Covalent Bonding of Alkene and Alkyne Reagents to Graphitic Carbon Surfaces

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Various aromatic and aliphatic alkynes and one alkene were covalently bonded to sp^2-hybridized carbon surfaces by heat treatment in an argon atmosphere. X-ray photoelectron spectroscopy, Raman, and FTIR spectra of the modified surfaces showed that the molecules were intact after the 400 °C heat treatment but that the alkyne group had reacted with the surface to form a covalent bond. Alkynes with ferrocene and porphyrin centers exhibited chemically reversible voltammetric waves that could be cycled many times. Atomic force microscopy of the modified surfaces indicated a thickness of the molecular layer consistent with monolayer coverage, and surface coverage determined by voltammetry was also in the monolayer range. Raman spectroscopy of the porphyrin monolayers formed from a porphyrin alkyne showed no evidence for dimer formation, although multilayer formation may occur at undetected levels. FTIR spectra of the porphyrin-modified carbon surfaces were well-defined, similar to the parent molecule, and indicative of an average tilt angle between the porphyrin plane and the surface normal of 37°. The bond between the molecular monolayer and the carbon surface was quite stable, withstanding sonication in tetrahydrofuran, mild aqueous acid and base, and repeated voltammetric cycling in propylene carbonate electrolyte. Heat treatment of alkynes and alkenes appears to be a generally useful method for modifying carbon surfaces, which can be applied to both aromatic and aliphatic molecules.

Introduction

A number of recent studies have reported covalent attachment of organic molecules to semiconductor[1−4] and metal surfaces.[5] These studies were motivated by both scientific questions about surface modification and by their potential application in the "bottom-up" fabrication of molecular electronic devices. For device fabrication purposes, most attachment studies in the open literature have been performed on metal or silicon surfaces,[6−8] with fewer reports on carbon-based materials such as diamond,[9−12] glassy carbon,[13−16] and pyrolyzed photoresist films

(PPFs).[17−19] The stability of both carbon substrates and a carbon−carbon bond between the modification layer and the substrate make molecular devices based on carbon substrates potentially attractive. Reported examples of carbon/molecule/metal molecular electronic junctions exhibit rectification and conductance switching, as well as a strong dependence of conductance on the structure of the molecular layer.[20−26]

Several laboratories have reported the covalent bonding of a variety of organic molecules to carbon surfaces via electrochemical reduction of aryldiazonium ions in both aqueous and organic solution.[13−16,18,27−30] Although the strong bonding and packing density of the modification layers produced by diazonium reduction have been well-established, several labs have reported multilayer formation during the reduction of aryldiazonium ions to yield organic films of varying thicknesses under diverse conditions.[14,15,18,31] On the basis of FTIR, X-ray photoelectron

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spectroscopy (XPS), and secondary ion mass spectrometry evidence, multilayer formation has been proposed to progress by additional diazonium reduction after the first monolayer forms and then subsequent radical attack of the initial monolayer.[15,32,33] Alternative methods for forming stable covalent carbon−carbon (C−C) bonds with the carbon surface have at least two objectives. First, a reduced tendency to form multilayers would more reliably limit the modification to a single monolayer. Second, the diazonium reduction route requires an aromatic diazonium reagent, which necessarily results in a phenyl ring coupling to the sp[2] carbon surface. An alternative modification reaction might be more general and permit both aliphatic and aromatic bonding between a carbon substrate and the chemisorbed monolayer.

Recently, several studies on the covalent attachment of conjugated alkenes, alkynes, and aromatics to silicon through a Si−C bond have been reported.[4,11,34−39] These studies have revealed that molecules such as 1-dodecyne and Zn(II) porphyrins can be covalently bonded to silicon. The attachment can be accomplished by anodic and cathodic "electrografting" methods[37,40,41] or by the heating of a reagent on a silicon surface at 400 °C in an inert atmosphere.[34] In these cases, excellent attachment of the reagents of interest was reported and characterized by scanning probe microscopy (SPM),[35] XPS, Fourier transform infrared spectroscopy (FTIR), and cyclic voltammetry (CV).[34] Covalent bonding of alkene and alkyne reagents to sp[2]-hybridized carbon surfaces by similar thermal routes has not been investigated, to our knowledge. We report here the formation of carbon−carbon bonds between a carbon surface and a modification layer by thermal activation of alkene and alkyne reagents. The resulting modified surface was characterized with atomic force microscopy (AFM), FTIR, Raman spectroscopy, XPS, and voltammetry.

Experimental Section

Chemicals and Materials. The molecules used for the attachment scheme are shown in Figure 1. The porphyrins 5-(4-ethynylphenyl)-10,15,20-trimesitylporphinatozinc(II), **1** (alkyne linker); 5,10,15-trimesityl-20-(4-vinylphenyl)porphinatozinc(II), **2** (alkene linker); and 5,10,15,20-tetraphenylporphyrinatozinc-(II), ZnTPP (no linker), were provided by Jon Lindsey after synthesis by published procedures.[42] Ethynylferrocene (**3**), 4-ethynyl-α,α,α-trifluorotoluene (**4**), and 5-Chloro-1-pentyne (**5**) were obtained commercially (Aldrich, 99+%) and used as received, as was positive photoresist AZ P4330-RS (AZ Electronic Materials, Somerville, NJ). Deionized water (from a Milli-Q purification system) had a resistivity ≥17 MΩ cm. The anhydrous solvents tetrahydrofuran (THF) and propylene carbonate (PC) (Aldrich
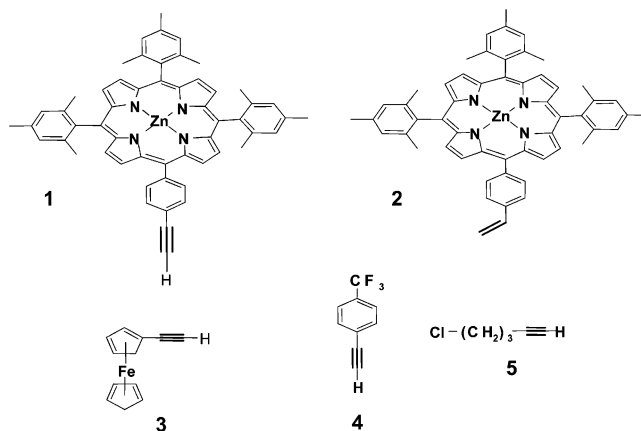

Figure 1. Molecular structures of the five molecules investigated for bonding to PPF surfaces: (**1**) 5-(4-ethynylphenyl)-10,15,20-trimesitylporphinatozinc(II), (**2**) 5,10,15-trimesityl-20-(4-vinylphenyl)porphinatozinc(II), (**3**) ethynylferrocene, (**4**) 4-ethynyl-α,α,α-trifluorotoluene, and (**5**) 5-chloro-1-pentyne.

99.7%) and electrochemical grade tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$) and silver hexafluorophosphate (AgPF$_6$) (Fluka) were all used as received.

Silicon wafers (Silicon Valley Microelectronics) were purchased (p-type boron-doped, 1 Ω cm, 2 mm thick) and diced into 2.2 × 1.4 cm pieces. A ~200 nm thick layer of silicon dioxide was grown on the wafer pieces by heating individual Si pieces in a quartz-lined box furnace (Riko Kiden, Japan). The furnace temperature was ramped to 150 °C, maintained at this temperature for 20 min, ramped at 8 °C/min to 1000 °C, and maintained for 1 h. Finally, the furnace temperature was passively decreased to room temperature. During heating and cooling of the samples, humidified N$_2$ flowed into the furnace at a flow rate of ≥3 L/min.

Preparation of Carbon Film. The procedure for preparing PPFs has been described previously[43,44] In brief, positive photoresist AZ P4330-RS was spin-coated onto clean silicon dioxide at 6000 rpm on a spin coater for 40 s. Two coatings were applied, to a final film thickness of 3−4 μm. The spin-coated samples were then soft baked at 90 °C for 2 min, and pyrolysis occurred in a tube furnace (Lindberg Blue) fitted with a quartz tube. The tube was flushed by a continuous flow of forming gas (95% N$_2$ + 5% H$_2$) at 100 mL/min during pyrolysis and cooling; samples were heated at 20 °C/min to 1000 °C, held at 1000 °C for 1 h, and then allowed to cool to room temperature while gas remained flowing. As noted previously,[43,44] PPF is similar in properties and conductivity to glassy carbon, with primarily sp[2]-hybridized bonding.

Counter/Reference Electrode Fabrication. Counter/reference electrodes were prepared as previously described.[45] The counter/reference electrode denoted as "Ag/wire" consisted of a bare silver wire placed inside a 10 μL polypropylene disposable pipet tip containing ~5 μL of 1.0 M Bu$_4$NPF$_6$ in PC. Where noted below, an alternative counter/reference electrode referred to as "Ag/Ag$^+$" included 100 μM AgPF$_6$ added to the 1.0 M Bu$_4$NPF$_6$ in PC. The electrolyte-filled pipet tip was then fastened onto a micropositioner for manipulation during electrochemical measurements. The electrochemical "cell" was formed by contact of a drop of electrolyte extruded from the pipet tip, which touched the modified PPF surface.

Electrochemical Studies and Monolayer Attachment Procedures. The molecular attachment scheme was the same as that used on the Si(100) surface.[2,34,41,45,46] Superior results were obtained under an inert atmosphere rather than in ambient lab air. In this report, the attachment procedure was conducted with an Ar purge unless otherwise indicated. The electrochemical experiments were performed with a BAS 100-W potentiostat

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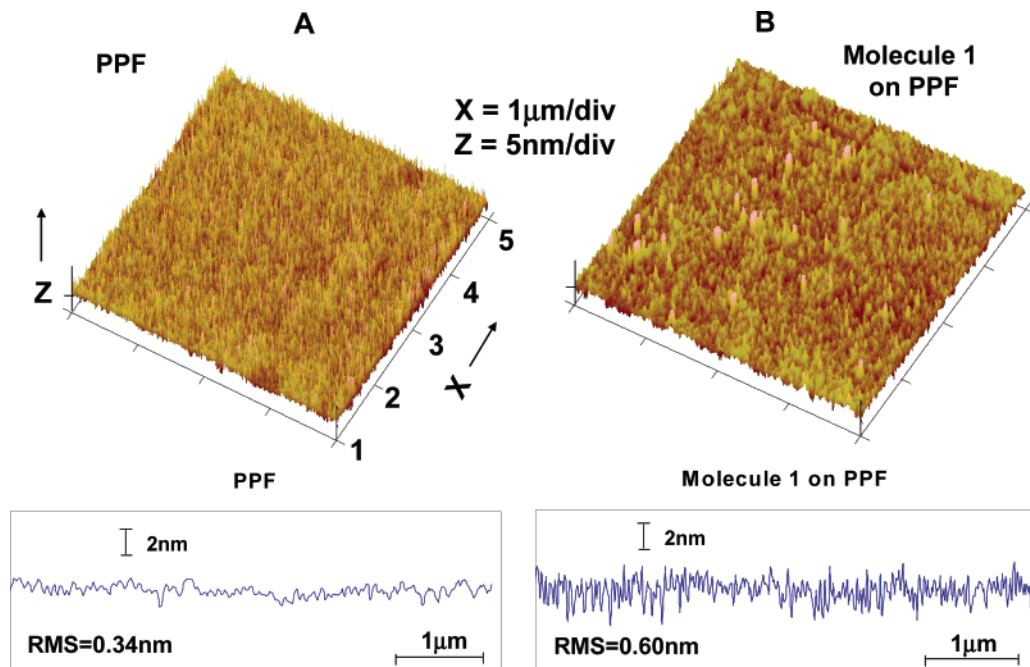
Figure 2. Typical AFM images of 5×5 μm areas of (A) PPF and (B) PPF modified with molecule **1**. The line scans illustrate rms roughness values of 0.34 nm for PPF and 0.60 nm for molecule **1** on PPF.

(Bioanalytical Systems, West Lafayette, IN). The surface coverage of the molecules was determined by integrating the charge under the first oxidation peak ($E_p \approx 0.5-0.6$ V) of a voltammogram of the modified surface in 1 M Bu$_4$NPF$_6$/PC with BAS software and then dividing this value by the area of the electrolyte drop in contact with the PPF ($\sim$0.008 cm^2). The temperatures reported below were those of the thermostated hot plate (Isotemp, Fisher), but a thermocouple positioned near the sample indicated that the sample temperature was approximately 70 °C lower than that of the hot plate during modification. The vial was inserted into a well cut in a 1 in. thick aluminum plate that was thermally equilibrated with the hot plate.

Reagents 1–3 were 1–2 mM in THF for modification, with the uncertainty of concentration caused by the very small amounts of porphyrin reagents available. Reagents 4 and 5 were applied as neat liquids. Prior to molecule introduction and subsequent heat treatment, the carbon film (PPF) was placed in a vial. The vial was sealed with a Teflon cap and purged with flowing Ar for 10 min through a syringe needle. A syringe containing the solution of the molecule under investigation was inserted through the Teflon cap and a drop of the solution placed onto the film. The solvent was then allowed to dry under a continued Ar purge. The vials were transferred to a hot plate at a preset temperature, and the film was heated under a continued Ar purge for a specified time. The hot plate temperatures investigated ranged from 175 to 480 °C and heating times ranged from 3 to 90 min. Vials were removed from the hot plate and allowed to reach room temperature under Ar purge. THF was twice syringed into the vials and the vials sonicated for 1 min to remove physisorbed alkene/alkyne molecules. The modified films were finally dried with a stream of Ar and removed from the vials for characterization.

AFM, X-ray Photoelectron Spectroscopy, and Vibrational Spectroscopy. Atomic force microscopy measurements were carried out in air with a Nanoscope IIIa Multimode instrument (Digital Instruments, Santa Barbara, CA). Rotated tapping mode etched silicon probes (RTESP), purchased from Veeco (Sunnyvale, CA) with resonant frequencies of $\sim$300 kHz were used for both contact and tapping mode AFM.

XPS analysis was performed with a Kratos Axis Ultra spectrometer equipped with a monochromatic Al Kα X-ray source. The base pressure of the analysis chamber was less than 1×10^{-9} Torr. Pass energies of 80 and 20 eV were used for survey and high-resolution spectra, respectively. A step energy of 0.1 eV was used for all acquisitions. Peak fitting and integration were performed using the software provided with the instrument.

All atomic ratios were calculated from the peak areas and were corrected for sensitivity factors using the Kratos software.

Raman spectra were collected in backscattered geometry with an incidence angle at the sample of 45°. An argon ion laser (514.5 nm) and high efficiency spectrograph (Kaiser Holospec, *f*/1.5) with holographic grating and back-thinned CCD (-110 °C) were used. Raman spectroscopy is capable of observing monolayers and submonolayers on surfaces,[13] but the sensitivity is a strong function of the cross section of the adsorbate.

FTIR spectra of the porphyrins in both solid and monolayer forms were collected at room temperature (Bruker Tensor 27 FTIR); in all cases the spectral resolution was 4 cm^{-1}. The spectra of the solid porphyrins were obtained in KBr pellets ($\sim$1–5 wt % porphyrin) using transmission mode and a room-temperature DTGS detector averaging over 32 scans. The IR spectra of the monolayers tethered to the graphitic surfaces were obtained using a Ge total reflection accessory (GATR; 65° incident angle, Harrick Scientific) and a liquid N$_2$-cooled MCT detector averaging over 256 scans. In this accessory, the carbon substrates are positioned in contact with the flat surface of a hemispherical Ge crystal that functions as the ATR optical element. All spectra of the monolayers were obtained using p-polarized radiation. The reader is referred to our previous publications for additional experimental details[2,34,46]

Results

The surfaces prepared by heating molecules **1**, **2**, and **3** on PPF as described above were examined using AFM, XPS, FTIR, and Raman spectroscopy. As noted in the Experimental Section, all samples were twice sonicated for 1 min in THF and then dried before surface analysis.

AFM. Figure 2 shows tapping mode AFM images of 5 μm $\times$ 5 μm areas of an unmodified PPF sample and a PPF sample modified with porphyrin **1**. Line profiles along a 5 μm line section of each of the images are also presented. These profiles illustrate the varying *z*-axis topography of each surface. The root-mean-square (rms) roughness along the lines was 0.34 and 0.60 nm for the unmodified and porphyrin **1**-modified PPF surfaces, respectively. The peak-to-valley maxima were 1.5 nm for unmodified PPF

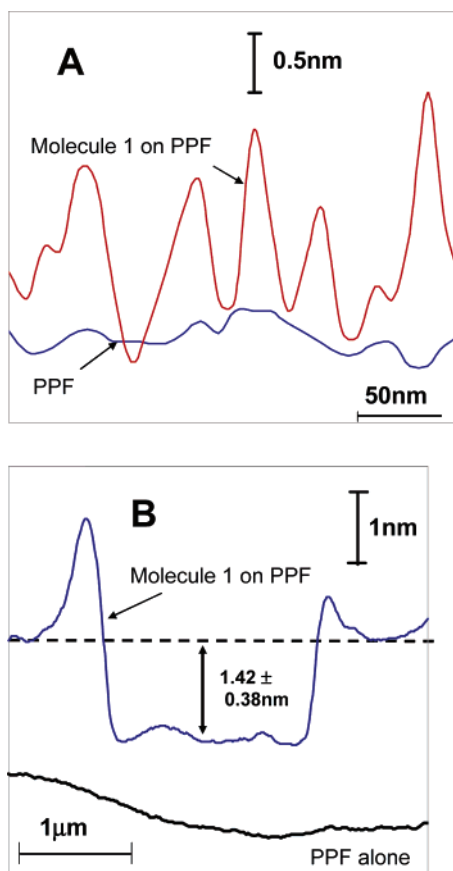(46) Yasseri, A.; Syomin, D.; Loewe, R.; Lindsey, J.; Zaera, F.; Bocian, D. *J. Am. Chem. Soc* **2004**, *126*, 15603.

Figure 3. Experimentally determined noncontact AFM line profiles. (A) Comparison between the line profiles of PPF and PPF modified with molecule **1** on a 250-nm scale. (B) Line profile through a scratch made in contact mode on PPF modified with molecule **1**. The lower trace shows a profile of a scratch made on unmodified PPF, offset vertically for clarity.
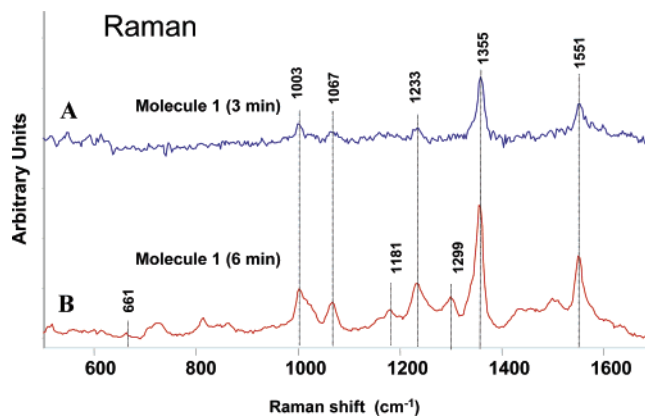

Figure 4. Raman spectra of molecule **1** on PPF after heat treatment for (A) 3 min and (B) 6 min. Spectra A and B were both obtained from samples heat-treated at 400 °C.

and 3.5 nm for the porphyrin-modified surface. Experimentally determined profiles of the surface of PPF modified with porphyrin **1** are shown in Figure 3. Figure 3A shows magnified line profiles of modified and unmodified PPF, showing a marked increase in the peak-to-peak variation of the two surfaces, corresponding to an increase in the rms of porphyrin **1**-modified PPF relative to that of unmodified but heat-treated PPF. Figure 3B shows a line profile through an intentional square "scratch" made on a porphyrin-modified surface in contact mode.[31] The height shown corresponds to an average of 10 line profiles collected across a 4 μm section of the porphyrin-modified PPF surface, which included the scratched section. A statistical procedure[31] that averaged many line profiles through the scratch yielded a depth of 1.42 ± 0.38 nm, corresponding to the average height of the porphyrin layer resulting from modification of PPF with molecule **1**. The distance between the opposite, outermost hydrogen atoms in molecule **1** is ~2 nm,[47] so the observed layer thickness is consistent with monolayer coverage of the PPF by a porphyrin having a tilted orientation with respect to the surface. This molecular tilt was confirmed by FTIR studies described below.

Raman and Infrared Spectroscopy. Surface Raman spectra obtained from PPF modified with molecule **1** are shown in Figure 4. The spectrum of unmodified PPF, which includes the sp[2] carbon "D" band (1360 cm^{-1}) and "G" band (1600 cm^{-1}), was subtracted from the raw spectra

before plotting in Figure 4. Prolonged heating of alkyne and alkyne reagents can lead to their polymerization,[48] so two heating times were used to test for multilayer formation. The Raman spectrum for a sample heated for 3 min (Figure 4A) corresponds closely to that of a Zn(II) porphyrin monomer reported by Jeong et al.[49,50] Heating for 6 min during modification yielded the spectrum of Figure 4B, which is significantly more intense than that of Figure 4A. Jeong et al. reported that porphyrin dimers show additional strong bands at 1292, 1179, and 656–677 cm^{-1}. Weak bands at these frequencies were observed for the 6-min heating time, implying that some porphyrin dimerization has occurred. The absence of these bands in the spectrum of the 3-min sample is indirect evidence for the absence of dimerization under the milder conditions. Peak frequencies and assignments for the Raman spectra of Figure 4 are listed in Table 1, using assignments from the literature.

Surface infrared spectra obtained for molecule **1** chemisorbed to PPF are shown in Figure 5, along with a spectrum of solid molecule **1** in a KBr pellet. PPF has weak IR absorptions at ~870 and ~1580 cm^{-1}, and the spectrum of unmodified PPF was subtracted before plotting the spectra of the porphyrins on PPF. Most of the IR bands observed for molecule **1** in KBr are clearly evident in the surface-bound molecule, indicating that the porphyrin ring structure is intact after surface modification. Figure 6 shows the ethyne C–C stretch at 2110 cm^{-1} in the parent molecule, which decreases from 0.003 absorbance units in molecule **1** in KBr to a negligible level (<0.0005 units) for the PPF-bound molecule. This observation indicates complete reaction of the ethyne group upon surface modification, and the lack of any detectable physisorbed porphyrin reactant. In attempts to determine the nature of the reaction of the alkyne with the surface, additional FTIR studies were conducted with an analogue of molecule **1** wherein both carbons in the alkyne were ^{13}C labeled. However, no bands could be identified that could be definitively attributed to the linker group.

The IR modes and assignments for molecule **1** are included in Table 1. The bands of particular importance are the out-of-plane C–H bend near 797 cm^{-1} and the in-plane pyrrole deformation at 997 cm^{-1}. The relative

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Table 1. Raman and IR Peak Frequencies for Zn(II) Porphyrin

| Raman, Zn(II) porphyrin | | Raman, 1 on PPF | | | |
monomer[a]	dimer/polymer[a]	3 min HT[b]	6 min HT[b]	IR, 1 on PPF:3 min HT[c]	assignment[d]
	656		661 ± 1.1		C−C ring bend
738			725 ± 3.3	725 ± 7.3	pyrrole deformation
				797 ± 2.0	out of plane C−H bend
1003	1009	1003 ± 1.3	1003 ± 3.9	997 ± 3.9	pyrrole breathing
1064	1076	1067 ± 2.2	1067 ± 2.2	1061 ± 1.5	C−H bend
	1179		1181 ± 4.9		C−H bend
1205		1236 ± 2.8	1233 ± 2.0	1203 ± 1.0	C−C ring stretch
	1292		1299 ± 2.5		C−C, CN stretch
1324				1334 ± 1.0	pyrrole quarter-ring breathing
	1353	1355 ± 0.6	1355 ± 1.0	1374 ± 1.0	pyrrole half-ring stretch
1354					C−C, CN stretch
				1457 ± 10.5	C−C stretch
1544	1546	1551 ± 3.4	1551 ± 3.3		C−C ring stretch

[a] Adapted from ref 49. [b] Mean ± standard deviation for seven samples, unless otherwise noted. [c] Mean ± standard deviation for four samples. [d] From refs 49 and 68.
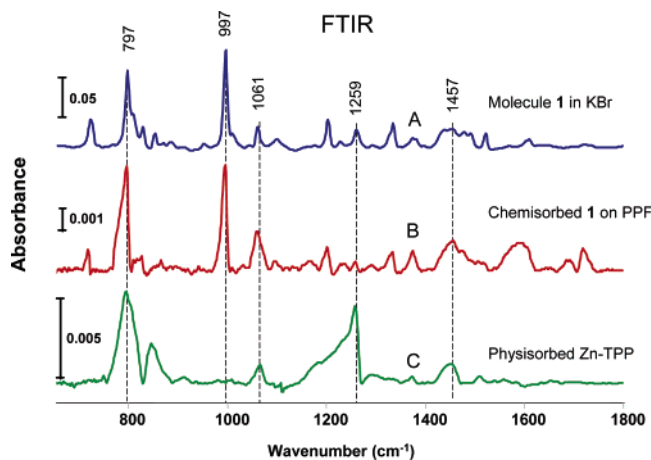

Figure 5. FTIR spectra of solid molecule **1** in a KBr pellet (A), the corresponding chemisorbed monolayer on PPF (B), and physisorbed ZnTPP on PPF (C).
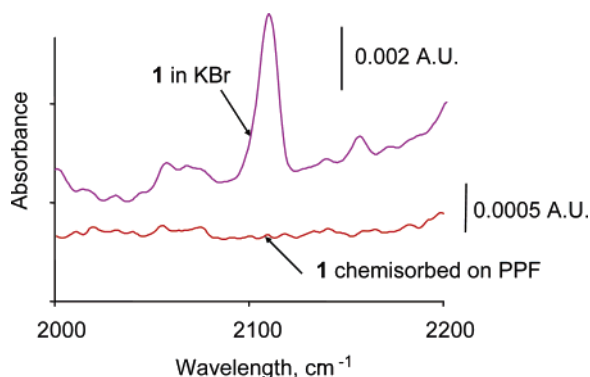

Figure 6. FTIR spectra of solid **1** in KBr and a chemisorbed monolayer of molecule **1** on PPF near 2100 cm^{-1} showing the loss of the ethyne vibrational mode at 2110 cm^{-1}

intensities of these two modes depend on the orientation of the porphyrin plane relative to the direction of the electric field vector of the p-polarized incident radiation, because the two modes have orthogonal dipole derivative vectors. For molecule **1** bonded to PPF, both the in-plane (997 cm^{-1}) and out-of-plane (797 cm^{-1}) vibrations are observed, indicating that the porphyrin ring is tilted with respect to the surface normal. The relative intensities of the in-plane and out-of-plane porphyrin vibrational modes can be employed to determine the average tilt angle (α) of the porphyrin with respect to the surface normal using standard methods.[51−55] A detailed discussion of the assumptions made to extract the average tilt angle can
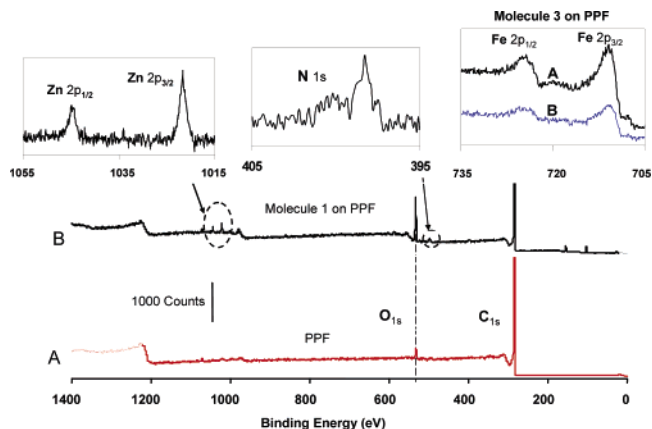

Figure 7. Survey XPS spectra of PPF (A) and PPF modified with molecule **1** (B). High-resolution scans of the Zn 2p$_{3/2}$ and N$_{1s}$ regions for PPF modified with molecule **1**. Inset at top right: high-resolution spectra of PPF modified with molecule 3 before (A) and after (B) treatment with mild acid.

be found in our previous publications.[2,46] The average tilt angle extracted from the spectral data from four different monolayers of molecule **1** was α = 37.4 ± 2.2° relative to the surface normal. Similarly, eight determinations of tilt angle on three separate samples of PPF modified with molecule **2** yielded α = 45.2 ± 0.7°. In addition, we note that, in the IR spectra of physisorbed ZnTPP (Figure 5C), the out-of-plane deformation (797 cm^{-1}) is quite intense, whereas the in-plane mode (997 cm^{-1}) is extremely weak, consistent with these molecules (that lack the linker group) lying flat on the carbon surface.

Photoelectron Spectroscopy. Representative XPS spectra of bare and modified PPF surfaces are shown in Figure 7. A survey spectrum for unmodified PPF (spectrum 7A) shows significant bands for only carbon and oxygen, with a surface oxygen coverage of 3.2 atom %. Exposure to THF and heat treatment increases oxygen coverage to 7.4%, as indicated in Table 2. Spectrum 7B is a survey spectrum of a PPF surface modified with molecule **1**, with insets showing high-resolution scans of the Zn$_{2p}$ and N$_{1s}$ regions. Porphyrin modification of the carbon surface is

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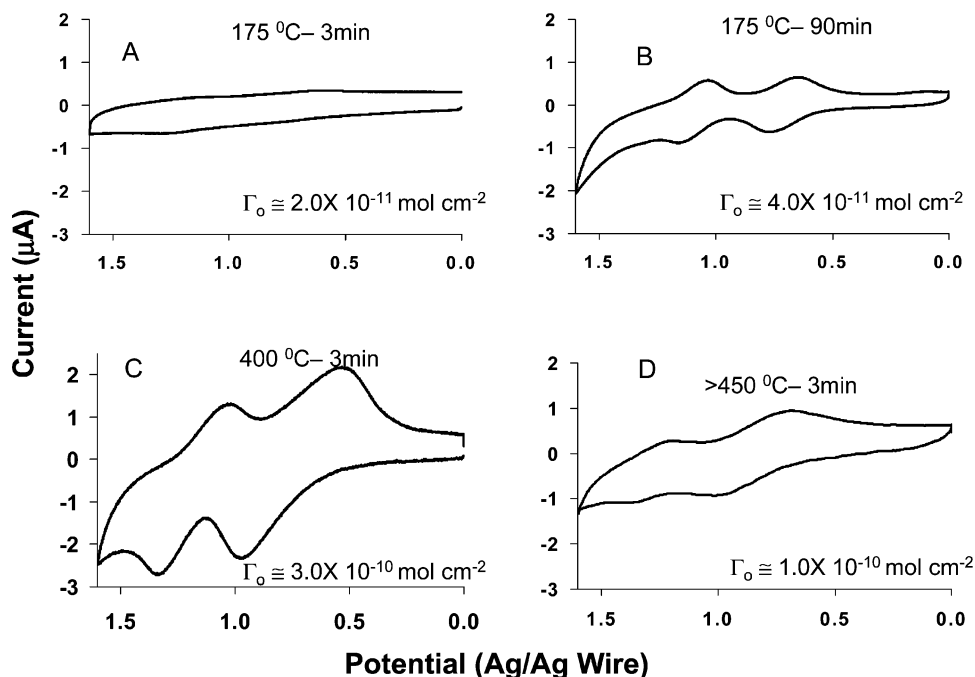(55) Zaera, F. *Int. Rev. Phys. Chem.* **2002**, *21*, 433.

Figure 8. Voltammograms $(1\,\text{V s}^{-1})$ of PPF modified with molecule **1** at various hot plate temperatures and heat treatment times. Porphyrin surface coverage was calculated from the integrated area of $E^{+1/0}$ cathodic wave, using an area of $0.008\,\text{cm}^2$. Potentials are all relative to a Ag/Ag$^+$ wire pseudoreference electrode.

Table 2. Surface Atomic Coverages from High-Resolution XPS Spectra

	%C	%O	%N	%Zn	%Fe	%F	%Cl
PPF (as prepared)	96.8	3.2					
PPF (heat-treated)[a]	92.6	7.4					
1	80.9	16.5	2.1	0.5			
2	80.3	17.5	1.8	0.4			
3	72.7	19.5			7.6		
3 (treated with H$^+$)	75.5	18.1			6.4		
4	75.6	12.6				11.8	
4 (treated with OH$^-$)	81.8	7.1				11.1	
5	81.3	17.4					1.3
5 (treated with OH$^-$)	80.1	18.5					1.3

[a] Heat-treated with same procedure as remaining samples, but without alkyne or alkene reactant.

indicated by the appearance of bands from the porphyrin molecule, Zn, and N, with a Zn/N atomic ratio of 0.24. In particular, porphyrin Zn $2p_{3/2}$ and N$_{1s}$ XPS signals are observed in all cases at $\sim$1022 and $\sim$399 eV, respectively.[56–59] The top right inset of Figure 7 shows a spectrum of PPF modified with the ferrocene-ethyne **3**. Although the binding energies of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ (711 and 725 eV, respectively) electrons were approximately 1.5–3 eV higher than those reported for free ferrocene,[60] the XPS results indicate that Fe was bound to the PPF surface, presumably by a process similar to that observed for molecule **1**.

The results of quantitative analysis of high-resolution spectra from various alkyne- and alkene-modified PPF surfaces are listed in Table 2. PPF surfaces modified with molecules **1**–**5** exhibited relatively consistent increases
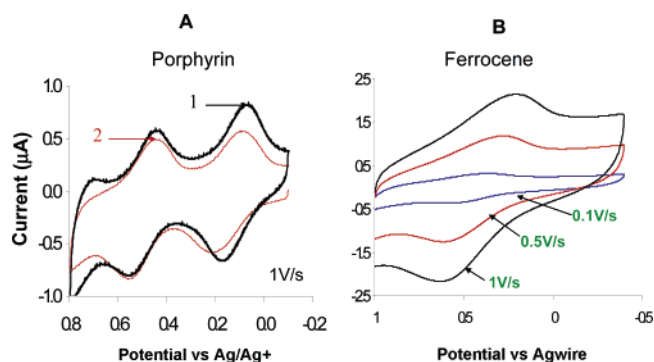
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Figure 9. Overlaid voltammograms $(1\,\text{V s}^{-1})$ of molecule **1** and **2** (A) and molecule **3** (B) bonded to PPF.

in oxygen coverage over that observed with a "blank" heat treatment with THF only. The reason for this substantial increase in oxygen coverage upon surface modification is currently unknown. The Fe-, Cl-, and F-containing reagents all yielded XPS bands for their respective elements following modification of the PPF surface. Neither sonication nor treatment with 1 M acid or base caused significant decreases in the coverage of the surface layers derived from molecules **3**–**5**, as shown in Table 2. This observation implies covalent attachment of the alkene and alkyne molecules to the PPF surface, which is stable in mild acid or base. The porphyrin-modified surfaces were not treated with acid or base, since they are unstable in aqueous conditions.

Voltammetry. Representative cyclic voltammograms of porphyrins **1** and **2** and molecule **3** bonded to PPF (TBAPF$_6$/PC electrolyte) are shown in Figures 8 and 9. The two waves observed for porphyrins **1** and **2** correspond to two one-electron oxidations, similar to that observed for porphyrins bonded to silicon or gold.[3,34,45,46,61] The voltammograms exhibited robust, quasireversible redox behavior stable for a large number of voltammetric cycles ($>$100). At least some of the peak separation apparent in Figures 8 and 9 is due to the ohmic potential losses in the PPF, combined with the relatively large electrode area

compared to past experiments. The redox activity of bound molecules provided a convenient means to monitor the stability and coverage of both the porphyrin and ferrocene groups on the PPF surface and was used to optimize attachment conditions.

The heat treatment and attachment procedure reported previously for Si(100)[2,3,34,42,45] was modified with respect to time and temperature for use with PPF. Voltammetry obtained for molecule **1** with varying heat treatment conditions are shown in Figure 8 and exhibited the following general trends: (1) the surface coverage of porphyrin increased monotonically with an increase in the treatment temperature up to 400 °C. For example, Figure 8A,C illustrates that increasing the treatment temperature from 175 to 400 °C for a heat treatment time of 3 min increased the surface coverage from 2×10^{-11} to 3×10^{-10} mol/cm^2. At temperatures significantly above 400 °C (Figure 8D), the coverage began to decrease and the voltammetric waves changed shape. (2) At temperatures less than 200 °C, an increase in the heating time led to a corresponding increase in the surface coverage of the porphyrin, evident through comparison of parts A and B of Figure 8. At 175 °C, increasing the heat treatment time from 3 to 90 min doubled the surface coverage of the porphyrin. Of the conditions examined, the highest coverage occurred when molecules **1** and **2** were heated on PPF at 400 °C for 3 min. Therefore, surface modification was carried out with a hot plate temperature of 400 °C for 3 min, corresponding to a sample temperature of ~330 °C.

A second set of cyclic voltammograms of PPF surfaces modified with porphyrins **1** and **2** and ferrocene **3** are shown in Figure 9. Figure 9A presents a comparison of porphyrin **1** and **2** on PPF at a scan rate of 1 V s^{-1}, while Figure 9B shows the voltammetry of a ferrocene-modified PPF surface at various scan rates. Note that a different reference electrode was used for Figure 9A (Ag/Ag$^+$) than for Figure 8 (Ag/wire), leading to the shift in porphyrin peak potentials.

Discussion

The results establish that heat treatment of alkyne derivatives on an sp^2-hybridized carbon surface forms a strongly bonded molecular layer that withstands sonication in organic solvents and/or prolonged treatment with mild aqueous acid or base. Porphyrin and ferrocene retain their redox activity when bonded to PPF for many voltammetric cycles. From the integrated areas of voltammetric peaks such as those shown in Figure 9A, the porphyrin coverage resulting from PPF modification with molecule **1** is between 9×10^{-11} and 1.5×10^{-10} mol/cm^2, which is somewhat larger than the surface coverage of $(6.2-9.7) \times 10^{-11}$ mol/cm^2 obtainable on silicon substrates.[2,34,46] We also note that the surface coverages of molecule **1** on both the carbon and silicon substrates are indicative of much less tightly packed monolayers than can be obtained in Langmuir–Blodgett films, wherein packing densities of ~3.3×10^{-10} mol/cm^2 are obtainable.[62] On the basis of the XPS results for three aromatic and one aliphatic alkyne with various substituents, the attachment method appears quite general for alkyne reagents with substituents that survive the heat treatment. Of particular note is the applicability to an alkyne with an aliphatic

substituent, as this possibility is not directly available with the diazonium reagents commonly used for carbon surface modification. Aliphatic diazonium reagents are unstable, and to date only aromatic diazonium reagents have been used for carbon surface modification. Furthermore, many alkyne reagents are available commercially with a wider range of structures than those available as diazonium reagents or their aromatic amine precursors. Although only one example of an alkene modifier was examined here, the similarity to the alkyne equivalent apparent in Figure 9 implies that thermal treatment of alkenes is also an effective route for bonding to carbon surfaces. It is reasonable to conclude that both diazonium and alkyne/alkene modifications of carbon surfaces have significant merit and in many ways are complementary.

The similarity of the surface Raman and IR spectra shown in Figures 4 and 5 to those of the isolated molecules provides strong evidence that the porphyrin ring system survives thermal treatment and covalent bonding to the PPF surface. The observed angle of the porphyrin relative to the surface normal is an average and does not provide information about the polar angle around the surface normal and the rotation around the main molecular axis with respect to the surface plane. In other words, no conclusions about packing or rotational disorder can be extracted. While the angle of 37° may indeed represent a useful average, the molecules are likely to be randomly rotated about the surface/porphyrin bond, and two-dimensional ordering on the surface seems unlikely. Since the PPF surface is itself quite disordered, we would expect randomly distributed porphyrin molecules across the surface, but with a common "tilt" angle. A 2.0 nm long molecule tilted 37° from the surface normal would yield a monolayer thickness of about 1.6 nm, which is generally consistent with the 1.4 nm monolayer thickness observed with AFM (Figure 3).

Several methods for forming a covalent bond to a carbon surface have been described, including the oxidation of primary and secondary amines, reduction of aryl diazonium cations, nucleophilic attack by amines, oxidation of aryl acetates, and oxidation in the presence of alcohols.[28,63,64] The melting points of molecules **1** (245 °C), **2** (430 °C),[42] and **3–5** (<100 °C) imply that the reagents are liquids or gases during surface bonding. However, all the reagents are adsorbed to the PPF, possibly strongly, so it is not clear in which phase the alkyne or alkene reacts with the surface. The literature provides some guidance regarding the mechanism of alkyne or alkene attachment to sp^2-hybridized surfaces. Mazur et al. reported that surface carbon radicals were formed by heat treatment of carbon surfaces under vacuum.[65] Since the attachment scheme in this report involves similar conditions, formation of surface carbon radicals under heat treatment could be followed by radical attack of the alkyne and alkene linkers of the reagent molecules, propagating several abstraction reactions in which covalent bonds would be formed between a molecule and the carbon surface. It is also possible that trapped radicals in the PPF surface might initiate a reaction with the alkyne or alkene. Alternatively, Wang et al.[66] and Roucoules et al.[67] have

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described the heat treatment of conjugated dienes on diamond and alkene-functionalized films under various conditions. They conclude that modification of these carbon surfaces occurs via Diels−Alder [4 + 2]- and [2 + 2]-cycloaddition reactions. These findings are consistent with the fact that these types of covalent attachment schemes have been observed on other group IV semiconducting surfaces such as silicon (100) and germanium (100).[1] From the current results, it is not yet possible to deduce the precise geometry and bonding of the linkage between the disordered carbon surface and the attached molecule. Nevertheless, several possibilities are shown schematically in Figure 10, based on Diels−Alder and cycloaddition reactions. Considering that the PPF surface is structurally disordered, it is surprising that the average tilt angles show quite narrow distributions (standard deviations of 0.7−2.3°). These narrow ranges presumably result from the very flat PPF surface (rms roughness < 0.5 nm) and imply that there is an abundance of binding sites available to the alkyne or alkene modifier. The difference in average tilt angle between the porphyrins derived from alkyne (37°) and alkene (45°) is statistically significant to >99.9% confidence, implying a difference in binding to the surface. One possibility is a difference in unsaturation, as illustrated in Figure 10. For either [2 + 2]- or [4 + 2]-addition reactions of an alkyne, the alkyne carbons become a double bond on the PPF surface, whereas the alkene **2** would be expected to yield a saturated C−C single bond. In the latter case, the tilt angle should be larger, as observed experimentally for the surface-bound porphyrin formed from the alkene **2**. While a difference in saturation of the bonded product is a plausible explanation for the difference in tilt angle, it could not be confirmed with direct observation of the vibrations of the surface bond,

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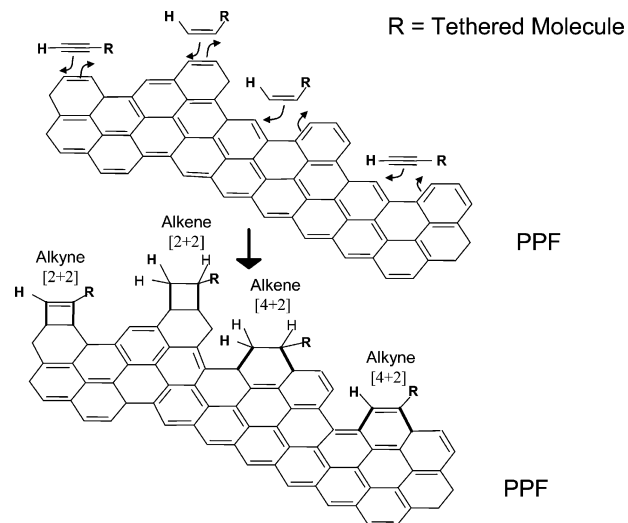

Figure 10. Likely products of [2 + 2]- and [4 + 2]-cycloaddition reactions of alkenes and alkynes on PPF. Distribution of hydrogen atoms and unsatisfied valences before and after the reaction may vary significantly depending on starting conditions, and only one possibility is shown.

due to the difficulty of distinguishing the PPF vibrationsfrom those of the bonded molecule.