Attaching Electronically Active Oligoanilines to Silicon Surfaces

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Diazonium salt-functionalized oligoanilines have been synthesized and assembled on hydride passivated silicon surfaces for subsequent incorporation into hybrid molecule−silicon device architectures. The targeted oligoanilines were synthesized using Buchwald/Hartwig Pd-catalyzed coupling reactions. A methodology using *N-tert*-butoxycarbonyl (Boc) protecting groups was essential to prevent *N*-nitroso formation during the diazotization step and to prevent rapid air oxidation and decomposition of the products. The molecules were assembled on silicon surfaces to form monolayer films, and thermal removal of the Boc protecting groups was achieved by heating the films to 215 °C for 4 h under argon. Single-wavelength ellipsometry verified the desired monolayer formation. X-ray photoelectron spectroscopy analysis confirmed the loss of the Boc groups and formation of the requisite oligoaniline monolayers. Assembly of **4** in a Molepore electronic test bed device followed by thermalization and retesting indicated that the current was doubled and a larger hysteresis was obtained after removal of the Boc protecting groups, thus underscoring the efficacy of this two-step assembly process. This study provides a route to interface the highly desirable electronically switching oligoanilines to the surface of highest relevance in the electronics industry, namely silicon, via the sequential Boc-based syntheses, diazonium assembly and final film thermolysis.

Introduction

Over the past few decades the semiconductor industry has been able to reduce transistor dimensions according to Moore's law[1] resulting in extremely powerful processors. However, due to physical limitations, barriers to continued miniaturization are being encountered.[2] It was proposed over 30 years ago that organic molecules a few nanometers in length might serve as switching and memory devices.[3] Organic compounds have already shown to be viable molecular switches.[2,4−9] As an emerging scientific technology, researchers in the molecular electronics field seek methods to combine electronically active organic molecules with existing complementary metal oxide semiconductor (CMOS) technology, thus producing hybrid devices.[2] Aryl diazonium salt-functionalized organic molecules,[10] previously shown to assemble on Si (hydride passivated single crystal or poly-Si: ⟨111⟩ or ⟨100⟩, p-doped, n-doped, or intrinsic),

GaAs, and Pd surfaces,[11] hold promise as potential components of such hybrid devices, and we recently demonstrated the efficacy of silicon−organic molecule hybrid memory devices.[11b]

We previously reported on the synthesis of thiol-functionalized oligoanilines for molecular electronic device candidates.[12] End-functionalized oligoanilines are promising compounds for molecular electronics applications because the parent polymer, polyaniline, is known to switch reversibly between numerous redox-active states, resulting in dramatic changes in conductivity. In recent work we reported on the redox and electrical behavior of these compounds in metal−molecule−metal nanowires.[13] Thiol-functionalized oligoanilines were found to behave as highly reproducible, reversible molecular switches at room temperature with on/off ratios greater than 10:1. We found that the observed hysteresis behavior of the devices was likely due to the oligoaniline[14] molecules undergoing conformational changes in the junction as a result of changes in their redox states. Additionally, work by Lindsay and co-workers[14a] found that a hepta-aniline oligomer attached to gold electrodes exhibited changes in conductivity associated with different oxidation states. In light of these results, we sought to synthesize

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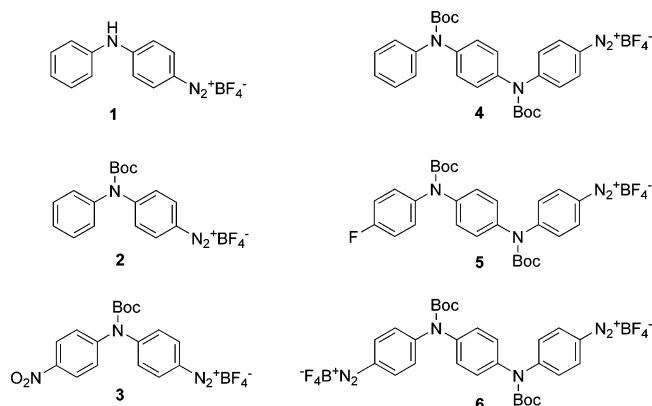
Figure 1. Diazonium salt-functionalized oligoanilines **1−6**.

diazonium salt-functionalized oligoanilines for assembly onto oxide-free silicon surfaces in attempts to exploit the electronic switching properties of the oligoanilines in silicon-based devices. However, two persistent problems had to be addressed. First, the nitrogen atoms along the backbone of the oligoaniline had to be protected to survive diazotization conditions. Second, once assembled on silicon, an efficient deprotection route had to be developed and further analytically confirmed.
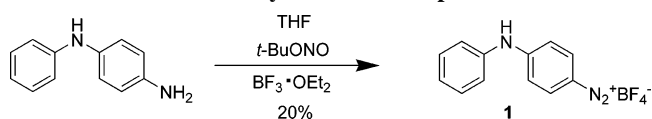
Synthesis of Oligoaniline Diazonium Salts

The target diazonium salt oligoanilines (**1−6**) are shown in Figure 1. In all cases except in **1**, the nitrogen atoms were protected with *N-tert*-butoxycarbonyl (Boc) to prevent *N*-nitroso formation from secondary nitrogen atoms of the substrate. The Boc protecting group is also convenient because it can be thermally removed[15] following film assembly.

The one-step synthesis of the two-ring oligoaniline **1** is shown in Scheme 1. Commercially available *N*-phenyl-*p*-phenylenediamine was treated with one equivalent of *tert*-butylnitrite (*t*-BuONO) in boron trifluoridediethyletherate to give a mixture of the *N*-nitroso adduct and the desired product, which was selectively precipitated to afford **1**. Hence, although the selective diazotization could be effected in this simple case without protection of the internal secondary amine, the yield suffered. Longer anilines could not be obtained without first protecting the secondary amines; hence, the Boc-protected route was developed on the short aniline **2** as shown in Scheme 2.

Aniline was coupled with 1,4-dibromobenzene by employing the conditions of Wolfe and Buchwald and Hartwig et al.[16,17] to give the monocoupled product **7**[18] which was treated with methyllithium followed by the addition of Boc₂O to afford **8**. The aryl bromide **8** was then converted to the aniline by coupling **8** with lithium hexamethyldisilazide[19,20] (LH-MDS) followed by removal of the silicon groups using

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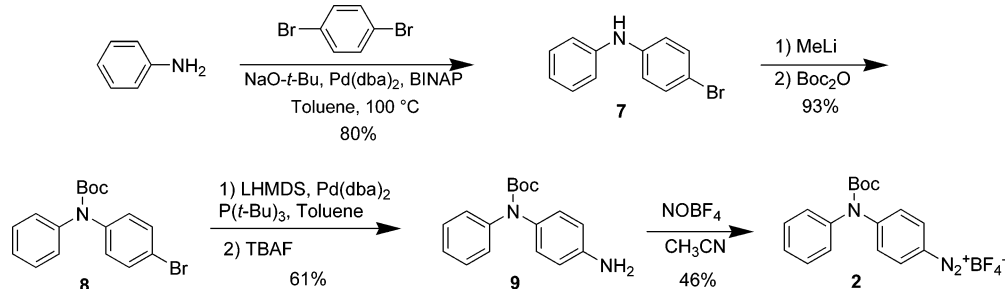(16) Wolfe, J. P.; Buchwald, S. L. *J. Org. Chem.* **2000**, *65*, 1144.
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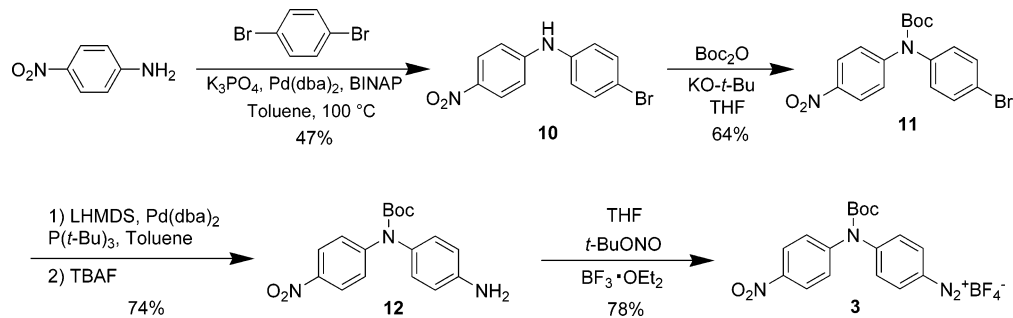(19) Lee, S.; Jørgensen, M.; Hartwig, J. F. *Org. Lett.* **2001**, *3*, 2729.
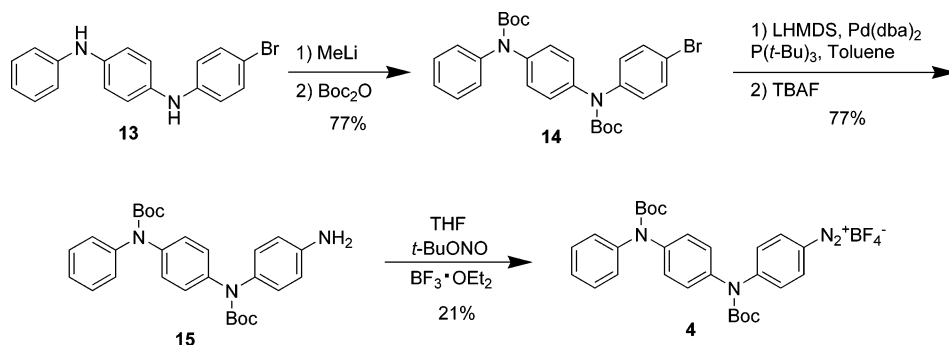(20) Huang, X.; Buchwald, S. L. *Org. Lett.* **2001**, *3*, 3417.
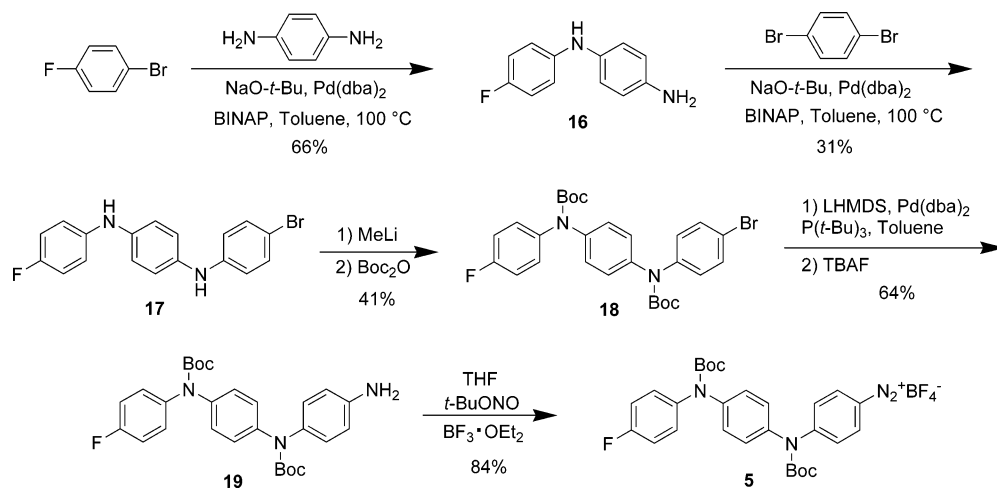
Scheme 1. Synthesis of Compound 1

tetrabutylammonium fluoride (TBAF) to give **9** which was then diazotized using nitrosonium tetrafluoroborate (NOBF₄) in acetonitrile to give the target **2**.

In general, we prefer the use of an alkylnitrite and boron trifluoridediethyletherate for the diazotizations over the use of NOBF₄ because the former protocol does not require the use of a glovebox. However, in the case of **2**, NOBF₄ gave better results, as it did in the synthesis of **6**, possibly as a result of partial Boc removal caused by the boron trifluoridediethyl etherate.

Compound **3**, containing a nitro group in the 4′ position, was synthesized as shown in Scheme 3. 4-Nitroaniline was coupled to 1,4-dibromobenzene to give **10** followed by installation of the Boc protecting group to give **11**. Compound **11** was coupled with LHMDS followed by exposure to TBAF to give the aniline **12**, which was diazotized using *tert*-butylnitrite in boron trifluoridediethyl etherate to give the desired diazonium salt **3**.

With several two-ring oligoaniline diazonium salts in hand, we sought to synthesize longer three-ring systems. Attempts to synthesize these with unprotected secondary nitrogen atoms were unsuccessful due to an inability to separate the multiple *N*-nitroso side products. Thus compound **13**[12] was treated with methyllithium followed by Boc₂O to afford **14**. Compound **14** was then coupled with LHMDS and after TBAF treatment afforded the aniline **15**. Diazotization gave the desired diazonium salt **4** (Scheme 4).

A three-ring oligoaniline diazonium salt with a fluorine atom in the 4″ position (**5**) was synthesized as shown in Scheme 5. 1-Bromo-4-fluorobenzene was coupled to *p*-phenylenediamine to afford **16** which was further coupled to 1,4-dibromobenzene to give **17**. Compound **17** was then treated with methyllithium followed by Boc₂O to afford **18**. Compound **18** was then similarly converted to **5** via the aniline **19**.

The synthesis of the bis-diazonium salt **6** is shown in Scheme 6. Compound **20**[12] was Boc-protected to afford **21**, and following LHMDS coupling, TBAF treatment, and diazotization, the desired diazonium salt **6** was formed via the bis-aniline **22**.

Monolayer Formation on Si and Boc Removal

With the completed molecules in hand, we carried out monolayer formation on heavily doped p-type Si(111)/H surfaces according to our previous report.[11] Using single-wavelength ellipsometry, the observed and theoretical thicknesses were compared to assess monolayer formation (Table 1). For **1−5**, monolayer formation was complete after assembly times of 0.5−1 h; **6** was unstable in solution. The observed layer thicknesses for compounds **1−5** were very close to the theoretical monolayer heights.

A silicon substrate on which a film from **4** had been formed was placed in a thermogravimetric analysis (TGA)

Scheme 2. Synthesis of Compound 2

Scheme 3. Synthesis of Compound 3

Scheme 4. Synthesis of Compound 4

Scheme 5. Synthesis of Diazonium Salt 5

furnace which was purged with argon and then heated at 10 °C /min to 215 °C (Scheme 7). The temperature was kept at 215 °C for 4 h and then cooled to room temperature, all under Ar.

The X-ray photoelectron spectroscopy (XPS) analysis indicated the presence of a carbonyl carbon peak at 289.4 eV (Figure 2a) in the sample before heating. The large C 1s

peak at 284.8 eV is due to the presence of both alkyl and aromatic carbons in the sample, as expected. The binding energy difference between the carbonyl carbon and the alkyl/ aromatic carbons is 4.6 eV, which corroborates with the expected values.[21] The C 1s peak at 286.1 eV is from carbon in the *tert*-butoxy (—C—O) bond; however, it is not reliably assigned to only the —C—O bond because contaminating
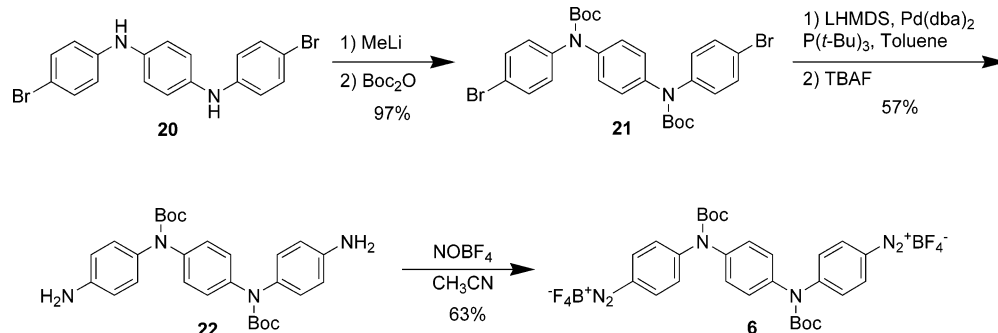
Scheme 6. Synthesis of Compound 6

Table 1. Calculated and Observed Thicknesses of Compounds 1–5 on Si(111)

		thickness (nm)	
molecule	reaction time (h)	found[a]	calcd[b]
1	1	0.9	1.0
2	0.5	1.2	1.0
3	1	1.2	1.2
4	1	1.7	1.7
5	1	1.9	1.7

[a] Value measured by ellipsometry with ca. ±0.2 nm error. All reported values are an average of three measurements for reactions of a 0.5 mM solution of the diazonium salt in CH_3CN. [b] The theoretical thicknesses were calculated by molecular mechanics, and they did not include the arene–silicon bond length.

Scheme 7. Thermal Removal of the Boc Protecting Groups
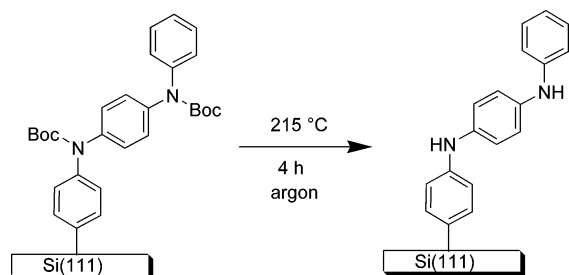
CO_2 on the surface notoriously leads to elevated counts for this peak.[22] Encouragingly, the carbonyl carbon peak at 289.4 eV disappeared after heating as shown in Figure 2b. When the counts from the XPS analyses are used, the ratios of –C=O carbon or –C–O/CO_2 carbon to the total amount of alkyl/aromatic carbon are listed in Table 2. As can be seen in the Table, the –C=O carbon content was removed after the thermal process; the experimental data agreed with that of calculated content. But as is common, CO_2 contamination does not permit us to quantitatively use the percentage of C 1s peak at 286.1 eV.[22] Moreover, CO_2 evolution is a byproduct of Boc loss; hence, surface adsorption of CO_2 is possible during the thermolysis process. Nonetheless, there was a decrease in the overall combined intensity of the –C–O/CO_2 signal. Heating for shorter times or at lower temperatures (200 °C) resulted in incomplete loss of the Boc groups. On the other hand, heating at 230 °C resulted in significant removal of the deposited films; hence, careful temperature control is essential.

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Table 2. Ratios of C 1s in –C=O and –C–O to C 1s in Alkyl and Aromatic C in the Film (a) before Heating and (b) after Heating the Surface-Bound Monolayer Film to 215 °C for 4 h[a]

	–C=O/(–C– and –C=)		–C–O + (CO_2)/(–C– and –C=)	
sample	found	calcd	found	calcd
(a)	0.06	0.07	0.29	0.07
(b)	0	0	0.16	0

[a] Note that the surface contamination with CO_2 makes the use of the –C–O signal only qualitative (see text).
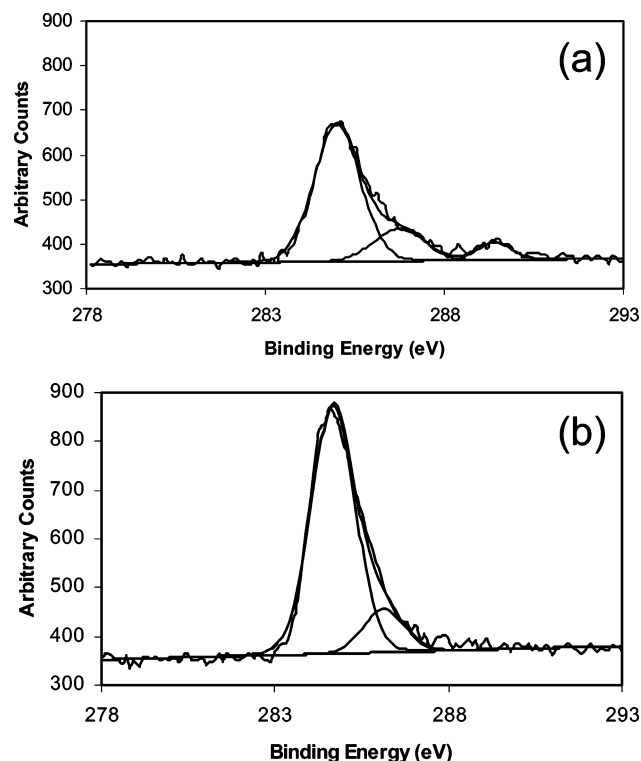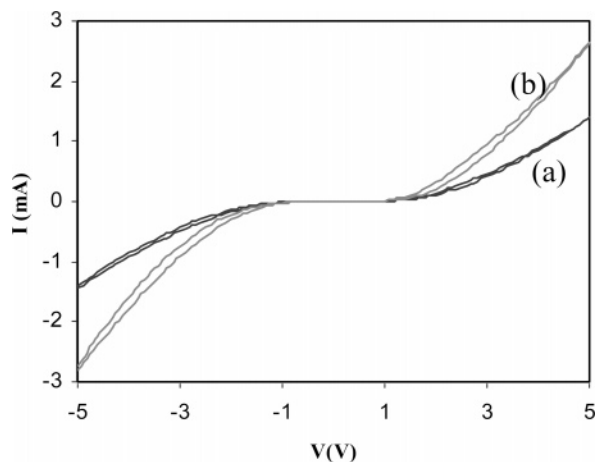

Figure 2. XPS data on the C 1s signals (a) before heating and (b) after heating the surface-grafted monolayer film to 215 °C for 4 h. The takeoff angle was 45°, and a 114.8 W monochromatic Al X-ray source was used for all the measurements.

Control tests with monolayer films derived from **1**, which has no carbonyl carbon in the molecule, shows no C 1s signal at 289.4 eV, thereby confirming that that signal does not arise from absorption of contaminates but indeed from –C=O carbon. Furthermore, the counts due to the CO_2 contamination at 286.1 eV in films derived from **1** remained about the same, relative to the 284.8 eV peak intensity, both before and after heating. Finally, attempts to remove the Boc groups using a 3 M HCl rinse resulted in complete monolayer removal. Hence, nonthermal routes were abandoned.

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Figure 3. *I*(*V*) characteristics of a Molepore test bed device containing a monolayer film derived from **4** (a) before thermal treatment and (b) after thermal treatment to remove the Boc protecting groups.

Molecule **4** was assembled on a Molepore electronic test bed device to form a monolayer on the silicon surface.[11b] The *I*(*V*) characteristics were measured under vacuum immediately after the film assembly. The device was then placed in a furnace and heated at 215 °C for 4 h, and the same measurements were made to compare the hysteresis and the current. Figure 3 shows the *I*(*V*) curves of a typical Molepore device assembled with molecule **4** before and after TGA treatment. The current was doubled, and a larger hysteresis was observed after removal of the Boc protecting groups. Therefore, the oligoanilines, when freed of their Boc groups, are more efficacious for molecular memory devices[11b] based on the results here.

Summary

We outlined the syntheses of oligoaniline compounds containing diazonium salt functionalities which allow monolayer grafting onto hydride passivated silicon surfaces. The synthesized molecules all form monolayers within 1 h as determined by ellipsometry. As confirmed by XPS, removal of the Boc protecting groups on the surface-grafted molecules was successful when using careful thermal treatment of the substrates. Assembly of **4** in a Molepore device followed by thermolysis indicated that the current was doubled and a larger hysteresis was obtained after removal of Boc protecting groups, underscoring the efficacy of this two-step approach to aniline grafting for silicon−molecule hybrid systems. This report demonstrates the controlled synthesis and direct formation of oligoaniline monolayer assemblies atop silicon and thereby paves the way for these established molecular electronic switches to be integrated with the surface of most interest to the semiconductor industry.

Experimental Section

Surface Preparation.[11] Si⟨111⟩ shards (prime grade, boron doped) were cleaned in piranha solution (2:1 H_2SO_4/H_2O_2; piranha solutions are hazardous; handle with care and appropriate personal protective clothing) at 100 °C for 30 min and rinsed with pure water (resistivity > 18 MΩ cm). The shards were immersed in Ar-sparged 40% NH_4F solution for 15 min to generate the hydrogen-terminated surface. The shards were rinsed thoroughly with water and dried in a stream of nitrogen gas.

Reactions with Diazonium Salts.[11] The freshly prepared H-passivated Si surfaces were immediately brought into an N_2 glovebox. A 0.5 mM solution of diazonium salt (diazonium salts can be hazardous to manipulate; work with the minimal amount required and use safety shielding) in anhydrous CH_3CN was freshly prepared in the glovebox, and the hydrogen terminated silicon substrates were immersed in the solution. The reaction vessel was sealed for the desired reaction time. Following assembly, the substrates were removed from the glovebox, rinsed with CH_3CN, and dried with N_2. The film thickness was immediately measured using ellipsometry.

TGA Analysis. A thermogravimetric analyzer was used to heat the monolayer film of molecule **4** on a silicon substrate. The substrate was placed in the TGA furnace which was purged with argon and then heated to 215 °C. The temperature was kept at 215 °C for 4 h in an Ar atmosphere and then cooled to room temperature in Ar. A Quantera XPS scanning microprobe was used in collecting the XPS data on the films before and after heating; the takeoff angle was 45°, and 114.8 W of a monochromatic Al X-ray source was applied for all the measurements.
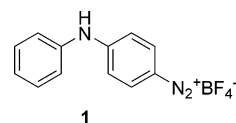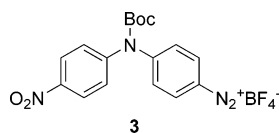

4-Phenylaminobenzenediazonium Tetrafluoroborate (1). To a 250 mL round-bottom flask was added *N*-phenyl-*p*-phenylenediamine (1.00 g, 5.43 mmol). Tetrahydrofuran (THF; 30 mL) was added, and the mixture was cooled to −50 °C. $BF_3\cdot OEt_2$ (2.75 mL, 21.72 mmol) was added dropwise followed by the dropwise addition of *t*-BuONO (0.86 mL, 6.52 mmol) in THF (5 mL). The reaction was allowed to warm to −10 °C at which point Et_2O (150 mL) was added. The suspension was allowed to stir for 10 min. The precipitated solid was collected by vacuum filtration to afford a mixture of **1** and the *N*-nitroso adduct. The collected solid was dissolved in a minimum of CH_3CN (10 mL), and Et_2O (150 mL) was added. The green solid was collected by vacuum filtration to afford the title compound as a light green solid (0.31 g, 20%). FTIR (KBr) 2244, 2186, 1603, 1579, 1531, 1493, 1366, 1323, 1112 cm^{-1}. ^{1}H NMR (400 MHz, (CD_3CN) δ 8.80 (s, 1H), 8.06 (d, *J* = 9.5 Hz, 2H), 7.50 (m, 2H), 7.35 (m, 3H), 7.10 (d, *J* = 9.5 Hz, 2H). ^{13}C NMR (100 MHz, (CD_3CN) δ 156.5, 137.3, 135.3, 130.5, 127.8, 124.5, 116.2, 92.6.
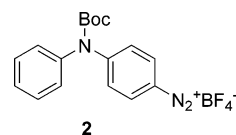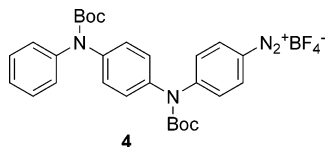

4-(*tert*-Butoxycarbonylphenylamino)benzenediazonium Tetrafluoroborate (2). To a 100 mL round-bottom flask was added $NOBF_4$ (0.07 mL, 0.55 mmol) in a nitrogen filled glovebox. A septum was affixed, and the flask was removed from the glovebox. CH_3CN (5 mL) was added, and the mixture was cooled to −40 °C. Compound **9** (0.15 g, 0.53 mmol) was added to a small vial under a nitrogen atmosphere and dissolved in CH_3CN (5 mL). The aniline was added dropwise to the $NOBF_4$ solution. Following addition, the solution was stirred at −40 °C for 20 min and then allowed to warm to room temperature. Et_2O (50 mL) was added to precipitate the diazonium salt. The solid was collected by vacuum filtration to afford the desired product as a shiny white solid (0.09 g, 46%). FTIR (KBr) 2982, 2267, 1723, 1577, 1494, 1370, 1327, 1309, 1278, 1253, 1167, 1101, 1057 cm^{-1}. ^{1}H NMR (400 MHz, (CD_3)$_2$CO) δ 8.68 (d, *J* = 9.5 Hz, 2H), 7.80 (d, *J* = 9.5 Hz, 2H),

7.56 (m, 2H), 7.51 (m, 1H), 7.40 (m, 2H), 1.49 (s, 9H). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 155.4, 153.0, 141.3, 134.9, 131.0, 129.54, 129.47, 124.7, 105.7, 84.4, 28.0.


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4-[*tert*-Butoxycarbonyl(4-nitrophenyl)amino]benzenediazonium Tetrafluoroborate (3). To a 250 mL round-bottom was added $BF_3 \cdot OEt_2$ (0.10 mL, 0.82 mmol), and the mixture was cooled to −40 °C. Compound **12** (0.09 g, 0.27 mmol) dissolved in THF (3.0 mL) was added dropwise. *t*-BuONO (0.06 mL, 0.54 mmol) was added dropwise, and the reaction mixture was then allowed to warm to room temperature. Et_2O (100 mL) was added to precipitate the diazonium salt. The solid was collected by vacuum filtration to afford the desired product as a pale solid (0.09 g, 78%). FTIR (KBr) 2262, 1735, 1574, 1523, 1344, 1315, 1275, 1252, 1153, 1085 cm^{-1}. ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 8.75 (d, $J = 9.5$ Hz, 2H), 8.41 (d, $J = 9.1$ Hz, 2H), 7.89 (d, $J = 9.5$ Hz, 2H), 7.75 (d, $J = 9.1$ Hz, 2H), 1.47 (s, 9H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 154.5, 152.2, 148.1, 147.2, 135.0, 130.8, 126.14, 126.07, 107.7, 85.3, 27.9.

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4-{*tert*-Butoxycarbonyl-[4-(*tert*-butoxycarbonylphenylamino)-phenyl]amino}benzenediazonium Tetrafluoroborate (4). To a 250 mL round-bottom flask was added $BF_3 \cdot OEt_2$ (0.10 mL, 0.76 mmol), and the mixture was cooled to −40 °C. **15** (0.12 g, 0.25 mmol) in THF (5 mL) was added dropwise. *t*-BuONO (0.06 mL, 0.51 mmol) was added dropwise, and the reaction mixture was then allowed to warm to room temperature. Et_2O (150 mL) was added to precipitate the diazonium salt. The solid was collected by vacuum filtration to afford the desired compound as a white solid (0.03 g, 21%). FTIR (KBr) 2978, 2280, 1737, 1716, 1579, 1509, 1371, 1338, 1322, 1271, 1252, 1164, 1085, 1055 cm^{-1}. ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 8.69 (d, $J = 9.5$ Hz, 2H), 7.84 (d, $J = 9.5$ Hz, 2H), 7.39 (m, 6H), 7.29 (m, 3H), 1.44 (s, 18H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 155.4, 153.9, 152.9, 144.5, 143.8, 138.0, 135.0, 129.8, 129.7, 128.8, 128.3, 127.0, 124.8, 105.7, 84.5, 81.6, 28.3, 28.0.

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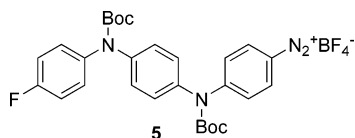
4-(*tert*-Butoxycarbonyl-{4-(*tert*-butoxycarbonyl(4-fluorophenyl)-amino]phenyl}amino)benzenediazonium Tetrafluoroborate (5). To a 250 mL round-bottom flask was added $BF_3 \cdot OEt_2$ (0.05 mL, 0.37 mmol), and the mixture was cooled to −40 °C. **19** (0.06 g, 0.12 mmol) in THF (5 mL) was added dropwise. *t*-BuONO (0.03 mL, 0.24 mmol) was added dropwise, and the reaction mixture was then allowed to warm to room temperature. Et_2O (200 mL) was added to precipitate the diazonium salt. The solid was collected by vacuum filtration to afford the desired compound as a light green solid (0.06 g, 84%). FTIR (KBr) 2901, 1615, 1506, 1430, 1372, 1318, 1163, 1113, 1059, 1033 cm^{-1}. ^{1}H NMR (500 MHz, $(CD_3)_2$-CO) δ 8.68 (d, $J = 9.5$ Hz, 2H), 7.83 (d, $J = 9.5$ Hz. 2H), 7.44 (d, $J = 8.8$ Hz, 2H), 7.35 (m, 4H), 7.17 (m, 2H), 1.44 (s, 18H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 155.4, 153.8, 152.9, 144.3, 140.0, 138.1, 134.9, 130.4, 130.3, 129.7, 128.6, 124.8, 116.5, 116.4, 105.8, 84.5, 81.8, 28.3, 28.0 (peak due to C−F coupling included).

6
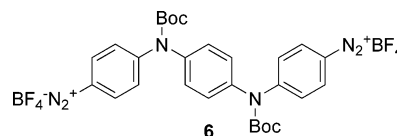
[4-(*tert*-Butoxycarbonylphenylamino)phenyl]phenyl-carbamic acid-4,4'-*tert*-butyl ester Benzenediazonium Tetrafluoroborate (6). To a 100 mL round-bottom flask in a nitrogen filled glovebox was added NOBF$_4$ (0.04 g, 0.34 mmol). A septum was affixed, and the flask was removed from the glovebox. CH_3CN (9 mL) and sulfolane[10] (1 mL) were added and cooled to −30 °C. To a separate 100 mL round-bottom flask was added **22** (0.08 g, 0.16 mmol) dissolved in sulfolane (16 mL) and CH_3CN (2 mL). The aniline solution was added dropwise to the NOBF$_4$ solution that was then allowed to stir at −30 °C for 30 min. The reaction was warmed to 0 °C, and Et_2O (25 mL) was added. The precipitate was collected by vacuum filtration to afford the desired product as an orange/brown solid (0.07 g, 63%). FTIR (KBr) 2977, 2274, 2224, 2166, 1729, 1578, 1508, 1370, 1313, 1109 cm^{-1}. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.69 (d, $J = 9.6$ Hz, 4H), 7.93 (d, $J = 9.6$ Hz. 4H), 7.62 (s, 4H), 1.48 (s, 18H). Attempts to acquire ^{13}C NMR spectral information were unsuccessful due to the instability of compound **6** in solution for extended time periods.

Supporting Information Available: General procedures, synthetic details, and characterization data for **7−12**, **14−19**, **21**, and **22** as well as copies of ^{1}H NMR spectra for **1−6** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.