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Communication

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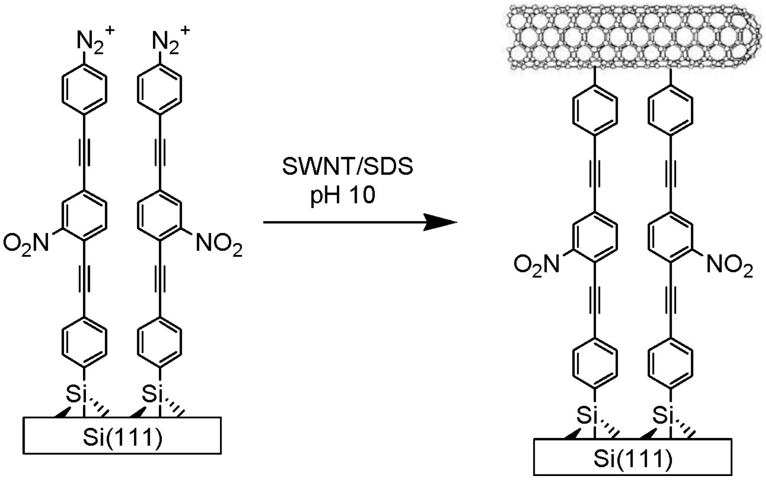

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Fabrication of Carbon Nanotube−Molecule−Silicon Junctions

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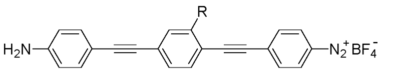
Previous work in our laboratory has demonstrated covalent attachment of arenes via aryldiazonium salts to Si (hydride-passivated single crystal or poly Si; ⟨111⟩ or ⟨100⟩, p-doped, n-doped, or intrinsic), GaAs, and Pd surfaces.[1] In the case of Si, this provides a direct arene−Si bond with no intervening oxide. We also reported on the use of aryldiazonium salts for the direct covalent linkage of arenes to single wall carbon nanotubes (SWNTs) where the nanotubes can exist either as bundles or as individual structures[2,3] (when surfactant-wrapped). Here, we merge these two concepts for the covalent attachment of individualized (unroped) SWNTs to Si surfaces via orthogonally functionalized oligo(phenylene ethynylene) (OPE) aryldiazonium salts.[4−10] To our knowledge, this is the first report of a procedure to covalently attach SWNTs to a silicon surface that does not require a CVD growth process. In addition to functioning as the linker units, OPEs and related conjugated molecules can serve as electronically active moieties in sensor and device embodiments.[11] Hence, the union of easily patterned silicon with the often hard-to-affix nanotubes can provide a critical interface methodology for electronic and sensor arrays.

Chemical orthogonality provides chemoselection for dual substrate/nanotube attachment, while OPEs provide a rigid structure to minimize molecular looping upon surfaces. The target OPE molecules contain a diazonium salt on one end and an aniline moiety on the other end (Figure 1). This design allows for selective assembly via the first diazonium salt onto a hydride-passivated silicon surface followed by diazotization of the aniline using an alkyl nitrite. Once formed, the new diazonium salt, covalently bound to the Si surface, will react with an aqueous solution of individualized sodium dodecyl sulfate (SDS)-wrapped SWNTs[12] (SWNT/SDS), resulting in covalent attachment of the SWNTs[13] to the silicon surface using the OPEs (Scheme 1).

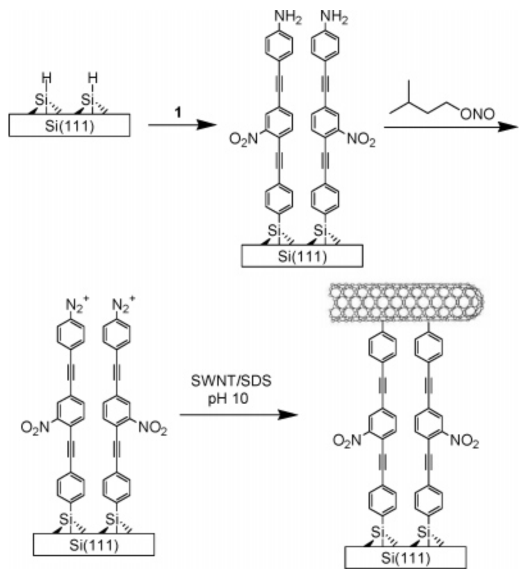


1, R = NO_2
2, R = H

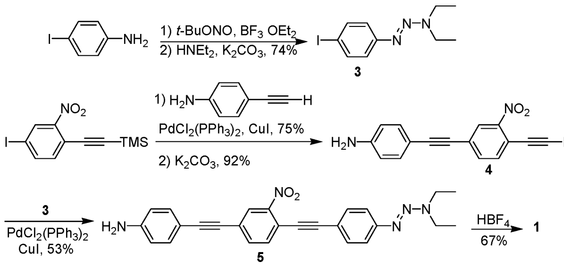
Figure 1. Oligo(phenylene ethynylene)s **1** and **2** used to covalently attach SWNTs to silicon.

The key to developing an orthogonal attachment chemistry was the formation of a diazonium species with a latent diazonium salt at the other end. An α-dialkyltriazenyl-ω-aniline proved to be efficacious upon the demonstration that the triazene could be converted to a diazo species[14] without affecting the aniline. The synthesis of the mononitro compound **1** is shown in eq 1, and compound **2** was similarly synthesized (see Supporting Information). Indeed, the triazene moiety on **5** was readily converted to the diazonium salt upon treatment with HBF_4, while the aniline remained intact, the latter thereby serving as a masked diazonium salt ready for generation after surface attachment. Attempts to use an α,ω-bisdiazonium salt OPE were unsuccessful due to the rapid loss of the terminal diazonium moiety during the silicon assembly.[1]

Scheme 1. Stepwise Attachment of Carbon Nanotubes to Silicon via **1**



In a typical experiment, the diazonium salt (**1** or **2**) in anhydrous CH_3CN (2.0 mM) was exposed to a hydride passivated silicon ⟨111⟩ surface according to our previous report[1] in a nitrogen-filled glovebox for the desired reaction time (vide infra). Following monolayer assembly, the substrate was removed from the glovebox and placed in a 0.3 M solution of isoamylnitrite in CH_3CN for 5 min to diazotize the terminal aniline (Scheme 1). The substrate was then removed and immediately immersed in an aqueous SWNT/SDS suspension[12] (0.7 μM) at pH 10 for 24 h. The SWNT remained predominantly as individualized SWNTs rather than in bundles. Following nanotube attachment, the substrate was removed, rinsed with water and CH_3CN, and dried with a stream of nitrogen to afford the desired structure (Scheme 1).



(1)

Molecular attachment to the silicon substrate was analyzed using ellipsometry (Table 1). Monolayer formation for **1** reached the theoretical height after 1 h. However, monolayer thicknesses for **2**

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Table 1. Calculated and Observed Thicknesses of **1** and **2** on Si⟨111⟩

	Thickness (nm)	
Molecule	found[a]	calcd[b]
1	2.0[c]	1.9
2	1.4,[c] 2.1[d]	1.9

[a] Value measured by ellipsometry with ca. ±0.2 nm error. All reported values are an average of three measurements for reactions of a 2.0 mM solution of diazonium salt in CH_3CN. [b] The theoretical thickness calculated by molecular mechanics (not including the arene−silicon bond). [c] Assembly performed inside a nitrogen-filled glovebox for 1 and 16[d] h.

averaged slightly below the theoretical SAM thickness, although thicknesses close to the theoretical value were attained by reacting the substrate with a solution of **2** for longer time periods.

Figure 2 shows the XPS spectrum of the N1s region of a monolayer of **1**. The smaller peak at 405.8 eV is due to the nitrogen atom of the nitro group, and the peak at 399.7 eV is due to the aniline plus nitrogen gas adsorbed from the atmosphere. Attempts to measure the nitrogen signal of the surface-tethered diazonium salt were unsuccessful due to its rapid decomposition during transfer in air.

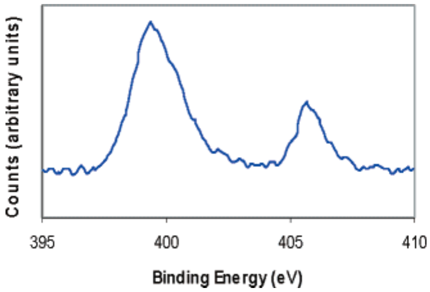

Figure 2. XPS spectrum of the N1s region of a SAM of compound **1** (45° take-off angle).

SWNT attachment was further verified using atomic force microscopy (AFM) (Figure 3). The AFM image shows a high coverage of SWNTs bound to the silicon substrate via the OPE molecules. The architectures are highly robust and able to withstand rinsing and 1 min of sonication. Many surface-bound nanotubes exist as individuals, although there may be small bundles present, as well. While the nanotube diameters range from 0.95−3.1 nm, as recorded by the height measurements, they can be difficult to precisely ascertain due to their projection upward from the molecule-grafted surface. We found SWNT coverage to be controllable by varying the SDS/SWNT reaction time with the terminal diazonium salt from 3 to 16 h.

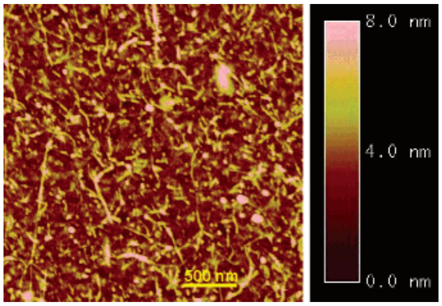

Figure 3. Tapping mode AFM image of SWNTs covalently bound via **1** (not seen) on a silicon surface.

Control experiments were performed to ensure both the OPE and diazotization steps were required for SWNT attachment (Supporting Information). When the OPE was not employed or when the second diazotization step was eliminated, there was no attachment of the SWNTs to the silicon surface. This leads us to conclude that the SWNTs are indeed covalently attached[13] to the assembled organic molecule via the in situ generated diazonium salt.

It is important to note that when using $NOBF_4$ to perform the diazotization (as opposed to the alkylnitrite) on the assembled monolayer, surface roughening in the form of large peaks and valleys (10−20 nm) was observed and there were no surface-bound nanotubes.

The lightly functionalized surface-bound SWNTs are likely to retain significant degrees of their electronic and optical properties since it takes functionalization of ca. 1 in 100 carbons along a SWNT to even cause a loss of the sensitive UV van Hove singularities.[15] Furthermore, when applied only to the end-segments of SWNTs that straddle patterned gap arrays, the active central portions of the SWNTs will remain unperturbed by the surface hybridization moieties. Thus, this Si−nanotube assembly strategy could provide the basis for directing SWNTs to precise junctions in electronic, optical, and sensor arrays.

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Supporting Information Available: Synthetic details and complete structure preparation and assemblies. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Stewart, M. P.; Maya, F.; Kosynkin, D. V.; Dirk, S. M.; Stapleton, J. J.; McGuiness, C. L.; Allara, D. L.; Tour, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 370−378.
(2) Dyke, C. A.; Tour, J. M. *J. Phys. Chem. A* **2005**, *108*, 11151−11159.
(3) Dyke, C. A.; Tour, J. M. *Chem.*−*Eur. J.* **2004**, *10*, 812−817.
(4) Kosynkin, D. V.; Tour, J. M. *Org. Lett.* **2001**, *3*, 993−995.
(5) Kosynkin, D. V.; Yang, J.; Tour, J. M. *Mater. Res. Soc. Symp. Proc. 660*, **2001**, JJ3.5.1−JJ3.5.5.
(6) Flatt, A. K.; Yao, Y.; Maya, F.; Tour, J. M. *J. Org. Chem.* **2004**, *69*, 1752−1755.
(7) Pollack, S. K.; Naciri, J.; Mastrangelo, J.; Patterson, C. H.; Torres, J.; Moore, M.; Shashidhar, R.; Kushmerick, J. G. *Langmuir* **2004**, *20*, 1838−1842.
(8) Hickman, J. J.; Laibinis, P. E.; Auerbach, D. I.; Zou, C. F.; Gardner, T. J.; Whitesides, G. M.; Wrighton, M. S. *Langmuir* **1992**, *8*, 357−359.
(9) Gardner, T. J.; Frisbie, C. D.; Wrighton, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 6927−6933.
(10) Walker, B. R.; Wassel, R. A.; Stefanescu, D. M.; Gorman, C. B. *J. Am. Chem. Soc.* **2004**, *126*, 16330−16331.
(11) Tour, J. M. *Molecular Electronics: Commercial Insights, Chemistry, Devices, Architecture and Programming*; World Scientific: River Edge, NJ, 2003.
(12) O'Connell, M. J.; Bachilo, S. M.; Huffman, C. B.; Moore, V. C.; Strano, M. S.; Haroz, E. H.; Rialon, K. L.; Boul, P. J.; Noon, W. H.; Kittrell, C.; Ma, J.; Hauge, R. H.; Weisman, R. B.; Smalley, R. E. *Science* **2002**, *297*, 593−596.
(13) Dyke, C. A.; Tour, J. M. *Nano Lett.* **2003**, *3*, 1215−1218.
(14) Kimball, D. B.; Haley, M. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3338−3351.
(15) Dyke, C. A.; Stewart, M. P.; Tour, J. M. *J. Am. Chem. Soc.* **2005**, *127*, 4497−4509.

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