate.⁶

Inspired by phenolato based enzymes, phenolato based Fe(II) complexes have been applied in oxidation catalysis,¹¹ for

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Figure 1. Structures of complexes 1 and 2.

Scheme 1. Mechanism for Oxidative Dimerization of 1 To Form a 4,4'-Bisphenolato 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)

example, with O_2 for catechol C–C bond cleavage by Velesumay et al.,^{15,16} and in the μ -oxo-diiron(III) polypyridyl complex (1),¹⁷ based on the ligand 2-(((di(pyridin-2-yl)methyl)(pyridin-2-ylmethyl)amino)methyl)phenol, in which each of the Fe(III) centers is coordinated to a phenolato ligand (Figure 1), applied over a decade ago by Feringa et al. to the selective oxidation of benzyl alcohols to aldehydes with H_2O_2 .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,^{12,19,20} as well as phenols,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.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.

Here, we report that electrochemical oxidation of 1 results in sufficient phenoxyl radical character for aryl C–C coupling of the phenol units to take place (Scheme 1). In dichloromethane, the coupling between phenoxyl radical units occurs at both 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, 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 groups¹⁰ at the *para* and *ortho* positions of the phenol units (i.e., 2).

EXPERIMENTAL SECTION

Synthesis. The ligand 2-(((di(pyridin-2-yl)methyl)(pyridin-2-ylmethyl)amino)methyl)phenol (**HL**¹) and the complex $[(\text{L}^1)\text{Fe}(\mu\text{-O})\text{Fe}(\text{L}^1)](\text{ClO}_4)_2$ (1) were prepared and isolated as previously reported.¹⁸ The ligand 3,5-di-*tert*-butyl-2-(((di(pyridin-2-yl)methyl)(pyridin-2-ylmethyl)amino)methyl)phenol (**HL**²) and the complex $[(\text{L}^2)\text{Fe}(\mu\text{-O})\text{Fe}(\text{L}^2)](\text{ClO}_4)_2$ (2) were prepared and isolated using an analogous synthetic route to that reported for 1¹⁸ and related compounds.²³ See the Supporting Information for details and

characterization (Figures S1–S18). Commercially available chemicals were used without further purification unless stated otherwise. Solvents for electrochemical and spectroscopic measurements were UVASOL (Merck) grade or better. For details for physical and computational methods used, see the [Supporting Information](#).

Caution! Perchlorate salts of metal complexes incorporating organic ligands are potentially explosive. These compounds should be prepared in small quantities and handled with suitable protective safeguards.

RESULTS AND DISCUSSION

Structure and Spectroscopic Characterization of $[(L^1)Fe(\mu-O)Fe(L^1)](ClO_4)_2$ (1) and $[(L^2)Fe(\mu-O)Fe(L^2)](ClO_4)_2$ (2). The ligand HL^1 and the complex $[(L^1)Fe(\mu-O)Fe(L^1)](ClO_4)_2$ (1) have been reported previously together with single-crystal X-ray structural determination of $[(L^1)Fe(\mu-O)Fe(L^1)](PF_6)_2$.¹⁸ HL^2 and 2 were prepared by analogous methods to HL^1 and 1, respectively. Synthesis and detailed FTIR and 1H NMR characterization of HL^1 , HL^2 , 1, and 2 are provided as [Supporting Information](#). The ESI/MS spectrum of 1 shows a base peak at m/z 445 ($[(L^1)Fe(\mu-O)Fe(L^1)]^{2+}(ClO_4)_2$) and of 2 at m/z 557 ($[(L^2)Fe(\mu-O)Fe(L^2)]^{2+}(ClO_4)_2$) (Figures S15 and S16). In both cases, ESI/MS spectra show no evidence for the presence of mononuclear species. The 1H NMR spectra of both 1 and 2 show signals in the range of -5 to 40 ppm in CD_3CN (Figures S13 and S14), which, together with broadening,²⁴ and the magnetic susceptibility, determined using Evans method,²⁵ of 2.78 BM and 2.76 BM for 1 and 2, respectively (Figures S17 and S18), 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.

Nonresonant Raman spectra of 1 and 2 (λ_{exc} 785 nm and λ_{exc} 1064 nm) were recorded in solution (acetonitrile and acetone, Figure S19) and in the solid state (Figure S20), whose peak positions compare well with the computed IR spectra (Figure S19). 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., $[Fe^{III}Fe^{III}(bpbmp)(CH_3CO_2)_2]ClO_4$ (1591, 1564, 1478, 1451, 1276, 1274, 1151, 1112, 890, 795, 636, 612, and 335 cm^{-1} , where bpbmp is 2-bis[(2-pyridylmethyl)-aminomethyl]-6-((2-hydroxybenzyl)(2-pyridylmethyl))-aminomethyl]-4-methylphenol).²⁶ The bands at 1279 and 602 cm^{-1} (found with DFT at 1251 and 582 cm^{-1} , Figure S19) are assigned to the $\nu(CO)_{phenol}$ mode and $\nu(Fe-O_{phenol})$ mode, respectively,²⁷ while the bands at 1595/1562 and 1475/1455 cm^{-1} 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 λ_{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 and 540 cm^{-1} are assigned to the $\nu(CO)_{phenol}$ mode and $\nu(Fe-O_{phenol})$ mode, respectively. The absence of change between the solid state spectrum (Figure S20) and those obtained in acetonitrile and acetone (Figure S19) indicates that the solid state structure is retained in solution, in agreement with EPR and ESI-MS data.

Both 1 and 2 show visible absorption (ϵ_{535} (1) $4.1 \times 10^3 M^{-1} cm^{-1}$, ϵ_{623} (2) $4.7 \times 10^3 M^{-1} cm^{-1}$) 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 elsewhere²⁸ and the longest wavelength absorption is assigned to a phenolato-to-Fe(III)

Figure 2. UV/vis absorption spectra of 1 (black) and 2 (red), 0.075 mM in acetonitrile.

charge-transfer transition (LMCT) based on resonance Raman spectroscopy (Figures S21–S23) and DFT (Figures S25, S26 and Table S2). 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, Figure S24), indicating that dissociation of a mononuclear complex is highly unfavorable.

Raman spectra recorded at λ_{exc} 561, 355, and 532 nm (Figures S21, S22, and S23) in dilute solution (0.25–0.5 mM) show resonance enhancement of some of the Raman bands of 1 and 2. The spectrum obtained at λ_{exc} 561 nm (Figure S20), although resonant with an absorption assigned as a phenolato-to-Fe(III) charge-transfer band, is similar to the Raman spectra obtained at 1064 and 785 nm (Figures S19 and S20). At λ_{exc} 355 nm, in resonance with an absorption band assigned to an oxo-to-Fe(III) charge transfer, bands at 411 and 430 cm^{-1} are enhanced strongly (Figure S22), which are ascribed, tentatively, to Fe-O-Fe modes that are observed typically between 380 and 540 cm^{-1} .²⁷ The computed IR spectrum shows these Fe-O-Fe modes at 432 cm^{-1} (4 km/mol intensity) and 453 cm^{-1} (35 km/mol intensity), respectively.

The electronic structure of complex 1 is confirmed by computational chemical data, which show that the spin ground state (at S12g/TZ2P²⁹ with ZORA³⁰ scalar relativistic corrections and COSMO³¹ solvation taken into account; see the [Supporting Information](#)) corresponds to the antiferromagnetically coupled Fe(III)-O-Fe(III) complex with other possible spin states higher in energy by at least 10 kcal·mol⁻¹ (Table S1). The corresponding geometric structure is also in good agreement with the X-ray structure (root-mean-square deviation 0.2 Å), with similar iron–ligand bond distances (mean absolute deviation 0.017 Å). Furthermore, the computed IR spectrum shows peak positions consistent with the nonresonant Raman spectra (Figure S19c). The TD-DFT UV/vis absorption spectrum for 1 (Figure S25), obtained at (COSMO+ZORA)SAOP/TZ2P,^{30,32} shows bands shifted to longer wavelengths (ca. 140 nm) compared to the experimental spectrum, and correspond to phenoxy-to-iron ligand-to-metal (LMCT) transitions (Figure S25).

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, 1.40, 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), with the

Figure 3. Cyclic voltammetry of **1** (black) and **2** (red, current axis is offset for clarity) (1.0 mM) in acetonitrile (0.1 M TBAPF₆) at a glassy carbon electrode ($d = 3$ mm) working electrode with a 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.

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 that two are electrochemically reversible redox processes assigned to phenolato centered oxidations at 1.04 and 1.23 V.

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 and Figure S29) electrode shows that both redox waves are electrochemically reversible.³³ A cyclic voltammogram from 0.3 V to between the first and second redox waves (Figure 4, left) 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 right, 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.

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 the 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.

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 [(NH₄)₂Ce(NO₃)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

Figure 4. Thin-layer voltammetry of **2** (5 mM) (left) at 0.01 V s⁻¹ in an OTTLE cell in acetonitrile (0.1 M TBAPF₆) (right) 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.

Figure 5. Thin-layer cyclic voltammetry of **1** (5.0 mM) in acetonitrile (0.1 M TBAPF₆ 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).

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 absorption of (b) **1** at 465, 785, and 850 nm with addition of 1 equiv of CAN, (d) **2** at 425, 488, and 625 nm with addition of 1 equiv of CAN.

to **1** in CH₃CN 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 and

850 nm. Resonance Raman spectra recorded at 473 and 785 nm during the oxidation provide insight in the species responsible for these absorption bands (vide infra).

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 and 1.2 V vs Ag/AgCl).

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

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 toward positive potentials, followed by two reduction waves at 0.55 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.

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-**1**²⁺ at ca. 0.34 and 0.55 V, respectively; i.e., one of the phenolate 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 conductivity³⁴ 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 (Figures S30–S32).

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 HL¹ 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 units³⁵ and, in particular, the phenol C4 positions. Indeed, DFT calculations 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**^{•+}. 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.

Hence, the redox chemistry of **1** in dichloromethane can be rationalized as an ECCE mechanism,^{21b,36} 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 aryl C–C coupling at the *para* position of the phenol unit to form H₂3²⁺, 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 $3^{\bullet+}$ 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

The formation of the coupled tetramer H_23^{2+} from two $1^{\bullet+}$ is slightly endothermic (+1.6 kcal·mol⁻¹), and the subsequent release of two protons is exothermic by 84.6 kcal·mol⁻¹, excluding twice the solvation energy of a proton (−260.2 kcal·mol⁻¹ in acetonitrile³⁷) for a total of more than 600 kcal·mol⁻¹ for the process of $H_23^{2+}(\text{solv})$ to $3(\text{solv}) + 2H^+(\text{solv})$.

Cyclic Voltammetry at Poly-1-Modified Electrodes. Poly-1-modified electrodes show two fully reversible oxidation waves at 0.34 and 0.55 V (Figure S33a) in monomer free solution. The cyclic voltammetry at the electrode modified with poly-1 shows a linear dependence (Figure S33b) 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., nondimerized 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 (Figure S35) in monomer free acetonitrile. However, in contrast to dichloromethane, a steady decrease in current was observed, indicating desorption of poly-1 over repeated cycles due either to ligand decomposition or to breakup of the μ -oxo bridging unit (Figure S35). 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.

vis–NIR Absorption Spectroelectrochemistry 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, and Figure S34). The

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).

spectra obtained for the singly and doubly oxidized poly-1²⁺ 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 nm 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.

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 λ_{exc} 785 nm. The bands at 1618, 1556, 1478, 1377, and 1131 cm⁻¹ observed are identical to the rRaman 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).^{11,38} 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 λ_{exc} 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 (λ_{exc} 473 nm) of **1** with 1 equiv of CAN (vide supra). The

Figure 10. Resonance Raman spectra of (red line) a poly- I^+ -modified gold electrode at λ_{exc} 785 nm, (black line) **1** in CH_3CN with 1 equiv of CAN at λ_{exc} 785 nm, (blue line) a poly- I^{2+} -modified gold electrode at λ_{exc} 488 nm, (gray line) **1** in CH_3CN with 1 equiv of CAN at λ_{exc} 473 nm. Identical spectra were obtained for poly- I^+ on ITO.

bands at 1608 and 1523 cm^{-1} are ascribed to $\text{C}=\text{C}$ and $\text{C}-\text{O}$ stretching modes, respectively.³⁸

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-electron oxidized 4,4'-bisphenolato species 3^{2+} 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^+).

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 phenoxyl 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 $\text{C}-\text{C}$ bond formation, followed by further oxidation (to form 3^{2+} , and related oligomers) and then slower reduction to the radical cation and then further reduction. The reduced $\text{C}-\text{C}$ 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 $\text{C}-\text{C}$ 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 $\text{C}-\text{C}$ 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 H_2O_2 is carried out.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b02378.

Details of computational data, experimental methods and syntheses, spectroscopic and electrochemical data (PDF)

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Notes

The authors declare no competing financial interest.

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