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The Electrode as Organolithium Reagent: Catalyst-Free Covalent Attachment of Electrochemically Active Species to an Azide-Terminated Glassy Carbon Electrode Surface

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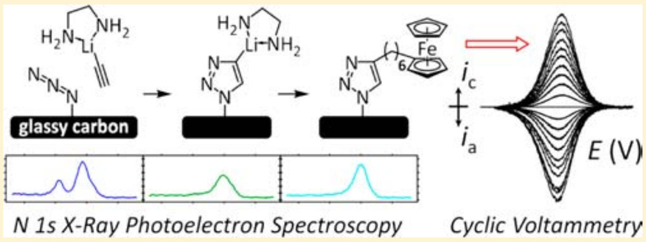
Ⓢ *Supporting Information*

ABSTRACT: The reaction of a lithium acetylide−ethylenediamine complex with azide-terminated glassy carbon surfaces affords 1,2,3-triazolyllithium surface groups that are active toward covalent C−C coupling reactions, including salt metathesis with an aliphatic halide and nucleophilic addition at an aldehyde. Surface ferrocenyl groups were introduced by reaction with (6-iodohexyl)ferrocene; the voltammetry of electrode samples shows narrow, symmetric peaks indicating uniform attachment. X-ray photoelectron and reflectance infrared spectroscopic data provide further support for the surface-attached products. Formation of the 1,2,3-triazolyllithium linkage requires neither a catalyst nor a strained alkyne. Coverages obtained by this route are similar to those obtained by the more common Cu(I)-catalyzed alkyne−azide coupling (CuAAC) of ethynylferrocene with surface azides. Preconditioning of the glassy carbon disk electrodes at ambient temperature under nitrogen affords coverages comparable to those reported with preconditioning at 1000 °C under hydrogen/nitrogen.



INTRODUCTION

Research at the interface between homogeneous catalysis and surface science leverages the synthetic and analytical capabilities of both disciplines. The development of homogeneous catalysts is aided by the fine control over structure and the wealth of detailed kinetic and thermodynamic information that solution methods offer; applying this knowledge to heterogeneous analogues requires a similar degree of control over surface structures.[1] Ideal strategies for coupling molecular species to surfaces accomplish robust surface binding in a facile, flexible, controlled, and uniform way and do not require harsh conditions such as high temperatures, strong oxidants, or large applied potentials.

The study of electrocatalysis of multiproton, multielectron reactions mediated by discrete species such as homogeneous catalysts,[2] surface-bound molecular catalysts,[3] or inorganic nanoparticles[4] relies on carbon electrodes, since these materials do not contribute substantial background hydrogen production or oxidation currents at modest applied potentials.[5] Several synthetic routes for covalent attachment to carbon materials are available;[6] the most prominent among these are the reductive cleavage of aryldiazonium salts to afford N_2 and an aryl radical that couples to the electrode[7] and the Cu(I)-catalyzed alkyne−azide (CuAAC) “click” route wherein alkyne and azide reactants undergo a 1,3-dipolar cycloaddition to afford a 1,4-disubstituted 1,2,3-triazolyl linkage.[8] Quite recently, ethynylferrocene has been directly attached to a carbon electrode surface by deprotonation of the terminal alkyne followed by electrochemical oxidation to generate a carbon radical that couples to the electrode.[9] In a complementary approach, the terminal carbon of (6-iodohexyl)ferrocene has been electrochemically reduced and the aliphatic C radical subsequently couples with the electrode surface.[10]

We have developed a new synthetic route to covalent modification of azide-terminated carbon surfaces that produces a 1,2,3-triazolyl linkage as with the CuAAC route, but which requires neither a catalyst nor a strained alkyne substrate.[11] This approach begins with the covalent binding of azide groups directly to glassy carbon following the method developed by Chidsey and co-workers,[8b,12] which we have modified to employ MeCN-soluble reagents in small quantities and commercially available plastic-encased disk electrodes. Treating these azide-terminated surfaces with (en)LiC≡CH (lithium acetylide−ethylenediamine complex) affords a triazolyllithium-terminated surface that couples cleanly with electrophilic reagents.

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Scheme 1. Reaction of (en)LiC≡CH with a Surface-Confined Azide Group and Subsequent Coupling with $Fc(CH_2)_6I$

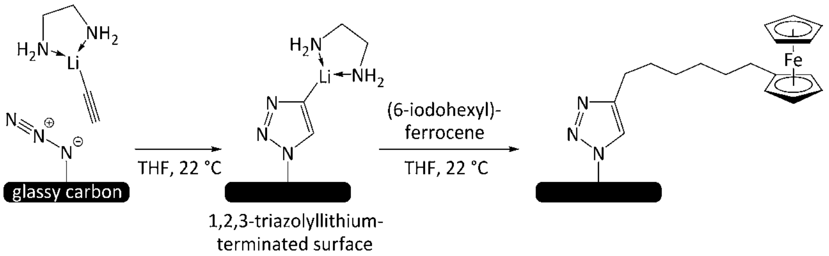


Table 1. X-ray Photoelectron Spectroscopic Data[a]

entry	preparation	atomic abundance AT% (atoms per 100 C atoms)							
		C	Li	N	O	S	Cl	Fe	I
1	lapped and polished	94.5	0.02 (0.02)	0.7 (0.7)	4.7 (5.0)	0.1 (0.1)	0.03 (0.03)	n.d.[b]	n.d.
2	... + ^{n}Bu$_4$N$^+$ [Cl–I–N$_3$]$^-$	82.5	n.d.	5.1 (6.1)	10.7 (13.0)	0.3 (0.4)	1.4 (1.6)	n.d.	0.1 (0.1)
3	... + (en)LiC≡CH	48.4	20.8 (43.1)	2.8 (5.8)	27.6 (57.1)	0.3 (0.6)	0.1 (0.2)	n.d.	n.d.
4	... + $Fc(CH_2)_6I$	84.3	4.9[c] (5.8)	4.0 (4.8)	5.7 (6.8)	0.6 (0.7)	0.1 (0.1)	0.4 (0.4)	n.d.

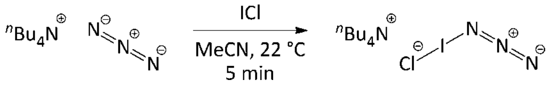
[a] Average of two measurements. High-resolution photoemission spectra are presented in Figure 1. Survey spectra are presented in Figures S1–S4 (Supporting Information). [b] None detected. [c] Overlaps with Fe 3p line.

■ RESULTS

We first describe our protocols for the activation of glassy carbon surfaces at ambient temperature and their subsequent reaction with in situ generated ^{n}Bu$_4$N$^+$[Cl–I–N$_3$]$^-$ and present the reflectance IR (infrared) and XPS (X-ray photoelectron spectroscopy) measurements accompanying these steps. We then describe the reaction of the azide-terminated glassy carbon surfaces with (en)LiC≡CH (lithium acetylide–ethylenediamine complex). This reaction is based on solution alkynylmetal–azide cycloaddition chemistry[13] and should by analogy proceed according to the pathway shown in Scheme 1. Subsequent reaction with $Fc(CH_2)_6I$ ((6-iodohexyl)ferrocene) affords an electrode exhibiting a voltammetric response consistent with a surface-confined ferrocenyl group; the presence of Fe is confirmed by XPS analysis. The voltammetry obtained with FcCHO (ferrocenecarboxaldehyde) as the coupling reagent also demonstrates surface attachment, indicating a synthetic flexibility similar to that demonstrated in the analogous solution chemistry.[13a] For comparison with these results we have optimized the conditions for nonaqueous CuAAC coupling using homogeneous analogues and have applied these conditions for the coupling of ethynylferrocene with azide-terminated surfaces.

Preparation of the Glassy Carbon Substrates. Plastic-encased glassy carbon disk electrodes for voltammetric studies and glassy carbon plates for XPS analysis were lapped with aluminum oxide films either by hand or on a mechanical lapping wheel and then polished with diamond paste. After rinsing and sonication in ethanol, these were stirred overnight in an ethanol suspension of activated carbon and then thoroughly rinsed with ethanol to remove adsorbed impurities.[6,14] Glassy carbon plate samples prepared in this way present O atoms (4.7 AT%; percentage of the total atoms measured) along with some N and S by XPS (0.7 and 0.1 AT%, respectively; Table 1, entry 1; Figure 1, red traces; Figure S1, Supporting Information shows the corresponding survey scans). All of these operations were carried out in the glovebox under N_2; comparisons of glovebox vs benchtop preparation and of mechanical vs hand lapping are given below.

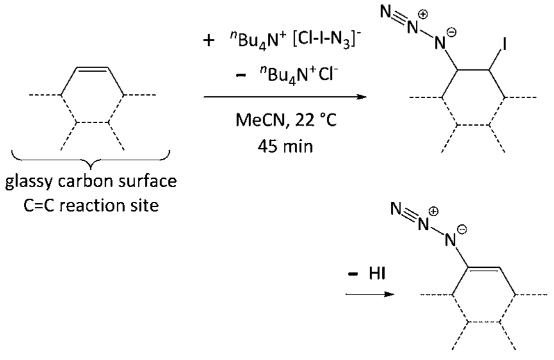
In Situ Generation of ^{n}Bu$_4$N$^+$[Cl–I–N$_3$]$^-$. ^{n}Bu$_4$N$^+$N$_3$$^-$ was reacted with ICl for 5 min in MeCN (eq 1) with all reactant



(1)

and product species remaining in solution. IR spectra showed bands at 2025 and 2000 cm^{-1} assigned to ^{n}Bu$_4$N$^+$[Cl–I–N$_3$]$^-$ (Figure S5, Supporting Information).[15] A shoulder at 2040 cm^{-1}, possibly corresponding to ^{n}Bu$_4$N$^+$[N$_3$–I–N$_3$]$^-$, and a small shoulder at 2005 cm^{-1}, assigned to excess ^{n}Bu$_4$N$^+$N$_3$$^-$, were also observed. The ^{n}Bu$_4$N$^+$[Cl–I–N$_3$]$^-$ bands diminished to 85% of their initial intensities over 45 min.

Reaction of Glassy Carbon Samples with ^{n}Bu$_4$N$^+$[Cl–I–N$_3$]$^-$. Glassy carbon samples were reacted with freshly prepared ^{n}Bu$_4$N$^+$[Cl–I–N$_3$]$^-$ solutions for 45 min and then rinsed with MeCN (eq 2). Reflectance IR spectroscopy of a



(2)

plate sample showed the characteristic band at 2104 cm^{-1} for the attached azide (Figure S6, Supporting Information). High-

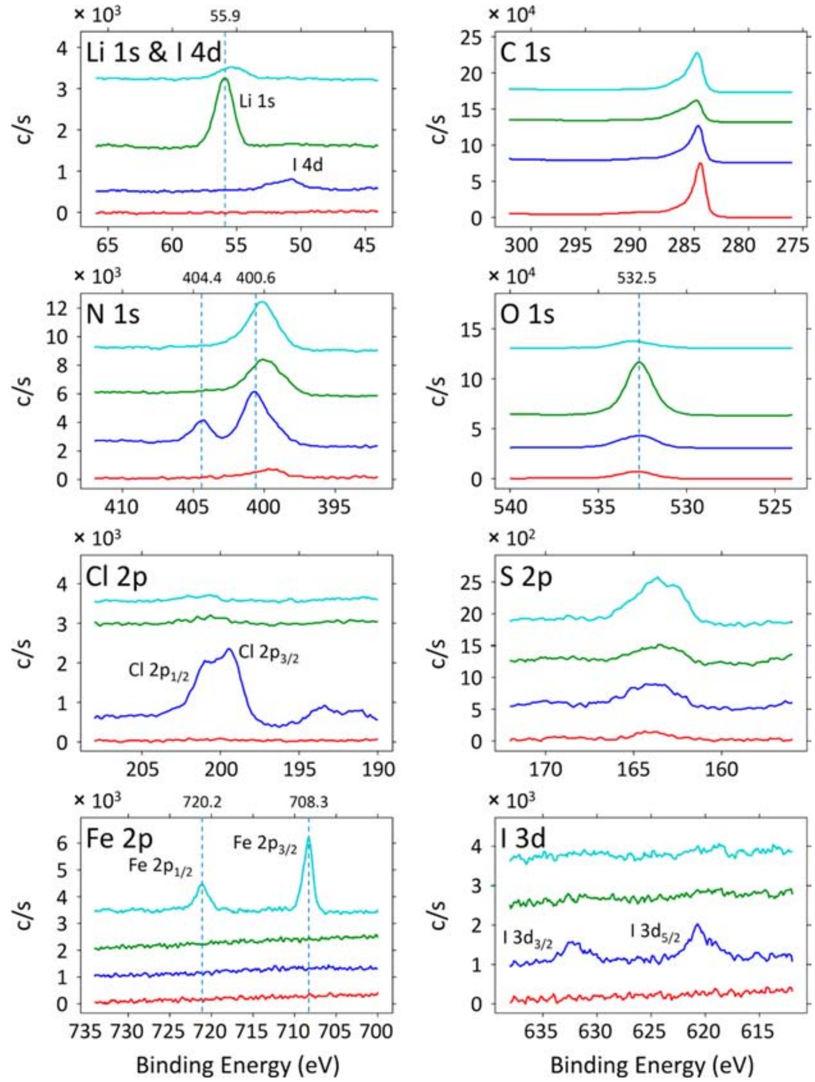


Figure 1. High-resolution photoemission spectra of glassy carbon plate samples at each stage in the (en)LiC≡CH reaction sequence: (red traces) after polishing, sonication in EtOH, and stirring in activated carbon/EtOH suspension; (blue traces) after subsequent reaction with ${}^{n}Bu_4N^+[Cl–I–N_3]^-$ in MeCN; (green traces) after subsequent reaction with (en)LiC≡CH in THF; (light blue traces) after subsequent reaction with $Fc(CH_2)_6I$ in THF.

resolution photoemission spectra showing the N 1s region are consistent with the presence of azide, with peaks at 400.6 and 404.4 eV in a 2:1 ratio (Table 1, entry 2; Figure 1, blue traces; Figure S2, Supporting Information);[8b,12b,16] Cl and I were also observed.

The azide-terminated electrodes were also examined by voltammetry in MeCN. Cathodic sweeps beyond −1.75 V vs $Fc^{+/0}$ (the half-wave potential $E_{1/2}$ for the ferrocenium/ferrocene couple, used throughout as the reference couple) showed a steady increase in current with applied potential. This wave was irreversible, and repeated sweeps caused this feature to decay toward the baseline (Figure S7, Supporting Information). We have assigned this to irreversible reductive decomposition of the surface azide groups.[17] While not examined here, this reductive decomposition may afford control over surface coverage. A similar response was observed with an azide-modified electrode that had been subjected to CuAAC coupling with ethynylferrocene, indicating the coupling did not consume the azide groups completely.

Reaction of Azide-Modified Glassy Carbon Samples with (en)LiC≡CH. Following azide deposition, glassy carbon samples were placed in dry THF over solid (en)LiC≡CH for 3 h at ambient temperature. A chalky blue film observed on withdrawing the sample from the solution was substantially removed on repeated rinsing with dry THF. The N 1s line at 404.4 eV was attenuated on reaction of the azide-terminated surface with (en)LiC≡CH, as is generally observed in reactions of surface azide groups with terminal alkyne species under CuAAC conditions (Table 1, entry 3; Figure 1, green traces; Figure S3, Supporting Information).[8b,12b,16] The IR band at 2104 cm^{-1} assigned to the azide also decreased substantially (Figure S6, Supporting Information).

The relative abundances of C, Li, and O as measured by XPS were 1.8:0.8:1 after reaction with (en)LiC≡CH (Table 1). The Li:N ratio was 7.4:1, indicating the formation of a relatively thick Li,C,O film with little remaining ethylenediamine. It is unclear whether ethylenediamine was lost during deposition or in the XPS vacuum chamber. Considering the oxophilicity of organometallic Li compounds,[18] samples used immediately for further reaction and samples set aside for XPS analysis might be expected to differ in their O abundances and hence in their

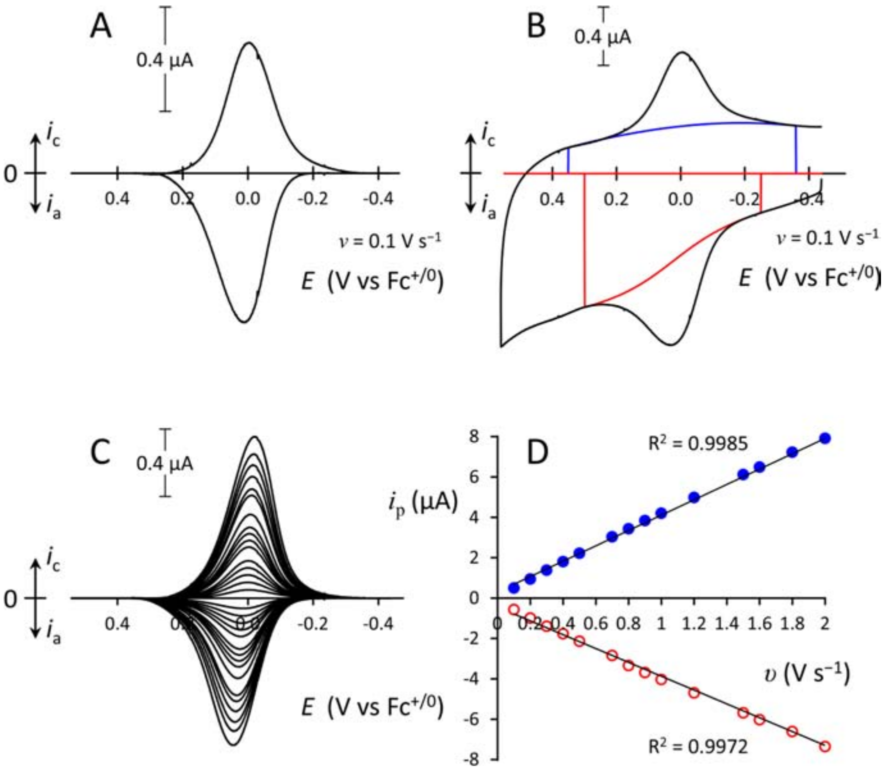


Figure 2. (A) Baseline-corrected and (B) raw voltammograms in MeCN (0.1 M $^n\mathrm{Bu_4N^+PF_6^-}$) showing the surface-confined ferrocenyl group obtained on reacting the azide-terminated electrode surface with (en)LiC≡CH followed by $\mathrm{Fc(CH_2)_6I}$; data are shown in Table 2, entry 1. (C) Baseline-corrected voltammograms collected with scan rates from 0.1 to 2 V $\mathrm{s^{-1}}$. (D) Dependence of corresponding cathodic and anodic peak currents on the scan rate.

Table 2. Voltammetric Results for Ferrocenyl-Terminated Electrodes[a]

sample	ferrocenyl synthon	coupling route	electrode area ($\mathrm{cm^2}$)[b]	coverage (10^{-13} molecules $\mathrm{cm^{-2}}$)	fwhm[c] (mV) redn	fwhm[c] (mV) oxidn	$E_{1/2}$ (V vs $\mathrm{Fc^{+/0}}$)	ΔE_p (mV)
1	$\mathrm{Fc(CH_2)_6I}$[d]	(en)LiC≡CH	0.0723	8.6	162	173	0.00	17
2	$\mathrm{Fc(CH_2)_6I}$[e]	(en)LiC≡CH	0.0725	5.7	136	144	0.00	16
3	$\mathrm{Fc(CH_2)_6Br}$[e]	(en)LiC≡CH	0.0737	4.4	132	148	0.00	30
4	FcCHO[f]	(en)LiC≡CH	0.0720	9.3	233	247	0.12	16
5	FcCHO[g]	(en)LiC≡CH	0.0720	10	298	230	0.25[h]	90
6	$\mathrm{Fc(CH_2)_6I}$[i]	HC≡CMgBr	0.0835	2.7	n.d.	n.d.	0.10	n.d.
7	ethynylferrocene	CuAAC (MeCN)	0.0839	7.0	206	218	0.17	20
8	ethynylferrocene	CuAAC (DMSO:water)	0.0554	11 (7.9)[j]	158	176	0.13	25

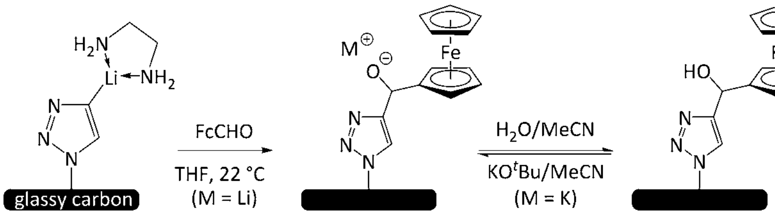
[a] Corresponding voltammograms are shown in Figure S9 (Supporting Information). [b] Determined by voltammetry and calibrated against a standard electrode, as described above. [c] Full-width at half-maximum current. [d] Voltammograms are shown in Figure 2. [e] Surfaces lapped by hand inside the glovebox. [f] After 30 s exposure to MeCN:water (1:1 by volume); see Figure 3. [g] After repeated shaking with MeCN:water. [h] Quasi-reversible wave. [i] Quasi-reversible response with poorly defined features; see Figure S9, entry 6. [j] The measured area was 22% smaller than the nominal area in this case; the value in parentheses assumes an area equal to the nominal area.

structure and reactivity, even when maintained under an inert atmosphere.

Both the Li 1s and the O 1s spectra show one peak (55.9 and 532.5 eV, respectively; Figure 1). These data are inconsistent with LiOH (having a Li 1s line at 54.7)[19] and $\mathrm{Li_2O}$ (having an O 1s line at 530.6 eV).[20] $\mathrm{Li_2O_2}$ (56.4 and 533.1 eV respectively) cannot be ruled out;[21] however, coordination of an alcohol or ether O atom to Li seems more likely, given the experimental conditions. Reaction of clean Li surfaces with ethanol has been reported to give Li 1s and O 1s lines at 56.4 and 533.1 eV, respectively.[22] No I atoms were detected in the present case, and the Li:Cl ratio was 220:1, ruling out substantial contribution from Li halides.

Reaction of 1,2,3-Triazolyllithium-Terminated Glassy Carbon Surfaces with $\mathrm{Fc(CH_2)_6I}$. After thorough rinsing with dry THF, the electrode and glassy carbon plate samples were held for 18 h in THF solutions of $\mathrm{Fc(CH_2)_6I}$ and then rinsed repeatedly with 1:1 $\mathrm{MeCN:H_2O}$. Figure 2 presents the voltammetric data obtained with the disk electrode. The surface area was calibrated against an electrode of known area (also having a nominal diameter of 3 mm) as described in the Experimental Section. The peak-to-peak separation and scan rate dependence are consistent with surface attachment. Baseline-corrected voltammograms are shown in Figure 2 (a description of the baseline correction appears in the Supporting Information); details are presented in Table 2. Control

Scheme 2. Reaction of the 1,2,3-Triazolyllithium-Terminated Surface Group with FcCHO



experiments omitting either the azide deposition or the reaction with (en)LiC≡CH afforded no measurable Faradaic signal, indicating that surface attachment of $Fc(CH_2)_6I$ by this route requires both of these reagents.

Photoemission spectra of a glassy carbon plate sample subjected to the same conditions (Table 1, entry 4; Figure 1, light blue traces; Figure S4, Supporting Information) show deposition of Fe. The Fe $2p_{3/2}$ and $2p_{1/2}$ lines at 708.3 and 720.2 eV are consistent with reported values for surface ferrocenyl groups.[8b,16a,23] The surface abundance of Fe as determined from XPS data (the calculation is described in the Experimental Section) is 7.4×10^{13} molecules cm^{-2}, in good agreement with the ferrocenyl coverage determined by voltammetry (8.6×10^{13} molecules cm^{-2}; Table 2, entry 1). The Fe:N ratio, calculated from the abundance per 100 C atoms (Table 1) and correcting for N present prior to the azide deposition, is 0.1; assuming all of these N atoms are in surface triazolyl groups, the Fe:triazolyl ratio is 0.3. The N 1s line at 400.0 eV (Figure 1) persists on reaction with $Fc(CH_2)_6I$. The decrease in measured surface abundance of N atoms per 100 C atoms (5.8 → 4.8 N per 100 C) may arise in part from screening by the carbon-rich hexylferrocenyl groups themselves and in any case indicates that loss of N from surface azide groups (e.g., by release of N_2, a common outcome for azide decomposition)[24] is minimal. No I is detected at the surface. This is significant because it indicates cleavage of I from the ferrocenyl synthon, consistent with the proposed salt metathesis reaction. The Li and O abundances (per 100 C atoms) are 87–88% lower than in the sample measured after reaction with (en)LiC≡CH, indicating that the Li,C,O film described above either did not form or was removed, either through the metathesis itself or in the subsequent water/MeCN work-up.

Coverage as a Function of Surface Preparation. Alternate methods for preparation of the glassy carbon electrode surface were examined by voltammetry following the reaction sequence presented above; these results underscore the importance of careful surface preparation in obtaining selective coupling chemistry. Higher surface coverages were obtained with samples that were lapped mechanically rather than manually (cf. entries 1 and 2 of Table 2). The lower coverages are accompanied by smaller fwhm values (full widths at half-maximum; see Figure S9, Supporting Information). Narrower waves indicate greater uniformity in the electrochemical environments of the attached molecules, having contributions from both surface density and variation in chemical structure.[25] These observations are addressed in the Discussion.

Mechanical lapping and hand polishing on the benchtop rather than in the glovebox, followed by sonication and stirring with activated carbon inside the glovebox, afforded a complicated voltammetric response (CV traces are shown in Figure S11, Supporting Information). The signal persisted on repeated rinsing, indicating that surface attachment had occurred. The apparent surface coverage was larger than that with the sample prepared in the glovebox, but the baseline-corrected peak currents did not evolve linearly with the scan rate, and the peak shapes were irregular, implying coupling pathways that were not available under the conditions we otherwise employed.

Reaction of the 1,2,3-Triazolyllithium-Terminated Glassy Carbon Surface With FcCHO. CV traces obtained with FcCHO as the ferrocenyl synthon (Scheme 2) after brief exposure to 1:1 water:MeCN showed a reversible wave with $E_{1/2}$ = 0.12 V (entry 4 of Table 2). Repeated shaking with 1:1 water:MeCN caused this first wave to diminish and a new quasi-reversible wave to grow in with $E_{p,ox}$ = 0.30 V ($E_{1/2}$ = 0.25 V; entry 5). The baseline-corrected voltammograms are shown in Figure 3. This evolution in the voltammetric response with exposure to water is attributed to the incremental protonation of the electron-deficient alkoxy intermediate generated by the C–C coupling reaction, as illustrated in Scheme 3. Placing the electrode in potassium *tert*-butoxide in MeCN for 5 min led to partial recovery of the reversible wave initially measured, although considerable broadening was also observed. Workup with $[(DMF)H]^+OTf^-$ (protonated dimethylformamide, a

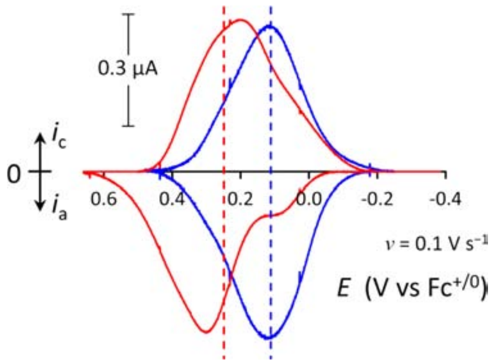
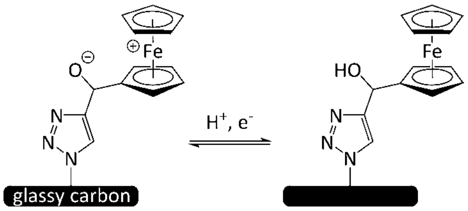


Figure 3. Baseline-corrected voltammograms showing the surface-confined ferrocenyl group obtained on reaction of the 1,2,3-triazolyllithium-terminated electrode with FcCHO, before (blue) and after (red) workup with 1:1 water:MeCN (Scheme 2). Vertical lines show the corresponding half-wave potentials.

Scheme 3. Proton and Electron Transfer of the FcCHO–Triazolyllithium Coupling Product



crystalline solid) in MeCN instead of water afforded a similar increase in current at the more positive potential. The species generated on protonation shows quasi-reversible voltammetry with the return reduction wave converging toward the response observed prior to workup, an effect we attribute to activation of the hydroxyl group toward proton transfer upon oxidation of the attached ferrocenyl group (Scheme 3).

Coupling with HC≡CMgBr vs (en)LiC≡CH. Alkynylmagnesium halide reagents cleanly cyclize with azides in homogeneous solution.[13a] In experiments using HC≡CMgBr (ethynylmagnesium bromide) as the alkynyl reagent rather than (en)LiC≡CH, Faradaic current corresponding to a surface-bound ferrocenyl group was only barely discernible after treatment with $Fc(CH_2)_6I$ (Table 2 and Figure S9, entry 6, Supporting Information). The failure itself is worthy of note, but we cannot confidently distinguish between the failure being due to the cyclization step or to the subsequent salt metathesis.

Optimization of CuAAC Coupling Conditions with Ethynylferrocene and Benzyl Azide. Different conditions for the Cu-catalyzed coupling were assayed using the reaction of benzyl azide with ethynylferrocene ($E_{1/2}$ = 0.16 V vs $Fc^{+/0}$) to afford 1-benzyl-4-ferrocenyl-1,2,3-triazole as a soluble model system ($E_{1/2}$ = 0.56 V vs $Fc^{+/0}$; Figure S12, Supporting Information). Variation in the spectroscopic yield with solvent (THF, 9:1 CH_2Cl_2:MeOH, MeCN, 1:1 DMSO:water), with Cu(I) source ($[Cu(MeCN)_4]^+PF_6^-$, CuI, $CuSO_4$ + sodium ascorbate), and with added base (none, NEt_3, N^iPr_2Et) are given in Table S2 (Supporting Information). Yields exceeding 80% were obtained at 24 h with CuI and triethylamine in THF, with $[Cu(MeCN)_4]^+PF_6^-$ and triethylamine in MeCN, and with $CuSO_4$ + sodium ascorbate in DMSO:water. The last two combinations were employed for reaction of the azide-terminated glassy carbon samples.

CuAAC Reaction of Azide-Terminated Glassy Carbon Samples with Ethynylferrocene. *Nonaqueous Conditions.* Samples were immersed in MeCN solutions of $[Cu(MeCN)_4]^+PF_6^-$, triethylamine, and ethynylferrocene (conditions identical with entry 6 of Table S1). These were withdrawn after 24 h, rinsed with MeCN, EtOH, and THF, and examined by cyclic voltammetry (CV). The initial anodic sweep generally showed a substantial irreversible anodic wave assigned to stripping of a physisorbed ferrocenyl species superimposed on a smaller reversible wave assigned to the covalently bound species. After this initial scan, reversible waves were observed (Figure 4). Peak currents increased linearly with v (R^2 = 0.9997). Voltammetric data are presented in Table 2, entry 7.

Aqueous Conditions. Samples were held for 24 h in water:DMSO solutions of $CuSO_4$ + sodium ascorbate and ethynylferrocene (conditions identical with those of entry 10 of Table S1, Supporting Information) and then rinsed as described above. The measured area for this electrode was 0.055 cm^2, 22% smaller than the nominal area of 0.071 cm^2. Calculated coverages are 11 × 10^{13} and 7.9 × 10^{13} molecules cm^{-2}, respectively, for the measured and nominal areas (Table 2, entry 8). The measured half-wave potential was also 40 mV negative of the value determined using the nonaqueous conditions.

■ DISCUSSION

Developing and demonstrating precise synthetic control over interfacial structures is essential to the study of structure−property relationships at complex interfaces. For example, the adsorption of alkanethiols in uniform ordered monolayers onto gold[26] made possible the detailed study of heterogeneous electron transfer kinetics in mixed monolayers of ferrocenyl-terminated and redox-silent alkanethiols.[27] Use of azide-terminated thiols with subsequent coupling to alkynes via copper-catalyzed azide−alkyne cyclization (CuAAC)[28,29] introduced new synthetic flexibility, and this platform was used in Chidsey and Collman's authoritative work showing the influence of electron transfer kinetics on productivity and selectivity in electrocatalytic oxygen reduction by cytochrome *c* oxidase.[30]

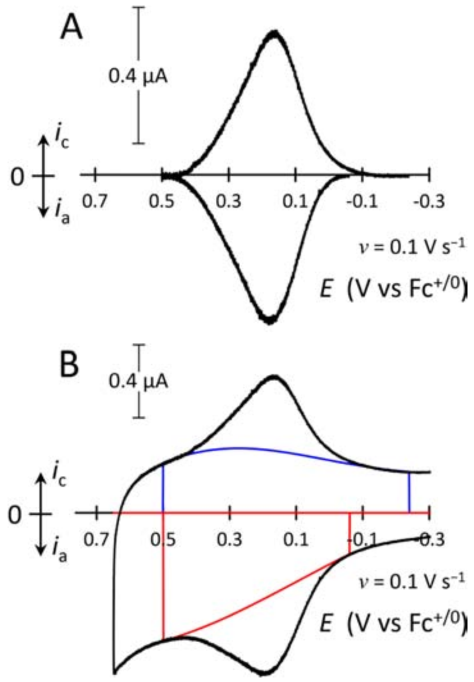


Figure 4. Baseline-corrected (A) and raw voltammograms (B) showing the surface-confined ferrocenyl group (ethynylferrocene + azide-terminated electrode surface, CuAAC conditions). Interpolated baselines are shown in red and blue.

Strategies for the covalent modification of carbon materials to afford robust films have also been developed.[6] Among these, the coupling of in situ generated aryl radicals to electrode surfaces by reduction of aryldizazonium ions has received broad application.[31] As with the gold−thiol approach, this method may also be used to introduce a coupling synthon. For example, attachment of either alkyne or azide groups followed by CuAAC coupling have both been achieved.[32] However, the aryldiazonium reductive coupling route may generate multilayered or nucleated structures, and obtaining precise control of surface structures remains a challenge.[33]

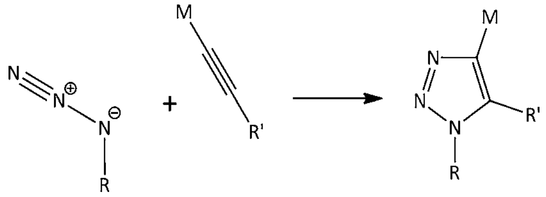
Azide groups may be introduced onto glassy carbon or other graphitic surfaces without an intervening linkage, by exposure to a source of iodine azide.[8b] The reaction is believed to proceed by addition of IN_3 across an arene C−C unsaturation followed by elimination of HI. The azide reactant may be generated by combining ICl with NaN_3 in approximately 5-fold excess suspended in MeCN.[8b] Solution IR spectroscopic evidence indicates that IN_3 is present as the adduct $[Cl{-}I{-}N_3]^-$ under these conditions.[15] This species also forms on reacting ICl with commercially available $^nBu_4N^+N_3^-$, which may be stored at ambient temperatures and is much more soluble in conventional organic solvents, thereby reducing the amount of azide waste generated, an important consideration given the attendant safety and health hazards.[34] Chidsey has recently reported a solvent-free method for generation of gaseous IN_3 from solid NaN_3 and ICl, also improving the utilization of azide;[12b] that work reports azide coverages obtained both with solution and gas-phase deposition methods along with detailed XPS and reactivity analyses, demonstrating that the gas-phase and solution routes both produce surface azide groups with minimal codeposited iodide.

While the $[Cl{-}I{-}N_3]^-$ ion and IN_3 may both be regarded as azide precursors, these reagents are not equivalent, since the inclusion of Cl atoms observed with the solution route is avoided in the gas-phase route.[12b] Deposition of azide from MeCN solution using the present method incorporates both Cl and I atoms (1.4 and 0.1 AT%, repsectively; Table 1, Figure 1), as has been observed using MeCN as the solvent and NaN_3 as the azide source.[12b] The measured Cl abundance is higher in the present case (1.4 vs 0.6 AT% by XPS); however, the I abundance is lower (0.1 vs 0.4 AT%).[12b] The N abundance itself is about the same: reaction with $^n\mathrm{Bu}_4\mathrm{N}^+[Cl{-}I{-}N_3]^-$ in MeCN increased the N:C ratio by 5.4 N atoms per 100 C (tracking the changes in the N:C ratio accounts for N atoms present prior to azide deposition), similar to the gas-phase route (also 5.4 N per 100 C) and somewhat lower than with NaN_3 + ICl in MeCN (7.1 N per 100 C).[12b] In their original[8b] report and in subsequent refinements[12a,b] Chidsey and co-workers activated substrates by heating to 1000 °C under H_2/N_2. We have found that coverage and selectivity are highly sensitive to surface preconditioning (see Figure S11, Supporting Information) and have obtained similar reactivity by activating conventional glassy carbon disk electrodes by lapping and polishing[10] under N_2 at room temperature, followed by sonication and stirring with activated carbon.[6] XPS analyses indicate that surfaces thus prepared present 4.7 AT% surface O atoms, 2.4 times that obtained by heating under H_2/N_2.[12b]

Azides react via Cu(I)-catalyzed 1,3-dipolar cycloaddition with terminal alkynes (the CuAAC reaction) to form stable 1,2,3-triazole linkages under a wide range of conditions and with excellent yields and selectivity, and coupling of ethynylferrocene to azide-terminated carbon surfaces proceeds cleanly.[8] We have obtained ferrocenyl surface densities of 7.0×10^{13} molecules cm^{-2} (determined voltammetrically) on reaction of azide-terminated glassy carbon electrodes with ethynylferrocene under nonaqueous CuAAC conditions, again similar to the results obtained by Chidsey's group.[8b,12a,b]

The rich chemistry of azides suggests a wider synthetic flexibility is attainable.[24] In 2004, Sharpless and co-workers reintroduced the 1,3-dipolar cycloaddition of alkynyl Grignard reagents to organic azides[13a] developed by Akimova and co-workers in 1967;[13b−d] the original work explored both bromomagnesium and lithium reagents. These reactions generate 4-metalated 1,2,3-triazolyl intermediates with various substituents in the 1- and 5-positions (R and R′; Scheme 4).

Scheme 4. Homogeneous Reaction of Organic Azides with Alkynylmetal Reagents[a]



[a]M = MgBr, Li; R, R′ = various.[13a]

This reaction is depicted for an idealized azide-terminated glassy carbon surface in Scheme 1. Changes to the N 1s spectral region on reaction with (en)LiC≡CH (Figure 1, Table 1) are essentially identical with those observed on subjecting surface-bound azides to CuAAC reaction conditions.[8b,12b,16] The total amount of N decreases only slightly throughout the synthesis, indicating that neither decomposition of the azide groups to release N_2 nor nucleophilic substitution occurs to an appreciable extent.[24] Both the Cl and I signals are also substantially mitigated, with Cl decreasing from 1.6 to 0.2 per 100 C and with I decreasing from 0.1 per 100 C to below the detection limit, respectively. This is important in cases where adventitious halides can act as poisons in metal-mediated reactions, and the use of gas-phase IN_3 offers an advantage in this respect.[12b]

In solution, the intermediates generated from alkynylmetal reagents and azides undergo subsequent reaction with a wide range of electrophiles, including aliphatic halides, aldehydes, acid chlorides, isocyanates, iodine, and other species.[13a] The surface obtained on treatment with (en)LiC≡CH reacts with $Fc(CH_2)_6I$ to afford (after water:MeCN workup) a surface-confined ferrocenyl group with near-complete removal of Li and without incorporation of I, consistent with a salt metathesis reaction. The O atom abundance decreases to 1.2 times the background level. Residual Cl again decreases in this step, from 0.2 to 0.1 per 100 C atoms (0.2−0.3 residual Cl atoms per deposited Fe atom). N abundance is preserved throughout the synthesis, in contrast with results obtained using aqueous CuAAC conditions.[12b]

Peak widths observed in the voltammetry of surface-confined redox species report on the electrochemical environment of the bound groups and depend on structural variability, redox kinetic effects, and the mutual proximity of redox centers.[16a,25] For perfectly uniform noninteracting surface-confined electroactive species, the fwhm value (full width at half-maximum) is 90.6 mV at 25 °C for a Nernstian redox process.[25a] fwhm values of 140 mV (average of reduction and oxidation waves) were obtained with $Fc(CH_2)_6I$ or $Fc(CH_2)_6Br$ (Table 2, entries 2 and 3) with manual lapping. Machine lapping increased coverage and also afforded broader peaks (average fwhm 168 mV; entry 1). This increase in peak width with coverage suggests that proximity effects are operative. Although the coverage was somewhat higher in this case in comparison to the coverage we obtained with the optimized nonaqueous CuAAC route (entry 7), the fwhm values were still lower. This may be due to differences in structural uniformity of the coupled species or to the conformational flexibility imparted by the long aliphatic spacer when $Fc(CH_2)_6I$ is used as the ferrocenyl source.[16a] Table 3, a sampling of reported data obtained with CuAAC-attached ethynylferrocene, places these fwhm values into context.

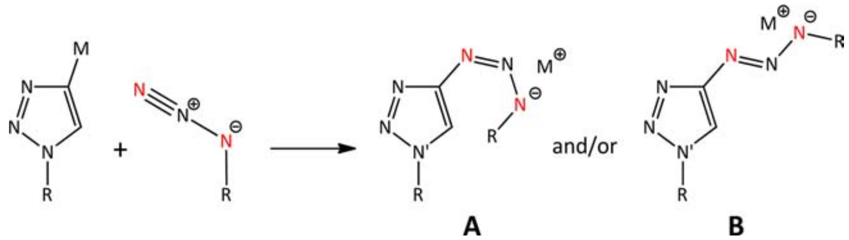
Selective production of a self-terminating monolayer is a challenge with radical coupling routes, as has been documented with the aryldiazonium route in particular,[33a] and may also be the case with other redox-mediated coupling routes.[9,10] If monolayer selectivity is indeed operative in the present case, this would constitute a key advantage. This is expected for two reasons. (1) Since the preparation of the surface 1,2,3-triazolyllithium group requires two discrete reactions, azide attachment and cyclization, the generation of multilayers by the route proposed herein would require these steps to be repeated in an alternating fashion; (2) Multilayer or nucleation−growth

Table 3. Survey of Surface Coverages and fwhm (Full Width at Half-Height) Values for Ferrocenyl Groups Attached to Azide-Terminated Glassy- Carbon Electrodes

coupling route	coverage ($\times10^{-13}$ molecules cm^{-2})	fwhm (mV)	ref
$^{n}\text{Bu}_4\text{N}^+\text{N}_3^-$ + ICl (MeCN), (en)LiC≡CH, Fc(CH$_2$)$_6$I[a]	5.7	140	this work
$^{n}\text{Bu}_4\text{N}^+\text{N}_3^-$ + ICl (MeCN), (en)LiC≡CH, Fc(CH$_2$)$_6$I[b]	8.4	168	this work
$^{n}\text{Bu}_4\text{N}^+\text{N}_3^-$ + ICl, MeCN, ethynylferrocene (nonaqueous CuAAC)	7.2	210	this work
$^{n}\text{Bu}_4\text{N}^+\text{N}_3^-$ + ICl, MeCN, ethynylferrocene (water:DMSO CuAAC)	11 (7.9)[c]	167	this work
$^{n}\text{Bu}_4\text{N}^+\text{N}_3^-$ + ICl, MeCN, ethynylferrocene (CuAAC)	2.0	150	8b
IN$_3$(g), ethynylferrocene (CuAAC)	8	170	12b
p-azidophenyldiazonium reduction, ethynylferrocene (CuAAC)	19.8	170	32
ideal close-packed ferrocenyl groups (as spheres with diameter 6.6 Å) on a planar surface[d]	24−27	91.6[e]	16

[a] Electrodes were lapped by hand. [b] Electrodes were lapped mechanically. [c] The measured area was 22% smaller than the nominal area in this case; the value in parentheses assumes an area equal to the nominal area. [d] Reference 16 provides a detailed examination of this estimate; the lower bound is for randomly packed spheres, and the upper bound is for spheres in a hexagonal close packing arrangement. [e] For a one-electron Nernstian response at 25 °C.[25a]

Scheme 5. Homogeneous Reaction of Organic Azides with Triazolylmetal Reagents[a]



[a] M = Li, Na, MgBr; R = various groups.[13,38]

structures might arise from radical intermediates; however, the 1,3-dipolar cycloaddition and nucleophilic substitution and addition reactions employed herein are not expected to proceed via radical routes under the present conditions. Diradical intermediates have been proposed to arise in 1,3-dipolar cycloaddition reactions; however, these reactions generally proceed with retention of stereochemistry rather than scrambling, suggesting that ring closure proceeds in a concerted fashion with all paired electrons remaining so.[35] Radical pathways in the alkylation of organolithium reagents with alkyl halides have been examined by both stereochemical retention and cyclizable radical traps. The majority of cases studied revealed no evidence for radical intermediates;[36] exceptions to this were with *tert*-butyl bromoacetate and benzyl bromide, both of which exhibit a propensity toward C−Br homolysis,[37] suggesting that the observed racemization was due to the choice of alkyl halide. Similarly, addition of organolithium species to carbonyls occurs predominantly by an ionic pathway unless a uniquely stable radical intermediate is possible, as with benzophenone.[36]

Triazolylmetal intermediates (M = Li, Na, MgBr) react with a second equivalent of azide in some cases to afford 4-triazenate-substituted triazoles, as shown in Scheme 5.[13,38] Analogous bis(tetrazolyl)triazenates, isolated as their Na$^+$ salts, are methylated by CH$_3$I at one of the terminal triazenate N atoms (these are shown in red in Scheme 5).[39] If this second azide coupling were operative in the present case, subsequent reaction with Fc(CH$_2$)$_6$I would then form a new C−N bond, which should affect the N 1s photoemission spectrum. Reaction with the triazolylmetal intermediate (Scheme 1) forms a C−C bond, and the N 1s photoemission spectrum is expected to change less in this case. Spectra obtained before and after reaction of the (en)LiC≡CH product surface with Fc(CH$_2$)$_6$I are nearly perfectly superimposable (Figure S13, Supporting Information), suggesting that the C−C coupling shown in Scheme 1 predominates.

We also examined the reactivity of the (en)LiC≡CH-treated surface with respect to nucleophilic attack at a carbonyl C atom, using ferrocenecarboxaldehyde as the reactant. The Brønsted basic surface ferrocenylalkoxide product shown in Scheme 3 was expected, and the oxidation peak potential of the ferrocenyl group shifted anodically with exposure to neutral water:MeCN, as predicted for protonation of the alkoxide.[9] These results demonstrate a reactivity pattern consistent with the solution 1,2,3-triazolylmetal analogues.

Surface attachment of FcCHO also affords coverage similar to that observed with the CuAAC coupling of ethynylferrocene. In this case the initial CV traces showed a broad, reversible wave with $E_{1/2}$ = 0.12 V vs Fc$^{+/0}$. On exposure to 1:1 water:MeCN, this wave decreased and a new quasi-reversible signal with $E_{\text{p,ox}}$ = 0.30 V vs Fc$^{+/0}$ emerged. We assigned this wave to the protonation product, surface-bound (1,2,3-triazolyl)(ferrocenyl)methanol. Workup using a stronger acid also produced this response, and subsequent reaction with potassium *tert*-butoxide partially restored the original response. Reaction with other carbon nucleophiles such as acid anhydrides and activated esters (e.g., bearing a succinimide substituent) should produce surface-bound species having a keto functionality rather than a hydroxy group.

■ CONCLUSIONS

This work demonstrates a catalyst-free route to produce surface organolithium groups from azides covalently attached to glassy carbon, allowing facile attachment of electrophilic coupling partners, again without a catalyst. Surface activation, required for successful deposition of azides, may be achieved straightforwardly within an inert-atmosphere glovebox using conventional commercially available glassy carbon electrodes.

Control experiments show that without either the azide or the lithium reagent no coupling chemistry is observed; analogy to known homogeneous reactions suggests a surface-bound 1,2,3-triazolyllithium synthetic intermediate is formed. Nucleophilic displacement and substitution chemistry beginning from this well-defined surface group offers entry into a broad array of subsequent chemistries for the mild, selective covalent modification of carbon materials.

■ EXPERIMENTAL SECTION

Materials and Methods. All manipulations were carried out in a N_2 glovebox unless otherwise noted. Methanol (MeOH; Aldrich) and acetone (Fisher, certified ACS) were used as received. Acetonitrile (MeCN; Burdick & Jackson BioSyn) and ethylene glycol (Aldrich anhydrous) were purified by sparging with nitrogen. Water was dispensed from a Millipore Milli-Q purifier (18 MΩ cm^{-1}) and sparged with nitrogen. Tetrahydrofuran (THF; VWR, anhydrous, not stabilized), dichloromethane (Fisher, not stabilized), and diethyl ether (Et_2O; Burdick & Jackson Brand) were purified by sparging with nitrogen and passage through neutral alumina, and ethanol (EtOH; Acros Organics, anhydrous, 200 proof) was purified by sparging with nitrogen and passage through $CaSO_4$, using a solvent purification system (PureSolv, Innovative Technologies, Inc.). Activated carbon (Vacuum Atmospheres) and permethylferrocene (Strem) were used as received. Aqueous HCl (37%), ${}^nBu_4N^+N_3^-$, ICl, lithium acetylide−ethylenediamine complex ((en)LiC≡CH), ethynylmagnesium bromide (HC≡CMgBr, 0.5 M in THF), $[Cu(MeCN)_4]^+PF_6^-$, CuI, Et_3N, ${}^iPr_2EtN$, hydroquinone, ethynylferrocene, and benzyl azide (Aldrich) were used as received. Ferrocene (Fc) and KO^tBu (Aldrich) were purified by sublimation. ${}^nBu_4N^+PF_6^-$ was prepared from ${}^nBu_4N^+I^-$ and $NH_4^+PF_6^-$ (Aldrich) and purified by crystallization from acetone.[40] (6-Iodohexyl)ferrocene ($Fc(CH_2)_6I$) was prepared from $Fc(CH_2)_6Br$ and NaI (Aldrich) in acetone.[10]

Glassy Carbon Substrates. Three millimeter glassy carbon disks encased in poly(chlorotrifluoroethylene) (for voltammetry, BAS Instruments) and 4 × 10 × 10 mm glassy carbon plates (for XPS and reflectance IR analysis, SPI-Glas 22 grade, SPI supplies) were preconditioned as follows: samples were first lapped in ethylene glycol with aluminum oxide films (12, 9, 3 μm, Buehler) on a mechanical wheel (Electron Microscopy Sciences Model 900) and then polished with diamond paste (3, 1, 0.25 μm, Buehler). After rinsing and sonication in ethanol, these were stirred overnight in an ethanol suspension of activated carbon, then thoroughly rinsed with ethanol. These operations were carried out in the glovebox; comparisons of glovebox vs benchtop preparation and of mechanical vs hand lapping are examined below. One plate sample was analyzed by XPS (Figure 1, red traces; Table 1, entry 1), and another was analyzed by reflectance IR spectroscopy (Figure S6, Supporting Information). Samples thus prepared were further modified and characterized as described below.

Instrumentation and Analytical Methods. X-ray Photoelectron Spectroscopic (XPS) Measurements. These were performed using a Physical Electronics Quantera Scanning X-ray Microprobe with a focused monochromatic Al Kα X-ray source (1486.7 eV), a spherical section analyzer, and a 32-element multichannel detection system. Glassy carbon plate samples were mounted for analysis inside a N_2 glovebox interfaced with the XPS vacuum introduction system (1×10^{-7} mmHg) and then moved to the main ultrahigh-vacuum system (1×10^{-10} mmHg). A 100 W X-ray beam focused to 100 μm diameter was rastered over a 1.3 × 1 mm rectangle on the sample. The X-ray beam was incident normal to the sample, and the photoelectron detector was at 45° off-normal. High-energy resolution spectra were collected using a pass energy of 69.0 eV with a step size of 0.125 eV. For the Ag $3d_{5/2}$ line, these conditions produced a fwhm of 0.91 eV. Surface densities were calculated from XPS data (Table S1, Supporting Information) using the method outlined in ref 41. The density of glassy carbon was taken as reported by the supplier (1.42 g cm^{-3}). The inelastic mean free path for the C 1s photoelectron (33.85 Å) was obtained from the Quases-IMFP-TPP2M (Tanuma, Powell, Penn) material properties database, corrected for the difference in density of the glassy carbon used vs that listed in the database (1.80 g cm^{-3}).

Infrared Spectroscopy. Solution IR spectra were recorded using a Nicolet iS10 FTIR spectrometer with demountable sealed liquid CaF_2 cells with a 0.1 mm path length (International Crystal Laboratories). Reflectance spectra of glassy carbon plate samples were recorded using a Bruker IFS66/S spectrometer configured to operate in the mid-infrared with a KBr beam splitter, Globar source, and liquid-nitrogen-cooled HgCdTe detector and fitted with a Bruker A513 specular reflectance accessory. Reflectance measurements were made using unpolarized light from the interferometer with both focusing mirrors set at an angle of 45° on opposite sides of the surface normal. Spectra were formed as $\ln(R_{sample}/R_{background})$, where R_{sample} is the sample reflectance spectrum and $R_{background}$ is the reflectance spectrum of the uncoated glassy carbon plate. Residual water signals were removed, and baselines were straightened in postacquisition data processing.

Electrochemical Measurements. These were conducted using a CH Instruments 620D potentiostat and a standard three-electrode cell. Glassy carbon-electrode samples preconditioned and subjected to chemical modification as described below were used as working electrodes. The counterelectrode was a 3 mm diameter glassy carbon rod (Alfa Aesar). The reference electrode was a silver wire (Alfa Aesar; 1 mm diameter, 99.9%) anodized for 5 min in aqueous HCl, washed with water and acetone, dried, and suspended in a glass tube containing neutral MeCN (0.2 M ${}^nBu_4N^+PF_6^-$) and fitted with a porous Vycor disk.

Standard Electrode Calibration and Measurement of Sample Electrode Areas. An electrolyte stock solution of ${}^nBu_4N^+PF_6^-$ (1.62 g, 4.18 mmol) in MeCN (8.0 mL) was prepared. Calibrant solutions of ferrocene in MeCN (0.2 M ${}^nBu_4N^+PF_6^-$) were then prepared as follows: ferrocene (50.6, 55.4, 54.5, and 50.9 mg) was diluted to 25.0 mL with neat MeCN. A 1.00 mL portion of each ferrocene solution was added to 2.0 mL of the electrolyte stock solution, and these mixtures were then diluted to 10.00 mL using MeCN. The resulting solutions were 0.10 M in ${}^nBu_4N^+PF_6^-$ and 1.09, 1.19, 1.17, and 1.09 mM in ferrocene, respectively. Using a 3 mm glassy carbon electrode, the following measurements were recorded with each calibrant solution: a cyclic voltammogram spanning the $Fc^{+/0}$ couple was recorded, affording $E_{1/2}(Fc^{+/0})$ vs E_{ref} (the equilibrium potential of the pseudoreference electrode). The electrode was polished, and a chronoamperogram was recorded with the voltage held at −0.5 V vs $Fc^{+/0}$ for 1 s, and then stepped to 0.5 V vs $Fc^{+/0}$ for 5 s, with data recorded at 0.001 s intervals during this period. The electrode was then polished, and the chronoamperogram was measured again. This was repeated one more time. For each calibrant solution, the chronoamperogram showing the largest mean current over t = 0.25−0.75 s was selected for data processing. Slopes were obtained using this data from linear least-squares regression to i vs $t^{-1/2}$, affording $R^2 > 0.999998$ for each calibrant solution. From these slopes, the electrode area was calculated using the Cottrell Equation with $D = 2.4 \times 10^{-5}$ cm^2 s^{-1} for ferrocene in MeCN,[42] affording A = 0.0758(4) cm^2 (confidence interval at the 2 × σ level). Areas for electrode samples were estimated by recording voltammograms of permethylferrocene in MeCN (0.10 M ${}^nBu_4N^+PF_6^-$) using both the standard and sample electrodes and taking the ratio of peak currents thus obtained as the ratio of the sample and standard electrode areas.

In Situ Generation of ${}^nBu_4N^+[Cl–I–N_3]^-$. *Warning!* Azide compounds may present explosion and/or toxicity hazards.[34] The products of this reaction *should not be isolated*. All glassware used in handling ICl, ${}^nBu_4N^+N_3^-$, or IN_3 was oven-dried and maintained under nitrogen. No metal was allowed to contact the reactants. A small storage tube containing ICl was attached to the Schlenk line and placed in a warm water bath. From this, ICl (50 μL, 0.95 mmol) was transferred under nitrogen by a PTFE-tipped volumetric micropipet (Drummond Wiretrol II) to a nitrogen-filled 5.0 mL volumetric flask fitted with a glass stopcock. This was then closed and removed to the glovebox, and the ICl was diluted to 0.19 M using neat MeCN. The ICl stock solution was stored at −35 °C. The following are from a typical experiment: MeCN (1.1 mL) was added to ${}^nBu_4N^+N_3^-$ (10.2 mg, 0.0359 mmol), and a 200 μL aliquot was transferred to a 2 mL screw-cap vial (6–7 μmol of $^n\mathrm{Bu_4N^+N_3^-}$). To this was added 25 μL of ICl stock solution (5 μmol). This mixture was allowed to stand for 5 min at ambient temperature. The reactant and product species all remained in solution during this procedure. Solution IR spectra showed bands at 2025 and 2000 cm^{-1} assigned to $^n\mathrm{Bu_4N^+[Cl{-}I{-}N_3]^-}$ (Figure S5, Supporting Information).[15] The peak intensities diminished by 15% over 45 min and were 0 on the following day.

Reaction of Glassy Carbon Samples with $^n\mathrm{Bu_4N^+[Cl{-}I{-}N_3]^-}$. Samples were rinsed with MeCN and sealed into a glass screw-cap vial containing freshly generated $^n\mathrm{Bu_4N^+[Cl{-}I{-}N_3]^-}$. After 45 min, the samples were removed, rinsed with MeCN and dry THF, and immediately reacted as described below. One electrode sample was examined by voltammetry and showed an irreversible reduction wave with a gradual slope that decayed with repeated scans (see Figure S7, Supporting Information). One plate sample was analyzed by XPS (Figure 1, dark blue traces; Table 1, entry 2), and another was analyzed by reflectance IR spectroscopy (Figure S6, red trace, Supporting Information).

Coupling with (en)LiC≡CH. In a typical experiment, (en)LiC≡CH (102.1 mg, 1.10 mmol) was suspended in dry THF (2 mL) in a screw-cap vial and an azide-treated electrode sample was placed in this solution for 3 h. Plate samples were prepared in the same way, one of which was analyzed by XPS without further modification (Figure 1, green traces; Table 1, entry 3). Another plate sample was analyzed by reflectance IR spectroscopy following 30 s exposure to 1:1 MeCN:water (Figure S6, black trace, Supporting Information).

Reaction of Azide + (en)LiC≡CH Modified Glassy Carbon Samples with $\mathrm{Fc(CH_2)_6I}$. $\mathrm{Fe(CH_2)_6I}$ (12.9 mg, 0.032 mmol) was dissolved in THF (300 μL) in a screw-cap vial. Following reaction with $^n\mathrm{Bu_4N^+[Cl{-}I{-}N_3]^-}$ and (en)LiC≡CH, a plate sample and an electrode sample were rinsed with dry THF and then placed in this solution for 18 h. The samples were then shaken for 30 s with MeCN:water (1:1 by volume), rinsed with MeCN, and analyzed by XPS (plate sample; Figure 1, light blue traces; Table 1, entry 4) or by voltammetry (electrode; Table 2, entry 1; Figure 2) as follows (this procedure was used for all electrode samples): a voltammogram spanning the potential range corresponding to the expected attached ferrocenium/ferrocene couple was collected (υ = 0.1 V s^{-1}); the potential was then cycled 40 times from −0.8 to 0.8 V vs Fc$^{+/0}$ (υ = 0.4 V s^{-1}). An initial decay toward a constant peak current was observed, with the constant current being 90–95% of the initial peak current. The electrode was then withdrawn, rinsed using the above sequence, and introduced into a new cell with fresh electrolyte solution. The electrochemical area of the electrode sample was then determined as described above. Voltammograms were recorded in select cases with υ ranging from 0.1 to 2 V s^{-1}.

Electrodes prepared by the above route but with either the $^n\mathrm{Bu_4N^+[Cl{-}I{-}N_3]^-}$ step or the (en)LiC≡CH step omitted did not exhibit a measurable Faradaic response. An electrode preconditioned by hand lapping rather than machine lapping in the glovebox afforded lower ferrocenyl coverages and narrower reduction and oxidation waves (Table 2, entry 2). Voltammetric data are shown in Figure S10 (Supporting Information). An electrode preconditioned by machine lapping on the benchtop rather than in the glovebox afforded the data shown in Figure S11 (Supporting Information). These data were judged unsuitable for coverage determination.

Reaction of Azide + (en)LiC≡CH Modified Glassy Carbon Electrode Samples with $\mathrm{Fc(CH_2)_6Br}$ or FcCHO. $\mathrm{Fc(CH_2)_6Br}$ (11.7 mg, 0.32 mmol) or Fc(CHO) (6.8 mg, 0.32 mmol) were dissolved in THF (300 μL) in a screw-cap vial. Hand-lapped electrodes that had been reacted with $^n\mathrm{Bu_4N^+[Cl{-}I{-}N_3]^-}$ and (en)LiC≡CH were rinsed with dry THF and placed in these solutions for 18 h and then shaken 30 s with MeCN:water (1:1 by volume) and rinsed with MeCN. Voltammograms of the $\mathrm{Fc(CH_2)_6Br}$-treated electrode sample are presented in Figure S9, entry 3 (Supporting Information); data appear in Table 2, entry 3. The FcCHO-treated electrode was examined by voltammetry after 30 s exposure to MeCN:water (Figure 3, blue trace; Figure S9, entry 4 (Supporting Information); Table 2, entry 4) and again after extended exposure to MeCN:water (Figure 3, red trace; Figure S9, entry 5 (Supporting Information); Table 2, entry 5). Subsequent exposure to saturated KO^{t}Bu in MeCN partially restored the initial response.

Reaction of an Azide-Modified Glassy Carbon Electrode Sample with HC≡CMgBr and Subsequent Reaction with $\mathrm{Fc(CH_2)_6I}$. Following reaction with $^n\mathrm{Bu_4N^+[Cl{-}I{-}N_3]^-}$, an electrode sample was sealed into a screw-cap vial containing 1 mL of HC≡CMgBr (0.5 M in THF, 0.5 mmol) and held for 3 h and then rinsed with dry THF. The electrode was then treated with $\mathrm{Fe(CH_2)_6I}$ in MeCN as described above and analyzed by voltammetry, showing a poorly defined Faradaic response with small peak currents (Figure S9, entry 6 (Supporting Information); Table 2, entry 6).

Optimization of Conditions for Nonaqueous CuAAC Coupling of Ethynylferrocene with Benzyl Azide. Different conditions were assayed using the reaction of benzyl azide with ethynylferrocene ($E_{1/2}$ = 0.160 V vs Fc$^{+/0}$) to afford 1-benzyl-4-ferrocenyl-1,2,3-triazole as a model system ($E_{1/2}$ = 0.56 V vs Fc$^{+/0}$; Figure S12, Supporting Information). Reactions were were conducted for 24 or 50 h at 22–25 °C. Variation in the spectroscopic yield with solvent (THF, 9:1 $\mathrm{CH_2Cl_2}$:MeOH, MeCN), with Cu(I) source ($\mathrm{[Cu(MeCN)_4]^+PF_6^-}$, CuI; 20 mol %), with added base (none, triethylamine, diisopropylethylamine), and with or without hydroquinone as reductant are given in Table S1 (Supporting Information). Yields exceeding 80% were obtained at 24 h both with $\mathrm{[Cu(MeCN)_4]^+PF_6^-}$ and triethylamine in MeCN and with CuI and triethylamine in THF (entries 6 and 9, respectively). The former mixture remained homogeneous, and this combination was employed for reaction of the azide-terminated glassy carbon samples. The following describes a typical procedure: $\mathrm{[Cu(MeCN)_4]^+PF_6^-}$ (7.3 mg, 17 mol %) and $\mathrm{Et_3N}$ (16 μL, 0.12 mmol) were added to a solution of ethynylferrocene (24.8 mg, 0.12 mmol) and benzyl azide (14 μL, 0.12 mmol) in 4 mL of MeCN in a 20 mL screw-cap vial. The mixture was stoppered and stirred at room temperature for 24 h. The suspension was filtered and the volume reduced to 2 mL. $\mathrm{Et_2O}$ (6 mL) was added, and the mixture was kept at −35 °C overnight. A precipitate was observed; it was collected via filtration, washed with $\mathrm{Et_2O}$, and dried.

CuAAC Reaction of $\mathrm{N_3}$-Modified Electrode with Ethynylferrocene. *Procedure 1.* Ethynylferrocene (8.4 mg, 0.040 mmol) and $\mathrm{[Cu(MeCN)_4]^+PF_6^-}$ (2.2 mg, 0.0059 mmol) were dissolved in MeCN (5.2 mL), and $\mathrm{Et_3N}$ (6 μL, 0.04 mmol) was added. A 1 mL aliquot of this solution was placed in a 2 mL screw-cap vial, and an electrode sample that had been reacted with $^n\mathrm{Bu_4N^+[Cl{-}I{-}N_3]^-}$ was suspended in this solution for 18 h, during which time a yellow precipitate formed.

Procedure 2. Ethynylferrocene (2.2 mg, 0.01 mmol), $\mathrm{CuSO_4}$ (10 μL of a 0.01 M $\mathrm{CuSO_4}$ solution), and sodium ascorbate (40 μL of 0.01 M Na ascorbate, 40 mol %) were dissolved in 1 mL of a DMSO:$\mathrm{H_2O}$ (2:1) solvent mixture in a 2 mL screw-cap vial. An electrode sample that had been reacted with $^n\mathrm{Bu_4N^+[Cl{-}I{-}N_3]^-}$ was suspended in this solution for 18 h, during which time a brown precipitate formed.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures, text, and tables giving characterization data and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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