

Direct Covalent Grafting of Conjugated Molecules onto Si, GaAs, and Pd Surfaces from Aryldiazonium Salts

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Abstract: Using aryldiazonium salts that are air-stable and easily synthesized, we describe here a one-step, room-temperature route to direct covalent bonds between π -conjugated organic molecules on three material surfaces: Si, GaAs, and Pd. The Si can be in the form of single crystal Si including heavily doped p-type Si, intrinsic Si, heavily doped n-type Si, on Si(111) and Si(100), and on n-type polycrystalline Si. The formation of the aryl-metal or aryl-semiconductor bond attachments was confirmed by corroborating evidence from ellipsometry, reflectance FTIR, XPS, cyclic voltammetry, and AFM analyses of the surface-grafted monolayers. A data-encompassing explanation for the mechanism suggests a diazonium activation by reduction at the open circuit potential, with aryl radical secondary products bonding to the surface. The synthetic details are included for preparing the surface-grafted monolayers and the precursor diazonium salts. This spontaneous diazonium activation reaction offers an attractive route to highly passivating, robust monolayers and multilayers on many surfaces that allow for strong bonds between carbon and surface atoms with molecular species that are near perpendicular to the surface.

Introduction

Recent advances in “wet” surface chemistry offer an increasingly sophisticated range of techniques for self-orienting molecular chemisorption on a wide variety of materials.^{1–3} These new techniques expand the broad, general applicability of synthetic chemistry to the heterogeneous phase and improve the prospects of future “bottom-up” fabrication strategies in nanotechnology. Specifically, work related to the construction of post-CMOS hybrid electronic devices using chemical techniques and molecular components^{4–6} to augment traditional fabrication schemes will require more control at the molecule/contact interfaces. In many experimental molecular electronic systems, molecules assembled between bulk metallic electrodes have chemical contacts that are highly polar, such as the sulfur-metal bond. This allows for undesired interfacial capacitance, possible electrochemical activity at the bond interface, and generally causes the molecule in the electrode gap to behave as a tunneling barrier.⁴ If we are to take further advantage of the electronic properties of various chemical substituents on

these molecular devices, a less polar, more electronically continuous chemical interface must be identified.⁷ A direct covalent bond, allowing stronger electronic coupling between the energy bands of a bulk contact and the frontier orbitals of a conjugated organic molecule, may allow for a greater deal of synthetic variation in device properties and make contact effects less dominant.⁸ Using aryldiazonium salts that are air-stable and easily synthesized, we describe here a one-step, room-temperature route to direct covalent bonds between fully conjugated organic molecules and three technologically important material surfaces: Si, GaAs, and Pd.

The covalent surface chemistry of organic diazonium salts has been known for some time on electrode surfaces. In the best understood reactions, a diazonium salt in solution with an electrolyte such as tetrabutylammonium cation is reduced with an externally applied potential, typically at around -1 V versus saturated calomel electrode (SCE), for reaction times of no more than a few minutes. The aryl radical intermediates that are locally formed rapidly react with the surface of the cathode. Electrochemical grafting of aryl groups onto carbon,⁹ silicon,¹⁰

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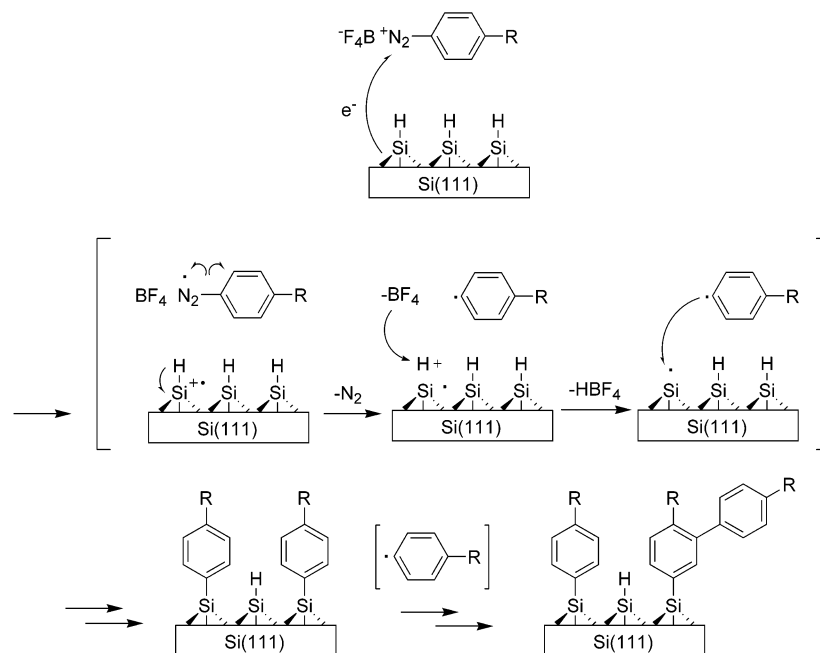
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Scheme 1. Example of Spontaneous Diazonium Activation by a Hydrogen-Passivated Si(111) Surface^a

^a An electron transfer from the surface at the OCP generates a diazenyl radical, and then an aryl radical upon loss of N₂. The complementary oxidative process generates a proton which eliminates as HBF₄. The radical generation process results in side products such as reduced aromatics (by aryl radical attack of the Si–H surface) and the formation of covalently bound multilayers. FTIR evidence shows the loss of an average of 65% of the surface hydride residues in the process of aryl radical generation. The multilayer formation can be retarded by the addition of BHT in situ, which may intercept the excess aryl radicals before they can attack the nascent monolayer.

and iron¹¹ electrode surfaces from diazonium salt precursors has been demonstrated previously by this kind of heterogeneous phase reduction.¹² The grafting of similar groups onto carbon,^{13–15} carbon nanotube,^{16,17} and metallic surfaces^{18,19} has also been carried out without electrochemical induction, using ancillary reagents. We now report the activation of aryldiazonium salts²⁰ alone, in the absence of an externally applied potential, or exogenous reductant species, to assemble covalently bound conjugated monolayers on hydride-passivated Si, GaAs, and Pd surfaces. This chemistry has the ability to be applied to samples where electrochemical means of surface activation are either unwieldy or impossible, such as isolated, highly nonplanar, or low-conductive substrates. Similar reactions might be possible on many other surfaces and materials that have not yet been studied, including many which have no known covalent attachment chemistry with organic molecules.

Results and Discussion

A tentative mechanism for the spontaneous heterogeneous activation of diazonium salts is tested and reconciled with our

experimental evidence. While specific details with regard to this mechanism may differ from surface to surface, or remain obscure, centrally we can propose a scheme in which the diazonium salts are activated at the surface in the absence of an externally applied potential, quickly forming a reactive intermediate, followed by surface attachment. This is most likely carried out by spontaneous electron transfer at the open circuit potential (OCP) of the substrate material in solution, which leads to the local generation of aryl radicals by loss of N₂,²¹ some diffusion of these radicals within the solution, and ultimately the formation of irreversible surface–molecule bonds (Scheme 1).

Silicon hydride-passivated surfaces are known to activate metal salts²² and dioxygen²³ in solution, undergoing OCP reduction at the Si(111):H electrode surface. This activation is also considered to be a corrosion potential, as there is a concomitant oxidation of the silicon surface in concert with the reduction. Yet, this technique diminishes incorporation of oxygen into the surface structure (in the form of SiO₂ for Si, or Ga₂O₃ and As₂O₃ for GaAs) and nonisolated contaminants such as HBF₄. This lack of contamination of the interface is corroborated by X-ray photoelectron spectroscopy (XPS) and by atomic force microscopy (AFM) studies which show that surface roughening²⁴ is minimal (vide infra). The required complementary reverse electron transfer for the diazonium activation at OCP has not been identified, but possibilities include backside surface decomposition and the presence of trace redox species in solution.

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Table 1. Calculated and Observed Layer Thicknesses (in nm) for Diazonium-Reacted Surfaces for Three Different Chemisorbates I, III, and III^a

	I	II	III
calculated length without surface bond	1.1	1.8	1.1
n ²⁺ -Si(111):H	1.3 ± 0.3	2.1 ± 0.5	1.4 ± 0.2
1 h			
n ²⁺ -Si(111):H	2.5 ± 0.5	3.1 ± 0.8	2.1 ± 0.4
6 h			
n ²⁺ -Si(111):H	1.8 ± 0.1	2.2 ± 0.2	1.9 ± 0.2
6 h with 0.01 M BHT			
GaAs(100)	1.0 ± 0.2	1.7 ± 0.3	0.9 ± 0.2
1 h			
GaAs(100)	2.8 ± 0.4	3.0 ± 0.9	2.5 ± 0.7
6 h			
GaAs(100)	1.8 ± 0.2	2.9 ± 0.2	1.9 ± 0.2
6 h with 0.01 M BHT			
Pd	1.4 ± 0.4	2.2 ± 0.3	1.4 ± 0.3
1 h			
Pd	2.1 ± 0.4	3.3 ± 0.7	2.3 ± 0.7
6 h			
Pd	1.5 ± 0.1	2.2 ± 0.1	1.8 ± 0.2
6 h with 0.01 M BHT			

^a Calculated length values are from Alchemy III software and do not include the organometallic bond length. All experimental values given are the average of three identically prepared samples for reactions of 0.5 mM solutions of diazonium salts in CH₃CN, reacted in the dark inside an inert atmosphere glovebox for the indicated time period. A monolayer of the chemisorbates tends to form within 1 h, followed by multilayer formation over extended time periods. Generally, the most defect-free layers were formed after a reaction time of 1 h, based on CV measurements. The presence of 0.01 M BHT in situ improves the layer quality by retarding the formation of multilayers over extended periods but does not prevent the reaction from occurring entirely.

Because the presence of an inert passivating layer, such as the native oxide of Si or GaAs, prevents any stable layers from forming, the native oxides must be removed by fluoride or ammonium hydroxide to see any reaction. This implies that a chemically reactive surface plays a part in the activation or bond-forming mechanism. Moreover, the reaction shows sensitivity to the presence of a radical scavenger like butylated hydroxytoluene (BHT), added in small amounts (ca. 0.1 mM), which retards the formation of organic multilayers but does not prevent the reaction from occurring (Table 1). A high-quality monolayer of the chemisorbates tends to be complete within 2 h under nitrogen atmosphere, according to ellipsometry and cyclic voltammetry (CV). The observed ellipsometric thickness for the monolayer corresponds to a near-vertical single molecular length. In light of these results regarding the BHT retarding-effect, it is implied that the multilayer formation on Si, Pd, and GaAs surfaces is radical-mediated.

For the assembly procedure, a cleaned surface is exposed to a solution of the diazonium salt (I–VI) in anhydrous acetonitrile (CH₃CN), in the dark, over a period of 2 h under an inert atmosphere. The presence of atmospheric oxygen seems to promote the formation of disordered multilayers, which have been observed in the electrochemical reactions as well.²⁵ Pd samples are freshly sputtered and used without further treatment, and GaAs samples are chemically cleaned^{26,27} with concentrated NH₄OH, which results in a metastable, stoichiometric surface

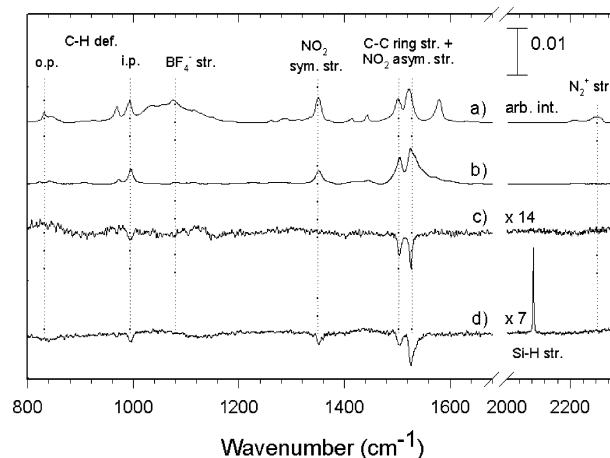
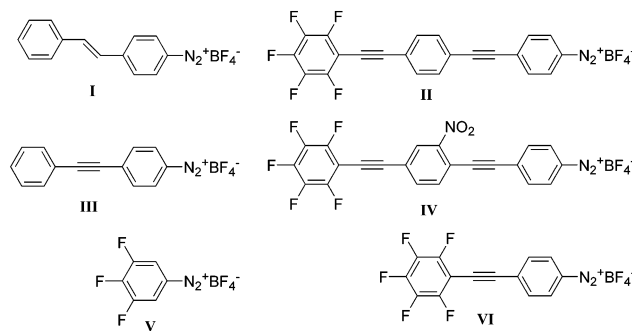


Figure 1. Reflectance FTIR spectra of ultrathin layers on 2'' wafers: (a) compound IV (KBr pellet), (b) polycrystalline Pd wafer reacted with IV, (c) n-type GaAs(100) wafer reacted with IV, (d) n²⁺-type Si(111):H wafer reacted with IV. The spectra show a selective enhancement of vibrational modes based on molecular orientation. In Figure 1c, molecules attached to GaAs(100) show less enhancement of the $\nu_s(\text{NO}_2)$ mode, most likely because of a slight tilt with respect to the surface. All surface samples were checked by ellipsometry for monolayer thickness (2 ± 0.2 nm on Si(111):H and Pd, around 1.7 nm on GaAs(100)).

that is free of As or Ga oxides. The reaction with diazonium salts has been successfully carried out on a wide range of oxide-free hydride-passivated²⁸ silicon surfaces: single crystal Si including doped p-type Si, intrinsic Si, heavily doped n-type Si, Si(111) and Si(100), and on n-type polycrystalline Si.



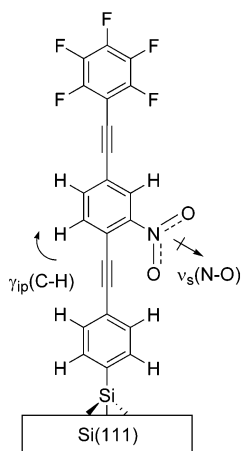
To analyze the samples by Fourier transform infrared spectroscopy (FTIR), a grazing angle experiment was used with heavily doped Si and GaAs wafers and sputtered polycrystalline Pd on Si wafers. The FTIR spectra in Figure 1b–d show structural features related to the organic chemisorbate IV and provide qualitative information about its alignment with respect to the surface. IR reflectance spectra with p-polarized light at angles of incidence greater than Brewster's angle on dielectric surfaces, such as Si and GaAs (Figure 1c and d), yield negative absorbance peaks and vibrational modes with components perpendicular to the substrate surface.²⁹ As compared to the structurally isotropic KBr pellet spectrum of the diazonium salt IV (Figure 1a), the monolayer spectra (Figure 1b–d) are dominated by vibrational modes with components perpendicular to the sample surface.

Qualitatively, this indicates the molecules adopt a more upright orientation rather than lying down with the molecular

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backbone parallel to the substrate surface. The most prominent features are the in-plane ring breathing $\nu(\text{C}=\text{C})$ modes at around 1525 and 1503 cm^{-1} , the antisymmetric NO_2 stretch $\nu_{\text{as}}(\text{NO}_2)$ mode at 1518 cm^{-1} (partially obscured by the ring breathing mode at 1525 cm^{-1}), the symmetric NO_2 stretch $\nu_{\text{s}}(\text{NO}_2)$ mode at 1351 cm^{-1} , and an in-plane aromatic C–H deformation $\gamma_{\text{ip}}(\text{C}-\text{H})$ mode at 995 cm^{-1} , which are seen in FTIR spectra of all three substrates; the strong breathing mode near 1600 cm^{-1} and an out-of-plane aromatic C–H deformation $\gamma_{\text{op}}(\text{C}-\text{H})$ mode at 825 cm^{-1} are present only in very weak intensity. The notable absence of vibrational features related to the diazonium tetrafluoroborate moiety on any of the samples, such as the $\nu(\text{N}\equiv\text{N}^+)$ peak near 2280 cm^{-1} and the strong and broad $\nu(\text{BF}_4)$ mode expected at around 1050 cm^{-1} (Figure 1a), suggests that it is no longer associated with the molecular layer. In Figure 1d, the spectrum for the assembly of **IV** on $\text{Si}(111):\text{H}$, loss of surface hydride residues is evident in a upward sharp $\nu(\text{Si}-\text{H})$ stretching peak at 2080 cm^{-1} . The peak is inverted as compared to the molecular signatures because a freshly hydride-terminated $\text{Si}(111)$ wafer is used as the reference sample. No silicon oxide signal is seen in the spectrum; if present, a large $\nu(\text{SiO}_x)$ peak around 1050 cm^{-1} and an oxide-back-bonded $\nu(\text{O}_x\text{Si}-\text{H})$ stretching peak at around 2220 cm^{-1} would be visible. Comparison of the Si stretching regions of $\text{Si}(111):\text{H}$ samples before and after reaction shows an average 65% net consumption of the surface hydride, indicating a maximal surface coverage on the part of the phenyl groups.^{10c} The hydride groups are possibly lost during the grafting reaction by aryl radical abstraction (leading to soluble side products) or by elimination as HBF_4 . In either case, it is direct proof that the activation of the diazonium salt and the subsequent formation of organic layers on the silicon surface cause chemical changes at the Si–H level of the $\text{Si}(111):\text{H}$ surface without incurring direct oxidation.

Oxide-free organic functionalization of the Si surface is corroborated by XPS. A $\text{Si}(111)$ sample reacted with **II** shows two peaks in the C 1s region, the smaller of the two being from the fluorocarbon terminus appearing at higher binding energy (Figure 2a), and a single peak in the F 1s region around 688.3 eV (see Supporting Information) corresponding to the pentafluorophenyl terminus. Clearly, the absence of the BF_4^- counterion which composes part of the diazonium salt (typically appearing at about 686.5 eV) is evidenced. There is no N 1s signal for $-\text{N}_2^+$ (approximately 403.8 eV) in any of the spectra, indicating that the diazonium moiety has been lost, although assemblies of **IV** on all surfaces showed a clear signal for the

$-\text{NO}_2$ group at 406.0 eV . The Pd 3d region and Si 2p regions (Figure 2b) of the XPS spectra indicate no oxide present in Pd or Si samples, respectively. For GaAs samples, the As 3d region sometimes shows a small amount of As^{III} oxide. If the samples are prepared in O_2 -containing atmospheres, the degree of oxidation in Si and GaAs samples increases slightly. Samples prepared with nonfluorinated diazonium salt **III** show only one signal in the C 1s region and no signal in the F 1s region (see Supporting Information).

Cyclic voltammetry (CV) analysis gives evidence of considerable physical passivation against ion currents on the Si and Pd surfaces reacted with **II** (Figure 3a and b). Our n-type GaAs samples showed passivation for only a few sweeps. The currents for the Pd and Si samples are both relatively potential-insensitive against the $\text{Fe}(\text{CN})_6^{3-/4-}$ couple, implying an overall low concentration of defects and pinholes in the films. For the GaAs samples, the putative Ga–C or As–C bond may not be chemically stable enough to allow good passivation against ion currents.

Because of the relative ease of preparing atomically flat $\text{Si}(111):\text{H}$ surfaces³⁰ from wet treatment in 40% NH_4F , Si samples reacted with diazonium compounds were checked for surface roughness effects by AFM. Our freshly made $\text{Si}(111):\text{H}$ samples typically showed RMS roughness of 0.2 nm or less over $1\text{ }\mu\text{m}^2$ areas, with atomic step edges being clearly visible. Samples reacted with diazonium salts using the normal conditions (0.5 mM for 2 h) showed slight increases in surface roughness to around 0.4 nm RMS, with complete loss of the atomic step edge features. It was then found that short reactions using more dilute solutions than normal (around 0.01 mM) left the surface sparsely reacted, enabling small vertical islands to be visualized (Figure 4a and b). A series of diazonium salts of different lengths were reacted with the flat surfaces to systematically observe these molecular features. Surfaces made with dilute solutions of diazonium salts **V** (observed height approximately 0.7 nm , although at this short length confusion with step edge features and defects is likely), **VI** (observed height approximately 1.5 nm), and **II** (observed height approximately 2.0 nm) showed these features consistently, with vertical heights corresponding to single perpendicular molecular lengths. The lateral dimension of the islands is limited by the radius of curvature of the AFM tip, which was typically around $30\text{--}40\text{ nm}$ in our images. Although AFM does not give chemical information within the images, given the XPS spectra that show the molecular signatures and no detectable Si oxide, it is plausible to affirm that the features are nucleation sites for film growth and not merely etch pits or oxide.

The exceptional chemical stability of the layers is indirect evidence of covalent bonding. Samples of the various substrates were reacted with **II**, exposed to various cleaning or etching treatments, and analyzed with ellipsometry and XPS. Pd samples reacted with **II** showed no loss of the molecular layers upon sonication in CH_3CN (10 min). If the molecules were simply physisorbed on the surface, this treatment would likely remove most of the organic residue. Similarly reacted GaAs samples were resistant to concentrated HCl etching solution (5 min), 30% aqueous citric acid etch solution, and concentrated $\text{NH}_4\text{-OH}$ followed by sonication in CH_3CN . Silicon samples reacted

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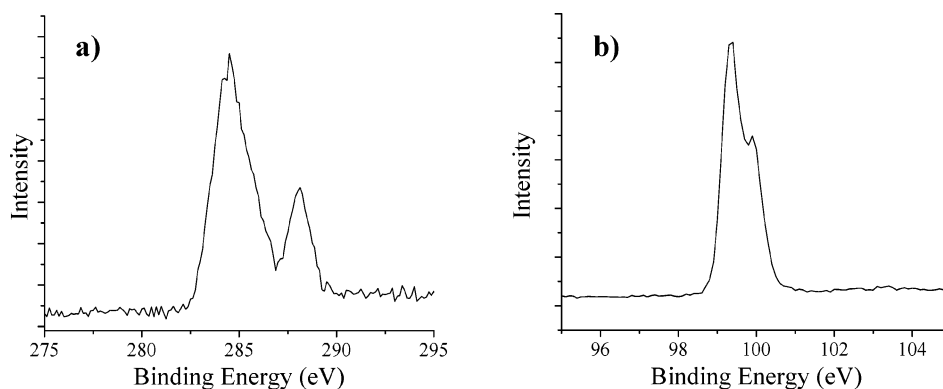


Figure 2. XPS spectra of reacted samples with monolayer thickness. (a) Spectrum of the C 1s region of the Pd sample reacted with **II**, taken at a 45° takeoff angle. The small peak at 288 eV is due to the pentafluorinated phenyl ring. (b) The spectrum of the Si 2p region of n²⁺-type Si(111) reacted with **II**, taken at a 30° takeoff angle, has a clear 2p^{1/2}–2p^{3/2} doublet and is free of the oxidation signal normally seen at around 103 eV.

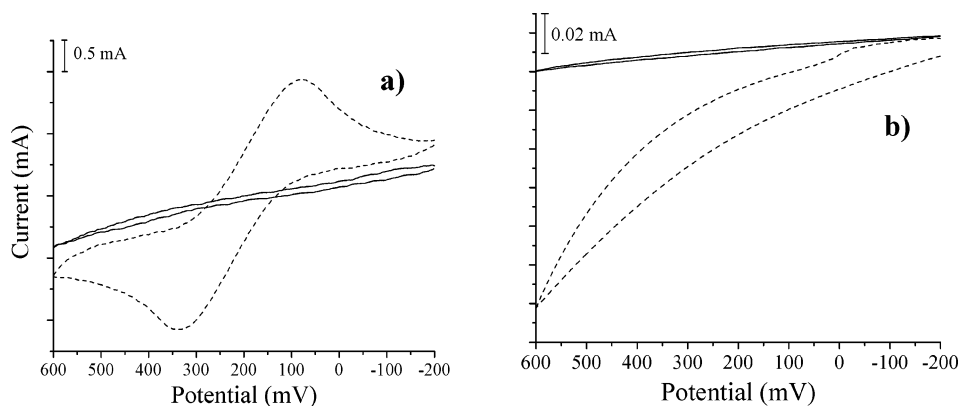


Figure 3. CV scans of reacted samples using a 0.01 M Fe(CN)₆^{3/4-} redox couple in 0.1 M KClO₃, with a 1 cm² area exposed. (a) Pd sample reacted with **II** (solid line) as compared to clean Pd (dashed line). (b) n²⁺-type Si(111) wafer reacted with **II** (solid line) as compared to the Si(111):H surface (dashed line).

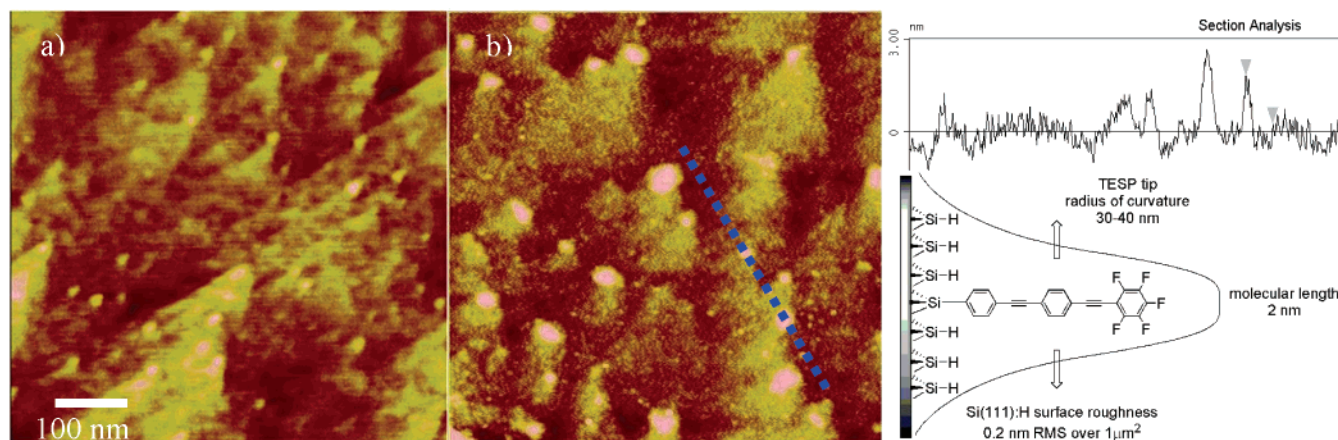


Figure 4. Tapping mode AFM images of sparsely reacted Si(111) surfaces before and after reaction with diazonium salt **II**, showing initial nucleation of perpendicularly oriented features of single molecular height. Scale bar is approximate. (a) Hydride-terminated Si(111) sample showing clear atomic step edges and RMS roughness of 0.2 nm over 1 μm². The vertical height of specklike features at step edge tips is less than 0.4 nm. (b) Si(111):H sample reacted for 15 min with 0.5 mM diazonium compound **II** shows initial growth of perpendicular molecules on step edges. The vertical height of the island is approximately 2.0 nm (Section Analysis, based on dashed blue line) measured from the terrace side of the feature. The lateral resolution of the molecular features is limited by the radius of curvature of the AFM tip, as depicted in the scheme.

with **II** were resistant to 7:1 buffered oxide etch solution (5 min), followed by pH 12 KOH solution at 25 °C (5 min), followed by sonication (10 min) in CH₃CN, CH₂Cl₂, or acetone. Because of the chemical endurance of the surface–molecule bonding, there was little or no loss of the chemisorbed molecular species or substantial oxidation of the substrate from any of these treatments.

Ellipsometric thickness measurements on monolayer films, FTIR spectroscopy, and AFM microscopy all provide evidence that implies that near-vertically oriented molecules are on the Si(111) surface. This is consistent with a covalent attachment between the aryl groups and the surface that would not allow for a large degree of deformation. XPS spectra show a low degree of chemical contamination within the attached layers and

at the critical surface–molecule interface. When combined with chemical tests that verify the robustness of the attachment at that interface, an overall review of the data is consistent with our model of covalently bound monolayers in high coverage on the surfaces in question. Now, we must use this model to justify our theory of how this reaction may activate the diazonium salts and form the layers.

Determining a consistent mechanism of the activation of the diazonium compounds is complicated by the broad chemical and physical differences between the metal, elemental semiconductor, and binary semiconductor materials used in this study. It is tempting, especially when considering the hydridic Si(111):H surface, to propose a cation exchange or charge injection mechanism for the aryl–surface bond-forming reaction. This might be qualitatively similar to charge injection from the ferrocenium cation as a surface activation method.³¹ In such a scheme (Scheme 1), elimination of N₂ from the aryl diazenyl radical would give an aryl cation intermediate, which would attack the Si(111):H surface, and then eliminate a proton and the counterion as HBF₄. However, reactions of diazonium salts with silanes,³² that likely do proceed via the aryl cation, tend to simply abstract hydride and form reduced aromatics and silyl halides. Although the hydride abstraction mechanism is a possibility, and would explain the very high degree of Si–H loss seen in FTIR spectra, inorganic surface fluoride from the counterion is something that we have not systematically observed on any of our surfaces. It also would not explain the formation of Si–C or other organometallic bonds. Finally, such a mechanism would not show significant sensitivity to the presence of BHT. As the major component of spontaneous diazonium activation, hydride abstraction can be ruled out.

Combella and coauthors¹⁵ have proposed an OCP-based mechanism for the spontaneous reduction of diazonium salts on a carbonaceous material made from an electrochemically reduced PTFE electrode surface. Is such a mechanism plausible for materials such as Si, GaAs, and Pd? The tendency of metastable surfaces such as Si(111):H to oxidize spontaneously, at OCP, provides a complementary means of reduction, as seen in Wade and Chidsey's experiments on the OCP-driven reduction of dioxygen to superoxide in fluoride solution.²³ If the OCP of the Si(111):H surface³³ in contact with 0.5 mM diazonium salt in CH₃CN is more negative than the reduction potential of the diazonium itself, about +0.3 V versus SCE,³⁴ it is possible to have the spontaneous reduction. Yet, unlike the dioxygen-superoxide system or reactions with metal salts,²⁴ we do not generally see the expected surface oxidation or major surface etching that might accompany the spontaneous reduction. The reverse electron transfer could instead have effects that were beyond our ability to analyze, such as a roughening of the opposite etched side or cleaved edges of the silicon wafer or reaction with a solution impurity species that we could not detect.

Nevertheless, the diazonium salts react with the surfaces and cleanly eliminate the N₂ and BF₄[−] byproducts from the surface, leaving no analytical traces on the surface. The effect of BHT

on the multilayer formation implies that aryl radical intermediates play a significant role in the surface reaction, which would be a secondary product of spontaneous electron transfer (the direct product being a short-lived diazenyl radical). This effect was most dramatic for diazonium assemblies on Pd and Si, and less so for the GaAs surface.

This spontaneous diazonium activation reaction offers an attractive route to highly passivating, robust monolayers and multilayers on many surfaces that allow for strong bonds between carbon and surface atoms. A data-encompassing explanation for the mechanism calls for an OCP-driven diazonium activation with aryl radical secondary products attacking the surface and forming the bonds. Covalently bound monolayers on Pd, Si, and GaAs offer possibilities for new applications in processing, electronic transport, and antistiction coatings for polysilicon-based MEMS devices, as well as a platform to study through-bond interactions between molecules chemisorbed on surfaces and the bulk materials to which they are attached. Current work includes improving the long-range order of the surface assemblies, determining molecular effects on the electronic structure of the interfaces, and adapting molecular assemblies with reported negative differential resistance (NDR) properties into silicon-based hybrid molecular electronic devices to assess molecular versus interfacial-based device behavior.^{4,8}

Experimental Section

Reagents and Solvents for Surface Reactions. Acetonitrile (CH₃CN, 99.5+%) for surface reactions was purchased from Aldrich packed under nitrogen in a SureSeal container. CH₃CN, dichloromethane (CH₂Cl₂), ethanol (EtOH), methanol (MeOH), and water used for rinsing were purchased at HPLC grade and used without further purification. Concentrated ammonium fluoride (NH₄F) was purchased at VLSI grade from J. T. Baker. Concentrated hydrochloric acid (HCl), concentrated NH₄F, concentrated ammonium hydroxide (NH₄OH), concentrated sulfuric acid (H₂SO₄), 49% hydrofluoric acid (HF), and 30% hydrogen peroxide (H₂O₂) were purchased at reagent grade. Before use, all diazonium salts were stored under nitrogen in tightly capped vials, in the dark at −30 °C.

Ellipsometric Measurements. Measurements of surface optical constants and molecular layer thicknesses were taken with a single wavelength (632.8 nm laser) Gaertner Stokes ellipsometer. The *n* value for the clean Pd surface was 1.9, and *k* was −4.2. The *n* value for the Si(111):H surface was 3.87, and *k* was −0.04. The *n* value for the clean GaAs surface was 3.85, and *k* was −0.2. The surface thickness was modeled as a single absorbing layer atop an infinitely thick substrate (fixed *n_s*). The observed error in repeated measurements of the same spot was typically 0.2 nm or less.

Cyclic Voltammetry (CV) Measurements. Electrochemical characterization was carried out with a Bioanalytical Systems (BAS CV-50W) analyzer. The reference was a saturated calomel electrode (SCE). The counterelectrode was a clean Pt wire. The aqueous redox couple and electrolyte were 0.01 M Fe(CN)₆^{3/4−} in 0.1 M KClO₄. Approximately 1 cm² of sample was exposed to solution during CV measurements. The scan rate was 100 mV s^{−1} from −200 to 600 mV.

Atomic Force Microscopy (AFM) Measurements. A Digital Instruments Nanoscope IIIa tapping mode instrument was used with freshly CHCl₃-cleaned TESP tips. Images were taken in air without using a purge box. Samples were prepared as normal and loaded into the AFM within a few minutes of their final rinsing. Samples prepared for Figure 4 were reacted for ≤15 min using approximately 0.05 mM diazonium solution in CH₃CN in a glovebox.

X-ray Photoelectron Spectroscopy (XPS) Measurements. A Physical Electronics (PHI 5700) XPS/ESCA system at 5 × 10^{−9} Torr was used to take photoelectron spectra. A monochromatic Al X-ray

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source at 350 W was used with an analytical spot size of 1.2 mm² and a 45° or 30° takeoff angle, with a pass energy of 11.75 eV.

FTIR Measurements. A customized analytical system, based on a Digilab FTS-7000 bench, was used, whose basic details are described in a previous publication.³⁵ FTIR spectra were obtained under an extended dry air purge using a liquid N₂ cooled wide-band MCT detector. External reflection *p*-polarized spectra used 1200 scans at 2 cm⁻¹ resolution at an 86° angle of incidence. A multipoint baseline correction and H₂O and CO₂ subtractions in GRAMS/32 are used for qualitative and presentation purposes.

Surface Preparation and Optical Constants. Pd samples were deposited by ion mill sputtering onto a 2-in. undoped oxidized Si wafer at 0.1 Å s⁻¹ until a final thickness of 2000 Å was reached. No surface adhesion layer was used. The Pd samples were reacted within 10 min after coming out of the vacuum chamber, without any surface cleaning. Highly doped 2-in. n-type Si(111) wafers (prime grade, As doped, 0.001–0.005 Ω cm) were first cleaned for 20 min in 2:1 H₂SO₄/H₂O₂ (piranha solution) followed by rinsing copiously with water and drying in a stream of N₂. The wafer was then hydride-terminated by immersion in N₂-sparged concentrated (40%) NHF₄ for 15 min, rinsed with water, and dried in a stream of N₂. Undoped GaAs(100) samples were cut (about 4 cm²) from a 3-in. wafer, sonicated in EtOH for 15 min, and UV/O₃ cleaned for 15 min. The oxidized GaAs shards were then treated with concentrated (40%) NH₄OH for 1 min, followed by a brief rinse in water, then EtOH, and finally a gentle stream of N₂. XPS experiments on GaAs used shards from a lightly Te-doped GaAs(100) wafer prepared and characterized with the same protocols.

Reactions with Diazonium Salts. The cleaned, prepared samples were brought inside a low-oxygen N₂-atmosphere glovebox (with levels of 1 ppm H₂O and O₂). Inside the glovebox, a solution of the diazonium salt was made to 0.5 mM concentration in CH₃CN, providing enough volume to completely cover the entire sample inside a glass screw-cap Nalgene jar. To adequately cover a 2-in. wafer, at least 10 mL must be prepared. For the smaller shards of GaAs, 5 mL of solution is sufficient. The surface samples are immersed in the diazonium solution, sealed to prevent evaporation, and covered with foil to prevent light exposure. The reaction time was 2 h, although shorter reaction times may be possible. Reaction times longer than 6 h tended to create multilayers up to 3.5–5 nm thick, depending on the molecule that was used (layer thicknesses were determined by ellipsometry). At the end of the reaction, the samples were brought out of the glovebox, rinsed with CH₃CN and soaked for 5 min (to remove residual diazonium salt), and then rinsed with CH₂Cl₂ (to remove physisorbed hydrocarbons) and soaked for 1 min. The samples were removed from the CH₂Cl₂ and then dried thoroughly with N₂.

Synthetic Materials and General Synthetic Procedures. Unless stated otherwise, reactions were performed in dried glassware under dry nitrogen atmosphere. Reagent grade diethyl ether (Et₂O) and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl. *N,N*-Diisopropylethylamine (Hünig's base), triethylamine (TEA), and *N,N*-dimethylformamide (DMF) were distilled from calcium hydride. Reagent grade hexanes, CH₂Cl₂, MeOH, EtOH, and ethyl acetate (EtOAc) were used without further distillation. Trimethylsilylacetylene (TMSA) was donated by FAR Research. All other commercially available reagents were used as received. Unless noted, reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) using E. Merck silica gel 60 F₂₅₄ precoated plates (0.25-mm). In general, the chromatography guidelines reported by Still were followed.³⁶ Flash chromatography (silica gel) was performed with the indicated solvent systems using silica gel grade 60 (230–400 mesh). ¹H and ¹³C NMR spectra were taken at 400 and 100 MHz, respectively, and chemical shifts are reported relative to CD₃CN (¹H, 1.96, ¹³C, 118.26) except when specified. All new compounds were named using AutoNom v. 2.2 under license of Beilstein Informationssysteme.

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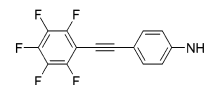
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General Procedure for the Coupling of a Terminal Alkyne with an Aryl Halide Utilizing a Palladium–Copper Cross-Coupling (Castro–Stephens/Sonogashira Protocol).^{37,38} To an oven-dried screw cap tube or a round-bottom flask and a magnetic stir bar were added the aryl halide, bis(triphenylphosphine)palladium(II) dichloride (5 mol % based on aryl halide), and copper(I) iodide (10 mol % based on aryl halide). The vessel was then sealed with a rubber septum, evacuated, and backfilled with nitrogen (3×). A cosolvent of THF was added followed by Hünig's base. The terminal alkyne was added, and the reaction was heated, if necessary, until complete. The reaction vessel was cooled to room temperature and quenched with water. The organic layer was diluted with CH₂Cl₂ and washed with a saturated solution of NH₄Cl (3×). The combined aqueous layers were extracted with CH₂Cl₂ (3×). The combined organic layers were dried over anhydrous MgSO₄, and the solvent was removed in vacuo. The crude product was then purified by flash or column chromatography (silica gel).

General Procedure for Alkaline Deprotection of Trimethylsilyl-Protected Alkynes. The TMS-protected alkyne was added to an open round-bottom flask equipped with a stirring bar and a solution of potassium carbonate in MeOH or tetrabutylammonium fluoride (TBAF) buffered with a mixture of acetic acid (AcOH) and acetic anhydride (Ac₂O). THF and CH₂Cl₂ were added to dissolve the organic compound. The reaction was monitored by TLC every 5 min until deprotection was completed. The reaction was quenched with water and extracted with organic solvents (3×). The combined organic layers were dried over anhydrous MgSO₄, and the solvent was removed in vacuo. The crude product was then purified by flash chromatography.

General Procedure for Diazotization of Anilines.³⁹ Into an oven-dried round-bottom flask equipped with a magnetic stir bar was added nitrosonium tetrafluoroborate (1.1 equiv per aniline) in the drybox, and the vessel was sealed with a rubber septum. CH₃CN was added to dissolve the salt and cooled to –30 °C. Separately, into an oven-dried round-bottom flask equipped with a magnetic stir bar was added the aniline that was dissolved in a minimum amount of CH₃CN. The organic solution was transferred dropwise via cannula, and the temperature was allowed to rise to 0 °C. Et₂O was slowly added until a precipitate came out from the slurry. The precipitate was collected by filtration, washed with Et₂O (3×), and dried.

4-Styrylbenzenediazonium Tetrafluoroborate (I). To a 25 mL round-bottom flask in a drybox was added NOBF₄ (0.1 g, 0.95 mmol). Acetonitrile (2 mL) was added, and the flask was cooled to –30 °C. A solution of 4-styrylaniline⁴⁰ (0.17 g, 0.86 mmol) and BHT (0.19 g, 0.86 mmol) in acetonitrile (5 mL) was added dropwise. The reaction was allowed to warm to –5 °C over 20 min. Et₂O (10 mL) was added, and the precipitate was filtered. The title compound was purified by reprecipitating from CH₃CN (3 mL) with ether (15 mL) to yield 0.82 g (34%) of the desired compound. IR (KBr): 3360, 3108, 2271, 1654, 1581, 1497, 1497, 1421, 1079 cm⁻¹. ¹H NMR (400 MHz, CD₃CN): δ 8.50 (d, *J* = 8.8 Hz, 2H), 8.39 (d, *J* = 8.8 Hz, 2H), 8.13 (d, *J* = 8.8 Hz, 2H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 16.8 Hz, 1H), 7.53 (d, *J* = 16.8 Hz, 1H). ¹³C NMR (100 MHz, CD₃CN): δ 159.8, 155.3, 150.1, 133.3, 133.7, 130.0, 112.9, 112.22.



4-Pentafluorophenylethynylaniline. Following the Sonogashira coupling protocol, pentafluorobromobenzene (9.6 mL, 77 mmol), PdCl₂(PPh₃)₂ (2.7 g, 3.9 mmol, 5 mol %), and CuI (1.5 g, 7.7 mmol, 10 mol %) were dissolved in THF (100 mL). Hünig's base (53 mL, 307 mmol) was added, followed by 4-ethynylaniline⁴¹ (9 g, 77 mmol), and the

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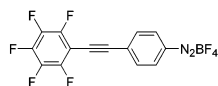
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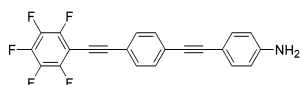
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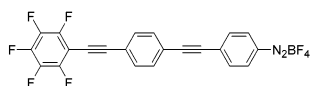
mixture was left overnight at 75 °C. Purification by flash chromatography (CH₂Cl₂ eluent) afforded the desired product (4.4 g, 21% yield) as a dark yellow solid. IR (KBr): 3482, 3394, 2206, 1610, 1501, 1446, 1290, 1176, 1133, 1033 cm⁻¹. ¹H NMR (400 MHz, CDCl₃ δ 7.27): 7.37 (m, 2H), 6.65 (m, 2H), 3.93 (br s, 2H). ¹³C NMR (100 MHz, CDCl₃ δ 77.23): 148.0, 133.6, 114.8, 110.8, 103.0, 71.4. HRMS calc'd for C₁₄H₆F₅N, 283.0420; found, 283.0423.



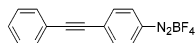
4-Pentafluorophenylethynylbenzenediazonium Tetrafluoroborate (VI). Following the general procedure for diazotization, 4-pentafluorophenylethynylaniline (400 mg, 1.4 mmol) was dissolved in CH₃CN (19 mL) and submitted under reaction with NOBF₄ (182 mg, 1.5 mmol). The desired product (487 mg, 91%) was isolated as a light yellow solid. IR (KBr): 3421, 2950, 2883, 2356, 2161, 1475, 1372, 1244, 1183 cm⁻¹. ¹H NMR (400 MHz, (CD₃)₂SO δ 2.54): δ 8.75 (d, *J* = 9.2 Hz, 2H), 8.21 (d, *J* = 9.2 Hz, 2H). ¹³C NMR (100 MHz, (CD₃)₂SO δ 40.4): 135.1, 134.4, 133.0, 117.8, 99.0, 82.9.



4-(4-Pentafluorophenylethynylphenylethynyl)aniline. 4-(4-Iodophenylethynyl)aniline⁴² (0.31 g, 1.0 mmol), PdCl₂(PPh₃)₂ (28 mg, 0.04 mmol), CuI (8 mg, 0.04 mmol), TEA (2 mL), THF (2 mL), and pentafluorophenylacetylene (0.28 g, 1.5 mmol) were used following the general procedure for couplings. The tube was capped and stirred at room temperature for 14 h. Flash column chromatography (1:1 hexanes:CH₂Cl₂) afforded the desired product as light yellow needles (0.16 g, 43% yield). IR (KBr): 3417, 2206, 1623, 1595, 1526, 1497, 1446, 1298, 1138 cm⁻¹. ¹H NMR (400 MHz, CDCl₃ 7.27): δ 7.47 (m, 4H), 7.34 (m, *J* = 8.7, 2.5, 1.8, 0.6 Hz, 2H), 6.64 (m, *J* = 8.7, 2.5, 1.8, 0.6 Hz, 2H), 3.85 (br s, 2H). ¹³C NMR (100 MHz, CDCl₃ 77.23): δ 147.2, 133.3, 131.9, 131.8, 131.5, 125.6, 120.5, 114.9, 112.2, 93.3, 87.1, 74.6.

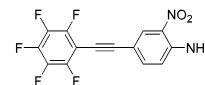


4-(4-Pentafluorophenylethynylphenylethynyl)benzenediazonium Tetrafluoroborate (II). Following the general diazotization procedure, 4-(4-pentafluorophenylethynylphenylethynyl)aniline (0.15 g, 0.04 mmol) was treated with NOBF₄ (52 mg, 0.52 mmol) in CH₃CN (4 mL) and sulfolane (4 mL). After the mixture was dried in vacuo, the desired product was isolated (0.12 g, 64% yield) as a yellow solid. IR (KBr): 3106, 2275, 2214, 1576, 1526, 1502, 1078, 989, 854, 832 cm⁻¹. ¹H NMR (400 MHz, (CD₃)₂SO δ 2.54): δ 8.71 (m, 2H), 8.15 (m, 2H), 7.74 (m, 4H). ¹³C NMR (100 MHz, (CD₃)₂SO δ 40.4): δ 133.8, 133.6, 133.0, 132.6, 132.2, 122.1, 114.9, 100.1, 98.3, 89.8, 75.5.

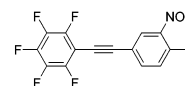


4-Phenylethynylbenzenediazonium Tetrafluoroborate (III). Following the general diazotization procedure, 4-phenylethynylaniline⁴³ (0.57 g, 3 mmol) was treated with NOBF₄ (0.36 g, 3.15 mmol) in CH₃CN (20 mL). Yellow needles of the desired product were precipitated with ether (0.75 g, 86% yield). IR (KBr): 3100, 2293, 2216, 1577, 1415, 1071, 1033 cm⁻¹. ¹H NMR (400 MHz, CD₃CN): δ 8.86 (m, *J* = 8.7, 2.4, 1.7, 0.5 Hz, 2H), 8.16 (m, *J* = 8.7, 2.4, 1.7, 0.5 Hz, 2H),

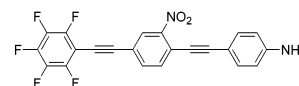
7.49 (m, 3H), 7.67 (m, 2H). ¹³C NMR (100 MHz, CD₃CN): δ 137.1, 134.6, 134.0, 133.1, 131.4, 129.8, 121.9, 114.3, 101.5, 88.2.



2-Nitro-4-pentafluorophenylethynylaniline. Following the general coupling procedure, 4-ethynyl-2-nitroaniline⁴⁴ (6.2 g, 38.7 mmol), PdCl₂(PPh₃)₂ (1 g, 1.5 mmol), CuI (0.6 g, 3 mmol), and TEA (27 mL, 155 mmol) were dissolved in THF (50 mL). Pentafluorobromobenzene (19 g, 77.3 mmol) was added, and the reaction was heated at 70 °C overnight. Purification by flash chromatography (CH₂Cl₂) afforded the desired product (3.7 g, 30%) as an orange solid. IR (KBr): 3468, 3364, 3099, 2469, 2428, 2221, 1933, 1801, 1728, 1631, 1583, 1550, 1413, 1338, 1284, 1243, 1163, 1117, 1077, 1033 cm⁻¹. ¹H NMR (400 MHz, CDCl₃ 7.27): δ 8.32 (s, 1H), 7.62 (d, *J* = 8.8, 1H), 7.53 (br s, 2H), 7.21 (d, *J* = 8.8, 1H). ¹³C NMR (100 MHz, CDCl₃ 77.23): δ 147.2, 138.0, 131.3, 130.1, 120.3, 108.4, 100.8, 71.8, 68.9. HRMS for C₁₄H₅F₅N₂O₂, 328.0271; found, 328.0273.



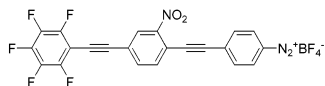
Pentafluoro-6-(4-iodo-3-nitrophenylethynyl)benzene. A solution of aniline 2-nitro-4-pentafluorophenylethynylaniline (2.9 g, 9 mmol) in CH₃CN (40 mL) was slowly added to NOBF₄ (1.5 g, 13.5 mmol) in CH₃CN (10 mL) at -20 °C. The resulting yellow solution was warmed to 0 °C, stirred for 30 min, and transferred via syringe into a flask containing a solution of NaI (2.7 g, 18 mmol) and I₂ (4.5 g, 18 mmol) in acetonitrile (50 mL). When the vigorous gas evolution was complete, the reaction mixture was diluted with water (500 mL), treated with urea (1.8 g, 30 mmol) and Na₂SO₃ (1.3 g, 11 mmol), and extracted with ether. The extracts were washed with water (50 mL) and brine (50 mL) and were evaporated. The crude product was purified by chromatography (CH₂Cl₂) to give lemon yellow needles (3.5 g, 90% yield). IR (KBr): 3093, 2879, 2629, 2428, 2229, 1940, 1780, 1594, 1518, 1501, 1443, 1356, 1266, 1151, 1036, 1017 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 8.07 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 1.6 Hz, 1H), 7.42 (dd, *J* = 8.4, 2.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 165.9, 142.4, 135.8, 128.3, 123.2, 117.7, 89.6, 87.8. HRMS for C₁₄H₃F₅INO₂, 438.9129; found, 438.9125.



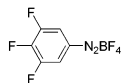
4-(2-Nitro-4-pentafluorophenylethynylphenylethynyl)aniline. 4-Ethynylaniline (0.28 g, 2.4 mmol), bis(triphenylphosphine)palladium(II) dichloride (70 mg, 0.1 mmol), copper(I) iodide (19 mg, 0.1 mmol), Hünig's base (0.51 g, 4.0 mmol), THF (4 mL), and 1-iodo-2-nitro-4-pentafluorophenylethynylbenzene (0.87 g, 2.0 mmol) were used following the general procedure for couplings. The bright red slurry formed after 14 h of stirring at room temperature was evaporated in vacuo, suspended in CH₂Cl₂ (10 mL), and filtered. The filter cake was washed with the same solvent (15 mL), dried, and recrystallized from THF–heptane to afford red silky needles (0.74 g, 87% yield). IR (KBr): 3505, 3401, 2200, 1624, 1597, 1538, 1524, 1496, 1444, 1351, 1136, 985 cm⁻¹. ¹H NMR (400 MHz, (CD₃)₂SO, 2.54): δ 8.26 (d, *J* = 1.4 Hz, 1H), 7.87 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 6.59 (d, *J* = 8.4 Hz), 5.88 (s, 2H). ¹³C NMR (100 MHz, (CD₃)₂SO, 40.4): δ 151.0, 148.46, 135.6, 134.1, 133.5, 127.5, 119.7, 119.3, 113.6, 106.4, 102.9, 98.4, 83.1, 76.5.

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4-(2-Nitro-4-pentafluorophenylethynylphenylethynyl)benzene-diazonium Tetrafluoroborate (IV). Following the general diazotization procedure, 4-(2-nitro-4-pentafluorophenylethynylphenylethynyl)aniline (0.42 g, 1 mmol) was treated with NOBF_4 (1.4 g, 1.2 mmol) in CH_3CN (20 mL) and sulfolane (20 mL). The product was precipitated with Et_2O (200 mL) and recrystallized from CH_3CN to give orange needles (0.26 g, 51% yield). IR (KBr): 3106, 2284, 2214, 15178, 1517, 1444, 1349, 1291, 1074 cm^{-1} . ^1H NMR (400 MHz, CH_3CN): 8.61 (d, $J = 2.4$ Hz, 1H), 8.56 (m, 2H), 8.36 (dd, $J = 8.8, 2.4$ Hz, 1H), 8.06 (m, 2H), 7.94 (d, $J = 8.8$ Hz, 1H) δ . ^{13}C NMR (100 MHz, CH_3CN): δ 149.0, 136.5, 135.4, 134.8, 133.7, 130.9, 128.8, 126.1, 125.8, 115.4, 96.8, 93.4.



3,4,5-Trifluorobenzenediazonium Tetrafluoroborate (V). Following the general procedure for diazotization, 3,4,5-trifluoroaniline

(300 mg, 2 mmol) was dissolved in CH_3CN (2 mL) and treated with NOBF_4 (262 mg, 2.2 mmol). The desired product (350 mg, 71%) was isolated as a pale yellow solid. IR (KBr): 3360, 3112, 2285.30, 2222, 1582, 1496, 1524, 1444, 1069 cm^{-1} . ^1H NMR (400 MHz, CD_3CN): δ 8.47 (m). ^{13}C NMR (100 MHz, CD_3CN): δ 121.5, 121.2.

Acknowledgment. This work was funded by the Defense Advanced Research Projects Agency, the Army Research Office, and the Office of Naval Research. Paul A. W. van der Heide (University of Houston, MRSEC) is thanked for assistance with XPS measurements. Dr. I. Chester (FAR Research, Inc.) is thanked for providing trimethylsilylacetylene used in the syntheses of the diazonium compounds.

Supporting Information Available: XPS spectra of samples reacted with fluorinated and nonfluorinated diazonium salts, and an FTIR spectrum of the Si(111):H surface (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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