Ethynylphenyl-derivatized Free Base Porphyrins:
Anodic Oxidation Processes and Covalent Grafting onto Glassy Carbon Electrodes

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Abstract

In six of seven cases, direct anodic oxidation of the ethynyl group of an ethynylphenyl-derivatized free-base porphyrin gave modified glassy carbon electrodes in which the porphyrin was strongly surface-bound, most likely in a perpendicular geometry through covalent attachment of the ethynyl group to a surface carbon atom. The porphyrins each contained an ethynylphenyl group in one meso position and varied in the groups present in the other three meso positions. Electrografted 5,10,15,20-tetrakis(ethynylphenyl)porphyrin, H₂1, which has ethynyl moieties in all four meso positions, has well-defined surface voltammetry and grows to multi-layer levels upon repeated cyclic voltammetry (CV) deposition scans. Multi-layering was not observed to the same degree for mono-ethynylphenyl-substituted porphyrins, and became progressively less for porphyrins having groups in the 15-meso position that were more protective against ethynyl radical attack. Clean molecular monolayer-level coverage was observed for 5-ethynylphenyl-10,20-bis(3-methoxyphenyl)-15-hexylporphyrin, H₂5. Owing to the fact that the ethynyl oxidation potential (1.1 to 1.5 V vs ferrocene) is more positive than that of the second macrocycle oxidation, the longevities and follow-up reactions of the porphyrin dications were also studied by CV, chemical oxidation, and optical spectroscopy in homogeneous solution. The primary follow-up products of the doubly oxidized porphyrins, whether surface-bound or in solution, were pyrrole-protonated species that were easily reduced back to the neutral porphyrin.

Introduction

Porphyrins and metalloporphyrins are well known for their ability to take part in chemical and photochemical processes such as electron-transfer mediation and catalysis¹⁻⁵. Accordingly, there is ongoing interest in development of methods whereby metallated or free-base porphyrins can be immobilized on the surfaces of electrodes that might be employed in optical and electronic devices as well as in electrocatalysis⁶⁻⁸. Among the known immobilization methods are chemisorption and Langmuir-Blodgett deposition^{4,9}, *in vacuo* sublimation^{10,11}, molecular self-assembly^{5,12}, reaction of a porphyrin with thionyl chloride-treated glassy carbon¹³, cathodic reduction of meso-substituted aryldiazonium^{14,15} or diazonium¹⁶ groups, and electrochemical polymerization¹⁷⁻²⁶, the last of these being the most common. Anodic polymerization of meso-substituted porphyrins is generally thought to involve coupling reactions at the meso positions of porphyrins in different redox states which, in the case of a one-electron process, is said to be a “radical-substrate” reaction²⁷. Although anilines, pyrroles, and thiophenes are the most commonly employed meso substituents for electrochemical polymerization processes^{19,22,23}, oxidation of aryl or polyaryl meso substituents have also been exploited for this purpose²⁴⁻²⁶.

We recently reported several approaches to the covalent attachment of molecules to carbon surfaces through an ethynyl linkage²⁸⁻³¹, in one case including a porphyrin containing ethynylphenyl groups in all four meso positions²⁹. In the so-called “direct oxidation” approach, anodic oxidation of a molecule’s terminal ethynyl group triggers its deprotonation, thereby producing an ethynyl radical which reacts with the electrode surface (Eq 1)^{29,31}. When this process was carried out on ethynylferrocenes (Eq 1, R = ferrocenyl derivative), surface

concentrations increased with the number of anodic deposition scans. In most cases, the surface growth continued past the point that would be consistent with molecular monolayer coverage, suggesting that electrochemical growth could occur by sequential ethynyl radical attack on vulnerable positions of already immobilized molecules. In the case of ethynylferrocenes, such multi-layering would involve coupling of an ethynyl-based radical to one of the cyclopentadienyl rings of the metallocene. A similar model is widely believed to be responsible for the multi-

layering observed in the aryldiazonium reduction method of surface deposition³². In our previous communication on direct oxidation of the ethynyl groups of 5,10,15,20-tetrakis(ethynylphenyl)porphyrin, (H₂TEPP, H₂1)²⁹, robust growth in surface coverage with multiple deposition scans was also observed. When H₂1 becomes ethynyl-linked to the surface, the remaining three ethynyl groups are available for continued radical-substrate coupling reactions, allowing continued growth of the porphyrin morphology. Oligomeric growth has also been observed in the anodic polymerization of porphyrins derivatized with multiple aryl or fluorenyl groups²⁴⁻²⁶, including the analogue of H₂1 that contains no ethynyl groups, namely tetraphenylporphyrin (H₂TPP)²⁴. Depending on the nature of the bond between the ethynyl and surface carbons, the surface geometries of mono-ethynyl-linked porphyrins might be more akin to those of self-assembled monolayers^{5,12,16,33,34} rather than those of porphyrin polymers (see discussion in section II.3).

The present work had two principal objectives. One was to detail the anodic deposition and surface voltammetry of H₂1, which had been only briefly described in a previous report²⁹. The second was to investigate the anodic grafting of porphyrins containing a *single* terminal ethynyl group and, in the process, explore how changes in the meso substituents might affect any sequential coupling reactions of the surface-bound species. The six mono-ethynylphenyl substituted compounds employed for the second aspect of the study, H₂2 through H₂7, are shown in Figure 1.

Figure 1. Structures of compounds discussed in this paper. Ring hydrogens are not shown.

A complication in the direct ethynyl oxidation approach to electrografting arises if the molecular backbone of the molecule (R in Eq 1) is oxidized at a less positive potential than the ethynyl group. For ethynylferrocenes, the fact that the ferrocenyl moiety oxidizes more easily than the ethynyl group is not detrimental, owing to the expected stability of the ferrocenium center. In that case, the ethynyl-linked ferrocenium compound that is electrodeposited on the surface is simply reduced to the neutral ferrocenyl moiety in the negative-going part of the CV scan³¹. The effects of a more facile oxidation of R become more complex when R is a porphyrin, which generally has two one-electron oxidations at sufficiently low potentials that a *trication* is initially formed when the ethynyl group is oxidized. The rich electrochemical literature of porphyrins indicates that doubly-oxidized porphyrins (i.e., porphyrin dications) are not always

persistent, even on the cyclic voltammetry (CV) time scale³⁶. Hence it was important to fully characterize the oxidation processes of the porphyrin backbones of compounds H₂1 through H₂7 in homogeneous solution. The first part of this paper addresses the five-membered family linked by four one-electron porphyrin redox processes at potentials E_{1/2}(2) through E_{1/2}(-2), as shown in Scheme 1. Within this group, we found that there is a correlation between the chemical

Scheme 1. Electron-transfer sequence proposed for the redox reactions of free-base porphyrins containing at least one ethynylphenyl group (PhC≡CH) at a meso position.

reversibilities of the porphyrin oxidations and the successful and clean (i.e., lacking side-products) anodic grafting of the compounds onto glassy carbon electrodes. The second part of the paper describes the electrografting process whereby proton loss following irreversible oxidation of the porphyrin ethynyl group at potential E_{pa}(3) appears to provide the radical which attaches to the electrode surface (Scheme 1).

Results and Discussion

I. Homogeneous electrochemistry

1.1 Tetrakis(ethynylphenyl)porphyrin, (H₂TEPP, H₂1) On the CV time scale, the four macrocycle-based redox reactions of H₂1 are chemically reversible, quasi-Nernstian, one-electron processes (Figure 2). As will become important in the discussion of the surface deposition of H₂1, this compound also has an irreversible anodic wave near 1.5 V that is assigned to oxidation of one or more of its ethynyl groups²⁹.

The five-membered, macrocycle-based, electron-transfer series observed for H₂1 is routine for a free-base porphyrin, and the difference in potential of the first oxidation and first reduction processes, ΔE_{1/2} (= E_{1/2}(-1) – E_{1/2}(1)), of 2.28 V in [PF₆]⁻ solution, is as expected for porphyrins (literature 2.25 V ± 0.15 V)³⁷. The potentials determined for the compounds in solution are collected in Table 1. Those determined for H₂1 are shifted positive by an average of 70 mV from

those measured by us for H₂TPP, showing that the porphyrin backbone of H₂1 experiences only a small electron-withdrawing effect from introduction of the four ethynyl groups.

Figure 2. CV scan at 0.2 V s⁻¹ of 1.0 mM H₂1 in dichloromethane/0.1 M [NBu₄][PF₆], 2 mm glassy carbon electrode.

Cmpd	E _{1/2} (2) [PF ₆] ⁻ (TFAB)	E _{1/2} (1) [PF ₆] ⁻ (TFAB)	E _{1/2} (-1) [PF ₆] ⁻ (TFAB)	E _{1/2} (-2) [PF ₆] ⁻ (TFAB)	Comments ^a E _{pa} (3) at 0.2 V s ⁻¹
H ₂ TEPP, H ₂ 1	0.90 (1.04)	0.61 (0.56)	-1.63 (-1.72)	-1.94 (-2.09)	Irrev ox 1.5 V
H ₂ 2	0.98 ^{pr} (1.08)	0.57 (0.52)	-1.68 (-1.71)	-2.04 (-2.06)	Irrev ox 1.3 V
H ₂ 3	0.88 ^{ir} (1.00)	0.47 (0.43)	-1.77 (-1.74)	-2.18 (n.m.)	Irrev ox 1.1 V
H ₂ 4	0.96 (1.11)	0.62 (0.56)	-1.64 ^{ir} (-1.68) ^{ir}	-1.88 (n.m.)	Irrev ox 1.2 V
H ₂ 5	0.86 (0.98)	0.50 (0.43)	-1.70 (-1.75)	-2.04 (-2.07)	Irrev ox 1.2 V
H ₂ 6	0.97 ^b (1.07) ^{pr}	0.59 (0.52)	-1.68 (-1.74)	-2.05 (-1.71)	Irrev ox 1.3 V
H ₂ 7	0.96 ^{ir} (1.13) ^{ir}	0.55 ^{ir} (0.47) ^{ir}	-1.73 (-1.76)	-2.10 (-2.13)	Irrev ox 1.4 V
H ₂ TPP	0.87 (0.99) (1.04, BArF ₂₄)	0.54 (0.46) (0.45, BArF ₂₄)	-1.70 (-1.75) (-1.74, BArF ₂₄)	-2.02 (-2.08) (-2.07, BArF ₂₄)	BArF ₂₄ is [B(C ₆ H ₃ (CF ₃) ₂) ₄] ⁻

Table 1. E_{1/2} potentials in V vs ferrocene. Medium was dichloromethane using either 0.1 M [NBu₄][PF₆] or 0.05 M [NBu₄][TFAB] as supporting electrolyte (TFAB = [B(C₆F₅)₄]⁻). Legend: pr = partially chemically reversible at CV scan rate of 0.2 V s⁻¹; ir = chemically irreversible up to 1 V s⁻¹, potential given for E_p at 0.2 V s⁻¹; n.m. = not measured; ^a measured in 0.1 M [NBu₄][PF₆]; ^b partially chemically reversible at CV scan rate of 2 V s⁻¹.

We observed that if the CV scans were carried out in dichloromethane that had not been rigorously dried, the second oxidation became chemically irreversible and a cathodic wave for a follow-up product appeared at E_{pc} = -0.9 V. This feature was also observed if the scan was taken

out to the irreversible ethynyl oxidation at $E_{pa}(3) = 1.5$ V (Figure 3). Owing to the fact that similar cathodic features were frequently encountered for electrodes that had been modified either by H₂1 or a number of other porphyrins (see section I.2), we carried out experiments that were designed to identify these common follow-up product(s).

Figure 3. CV scan at 0.2 V s^{-1} of $1.0 \text{ mM H}_2\mathbf{1}$ in dichloromethane/ $0.1 \text{ M [NBu}_4\text{][PF}_6\text{]}$, glassy carbon electrode, extended to the potential of the ethynyl oxidation process at 1.5 V . The reverse scan shows a large cathodic wave near -0.9 V which is ascribed to the reduction of the protonated follow-up product $[\text{H}_4\mathbf{1}]^{2+}$.

Attempts at exhaustive anodic electrolysis at the potential of the second oxidation of H₂1 in dichloromethane containing either $[\text{NBu}_4][\text{PF}_6]$ or $[\text{NBu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$ electrolyte were unsuccessful, owing to formation of a blocking coating on the platinum basket anode. We therefore generated the follow-up product(s) of the porphyrin dication by chemical oxidation, wherein a dichloromethane solution of H₂1 was treated with two equivalents of the strong oxidant $[\text{N}(\text{C}_6\text{H}_3\text{Br}_2)_3]^+$ (“magic green”, $E_{1/2}^{0/+} = 1.14 \text{ V}$)³⁸ (Eq 2) introduced as the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ salt^{39,40}. Optical spectra recorded on the solution of “twice oxidized” H₂1 showed red shifts in

both the Soret band (426 nm to 438 nm; Supplementary material, Figure S1) and the long-wavelength Q-band (649 nm to 679 nm, Figure 4). CVs of the product solutions showed a single irreversible cathodic wave at $E_{pc} = -0.95 \text{ V}$.

Similar optical shifts have been reported by a number of groups who characterized the follow-up products after two-electron chemical oxidation of closely-related H₂TPP as $[\text{H}_4\text{TPP}]^{2+}$,

wherein two pyrrole nitrogens have been protonated⁴¹⁻⁴⁴. Repeating the literature experiments on H₂TPP under our conditions (oxidation of H₂TPP by two equivalents of [N(C₆H₃Br₂)₃][B(C₆F₅)₄] in dichloromethane/0.05 M [NBu₄][B(C₆F₅)₄]), confirmed these findings, as red-shifted values of 422 → 430 nm and 598 → 646 nm were measured for the Soret and lowest-energy Q-bands, respectively, in going from the neutral compound to twice-oxidized H₂TPP. We also recorded the CV scans as the double oxidation proceeded. As the CV waves of H₂TPP became smaller, irreversible reductions appeared in the range -0.7 V to -1 V, permitting assignment of cathodic

Figure 4. Visible spectra of a 1×10^{-4} M solution of H₂1 in dichloromethane before and after addition of 1 equivalent (dashed line) and 2 equivalents (dotted line) of [N(C₆H₃Br₂)₃][B(C₆F₅)₄].

waves in this region to the protonated follow-up products [H₃TPP]⁺ and [H₄TPP]²⁺, the latter being responsible for a dominant cathodic peak between -0.9 V and -1.0 V.

Taken together, the similarities of the optical and voltammetric data for the H₂1 and H₂TPP oxidations provide strong support for assignment of the major follow-up product after formation of [H₂1]²⁺ being doubly-protonated species [H₄1]²⁺. Equation 3 gives the overall two-electron process, assuming that the solvent (SH) is the source of the hydrogen atoms required to form [H₄1]²⁺. The reaction is written as reversible owing to the fact that the protonated product can be reduced back to the neutral starting material. In terms of the underlying mechanism of this

reaction for porphyrins (Por) in general, we offer the sequence of Eqs 4-6, which is similar to that proposed earlier by Iniser *et al* for the anodically-driven protonation of Por = H₂TPP⁴¹. In the present case, we add the disproportionation of [H₃Por]⁺ (Eq 6) in order to account for the fact that some CV evidence was obtained for diprotonated [H₄Por]²⁺ after addition of just one

equivalent of chemical oxidant to the H₂1 solution. As we will show, evidence for protonated follow-up products [H_nPor]^{m+} (n = 3, m = 1; n = 4, m = 2), was also obtained for the surface-bound porphyrins. In fact, the chemical reversibility of these electron-transfer promoted protonation/deprotonation reactions accounts for some of the most common features of the voltammetry of the surface-bound porphyrins reported in this paper.

I.2 Mono-ethynylphenyl porphyrins H₂2 to H₂7

All of the mono-ethynylphenyl porphyrins, H₂2 to H₂7, had one-electron oxidations and reductions at potentials that are qualitatively consistent with the well-known minor electronic effects introduced by the various meso substituents. There were only two exceptions to chemical reversibility in the first oxidation or reduction processes: the 0/+ oxidation, E_{1/2}(1), of H₂7 and the 0/- reduction, E_{1/2}(-1), of H₂4 were irreversible up to a scan rate of 1 V s⁻¹. The follow-up reaction for [H₂4]⁻ is the loss of bromide ion, as will be discussed, but that of [H₂7]⁺ remains unknown. Variability in chemical reversibility was seen for the second oxidation of compounds H₂2 to H₂6. In a [PF₆]⁻ - based electrolyte scanned at 0.2 V s⁻¹, the +/2+ couple, E_{1/2}(2), was fully reversible for H₂4, H₂5, and H₂6, partially reversible for H₂2, and irreversible for H₂3. Interestingly, however, the second oxidation of H₂2 and H₂3 became fully reversible when the electrolyte anion was [B(C₆F₅)₄]⁻ (Figure 5), a finding that will be discussed below. Each of these compounds had an irreversible oxidation at more positive potentials (1.1 V to 1.5 V: see last column of Table 1) which is ascribed to oxidation of their ethynyl group.

The potential separation between the first oxidation and reduction processes, $\Delta E_{1/2}$, often referred to as the HOMO-LUMO gap of porphyrins, averages $2.23 \text{ V} \pm 0.06 \text{ V}$ in $[\text{PF}_6]^-$ and $2.20 \text{ V} \pm 0.05 \text{ V}$ in $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ⁴⁵, indicating that the π/π^* electronic structures of the porphyrin cores are not significantly affected by the meso substituents.

Figure 5. CV scans of 1 mM $\text{H}_2\mathbf{3}$ in dichloromethane containing either 0.1 M $[\text{NBu}_4][\text{PF}_6]$ (black line) or 0.05 M $[\text{NBu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$ (blue line); 2 mm GC electrode, scan rate 0.2 V s^{-1}

Replacement of the $[\text{PF}_6]^-$ electrolyte anion with $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ affects both the difference in potential between the two porphyrin oxidations and the kinetic stability of the porphyrin dications. The thermodynamic effects are straightforward and follow a model in which the value of $E_{1/2}(2) - E_{1/2}(1)$ is larger in $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ than in $[\text{PF}_6]^-$ electrolytes^{46,47}, owing principally to weaker ion-pairing of the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion with the porphyrin dication. The average anion-related increase in $E_{1/2}(2) - E_{1/2}(1)$ for H_2TPP and $\text{H}_2\mathbf{1}$ through $\text{H}_2\mathbf{6}$ is smaller (170 mV) than observed for bis(fulvalene)dinickel (273 mV)⁴⁷, perhaps owing to ion-pairing effects being somewhat less in the highly charge-delocalized macrocycle dications. The present observations are similar to those reported in much greater depth by DiMango and co-workers for H_2TPP , wherein the $E_{1/2}(2) - E_{1/2}(1)$ values in 1,2-difluorobenzene were compared for a number of traditional anions (including $[\text{PF}_6]^-$) and the weakly-coordinating anion $[\text{B}(\text{C}_6\text{H}_3(\text{CF}_3)_2)_4]^-$ ⁴⁸.

As pointed out in the Introduction, the kinetic stabilities of the porphyrin dications are relevant to the exact nature of the species that is grafted onto a surface when the ethynyl group of the porphyrin is oxidized. The fact that the second oxidations of $\text{H}_2\mathbf{2}$ and $\text{H}_2\mathbf{3}$ become more

reversible when the electrolyte anion is changed from $[\text{PF}_6]^-$ to $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ raises the possibility that the dications $[\text{H}_2\mathbf{2}]^{2+}$ and $[\text{H}_2\mathbf{3}]^{2+}$ undergo nucleophilic attack by the $[\text{PF}_6]^-$ anion. Although examples of reactions of modestly nucleophilic anions such as $[\text{PF}_6]^-$ with highly oxidized organometallic⁴⁹⁻⁵² and organic^{39,53,54} radical cations and dications are known, we are not aware of them being reported for free-base porphyrins in higher oxidation states. Certainly, stronger nucleophiles such as nitrite, hydroxide, and nitrogenous bases are known to react with porphyrin cations at either a meso position or at the β position of a pyrrole ring (see below), giving

isoporphyrins and meso-or β -substituted porphyrins^{16,55-61}. Although we cannot rule out the possibility of nucleophilic attack by $[\text{PF}_6]^-$ in the present case, the voltammetry of the dominant follow-up products is more consistent with that of simple pyrrole-protonated products. Thus, a CV scan through the second oxidation of $\text{H}_2\mathbf{2}$ or $\text{H}_2\mathbf{3}$ in $[\text{PF}_6]^-$ solution gives a new, irreversible, cathodic feature at ca -0.9 V, similar to what was seen for electro-deposited $\text{H}_2\mathbf{1}$ (Figure 3) or after chemical oxidation of $\text{H}_2\mathbf{2}$ by $[\text{N}(\text{C}_6\text{H}_3\text{Br}_2)_3][\text{B}(\text{C}_6\text{F}_5)_4]$ in a $[\text{PF}_6]^-$ - free medium. For example, after addition of magic green oxidant to a solution of $\text{H}_2\mathbf{2}$, the positive-going part of the CV scan (Figure 6) shows that the reversible oxidation wave for $[\text{H}_2\mathbf{2}]^{0/+}$ ($E_{1/2} = 0.52$ V, feature A) has shrunk to about $\frac{1}{4}$ of its original size. The extent of the loss of $\text{H}_2\mathbf{2}$ suggests that both its monocation and dication are prone to oxidatively-induced protonation. When the scan is reversed at 0.75 V, a cathodic wave assigned to reduction of the protonated follow-up product $[\text{H}_4\mathbf{2}]^{2+}$ is seen at $E_{\text{pc}} = -0.95$ V (feature B) as the major electroactive product in solution. As the scan continues negative, the original reduction wave for $[\text{H}_2\mathbf{2}]^{0/-}$ (feature C, $E_{1/2} = -1.71$ V) is observed to have essentially the same current that was observed before addition of the oxidant. This shows that when $[\text{H}_4\mathbf{2}]^{2+}$ is reduced, neutral $\text{H}_2\mathbf{2}$ is produced in the electrochemical reaction layer (back reaction of Eq 3) and then reduced at the more negative potential.

The follow-up reactions of oxidized $\text{H}_2\mathbf{2}$ were also followed by optical spectroscopy. Addition of either one or two equivalents of $[\text{N}(\text{C}_6\text{H}_3\text{Br}_2)_3][\text{B}(\text{C}_6\text{F}_5)_4]$ to a 1×10^{-5} M solution of $\text{H}_2\mathbf{2}$ in dichloromethane resulted in a shift of the Soret band from 418 nm to 426 nm (Suppl. material, Figure S2). When this was repeated on a 1×10^{-4} M solution, the most-intense Q-band absorption of $\text{H}_2\mathbf{2}$ at 512 nm disappeared, and a strong band grew in at 643 nm, which is again

consistent with formation of a protonated species as the oxidation product. (Suppl. material, Figure S3).

Figure 6. CV scan (1 mm GC electrode; 0.2 V s^{-1}) in dichloromethane/ $0.05 \text{ M } [\text{NBu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$ after addition of one equivalent of $[\text{N}(\text{C}_6\text{H}_3\text{Br}_2)_3][\text{B}(\text{C}_6\text{F}_5)_4]$ to a 1 mM solution of $\text{H}_2\mathbf{2}$.

The dominant follow-up reactions of the mono-ethynylporphyrin dications in homogeneous solution are therefore seen as H-atom additions which result in pyrrole-protonated products, most likely by the same mechanism proposed for $[\text{H}_2\mathbf{1}]^{2+}$ (Eq 4-6). Changing the electrolyte anion from $[\text{PF}_6]^-$ to $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ appears to slow down, but not eliminate, the follow-up reactions.

II. Anodic Grafting

Anodic grafting was carried out successfully for $\text{H}_2\mathbf{1}$ and, with the exception of $\text{H}_2\mathbf{7}$, for all of the mono-ethynyl substituted compounds in one or more triangular CV scans, generally at 0.2 V s^{-1} , between the rest potential and the ethynyl group oxidation potential $E_{\text{pa}}(3)$. In the discussion below, potentials refer to those measured in $[\text{NBu}_4][\text{PF}_6]$ electrolyte, and the working electrode was glassy carbon (GC).

After completion of one or more grafting scans, the modified electrode was removed from solution, washed and sonicated as described in the Experimental section, and placed in a fresh dichloromethane/supporting electrolyte solution for voltammetric analysis. Surface concentrations were calculated by integration of the current/time curves of CV scans obtained on the modified electrodes.

II.1 Grafting of tetrakis(ethynylphenyl)porphyrin, (H₂1). Single-to-multiple CV scans of H₂1 to 1.6 V gave modified electrodes with a single electroactive product having well-shaped⁶² reversible waves (Figure 7) at the expected potentials ($E_{1/2}(1) = 0.57$ V; $E_{1/2}(-1) = -1.71$ V) for surface-bound H₂1⁶³. The other two porphyrin redox processes at $E_{1/2}(2) = 0.87$ V and $E_{1/2}(-2) = -2.08$ V were also observed. The second oxidation process was less chemically reversible in [PF₆]⁻ than in [B(C₆F₅)₄]⁻, mimicking the oxidative behavior of H₂1 in homogeneous solution.

Figure 7. CV scans at 2 mm GC electrode modified with H₂1, 0.2 V s⁻¹ in dichloromethane containing either 0.1 M [NBu₄][PF₆] (solid lines) or 0.05 M [NBu₄][B(C₆F₅)₄] (dashed lines). The positive-going scan in [PF₆]⁻ preceded the negative-going scan, accounting for the absence of a sharp anodic pre-peak. The small irreversible cathodic peaks in [PF₆]⁻ near -1 V are assigned to reduction of pyrrole-protonated oxidation products.

Although the faradaic currents increased linearly with scan rate (Supplementary material, Figure S4), as expected for surface-bound species⁶², the oxidation waves showed a gradual loss of current if the scans were conducted in a [PF₆]⁻ - based electrolyte. There does not appear to be net loss of porphyrin from the electrode surface. Rather, irreversible cathodic waves began to appear between -0.8 V and -1 V (see solid line in Figure 7). Based on the information given in section I, the new cathodic features are assigned to reductions of surface-bound pyrrole-protonated products. When the surface oxidations were recorded in [B(C₆F₅)₄]⁻ - based electrolyte, the follow-up reactions were minimal over at least five scans (Supplementary Material, Figure S5).

Surface coverages increased progressively from about $2\text{--}3 \times 10^{-10} \text{ mol cm}^{-2}$ for a single scan to as much as $5 \times 10^{-9} \text{ mol cm}^{-2}$ for 20 scans. There is a very high probability that the grafting of H₂1 begins with the covalent attachment of an ethynyl carbon atom to a surface atom, and builds from there by two- or three-dimensional²⁶ ethynyl/ethynyl coupling reactions. This coupling model is supported by the observation that the more highly concentrated electrodes display the sharp cathodic and anodic “pre-peaks” (Figure 7) that are commonly observed for electroactive oligomeric films, and widely attributed to charges trapped in the film⁶⁷⁻⁷². Scanning through the faradaic reduction wave at -1.71 V produced the anodic pre-peak at 0.25 V , and scanning through the faradaic oxidation wave at 0.57 V produced the cathodic pre-peak at -1.57 V . Noting that observed or calculated surface coverages for perpendicular-bonded porphyrin monolayers have been reported as $3.5 \times 10^{-10} \text{ mol cm}^{-2}$ ^{64,65}, $5.8 \times 10^{-10} \text{ mol cm}^{-2}$ ¹⁵, and $5.0 \times 10^{-10} \text{ mol cm}^{-2}$ ¹⁶ for gold, glassy carbon, and platinum, respectively, it is clear that repeated CV scans of H₂1 resulted in a multi-layered assembly of the porphyrin on the electrode surface. Photographs of the modified electrodes show that the surface coverage is irregular (Figure 8).

Figure 8. Photograph of GC electrodes after being electrografted with H₂1: left, surface coverage of $2 \times 10^{-9} \text{ mol cm}^{-2}$; right, surface coverage of $5.8 \times 10^{-10} \text{ mol cm}^{-2}$.

Increased “blockage” of the redox reactions of solution analytes⁶⁶ was observed for electrodes having higher levels of surface coverage. As shown in Figure 9, mild blockage of the oxidation

of ferrocene was observed when the surface coverage was at the equivalent of about a monomolecular level, but the oxidation became essentially irreversible at this scan rate when the surface coverage was $2 \times 10^{-9} \text{ mol cm}^{-2}$. The latter translates to about a four-molecular-layer level of coverage.

Figure 9. CV scans (0.2 V s^{-1}) of $5 \times 10^{-4} \text{ M}$ ferrocene in dichloromethane/ 0.05 M $[\text{NBu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$ at 2 mm GC electrodes that were either porphyrin-unmodified (solid line) or contained surface-bound $\text{H}_2\mathbf{1}$ at concentrations of $5.8 \times 10^{-10} \text{ mol cm}^{-2}$ ($\cdots$) or $2 \times 10^{-9} \text{ mol cm}^{-2}$ ($-\cdots$).

Square-wave (SW) voltammetry was recorded on modified electrodes over the frequency range $10\text{--}200 \text{ Hz}$ in dichloromethane/ 0.05 M $[\text{NBu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$. It was generally observed that the square wave current for the second porphyrin oxidation was smaller than the first (Figure 10), a phenomenon reported previously for the two oxidations of surface-bound ethynylbis(fulvalene)diiron in $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ -based electrolyte, and ascribed to mixed diffusivity of the large counter-anion at the solution/surface interface⁷³. Brennan et al. have also reported examples of overall decreased currents for porphyrin electropolymers in solutions containing large anions⁷⁴. In the present case, comparison with the behavior in smaller-anion electrolytes was not carried out owing to the complication of faster follow-up reactions of $[\text{H}_2\mathbf{1}]^{2+}$ in small-anion media. An important aspect of the square-wave data is that the forward and reverse components of the SW voltammograms had almost identical peak potentials, showing that the electron-transfer reactions of surface-bound $\text{H}_2\mathbf{1}$ are fast^{75,76}.

Figure 10. Square-wave voltammogram at 60 Hz for surface-bound **H₂1** on GC electrode immersed in dichloromethane/0.05 M [NBu₄][B(C₆F₅)₄]. Gray line gives forward current (i_f) minus reverse current (i_r), which is the traditional way to display square-wave voltammograms. Black line gives $i_f + i_r$, which allows visual comparison of the forward and backward currents.

II.2 Grafting of mono-ethynylphenylporphyrins **H₂2** to **H₂6**. Some aspects of the grafting results for the six mono-ethynylphenylporphyrins are collected in Table 2. Only **H₂7**, which was alone in displaying an irreversible first oxidation in solution, failed to show significant deposition on glassy carbon electrodes scanned to the ethynyl oxidation potential.

We took the following facts to be the most important for surface-bound **H₂2** to **H₂6**:

1) Well-defined surface waves were obtained at potentials (see Table 2) which indicated that the parent porphyrin had been deposited onto the electrode surface.

Table 2. Selected anodic electrografting results for ethynylphenyl porphyrins (Por). Potentials in V vs ferrocene, recorded in dichloromethane/0.1 M [NBu₄][PF₆]. The meso groups are designated as para- or meta- to the surface-bound PhC≡C moiety.

Por	Para (p) or meta (m) meso groups	Grafting onto glassy carbon			
		Por E _{1/2} values	ΔE _{1/2} ^a (V)	Coverage, two scans, ^b Γ in mol cm ⁻²	Side products ^c
H ₂ 1	p, m-(PhC≡CH) ₃	Ox: 0.56, 0.87 Red: -1.71, -2.08	2.27	6.0 x 10 ⁻¹⁰ Multi-layering possible	[H ₄ 1] ²⁺
H ₂ 2	p-H, (m-Ph) ₂	Ox: 0.56, 1.05 ^d Red: -1.68, -2.09	2.24	4-6 x 10 ⁻¹⁰ Multi-layering possible	[H ₄ 2] ²⁺ ; Ox, 0.34 V
H ₂ 3	p-H, (m-hexyl) ₂	Ox: 0.44, 1.1 ^d Red: -1.78, -2.20, irrev	2.22	4.2 x 10 ⁻¹⁰	[H ₄ 3] ²⁺ ; Ox, 0.15V Red, -1.04 V, -1.34 V
H ₂ 4	p-Br, (m-Ph) ₂	Ox: 0.57 Red: -1.62, irrev -1.7, rev, -2.09, rev	2.19	4.0 x 10 ⁻¹⁰	[H ₄ 4] ²⁺ ; Ox, 0.03, 0.21 (v. small)
H ₂ 5	p-hexyl, (m-[C ₆ H ₄ (OMe)]) ₂	Ox: 0.32, 0.66 Red: -1.51, -1.70	1.83	3.2 x 10 ⁻¹⁰	[H ₄ 5] ²⁺
H ₂ 6	p-H, (m-[C ₆ H ₄ (OMe)]) ₂	Ox: 0.38, 0.76 Red: -1.52, -1.71	1.90	8 x 10 ⁻¹⁰	[H ₄ 6] ²⁺ ; Ox, 0.41 (v. small) Red, -0.51 (v. small)
H ₂ 7	p-Ph, (m-Ph) ₂	No deposition (irrev 0/+ oxdn in homogen soln)			

^a ΔE_{1/2} = E_{1/2}(1) – E_{1/2}(-1). ^b Direct oxidation of ethynyl group, two successive scans to 1.7 V vs FcH, 1 mM analyte in dichloromethane/[PF₆]⁻. ^c Smaller surface waves observed in first cathodic or anodic scans after anodic grafting. Diprotonated species assigned to irreversible cathodic waves in range -0.7 V to -1.0 V. ^d Semi-reversible in [PF₆]⁻ electrolyte, reversible in [B(C₆F₅)₄]⁻, E_{1/2}(2) = 1.0 V.

2) After two grafting scans, the surface coverage, Γ, was at an estimated mono-molecular level^{15,16,64,65} (ca 5 x 10⁻¹⁰ mol cm⁻²) for compounds H₂3, H₂4, and H₂5, and did not increase significantly with further scans (it took eight scans to reach this level for H₂6, perhaps owing to its faster anodic follow-up reactions). Compounds H₂3 to H₂5 have protecting groups in meso positions: 3-pentyl groups in the 10 and 20 (meta) positions of H₂3; bromide in the 15 (para) position of H₂4; and hexyl in the 15 (para) position of H₂5. The only mono-ethynyl compound to show significantly more extensive layering (maximum Γ = 1.7 x 10⁻⁹ mol cm⁻² reached after eight grafting scans) was H₂2, which has either an H atom or a phenyl group in all three meso

positions. In no case, however, did the surface concentration of a mono-ethynylphenyl compound approach that observed for H₂1 (5×10^{-9} mol cm⁻² for twenty scans).

3) Within the set of mono-ethynyl porphyrins, the structural aspect that appears to correlate best with the character of the grafted electrodes is the substituent in the 15-position (i.e., the meso position para to the ethynylphenyl group). Thus, electrodeposited H₂5, which has a protecting hexyl group at that position, gave four very clean surface waves, the only secondary product being a very small amount of the pyrrole-protonated species. The two faradaic reductions of surface-bound H₂5 are shown in Figure 11. The small “pre-peak” near -1.3 V may arise from the trapped-charge effect described earlier for surface-bound H₂1. All three porphyrins having H-atoms in the 15-position (H₂2, H₂3, and H₂6) give greater quantities of side products on the modified electrodes (see last column in Table 2). In this context, the much cleaner surface deposition of H₂5 compared to H₂6 is particularly striking, for they differ only in the substituent (hexyl vs H, respectively) at the 15-position.

Figure 11. Second negative-going CV scan at 0.2 V s^{-1} for modified GC electrode in dichloromethane/0.1 M [NBu₄][PF₆] after anodic grafting of H₂5.

4) The grafting processes always produced a modified electrode that showed one or two irreversible cathodic waves in the range -0.7 to -1 V, assigned to protonated species, on the first negative-going scan after completion of the anodic deposition. Owing to the fact that scanning through those waves results in reduction of the protonated species back to the parent porphyrin, they disappeared from subsequent cathodic scans. Similar first-scan-only cathodic features,

reported for unspecified side products of anodically-deposited aryl-substituted porphyrins^{24,25}, may also be arising from the reduction of protonated products.

5) For several compounds, namely H₂2, H₂3, and H₂4, the grafted electrode also displayed smaller *reversible* waves arising from oxidative side products (see last column of Table 2). Outside of those arising from pyrrole protonations, they were not identified. The lesser side products may be isoporphyrins or beta-substituted porphyrins^{16,55-61}, as discussed above. To see if a lower temperature reduced the degree of side products, the grafting of H₂2 was carried out at both 268 K and 297 K. Indeed, the modified electrode prepared at the lower temperature had significantly cleaner voltammetry (Supplementary Material, Figure S6).

6) CV scan-dependent electrochemistry was seen for electrografted H₂4. After anodic deposition, the first negative-going scan (Figure 12) shows the cathodic waves between -0.7 V and -0.9 V of protonated follow-up products (feature A in Figure 12), a small cathodic pre-wave near -1.4 V, followed by two dominant reductions. The latter are ascribed to the irreversible one-electron reduction of surface-bound H₂4 at -1.62 V (feature B in Figure 12) and the reversible one-electron reduction of surface-bound H₂2 at $E_{1/2} = -1.7$ V (feature C in Figure 12). The sequence for this reaction process (Scheme 2) has the radical formed after loss of bromide from the putative monoanion [H₂4]⁻ (-1.62 V) picking up a hydrogen atom from solvent, thereby producing surface-bound H₂2 ($E_{1/2} = -1.7$ V).

Figure 12 First negative-going CV scan of surface-bound H₂4 on GC electrode, 0.2 V s⁻¹.

Scheme 2. The sequence in which cathodic reduction of surface-bound $\text{H}_2\mathbf{4}$ gives $\text{H}_2\mathbf{2}$. The H-atom donor is assumed to be solvent (SH).

The efficient cathodic conversion of surface-bound $\text{H}_2\mathbf{4}$ to $\text{H}_2\mathbf{2}$ was confirmed by a second cathodic scan of the modified electrode, which shows only the voltammetry of surface-bound $\text{H}_2\mathbf{2}$ (see Figure 13).

Figure 13. The second negative-going CV scan of surface-bound $\text{H}_2\mathbf{4}$, taken immediately after that shown in Figure 12. The remaining features are ascribed to $\text{H}_2\mathbf{2}$.

7) The $\Delta E_{1/2}$ values for surface-bound $\text{H}_2\mathbf{1}$ through $\text{H}_2\mathbf{4}$ are $2.22\text{ V} \pm 0.03\text{ V}$, whether the measurements are made in $[\text{PF}_6]^-$ or $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ electrolytes. This is in concert with the measurements made for these compounds in solution (section I.2) and with general expectations for porphyrins. The $\Delta E_{1/2}$ values are considerably smaller, however for surface-bound $\text{H}_2\mathbf{5}$ (1.83

V in $[\text{PF}_6]^-$, 1.87 V in $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ and **H26** (1.90 V in both electrolytes). The reason for this lowering of the apparent HOMO-LUMO gap by *ca* 350 mV is not readily apparent to us. The decrease appears insufficient to argue for the presence of isoporphyrin surface structures, for which $\Delta E_{1/2}$ values of 1.4 V or less would be expected, based primarily on a positive shift in the reduction potential^{55-57,60}. More often, a reduced $\Delta E_{1/2}$ value for a porphyrin has been taken to indicate a variation in its planarity, causing a diminution in the conjugation of the macrocycle⁷⁷. This appears to be less probable for a free-base porphyrin than a metallated porphyrin. Furthermore, β substitution of the macrocycle or variations in its planarity generally affect one of the redox potentials (either $E_{1/2}(1)$ or $E_{1/2}(-1)$) much more than the other.⁷⁸⁻⁸¹ In the present case, the shrinking of the $\Delta E_{1/2}$ values for surface-bound **H25** and **H26** arises from essentially equal easing of both the $E_{1/2}(1)$ and $E_{1/2}(-1)$ potentials that were measured in solution. We note that a somewhat comparably reduced $\Delta E_{1/2}$ value (1.97 V) has been reported for an aniline-based porphyrin polymer⁸². Further inquiries into this interesting constriction of the porphyrin $\Delta E_{1/2}$ values are warranted.

II.3 Electrografting Model After bonding of one ethynyl group to the electrode surface, **H21** has three ethynyl groups still available for either radical-radical or radical-substrate coupling with the ethynyl group of an incoming molecule. In this sense, the mechanism by which surface growth of the tetra-ethynyl-substituted compound **H21** occurs is not unlike that common to the anodic electropolymerization of other multiply-meso-substituted porphyrins^{24,26,83,84}. The reports on electropolymerization of porphyrins that are conceptually most closely related to the present findings for **H21** are those of Paul-Roth *et al*, who employed the direct oxidation of meso-positioned aryl groups (phenyl, 3,5-dimethoxyphenyl, or fluorenyl moieties) to produce electroactive polymer films of both free base and metallated porphyrins on platinum and ITO electrodes²⁴⁻²⁶.

Electrode deposits of anodically-grafted **H21** certainly share some characteristics with electroactive polymer films, a few of them being: similarities in the redox potentials of monomers and oligomers; a capacity to increase the surface coverage by repeated electro-deposition or prolonged electrolysis; trapped-charge anodic and cathodic pre-peaks for more concentrated deposits; and physical and chemical robustness. However, the surface geometries of anodically-grafted multilayers of **H21** are more likely similar to those obtained by the

aryldiazonium reduction method. Whereas the aryldiazonium process produces multilayers owing to aryl-aryl coupling^{32,85} and H₂1 oxidation produces multilayers through ethynyl-ethynyl coupling, comparable patterns of growth away from the electrode surface are expected. One such set of alignments for H₂1 is shown in Scheme 3. Although the drawing uses a perpendicular orientation between the attached species and the surface, a 90° extrusion angle cannot be assumed.

Scheme 3. Two possibilities for idealized multi-layering geometries of ethynyl-attached porphyrins capable of coupling at either the para meso position alone or both the para and meta meso positions. The small rectangle represents an ethynyl group. This model draws directly on the multi-layering known to occur in aryldiazonium electro-deposition processes.^{32,85}

The fact that mono-ethynyl substituted porphyrins H₂2 through H₂6 all give strongly-bound surface deposits in spite of having considerable variability in their meso substituents

argues convincingly that they are covalently bonded to the surface through the ethynyl group, and that molecular coupling reactions (i.e., oligomerizations) are not required to initiate the anodic deposition process. Deposition of the mono-ethynyl substituted porphyrins may be compared to those reported for three other porphyrins (Figure 14) having a single redox-active substituent that is used to trigger an electrografting process. The nickel(II) porphyrin **8** was successfully attached as a *monolayer* to a platinum electrode by reduction of its meso-diazonium ion¹⁶. In contrast, direct anodic oxidation of the 3,5-dimethoxyphenyl group in H₂**9**²⁶ and the aniline group in H₂**10**⁷⁴ gave *oligomers*, apparently owing to coupling reactions at the meso-carbon (H) positions of the porphyrins.

Figure 14. Three porphyrins having a single redox-active substituent that have been previously electrografted onto electrode surfaces. See text for literature references.

Although ethynyl/meso-carbon (H) coupling reactions are certainly possible in our mono-ethynyl systems, the observation that H₂**2** shows facile multi-layering, whereas H₂**3** does not, suggests that ethynyl/phenyl coupling is more facile in these systems. Furthermore, the fact that the electrografted surface concentrations of H₂**5** did not rise above a monolayer level suggests that ethynyl/anisole coupling is slower than ethynyl/phenyl coupling. The tendency for ethynyl-to-meso-substituent coupling therefore appears to decrease in the order ethynyl >> phenyl > anisole $\approx$ meso-carbon (H) >> 1-hexyl $\approx$ 3-pentyl. The two aliphatic substituents appear to block ethynyl coupling at those positions, as is also likely in the case of meso-bromide substituted H₂**4**.

It is also worth reiterating that electrodes grafted by the oxidation of H₂**3** and H₂**6** show redox-active side products which may arise from nucleophilic attack at the meso-carbon (H) position.

Finally, we note that electron-transfer chemistry can be performed on the immobilized ethynyl porphyrins with, in many cases, minimal loss of porphyrin from the electrode surface. This was seen in the chemically reversible redox-coupled protonation/deprotonation reactions of the porphyrins as well as in the hydrogen-for-bromine substitution process induced by the reduction of surface-bound H₂4. The chemical resiliency of the surfaces holds promise for the application of ethynyl-bound porphyrins and their metallated derivatives to electron-transfer catalysis.

Experimental

All experiments were carried out under nitrogen, using Schlenk conditions or a Vacuum Atmospheres drybox operating below 5 ppm oxygen. The dichloromethane used for electrochemistry was obtained by passing reagent-grade solvent through an alumina/argon purification system. Electrochemistry was carried out using a PARC model 273A potentiostat interfaced to a personal computer operated by homemade software. [NBu₄][PF₆] (Tokyo Chemical Industry) was thrice recrystallized from absolute ethanol and vacuum dried at 373 K. [NBu₄][B(C₆F₅)₄] was prepared as described elsewhere⁸⁶, recrystallized from dichloromethane/diether ether, and vacuum dried. The following were also prepared by literature procedures: [N(C₆H₃Br₂)₃][B(C₆F₅)₄]³⁹; H₂1⁸⁷; H₂2⁸⁸; H₂3 and H₂4⁸⁹; H₂5⁹⁰; H₂7⁹¹.

5-(4-ethynylphenyl)-10,20-bis(3-methoxyphenyl)porphyrin, H₂6. [5-Bromo-10,20-bis(3-methoxyphenyl)porphyrin (77 mg, 0.128 mmol, 1 eq.) was dried together with Pd(PPh₃)₄ (33 mg, 0.028 mmol, 0.22 eq.), K₃PO₄ (273 mg, 1.28 mmol, 10 eq.) and the 4-[(trimethylsilyl)ethynyl]phenylboronic acid pinacol ester (77 mg, 0.256 mmol, 2 eq.). The porphyrin was dissolved in dry THF. Three freeze-thaw cycles were done and the reaction was stirred at 70 °C for 18 h. After an aqueous work up with NaHCO₃ and Na₂SO₄, the sample was eluted through a silica column with 7:1 hexane:ethyl acetate. The TMS-protected porphyrin was obtained in 61 % yield (54 mg, 0.078 mmol). This porphyrin was directly deprotected without further purification. The porphyrin was again dissolved in dry THF and 0.3 mL 1M [NBu₄][F] (4 eq) was added. The reaction was stirred at room temperature until completion. The crude mixture was then added to H₂O and extracted with dichloromethane. After an aqueous wash, the desired porphyrin (48 mg, 0.076 mmol, 98 %) was obtained. M.p: > 300 °C; *R*_f = 0.33 (hexane/dichloromethane, 1:2, v/v); ¹H NMR (400 MHz, CDCl₃) δ 10.22 (s, 1H, *H*_{meso}), 9.33 (d,

$J = 4.7$ Hz, 2H, H_β), 9.06 (d, $J = 4.6$ Hz, 2H, H_β), 8.95 (d, $J = 4.7$ Hz, 2H, H_β), 8.83 (d, $J = 4.8$ Hz, 2H, H_β), 8.17 (d, $J = 7.7$ Hz, 2H, phenyl- H), 7.88 (d, $J = 8.0$ Hz, 2H, phenyl- H), 7.85 – 7.77 (m, 4H, phenyl- H), 7.67 (m, 2H, phenyl- H), 7.38 – 7.32 (m, 2H, phenyl- H), 4.00 (s, 6H, OCH_3), 3.31 (s, 1H, $C\equiv CH$), -3.04 (s, 2H, NH); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 158.1$, 134.4, 130.4, 127.7, 120.6, 113.5 and 55.5 ppm; UV/Vis (dichloromethane): λ_{max} (log ϵ) 416 (6.11), 511 (4.72), 546 (4.23), 584 (4.23), 639 nm (3.85); HRMS (MALDI) m/z calcd. for $C_{42}H_{30}N_4O_2$ $[M]^+$: 622.2369, 622.2382 found.

Electrochemistry A three-electrode configuration was used for electrochemical work. The auxiliary electrode was a platinum wire. Although the experimental reference electrode was a silver chloride-coated silver wire separated from the working electrode compartment of the cell by a glass frit, the in-situ method of Gagne et al.⁹² was used to convert the experimentally measured potentials to the ferrocene/ferrocenium potential^{38, 92, 93}. All the potentials reported in this paper are referenced to ferrocene. If decamethylferrocene was used as the in-situ reference, the analyte potential vs ferrocene was obtained from the experimental value by subtraction of 0.56 V if the measurement was obtained in dichloromethane/ $[PF_6]^-$, or 0.61 V if it was obtained in dichloromethane/ $[B(C_6F_5)_4]^-$. Glassy carbon electrodes (Bioanalytical Systems) were polished before use with Bühler diamond paste, washed with acetone, sonicated in dichloromethane, and dried under antechamber vacuum. Electrochemically grafted electrodes could be reused for new experiments after a polishing procedure. Bulk electrolysis was carried out using a standard three-compartment cell in which a platinum basket was used as the working electrode. The electrografting procedures were carried out on solutions having an analyte concentration of 1 mM in dichloromethane containing either 0.1 M $[NBu_4][PF_6]$ or 0.05 M $[NBu_4][B(C_6F_5)_4]$. After the anodic grafting scans were completed, the working electrode was removed from the drybox, washed with acetone, sonicated in dichloromethane, vacuum dried, and placed in a fresh solution containing only dichloromethane and the supporting electrolyte for analysis.

Supporting Information Two visible-region spectra of **H22** chemical oxidation products and two CV scans of surface-bound products.

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