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VIP **Electrochemistry** **Very Important Paper**

Covalent Attachment of Porphyrins and Ferrocenes to Electrode Surfaces through Direct Anodic Oxidation of Terminal Ethynyl Groups**

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The structural rigidity and suitable electronic properties of the C≡C moiety make the alkynyl group an attractive linkage for electron transfer between redox-active metal centers[1] or between an electrode and a covalently bonded redox-active molecule.[2] Given the wide application of terminal alkynes in molecular derivatization,[3] electrografting methods based on this group hold promise for a diverse collection of molecularly altered electrodes and other metal surfaces. A radical-based electrografting procedure,[4] which requires generation of the alkynyl radical close to the electrode surface, involves the loss of a hydrogen atom from the end carbon. We recently described a two-step method for such a process based on anodic oxidation of a lithio-activated ethynyl group.[2] This process requires the in situ formation of a Li-stabilized carbanion [Eq. (1)], followed by one-electron oxidation [Eq. (2)], thereby producing an ethynyl radical, which reacts with the electrode.

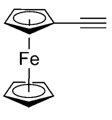
$$\mathrm{RC{\equiv}C{-}H} \xrightarrow{\mathrm{BuLi}} \mathrm{RC{\equiv}C^{\delta-}{-}Li^{\delta+} + BuH} \qquad (1)$$

$$\mathrm{RC{\equiv}C^{\delta-}{-}Li^{\delta+} - e^- \rightarrow RC{\equiv}C^{\cdot} + Li^+} \qquad (2)$$

We have since sought an alternative method that obviates the need for chemical activation of the alkynyl group [Eq. (1)]. It was reasoned that one-electron oxidation would increase the already high acidity[5] of a terminal alkyne, thereby causing rapid loss of a proton and the production of the desired alkynyl radical [Eq. (3)].

$$\mathrm{RC{\equiv}C{-}H - e^- \rightarrow RC{\equiv}C^{\cdot} + H^+} \qquad (3)$$

We now report the successful application of this method to the covalent attachment of ferrocenyl derivatives and 5,10,15,20-(4-ethynylphenyl)porphyrin through ethynyl linkages to glassy carbon and other electrode surfaces, including platinum and gold. We also describe the covalent attachment of vinylferrocene to glassy carbon through direct anodic oxidation of the vinyl group.



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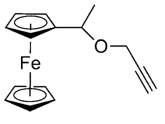

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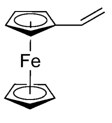

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A cyclic voltammetry (CV) scan of ethynylferrocene (**1**, 0.65 mM) in dichloromethane/$[Bu_4N][PF_6]$ (0.1 M) shows two oxidation waves (Figure 1), the first of which $[E_{1/2}{}^{Ox1} = 0.14$ V vs. ferrocene(FcH)] forms the ethynyl ferrocenium ion $\mathbf{1}^+$. The second wave at $E_{pa}{}^{Ox2} = 1.56$ V is attributed to the ethynyl group.[6,7] Although the multi-electron nature of the second wave implies complexity beyond simple formation of the putative biradical $\mathbf{1}^{2+}$, the functional consequence of a single scan into this wave is the efficient deposition of ethynylferrocene on the electrode, as determined by CV after transferring the sonicated modified electrode into a pure electrolyte solution (Figure 1, inset). Having an $E_{1/2,s}$ of −0.01 V and peak currents that are proportional to the scan rate, the new redox

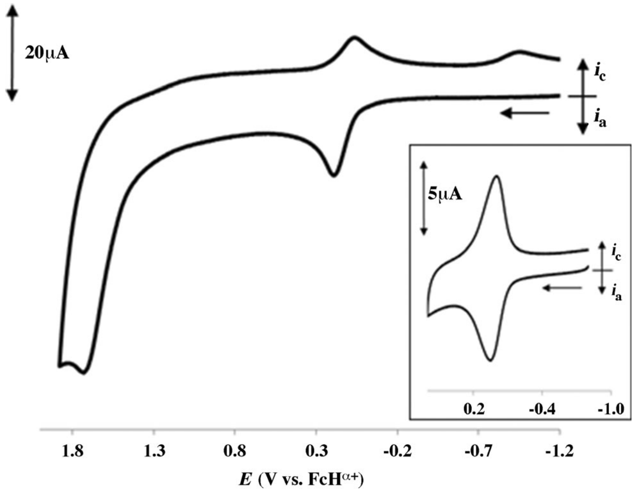

Figure 1. CV of **1** (0.65 mM) in $CH_2Cl_2/[Bu_4N][PF_6]$ (0.1 M) at a glassy carbon electrode; inset shows the resultant modified electrode in pure CH_2Cl_2/0.1 M $[Bu_4N][PF_6]$; scan rate 0.5 V s^{-1}. i_c and i_a are the cathodic and anodic currents, respectively.

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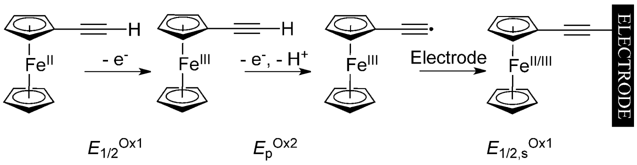


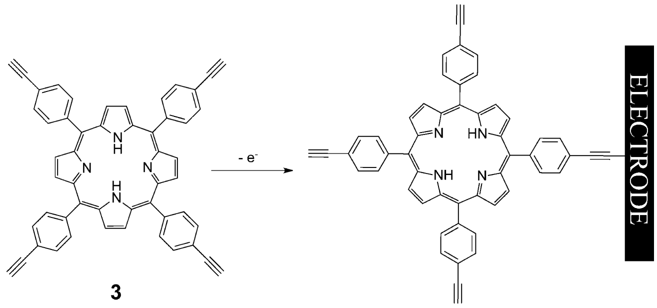
Scheme 1. Likely mechanism for the deposition of ethynylferrocene after application of potential E_p^{Ox2}, which is sufficient to oxidize the ethynyl group. The formal biradical is initially deposited as the ferrocenium (Fe^{III}) complex and then reduced to the ferrocene (Fe^{II}) form when the potential is returned negative of $E_{1/2,s}$.

pair is clearly the ferrocene/ferrocenium couple of surface-bound **1** (Scheme 1).

Integration of the anodic peak current gave an apparent surface coverage (Γ) of 8.1×10^{-10} mol cm^{-2}, equivalent to about 1.8 monolayers. Only small changes in coverage resulted from variation of either the concentration of **1** (0.65 to 5.2 mM) in the deposition solution or the CV scan rate (0.1 to 1.0 V s^{-1}), as long as only a single scan was employed.[8]

The ether-derivatized ethynylferrocene **2** ($E_{1/2}^{Ox1}=-0.03$ V; $E_{pa}^{Ox2}=1.31$ V) behaved similarly, except that in this case, the analyte concentration affected the surface coverage. A single scan through the second wave at the lowest concentration studied (0.54 mM) gave a surface coverage of 1.9×10^{-10} mol cm^{-2}, whereas higher concentrations (up to 4.2 mM) produced coverages of up to 3.4×10^{-10} mol cm^{-2}, equivalent to a nominal monolayer.[8] When electrode modifications were performed for **2** (3 mM) in tetrahydrofuran (THF), surface coverage increased to 1×10^{-9} mol cm^{-2} (or 2.2 monolayers). Multilayers most likely arise from radical attack on already surface-confined species.

The modification of electrodes with porphyrins or metal porphyrins is an area of intense activity, attracting wide-ranging approaches that include electropolymerization,[9] self-assembly through tethered functional groups,[10] thermolysis,[11] click chemistry,[12] and covalent attachment through reduction of a pendant aryl diazonium group.[13] The direct alkyne-oxidation method was employed to attach the phenylacetylene-substituted porphyrin **3** to electrodes (Scheme 2), and metalation of the porphyrin with zinc was carried out on the immobilized porphyrin.



Scheme 2. Anodic attachment of 5,10,15,20-(4-ethynylphenyl)porphyrin to an electrode. The scheme does not take into account the first two (porphyrin-based) oxidations and assumes that the alkynes not bound to the surface are unchanged.

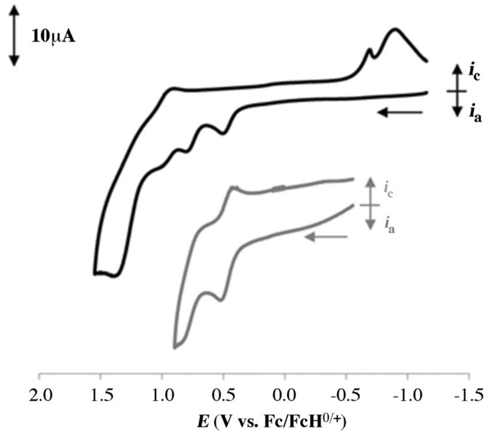


Figure 2. CV of **3** (1.0 mM) in CH_2Cl_2/[Bu_4N][PF_6] (0.1 M) at a glassy carbon electrode, $\nu=0.2$ V s^{-1}.

The anodic voltammetry of **3** in solution is similar to that reported for other tetraphenylporphyrins[9b,13a,14] in displaying two porphyrin-based one-electron oxidations (0.58 V, 0.90 V).[15] However, there is additional activity at more positive potentials (Figure 2), and the multi-electron wave at $E_{pa}=1.36$ V can be ascribed to oxidation of one or more of the ethynyl groups. A single scan to 1.5 V produced a modified electrode with reversible oxidation ($E_{1/2}=0.50$ V) and reduction ($E_{1/2}=-1.80$ V) couples consistent with an attached porphyrin (Figure 3).

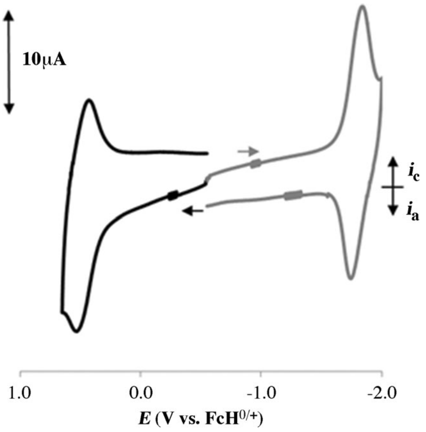


Figure 3. CV of a glassy carbon electrode modified with **3** in pure CH_2Cl_2/[Bu_4N][PF_6] (0.1 M) at $\nu=1$ V s^{-1}.

The average surface coverage obtained by using the single-scan procedure, determined by integration of the cathodic wave of the modified electrode, was 6×10^{-10} mol cm^{-2}, a result indicative of a perpendicular orientation of **3** with respect to the electrode surface.[16] There is some electrode 'scan history' for surface-confined **3**; repeated scans through the oxidation wave give slow degradation of the wave at 0.5 V (Figure S2 in the Supporting Information). Voltammetric changes are also observed in scans through the reduction wave (Figure S3 in the Supporting Information). Similar redox-induced changes have been reported for porphyrins in diazonium-modified electrodes.[13a]

Chemical confirmation of an active porphyrin on the electrode was obtained by treating a modified electrode overnight with a solution of $ZnCl_2$ (1 M) in diethylether. After sonication and transfer into a pure electrolyte solution, the electrode gave CV results consistent with the electrochemistry of the zinc complex of **3**, with two reversible oxidations (Figure 4) at the expected potentials (0.34 V, 0.64 V).[9c] Repeated CV scans caused little change in the voltammetry of the metalated porphyrin electrode.

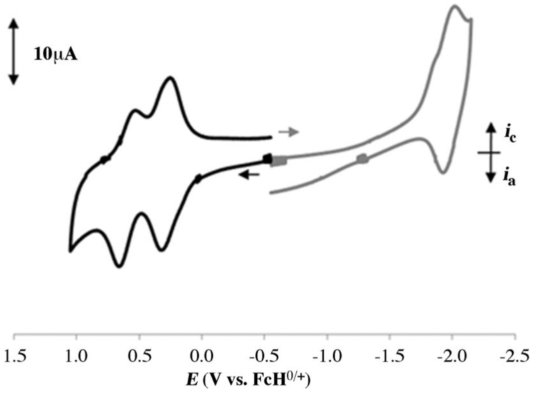


Figure 4. CV of a Zn-treated glassy carbon electrode modified with **3** in $CH_2Cl_2/[Bu_4N][PF_6]$, $\nu = 1\ V s^{-1}$.

The porphyrin deposition and metalation processes were confirmed spectroscopically through monitoring of the optical spectra on indium tin oxide (ITO) slides. After anodic oxidation in a solution of **3**, ITO slides (Figure 5) showed the characteristic Soret band at 432 nm.[13a] After functionalization with zinc, this band underwent the expected shift to 440 nm characteristic of the zinc porphyrin.[17]

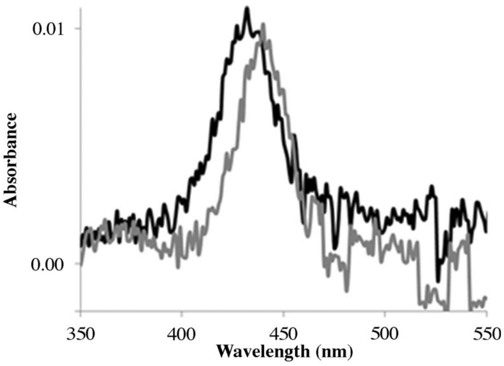


Figure 5. UV/Vis spectrum of an ITO electrode modified by **3** (black), and the same electrode after undergoing zinc treatment (gray).

Finally, we report an interesting adaptation of the anodic deposition theme to vinylferrocene (**4**). This compound also has an irreversible multi-electron wave at a fairly positive potential ($E_{pa} = 1.3$ V in $CH_2Cl_2/[Bu_4N][PF_6]$; Figure S7 in the Supporting Information). Single scans into this wave (0.4 to 1 mM **4**, 0.2 $V s^{-1}$) give an electrode which, in pure electrolyte solution, shows a well-defined surface wave (Figure 6) consistent with nearly monolayer coverage with a ferrocenyl group ($E_{1/2,s} = -0.03$ V, $\Gamma = 2.7 \times 10^{-10}\ mol\,cm^{-2}$). Although the precise nature of the molecule-to-surface bonding is still being investigated, the fact that the modified electrodes are impervious to sonication, solvents, and hundreds of CV scans appears to rule out the presence of oligovinylferrocene on the electrode. A working hypothesis is that a vinyl-based radical cation is responsible for the anodically-induced deposition of vinylferrocene.[18]

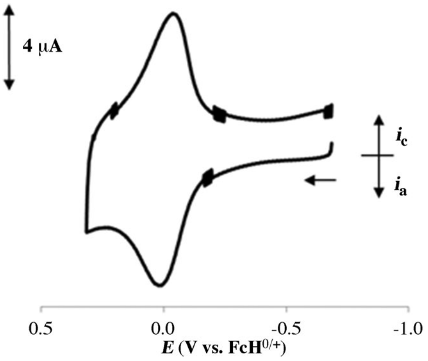


Figure 6. CV of a glassy carbon electrode modified with vinyl ferrocene in pure CH_2Cl_2/0.1 M $[Bu_4N][PF_6]$ at $\nu = 1\ V s^{-1}$.

In conclusion, we report a single-step anodic electrografting method for the covalent attachment of molecules to electrodes through an ethynyl linkage. This technique takes advantage of the increased acidity of the radical cations of terminal ethynyl groups, thus allowing the generation of a radical that bonds to the metal surface through the end carbon. Surface coverages of one to two monolayers are possible with one CV scan. Although emphasis to date has been on modification of glassy carbon electrodes, the ethynyl-linked compounds reported herein have also been deposited on gold, platinum, and ITO electrodes. We also report what appears to be the first covalent attachment of porphyrin monolayers on carbon and their efficient zinc metalation. Electrode modification through direct anodic oxidation of a terminal alkynyl group has advantages over the recently reported method of lithium activation of alkynes[2] in cases where lithiation of the substrate is problematic or the deposition needs to be carried out at submillimolar concentrations. Anodically induced monolayer-level electrode coverage has also proved possible for vinylferrocene.

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