VOLUME 72, NUMBER 20 JOC Perspective SEPTEMBER 28, 2007

# Transition to Organic Materials Science. Passive, Active, and Hybrid Nanotechnologies

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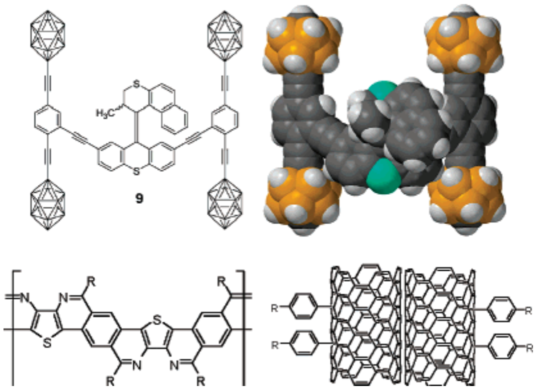
*Received March 15, 2007*



This article covers the author's transition from small molecule organic synthesis into polymeric materials and nanotechnology which led to receipt of the Arthur C. Cope Scholar Award in 2007. This includes his start in organometallic reaction development, synthesis of precisely controlled oligomers, conjugated polymers, planar conjugated polymers, and his work on fullerenes. Also mentioned are the people of influence in his life during that formative period. The meaning of nanotechnology is explained in light of bottom-up vs top-down construction and then more specifically related to the passive, active, and hybrid sides of nanotechnology research. These three areas are explained using examples from the author's laboratory: from the passive side, functionalization of carbon nanotubes and their use in composites; from the active side, molecular electronics and nanocars; and finally, the hybrid side, complementing silicon with molecules.

## From Small Molecule Synthesis to Organic Materials Science

I distinctly recall when I was hovering over the thermal printout recorder of our lab's gas chromatograph at Purdue University in 1984, when my professor and mentor, Ei-ichi Negishi, entered. He began speaking with me about the future of synthetic chemistry. He started to tell me that natural product synthesis and related synthetic methodology would have minimal sustainable funding in the coming years. Science was evolving, as it always had, and Negishi predicted that there would be two "hot" areas where synthetic chemists might have thriving funding in the future: bioorganic chemistry and materials−polymer chemistry. It was at that moment that my mind raced to the future: Where I should hoist my banner of independence?

Over the next 3 years, the field of bioorganic chemistry started to blossom through the exploits of some enormously talented organic chemists, most of them assistant professors that were destined to become stars in their own right. So I started to think more of materials science, and synthetic organic materials in particular, because the area seemed less crowded. About that time, Robert Grubbs (Cal Tech) was beginning to publish some

10.1021/jo070543s CCC: $37.00 © 2007 American Chemical Society
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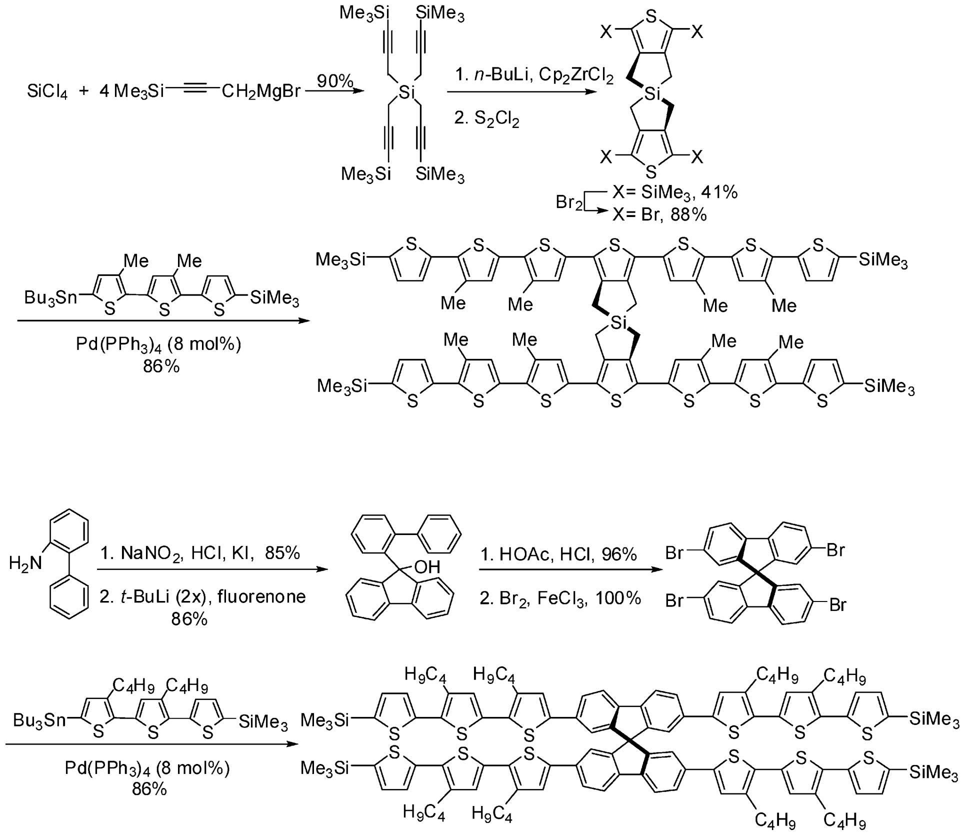
**SCHEME 1. First Examples of Spirofused Molecular Switches That Were Synthesized in Our Laboratory[3,4]**



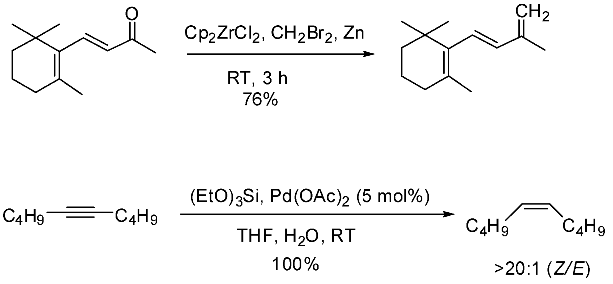
remarkable polymerization methods using Schrock-type carbene catalysts, and Richard Schrock (MIT) was doing similar work. George Whitesides (Harvard) was pioneering, as he did in most areas that interested him, the use of self-assembled monolayers (SAMs), a topic that he had learned with guidance from David Allara (then at Bell Labs, now Penn State). Further, in 1986, while doing my postdoctoral studies at the University of Wisconsin and then Stanford University with Barry Trost, I tried binding a new Ni−Cr bimetallic catalyst system to derivatized polystyrene to enhance the catalyst's stability and selectivity.[1] It worked remarkably well.

In 1988, John Stille (Colorado State) came through for a departmental seminar. Graduate students and post docs at Stanford could sign up to have a department-paid lunch at a local restaurant with the seminar speakers, and Stille was high on my list. I asked him how a synthetic chemist like himself had learned so much polymer chemistry. Stille clarified that he had started out as a polymer chemist and moved into synthetic organic methodology as his career progressed. After scribbling some of my polymer-based ideas on a napkin, Stille recommended that I visit C. Grant Willson at the IBM Almaden Research Center, a 35-minute drive, baring traffic, down Highway 101 from Stanford. So I did. And Willson (now at the University of Texas at Austin), an organic chemist from academia who had moved to IBM and risen to the premier fellow status for his work on chemically amplified resists, welcomed me for a lunch at the Almaden facility. I described to Willson some of my synthetic chemistry ideas for making novel polymers, which as I recall now were quite naïve, yet I shared them with youthful enthusiasm. He then introduced me to Bob Miller, a synthetic organic chemist at IBM working in the area of polysilanes. Willson then invited me to spend a week at the IBM labs working on polysilane syntheses with Miller, an opportunity I immediately accepted. I took one week of my two weeks of vacation from the Trost lab to spend it at the IBM Almaden facility making polysilanes by treating dichlorodiarylsilanes with sodium metal. I spent many hours quizzing Miller over lunch and talking with the analytical lab technicians and my office mates (such as the polymer chemist William Daly, who was there on sabbatical leave from Louisiana State University) in a desire to learn as much polymer chemistry as possible.

During the fall of 1988, while setting up my aged yet freshly painted laboratory at the University of South Carolina, I read an article by Ari Aviram, then at IBM Yorktown, in the *Journal of the American Chemical Society* (*JACS*) on a proposed spiro-fused "molecular switch".[2] He claimed that if one could build such a molecule, and then place it between six juxtaposed address probes, it could respond like a molecular switching device. I called Aviram and inquired whether anyone had ever made such a molecule. He said, "No." But he was delighted that I would try, and he has been a kind supporter of my career ever since. Upon my first students' completion of the core of the spiro-fused molecular switch, I was overjoyed that Lou Hegedus (Colorado State University), the associate editor of *JACS*, agreed to accept this simple synthetic contribution.[3] And then once we extended the conductive arms of the switch molecule, it was also accepted to *JACS* (Scheme 1)[4] (again through the good graces of Hegedus who was most kind to the assistant professor).

Shortly after publication of the molecular switch, an odd thing happened. I received a phone call (no email in those days) from a reporter at *Scientific American* magazine. She said something like, I understand that you've made the most complex molecule

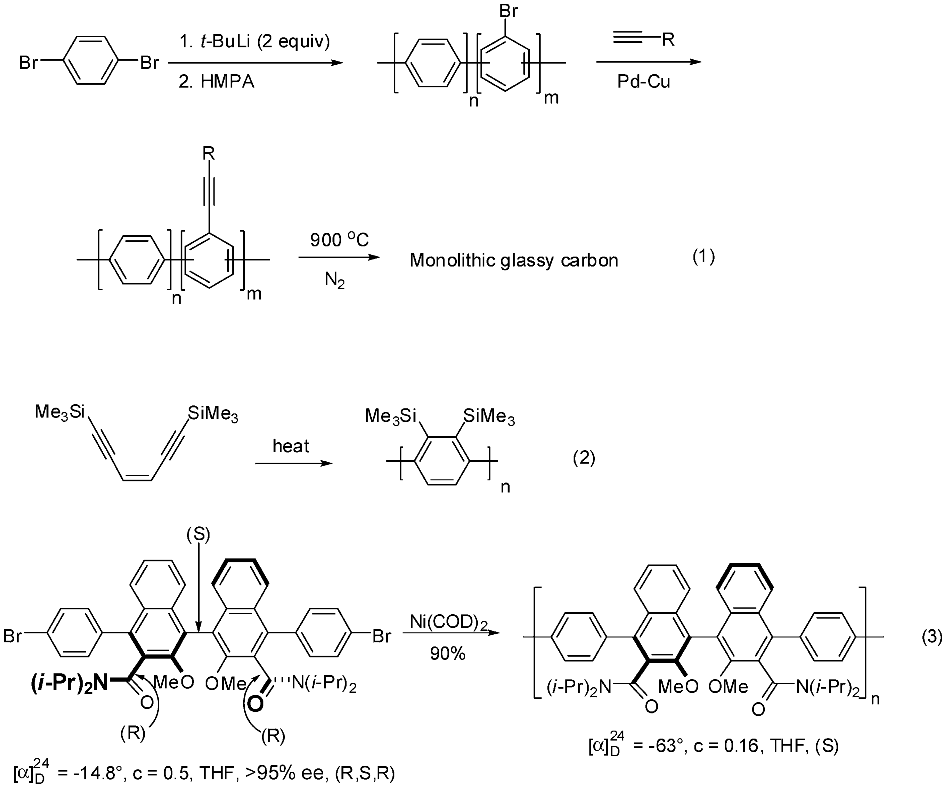
**SCHEME 2. Simple Methylenation of Carbonyl Compounds[6] and a Sol−Gel-Based Selective Hydrogenation Protocol[7] That Was Developed in Our Laboratory Before We Moved Concertedly into the Area of Synthetic Organic Materials**



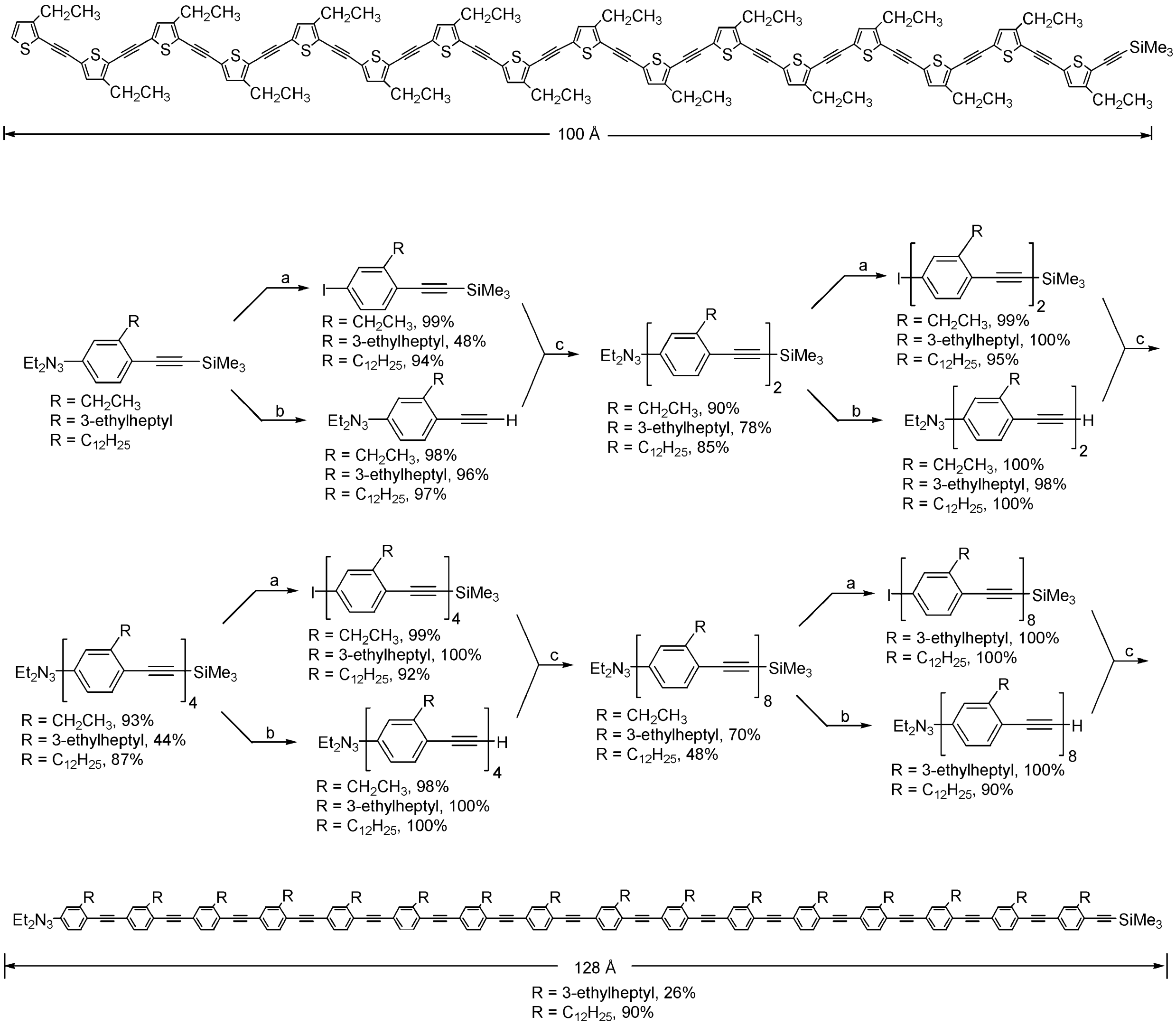
ever synthesized. “Huh?,” I replied, all the while thinking that Kishi (Harvard) had recently published the synthesis of palytoxin.[5] But not wanting to diminish her interest, I replied that though the spiro switch was not the most complex molecule ever synthesized, it was reasonably intricate and certainly the first completed synthesis of a proposed molecular switch for molecular electronics. That is when I realized something that was, for me, profound: if I make a natural product investing tens of person years and painstaking effort, few beyond the synthetic organic community will generally take interest. But if I take my synthetic background and apply it to the materials science world, then I would get far more recognition than I rightly deserved. That seemed wonderful in allaying my assistant professor insecurities.

Concurrent with my carrying out these efforts in molecules for molecular electronics, I was writing all the standard synthetic methodology proposals to the NIH and NSF, the two funding agencies that underwrote most of my Ph.D. and postdoc careers through grants to Negishi and Trost. But none of my independent proposals in synthetic methodology were being funded. I submitted 37 proposals in my first 36 months as a faculty member! And most of those as a single PI since collaborative proposals were less common in those days. Furthermore, word processors were far less efficient than they are now; the insertion of chemical graphics meant leaving an open space and then physically cutting and pasting in the structures, for example. Of course, some of those proposals, if rejected, were reworked and resubmitted the following year, and several similar proposals were sent to different agencies wherein I explained that if both were funded, I would only accept funding from one source. However, double-funding was not a problem because my success rate was sufficiently low. Hence, my approach was to work like the dickens while seeking funds from every source that had something to offer: a few from the university, some from the state, some from private sources such as the PRF and corporations, and every federal agency that I could imagine that had an interest in organic chemistry or polymers. I am aware that others have been successful with a more precision-targeted proposal-writing approach. But my success rate was far too low to have ever been successful with that method. The Office of Naval Research through their polymer program managed by Ken Wynne (now at Virginia Commonwealth University) and the Defense Advanced Research Projects Agency were the mainstay of my research program for many years, and to them I am greatly indebted. Interestingly, I was able to ultimately receive support from the NSF, not from the chemistry program (which came later) but from the polymers program, where I received

**SCHEME 3. Process for the Synthesis of Brominated Polyphenylenes and the Alkynation and Conversion to Monolithic Glassy Carbon through Thermolysis (eq 1).[8a−f] Enediyne Polymerization Route to Polyphenylenes (eq 2)[8g,h] and Synthesis of Linear Chiral Nonracemic Polyarylenes (eq 3)[8i]**



**SCHEME 4. 100 Å Long Oligo(thiophene ethynylene)[9r] and 128 Å Long Oligo(phenylene ethynylene),[9s] Both Prepared by Selective Iterative Divergent/convergent Approaches (These were Early Candidates Tested in Our Molecular Wire Studies for Molecular Electronics)[a]**



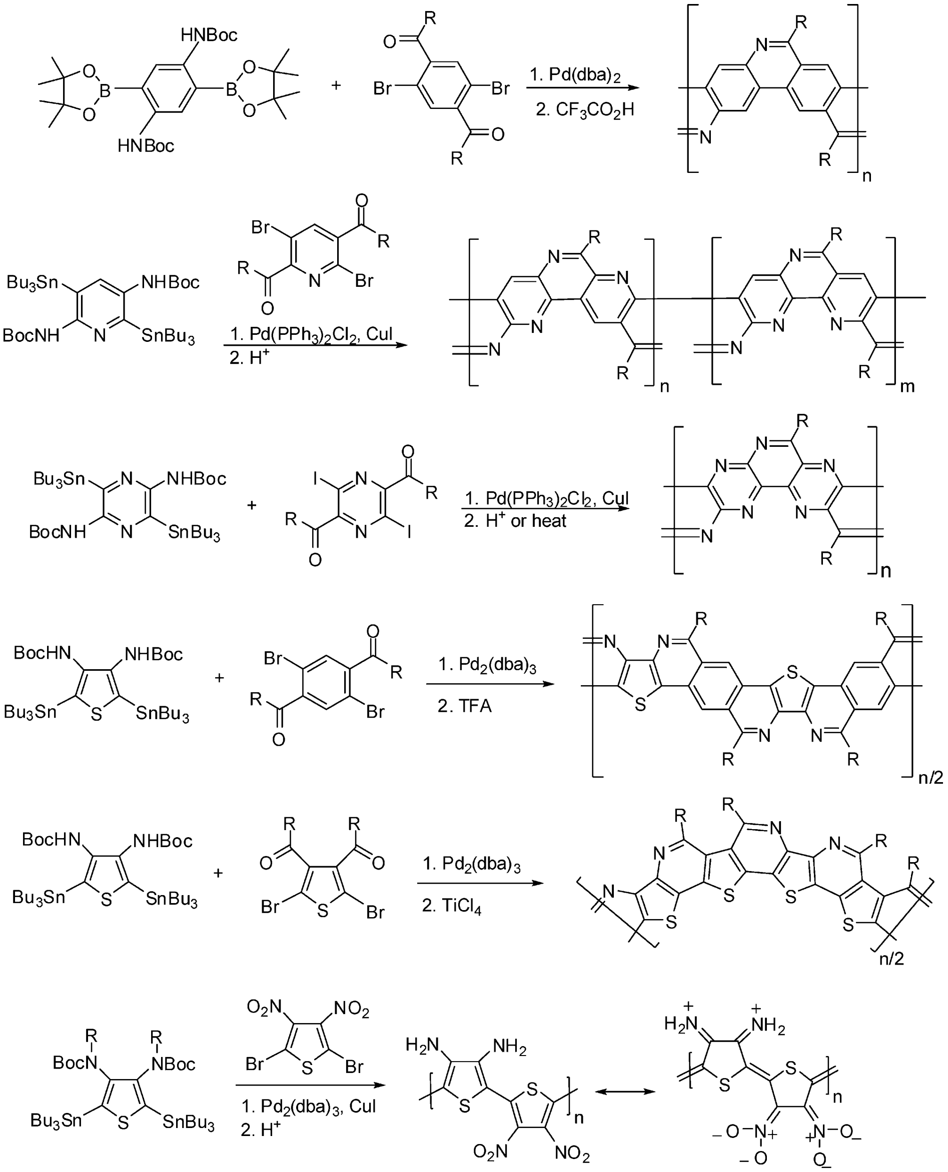
[a] Reagents: (a) MeI as solvent, 120 °C in a screw cap tube; (b) $K_2CO_3$, MeOH, 23 °C or *n*-$Bu_4NF$, THF, 23 °C; (c) $Pd(dba)_2$ (5 mol %), CuI (10 mol %), $PPh_3$ (20 mol %), *i*-$Pr_2NH$/THF (1:5) 23 °C.

the Presidential Young Investigator Award. I never was successful at securing funding from the NIH, and after the third unsuccessful attempt, I moved wholeheartedly into the organic materials area. In part, I credit the NIH and its extremely high threshold for securing funding in the late 1980s for my move in the organic materials area. On the days of receiving the declination of funding letters from the NIH, sadness certainly followed. I would always call my wife, Shireen, because she was repeatedly there to reassure me of my self-worth, and my children were still there to call me “Daddy”. And by the following day, I was back at my Mac SE (with its 1 MB of RAM), writing another proposal. Another lesson: academic research is not for cowards or those with thin skin. I endeavored to dwell only momentarily on the harsh, sometimes even unnecessarily personal, comments of reviewers, while seeking to learn as much as I could from their constructive criticisms and then rewrite and resubmit the proposal right back to the same agency while inserting any new preliminary data that we had gotten.

In 1989, when I wanted to learn about conducting polymers, I cold-called Alan MacDiarmid (University of Pennsylvania) and asked if I could visit his lab with one of my graduate students, Eric Stephens. He was enormously gracious, kindly entertaining Eric and me at dinner, and opening his lab and his heart to us. He likewise became an active supporter of my career for the next many years. With his recent passing, I have lost the company of one of materials chemistry’s finest gentlemen.

Although I was quite content at the University of South Carolina and they had been extremely good to me over the past 11 years, in 1999, at the request of Richard (Rick) Smalley, I moved to Rice University’s Department of Chemistry and their Center for Nanoscale Science and Technology. This opened new doors for me, particularly in the areas of nanotechnology and specifically in the use of carbon nanotubes. I learned so much from Rick. He became a dear friend and a personal hero, and his passing away was tough to bear.

**SCHEME 5. Various Routes to Planar Polymers That We Conducted. Illustrated Are the Routes to Planar Polyphenylenes, Planar Polypyridines, Planar Polypyrazines, Linear Planar Poly(thiophene pyridine)s, Bent Planar Poly(thiophene pyridine)s, and Planar Polythiophenes that Are Rendered Planar through Alternating Donor/Acceptor Interactions. All of These Extended $\pi$-Conjugated Systems Have Unusually Low Optical Bandgaps for Their Parent Repeat Unit Types[10]**

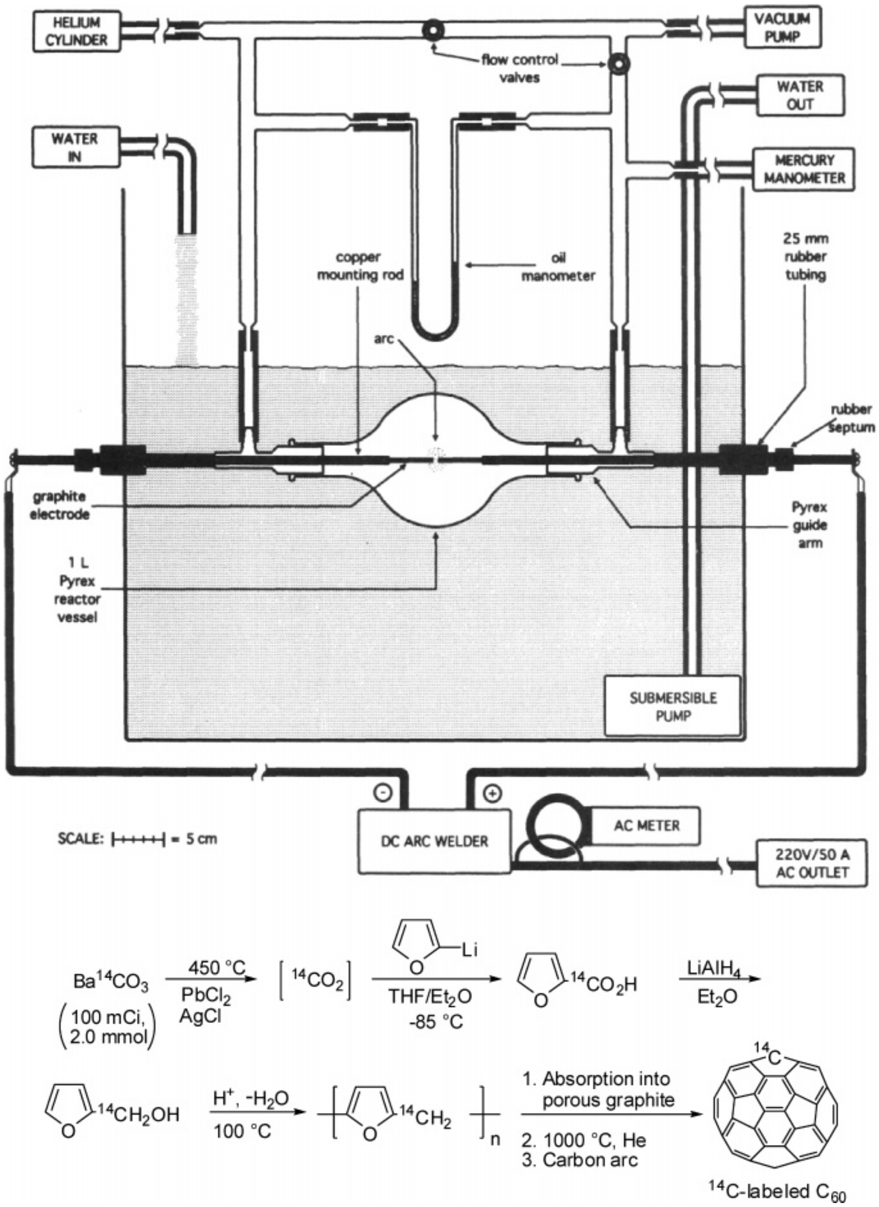


The early work at South Carolina took us through simple organometallic reactions such as methylenations[6] and sol−gel-based metal-catalyzed hydrogenations[7] (Scheme 2); into more materials-related fields of polyarylenes such as polyphenylene syntheses for glassy carbon monoliths, an enediyne route to polyphenylenes, and chiral linear polyarylenes[8] (Scheme 3); precisely controlled conjugated oligomers for electronics and optics[9] (Scheme 4), planar conjugated polymers for band gap minimization via covalent and alternating donor−acceptor strategies[10] (Scheme 5); large-scale (at the time) fullerene syntheses in a round-bottomed flask,[11] the first gram quantity purifications of $C_{60}$ and $C_{70}$ using simple column chromatography,[12] fullerene modifications,[13] and early biological studies including in vitro and in vivo use[14] of radiolabeled fullerenes[15] (Scheme 6); and then into the development of flame-retarding polymers and additives for plastics.[16] This developed into three main areas of organic nanotechnological interest for our group: carbon nanotubes, molecular electronics, and nanomachines. On the basis of these three areas, I shall present nanotechnology in its three facets: the passive, active, and hybrid sides.

## Nanotechnology

The NSF definition of nanotechnology is as follows: "Research and technology development at the atomic, molecular or macromolecular levels, in the length scale of approximately 1−100 nanometer range, to provide a fundamental understanding of phenomena and materials at the nanoscale and to create and use structures, devices and systems that have novel properties and functions because of their small and/or intermediate size."[17] Hence, the "technology" part of nanotechnology implies the connection to the macroscopic world in a way that small molecule chemists, generally, did not consider. An important distinction is that although small molecule chemists did not usually make the connection to the macroscopic world,

**SCHEME 6. Round-Bottomed Flask-Based Method[11] for the Preparation of $C_{60}$ and Some Other Higher Fullerenes That also Led to the Simple Column Chromatography Separation of Gram Quantities of $C_{60}$ and $C_{70}$ Using Activated Charcoal and Derivatized Polystyrene as Stationary Phases,[12] Respectively. The Bottom Synthetic Scheme Shows Our Route to $^{14}C$-Labeled $C_{60}$ That Was Used for in Vivo and in Vitro Toxicity Studies[13−15]**



polymer chemists did. The polymer chemist routinely considered a broad range of nanoscale and macroscale properties ranging from monomer reactivity and interchain interactions to bulk phase and property behavior such as toughness, electrical conductivity, bio-degradability, or flame retardancy. Hence, in a very realistic sense, some types of chemists have been nanotechnologists for over a century. But the technology part also implies a strong interface with nonchemists, something that had not been traditionally taught in synthetic chemistry graduate departments. But these days, working with engineers and physicists has become commonplace in university settings. This is often required if one is going to see the nano become a nanotechnology. So collaborations have become the order of the day, and that is a welcomed experience that enriches the science and the technology.

Another thing that nanotechnology provides is the purposeful bottom-up construction approach rather than the more typical top-down approach. An easy way to illustrate this is by comparing Nature's construction methods to humankind's construction methods. All biological systems are constructed from the bottom up. Within biology's toolkit, there is molecular arrangement into larger structures through thermodynamically controlled methods such as self-assembly. There are also enzymatically controlled assembling routes that provide the precise placement of molecular-sized entities for the construction of higher order structures in biological systems. Humankind, on the other hand, constructs its systems primarily through a top-down approach where large objects are fashioned into smaller ones. For example, when humans want to make a table, they generally find a large tree, cut it down and fashion it into the table. Likewise, to make micron- or sub-micron-sized transistors, the semiconductor industry presently takes large silicon wafers and patterns and etches them to form the small desired features using billion-dollar fabrication facilities. Is

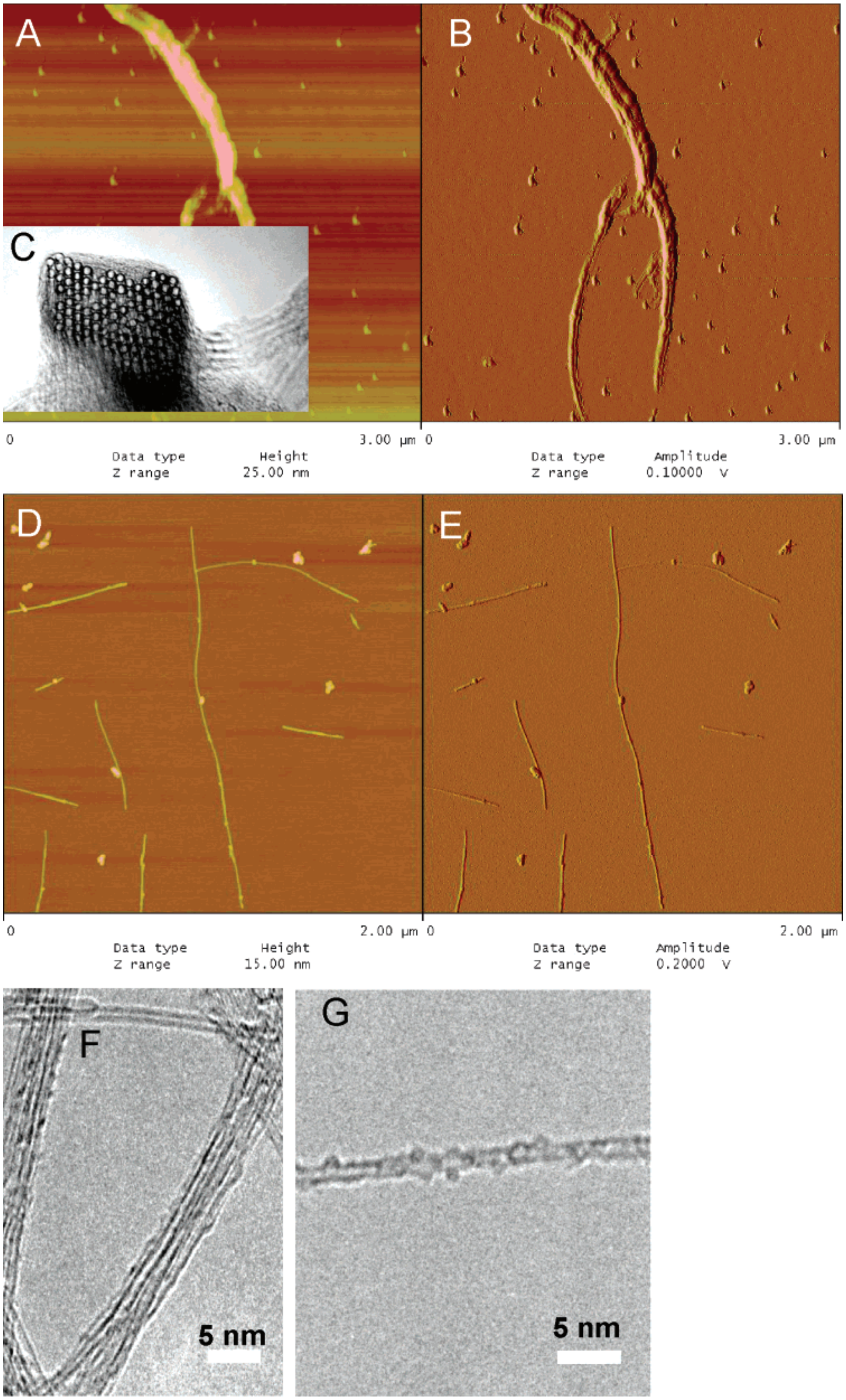
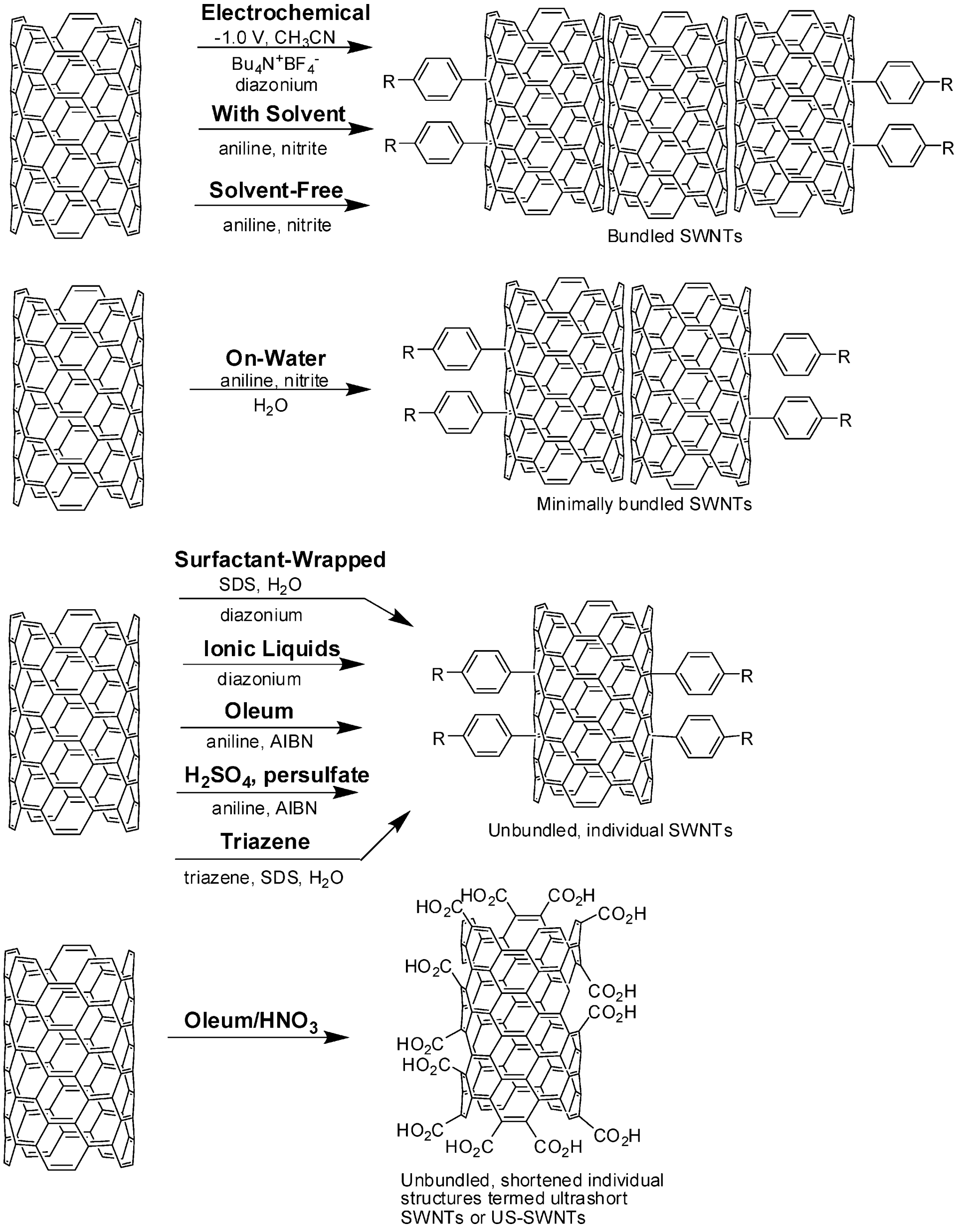


**FIGURE 1.** Atomic force microscopy (AFM) analysis (spin coated onto freshly cleaved mica) by (A) height and (B) amplitude of unfunctionalized SWNTs that were washed free of their sodium dodecyl sulfate (SDS) wrappings (3 $\mu$m picture edge). (C) A sample of roped SWNTs as viewed by transmission electron microscopy (TEM); each SWNT in the sample is approximately 1 nm in diameter. Notice their tendency to rebundle, unlike the functionalized SWNTs in (D) and (E). The AFM analysis (spin coated onto freshly cleaved mica) by (D) height and (E) amplitude of 4-*tert*-butylphenylene functionalized individual SWNTs that had been treated as SDS-wrapped SWNTs in water (2 $\mu$m picture edge). These functionalized SWNTs were washed free of their SDS wrapping prior to imaging yet they remain unbundled throughout their entire lengths. (F) Another TEM view of unfunctionalized and therefore roped SWNTs on a lacy carbon grid. (G) TEM of a functionalized carbon nanotube on a lacey carbon grid; the aryl addends can seen as bumps along the SWNT sidewall. There is no tendency to re-bundle for the 4-*tert*-butylphenylene functionalized SWNT.[20]

**SCHEME 7. Various Carbon Nanotube Functionalization Reactions That We Have Developed along with the Types of Products (Bundled, Minimally Bundled, or Unbundled) That Can Be Obtained**[21−30]



bottom-up construction practical? If we look at the ubiquitous modes of biology around us, and we accept that biology is the most elegant of artisans, then bottom-up construction could make great sense. Moreover, biology is not magical. It is sophisticated yet efficient in its modes of operation. Therefore, it underscores our need to imitate this mode of construction, at least in many design scenarios, and it behooves us to begin investigations into the purposeful bottom-up fabrication of micron and then macroscopic objects and systems.

In an attempt to further define nano so that it can be more precisely categorized, I think that it is useful to separate nanotechnologies into three groupings.[18]

*Passive nanotechnology:* The nano part does nothing particularly elaborate. Just its presence adds a significant increase to the performance of the system. For example, the addition of functionalized carbon nanotubes to rubber can greatly enhance the toughness of the rubber without a loss in the strain-at-break (the distance that it can be stretched before unrecoverable failure). The applications of these passive systems are being realized today in commercial products, and the time from lab to market is generally shorter than in active systems.

*Active nanotechnology:* In this case, the nano entity does something quite elaborate such as taking up a photon and releasing an electron or moving in a specific and definable fashion across a surface. The applications of these active systems in commercial products are generally further in the future.

*Hybrid nanotechnology:* The complementing of a known platform through the attachment of a nanosized entity but where the platform carries the bulk of the burden. For example, using a silicon platform to carry out electronics, but making the silicon work with higher performance through the attachment of a surface layer of organic molecules that donate or accept charge.

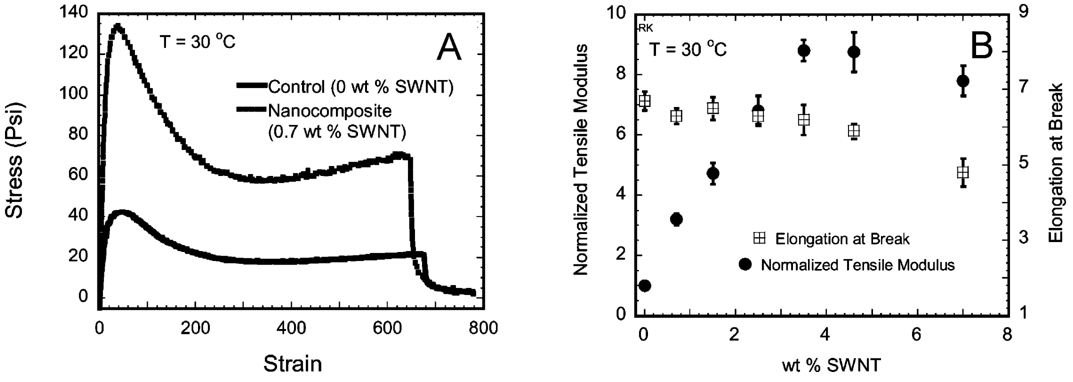
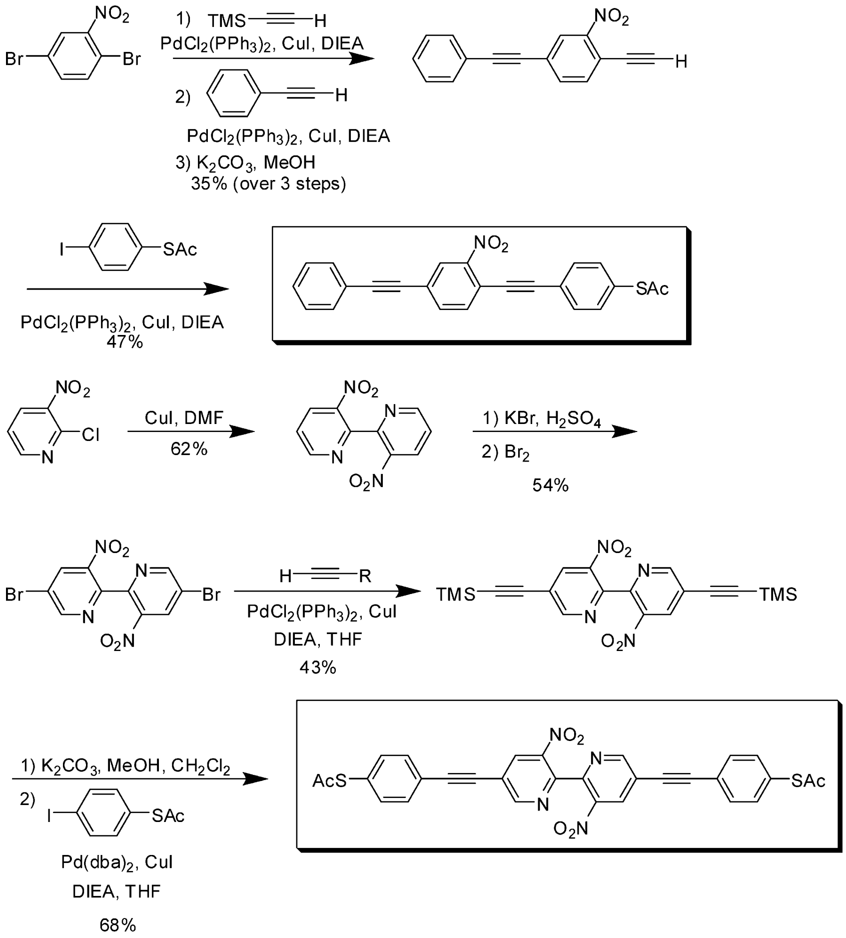


**FIGURE 2.** (A) Tensile testing of a 0.7 wt % functionalized [$C_6H_4$-$(CH_2)_{10}$-OH addends by the dry functionalization protocol[23]] using SWNT-filled PDMS nanocomposite[20b] compared to a similarly cross-linked PDMS network that contains no nanotubes. The sample was stretched at a rate of 2 mm/min in a mini-Instron tester. (B) Composition dependence and elongation-at-break for the SWNT-functionalized material in a PDMS nanocomposite. These plots were obtained by R. Krishnamoorti from the University of Houston.

**SCHEME 8. Synthesis of the Most Commonly Used Molecular Switches for Molecular Electronics Studies: The "mononitro OPE" (Top) Which Shows Consistent NDR in Several Testbeds[36] and the "BPDN" (Bottom) Switches[38] Which Show Consistent Hysteresis across Several Testing Methods. This Exemplifies the Simplicity of Synthesis and Structure That Has Proved Most Important in the Development of Organic Molecular Electronics Devices**

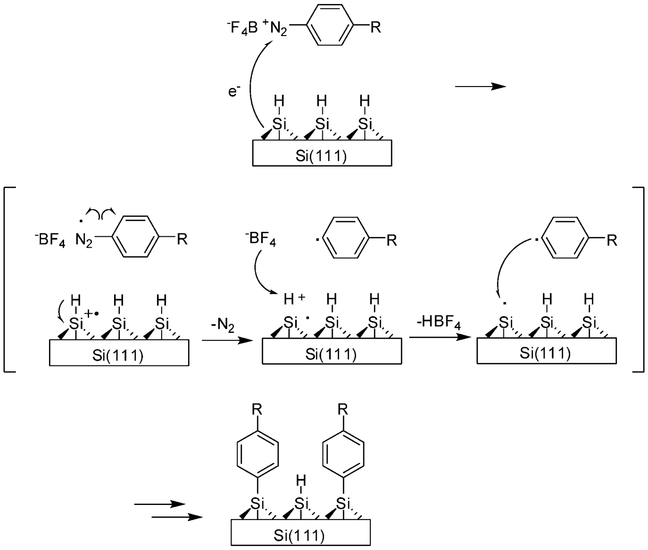


I concede that the definition here could be somewhat difficult to separate from passive or active systems, and some might want to only have the two former areas of definition. I would not argue otherwise, but in some cases this third category can add further clarity: a hybrid, of sorts, between the passive and active sides. And as suspected, the commercial realization of hybrid systems would often reside between the passive and hybrid development periods.

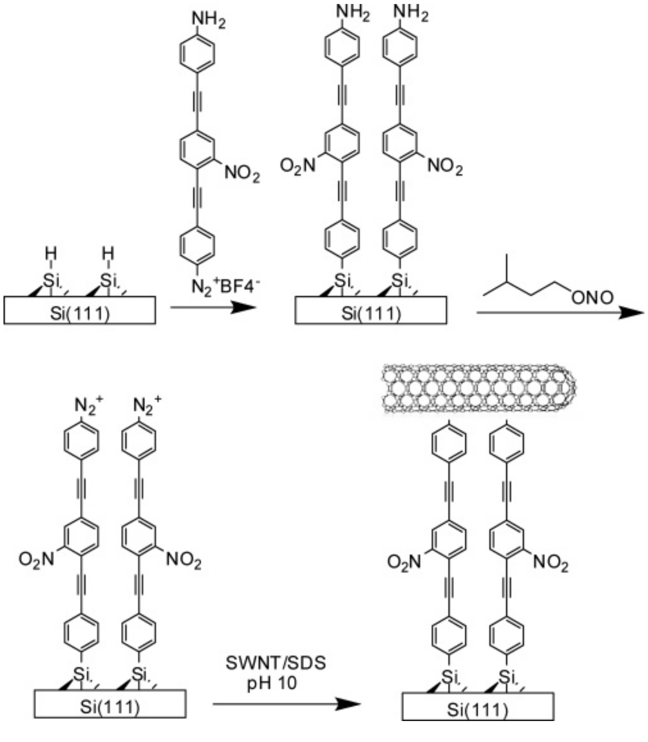
## Passive Nanotechnology: Functionalized Nanotubes and Composites

Passive nanotechnology, where the simple presence of the nano entity adds enormously to the performance of the system, can be illustrated through our incorporation of covalently functionalized single-walled carbon nanotubes (SWNTs) into composite materials. Covalent functionalization of SWNTs has

**SCHEME 9. Molecular Grafting Method That We Developed for Attaching Arenes Directly to Silicon via the Hydrogen-Passived Silicon Surface with No Intervening Oxide**[39]



**SCHEME 10. Attachment of SWNTs to a Silicon Surface Using Orthogonally Functionalized OPEs**[40]



given scientists and engineers the ability to manipulate these astonishing structures in ways that would otherwise be unattainable. SWNTs consist of only carbon and can be considered theoretically as a graphene sheet rolled into a seamless cylinder. SWNTs are ladder polymers, i.e., more than one bond needs to be broken to cleave the backbone. Typical ladder polymers are fully joined by only two repeating bonds. However, depending on the tube type, SWNTs have 10−20 carbon−carbon bonds per repeat unit that would need to be broken for polymer strand rupture to occur. Furthermore, each of those 10−20 carbon−carbon bonds has a bond order of ca. 1.3 rather than simple a single bond. And since the carbon−carbon bond is among the strongest bonds in the universe, it is unlikely that we will ever find more robust polymeric chains than a SWNT.

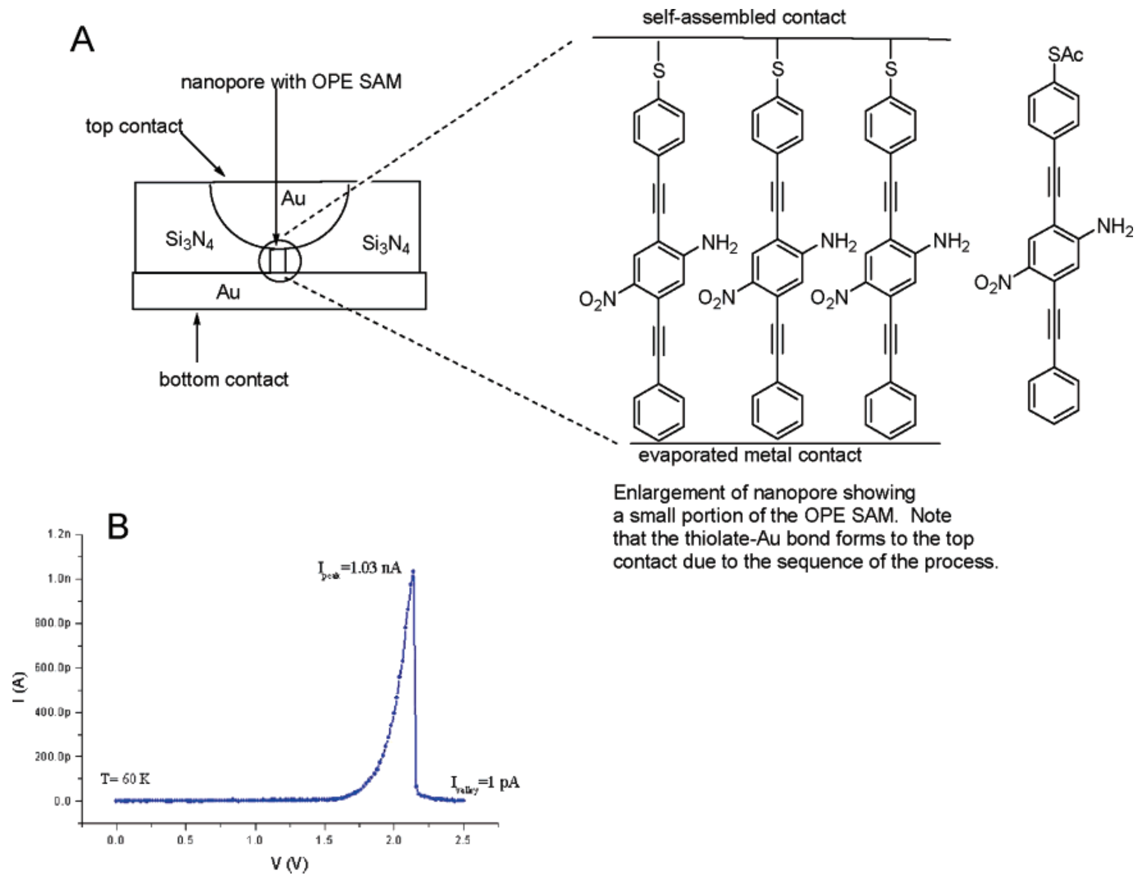
Carbon nanotubes are highly polarizable, smooth-sided compounds with attractive interactions of 0.5 eV per nm of tube to tube contact. Due to these extreme cohesive forces, SWNTs exist as bundled structures that are often referred to as ropes. We can functionalize these ropes so that the outer nanotubes are more highly functionalized than the inner ones, or we can functionalize all of the nanotubes rendering them far less able to rope together (Figure 1). This bundling or roping phenomenon contributes to the bulk materials having limited solubility and poor dispersion in polymers. In fact, pristine carbon nanotubes tend to agglomerate in polymer hosts, which often weakens the mechanical strength of these composite materials. Another problem associated with pristine nanotubes in composites and blends is the lack of interfacial bonding (SWNT to matrix material), which leads to fiber pull-out during stress followed by catastrophic failure. Covalent sidewall functionalization of SWNTs generates the ability to solubilize and disperse these nanotubes into polymer matrices. Covalent functionalization of carbon nanotubes was recently very well-reviewed by Prato,[19] so I will cover here only our contributions to this growing area.[20]

The main categories of functionalization methods that we have developed for SWNTs involve, generally, an aryldiazonium species as a reagent or intermediate (via the aniline or triazene), and they are used to generate (Scheme 7):

- *Functionalized Bundled SWNTs* (Scheme 7): electrochemical,[21] solvent-based[22] and solvent-free[23] methods.
- *Functionalized Minimally Bundled SWNTs*: on-water reaction methods.[24]
- *Functionalized Unbundled SWNTs*: surfactant wrapping,[25] ionic liquids,[26] oleum,[27] concentrated sulfuric acid with ammonium persulfate,[28] triazene,[29] and oleum/nitric acid oxidation[30] methods.

Several of these methods can generate water-soluble and phosphate-buffered solution-soluble SWNTs, making them particularly useful for biological applications.[31]

*Carbon Nanotube-Modified Composites.* Polymer-based composites and blends, where polymers serve as the matrices for inorganic, organic, or carbon fillers, have had enormous impact as engineering materials, and they are widely used in commercial products. One class of such composite materials is elastomers. Elastomers are used commercially in a wide range of applications in market segments including rubber tires, which is the largest consumer of natural and synthetic rubber. Traditionally, additives are applied within elastomers to make them have a higher tensile modulus (stiffness), but the result is generally a concomitant large reduction in the strain-at-break (the stretch point at which the polymer will break). For the sake of illustration, polyisobutylene shows a strain-at-break of ca. 10 (i.e., 1000%) or higher, meaning that it can stretch to 10 times its original length with nearly complete return to its original state upon release. By adding 40−50 wt % carbon black, the tensile modulus could increase 10-fold, but the strain-at-break could fall to 1.25 (125%); hence it would no longer respond as an elastomer but as a thermoplastic in dynamic mechanical properties. The development of high strength elastomers with high breaking strains and low densities is crucial



Enlargement of nanopore showing a small portion of the OPE SAM. Note that the thiolate-Au bond forms to the top contact due to the sequence of the process.

**FIGURE 3.** (A) Nanopore testbed structure containing a SAM of the functionalized OPE shown to the right. (B) Current−voltage characteristics of a nanopore testbed device containing a SAM of molecules shown in (A) at 60 K. The peak current density is ∼50 A/cm$^2$, and the peak-to-valley ratio of the switching response is 1000:1. This plot was obtained by M. Reed from Yale University.[36b,c]

in many applications including tires, belts, hoses, seals, O-rings, etc. that affect industries such as automotive, engine, aerospace, oil drilling, and refining. Therefore, to be able to stiffen elastomers while retaining the strain-at-break properties is highly desirable.

We have recently developed model-functionalized SWNT reinforced networks of an amine-terminated poly(dimethylsiloxane) (PDMS) which typifies the extraordinary effects of functionalized SWNT-filled elastomeric composites.[20a,b] Typical data suggest a 3-fold increase in the modulus of the elastomer with no change in the strain-at-break (Figure 2A). These results are remarkable because the tensile modulus and strength are considerably increased while the strain-at-break is largely unchanged. Further, the data suggest an optimal network structure at 3−4 wt % addition of the functionalized SWNT with an 8-fold increase in the modulus with no change in the strain-at-break (Figure 2B).[20a,b] This has now been extended into the use of functionalized SWNTs in nitrile-butadiene rubber (NBR) systems, a commonly used high-performance elastomer for seals and into mammalian bone composites.[32] One only needs a compatiblizing nanotube functionalization pendant for efficient polymer blending and miscibility, and it should be readily extendable to a wide range of elastomers and network forming polymers including high-temperature epoxies, an effect that we are seeing from our ultrashort SWNTs.[30]

**Passive Nanotechnology Conclusions.** Through passive nanotechnology, a significant increase in the performance of the system can be realized simply by the presence of the nanoscale entity. Covalent functionalization of carbon nanotubes gives researchers the ability to manipulate these nanostructures in typical organic solvents, water, or even in solvent-free conditions, making them easily dispersed in host matrices. This leads to unprecedented ultrahigh performance composites. The applications of these passive systems are being realized today in commercial products, and the time from lab to market is generally short compared with the active systems.

## Active Nanotechnology: Molecular Electronics and Nanocars

In active nanotechnology, the nano entity does something elaborate when compared to the passive systems. As we will see here in molecular electronics, upon the influence of an electric field, the molecules need to undergo a state change. This state change might be precipitated by a conformational twisting or by an electron injection into or out of the molecule.

**Molecular Electronics.** The rapidly developing field of ultrasmall electronics was one of the driving forces behind our interest in the synthesis of new molecules as candidates for molecular electronics. We have separately reviewed some of the syntheses of these molecules as well as the large body of work concerning the theoretical aspects of molecular conduction.[33] However, the limitations of the present top-down method of producing semiconductor-based devices have been the subject of debate and conjecture since Gordon Moore's prediction in

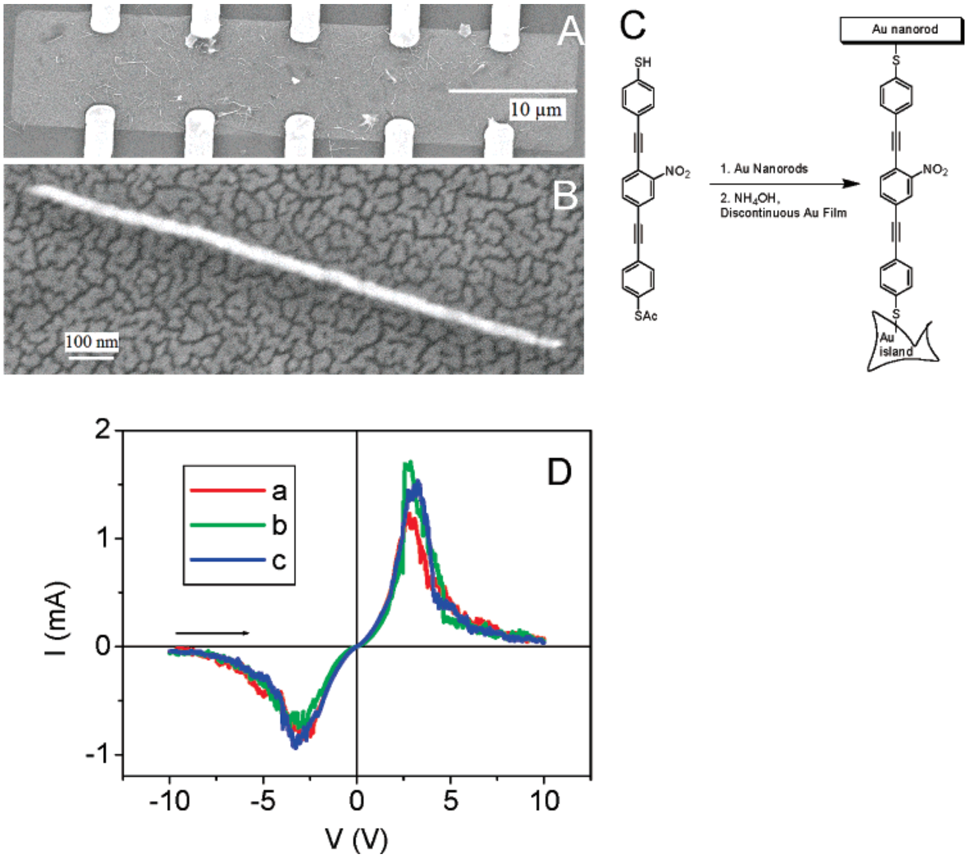


**FIGURE 4.** Scanning electron micrographic (SEM) image of the nanocell after assembly of the Au nanowires and OPEs. (A) The five juxtaposed pairs of fabricated leads across the nanocell and some Au nanowires are barely visible on the internal rectangle of the discontinuous Au film. (B) is a higher magnification of the nanocell's central portion showing the disordered discontinuous Au film with an attached Au nanowire which is affixed via the OPE-dithiol as shown in (C). (D) is three successive (a−c) current−voltage sweeps to show the device-like behavior obtained from a pair of juxtaposed leads.[43a]

1965 that the number of components per integrated circuit would double every 18 months.[34] It was thought that the inherent limitations of the present technology would lead to a dead-end in the next few years. For instance, silicon's band structure disappears when silicon layers are just a few atoms thick. Lithographic techniques that are used to produce the circuitry on the silicon wafers are limited by the wavelengths at which they work. Interestingly, leaders in the semiconductor manufacturing world continue to make advances that appear to be pushing "Moore's Law" beyond its prior perceived limits. In 2004, Intel projected that "Moore's Law" is here to stay for the next 15−20 years.[35]

A class of molecules that has been studied extensively in our lab and by others is the oligo(1,4-phenylene ethynylene)s (OPEs), and they form reasonably well-ordered monolayers on Au surfaces. OPEs can be rapidly synthesized using transition-metal-catalyzed coupling reactions. In this case, the compounds were synthesized in both solution phase and on a polymer-based solid resin (Scheme 8). These and related OPEs have been studied for their switching behavior in a number of testbed devices and on surfaces by STM. In many modes, they exhibit repeatable switching that is often controllable,[36] while in other testbeds only by stochastic mechanisms based on molecular tilting.[37] Another compound that has been shown to switch in numerous testbeds is the bipyridyl-dinitro (BPDN) compound (Scheme 8).[38] These simple structures are some of the most used compounds for electronic switching in molecular electronics.

Using aryldiazonium salts that are air-stable and easily synthesized, we developed a one-step, room-temperature route to the formation of direct covalent bonds between $\pi$-conjugated organic molecules on three material surfaces: Si, GaAs, and Pd.[39] 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 (Scheme 9). The formation of the aryl−metal or aryl−semiconductor bond attachments were confirmed by corroborating evidence from ellipsometry, reflectance Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV), and AFM analyses of the surface-grafted monolayers. This spontaneous diazonium activation reaction offers an attractive route to highly passivating, robust monolayers or multilayers on many surfaces that allow for strong bonds between carbon and surface atoms with molecular species that are near perpendicular to the surface.

Union of easily patterned silicon with the often hard-to-affix nanotubes can provide a critical interface methodology for electronic and sensor arrays. For example, 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

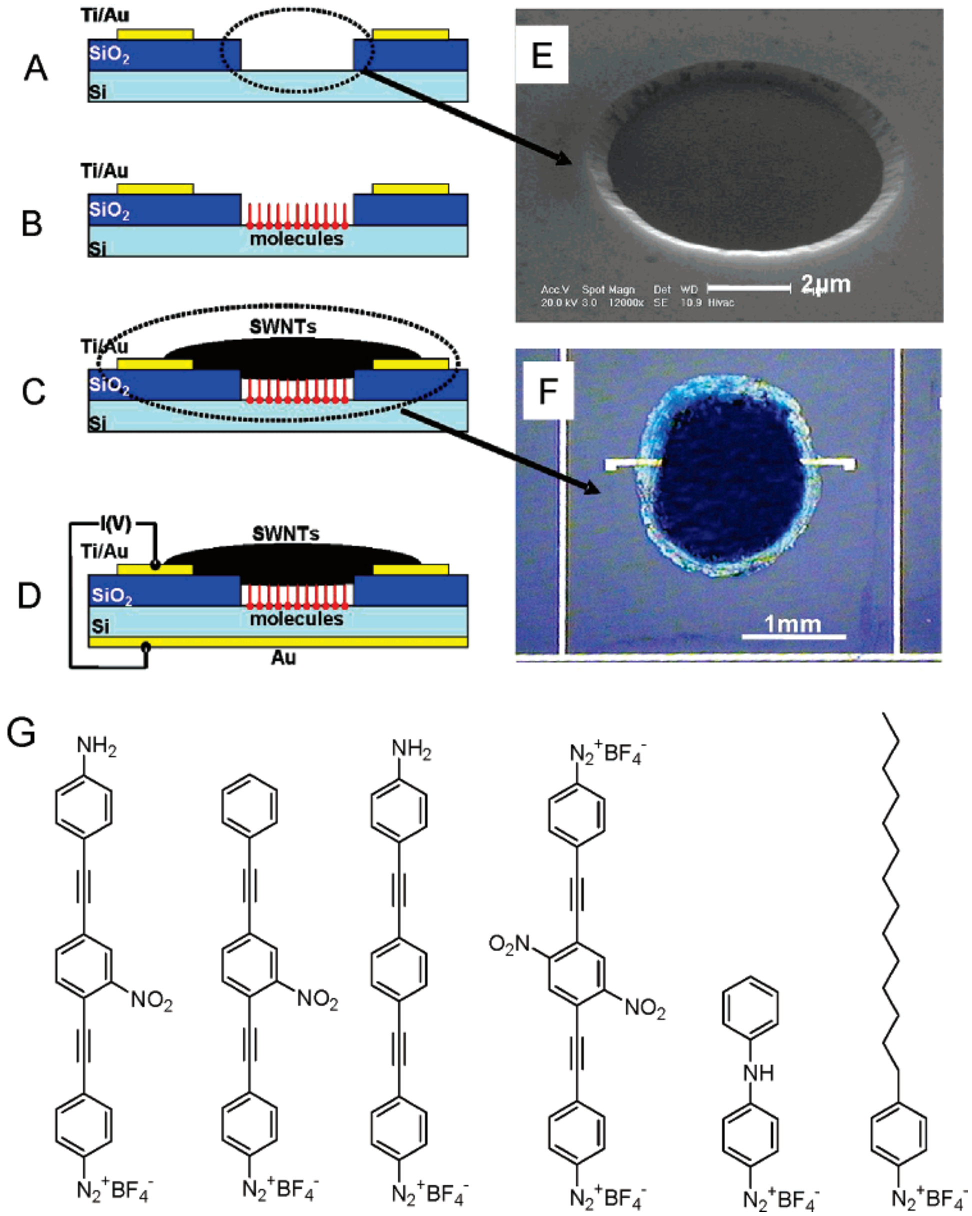
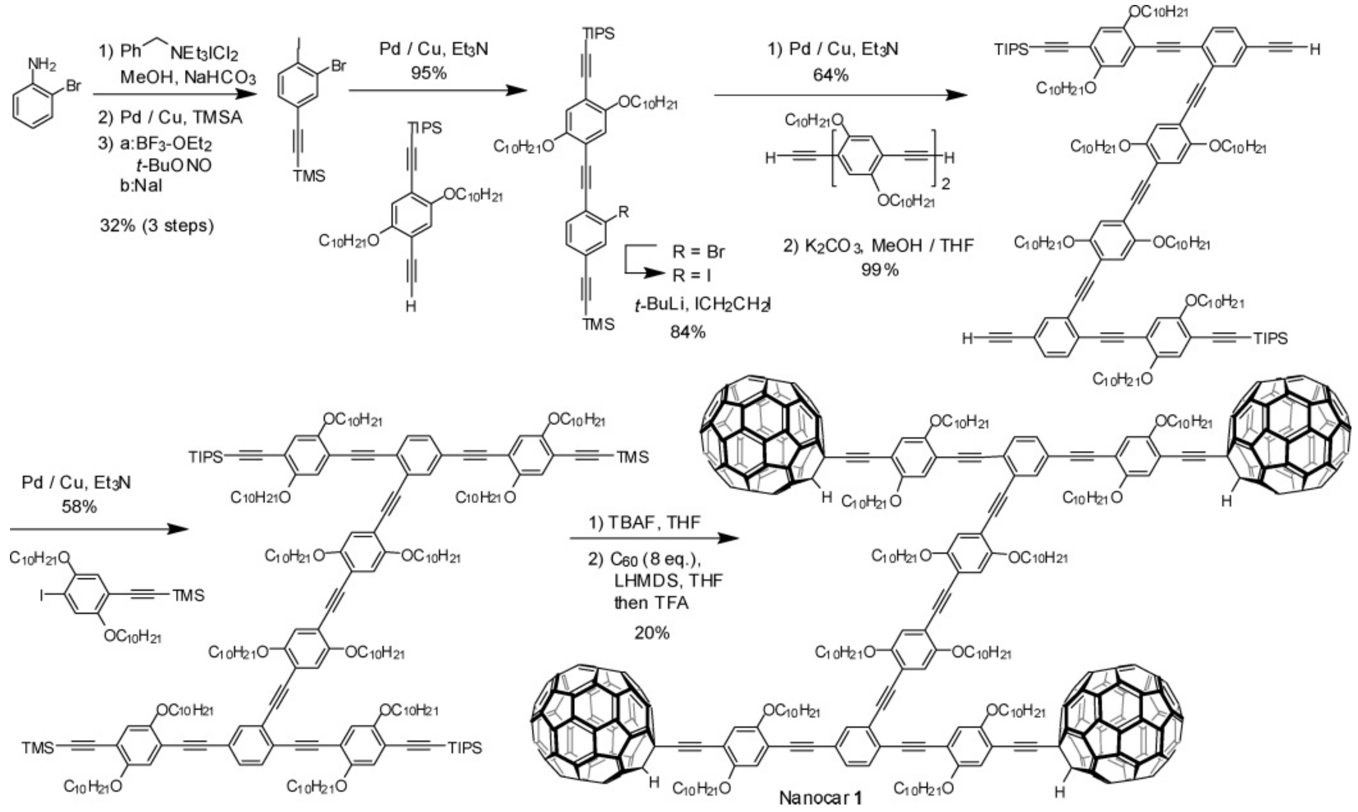


**FIGURE 5.** Schematic showing the Si-molecule-SWNT device and its fabrication process: (A) the starting lithographically defined structure, (B) formation of a molecular monolayer in the well by surface grafting to form a direct Si−arylcarbon bond, and (C) deposition of a SWNT mat atop the molecules and across the well, electrically connecting the molecular layer to the metal pads to give the finished device in (D) after bottom-side Au contact formation. (E) An SEM image of a 5 $\mu$m well showing its ramped oxide edges and (F) the top view of a finished device ready for testing where the SWNTs drape across both the Au contacts and the molecular layer in the well, the latter being a minute portion in the center of the image that is not visible due to the SWNT mat and the resolution of the image. (G) The set of molecules grafted in the device to form the direct silicon−aryl bond after loss of $N_2$ as in Scheme 9.[44]

contain a diazonium salt on one end and an aniline moiety on the other end. 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 SDS-wrapped SWNTs[25] resulting in covalent attachment of the SWNTs to the silicon surface using the OPEs (Scheme 10).[40] In this particular molecular electronic embodiment, we seek to store charge above silicon, in the SWNTs, and thereby build a molecular electronic memory that would be somewhat similar to nanocrystal flash memory which uses metallic particles for the charge storage above a transistor channel.

In early work to lay the foundation for the use of self-assembly in construction of electronic devices from molecules, SAMs of various thiol-containing molecules were formed on the surface of Au and analyzed using ellipsometry, XPS, and external reflectance FTIR.[9m,41] It was found that the thiol moieties dominated the adsorption on the Au sites, with the direct interaction of the conjugated $\pi$-systems with the Au surface being weaker (Figure 3A). In 1999, large ON:OFF ratios and negative differential resistance (NDR, where the current increases and then decreases as the voltage is increased) were measured in molecular electronic devices constructed using functionalized OPEs and a nanopore testbed (Figure 3B).[36b]

**SCHEME 11. Synthesis of the Nanocar 1**[46]



Our next approach at building devices involved the nanocell embodiment.[42] The nanocell approach is not dependent on placing molecules or nanosized metallic components in precise orientations or locations. The internal portions are, for the most part, disordered, and there is no need to precisely locate any of the switching elements. The nanosized switches are added in abundance between the micron-sized input/output electrodes, and only a small percentage of them need to assemble in an orientation suitable for switching. The result of the nanocell architecture is that the patterning challenges of the input/output structures become far less exacting since standard micron-scale lithography can afford the needed address system. Also, fault tolerance is enormous. However, programming is significantly more challenging than when using ordered ensembles. Remarkably, the nanocell exhibits reproducible switching behavior with excellent peak-to-valley (PVR) ratios, peak currents in the milliamp range, and reprogrammable memory states that are stable for more than a week with substantial 0:1 bit level ratios. A discontinuous gold film was vapor deposited onto the $SiO_2$ in the central region (Figure 4A,B). Figure 4C shows the molecule type and sequence that was used to assemble the gold nanowires on the discontinuous gold film, and Figure 4D shows the current−voltage response across two of the juxtaposed leads.[43]

We later developed a new testbed, the molepore, for exploring the electrical properties of molecules while eliminating the possibility of metal nanofilament formation and to ensure that molecular effects are measured.[44] This metal-free system uses single-crystal silicon and single-walled carbon nanotubes as electrodes for the molecular monolayer. As discussed earlier, the direct Si−arylcarbon grafting protocol[39] was used (Scheme 9), and Figure 5 shows the fabrication flow for the metal-free Si-molecule-SWNT testbed. The molecules being tested were grafted to the H-passivated silicon substrate to form a monolayer in a small well made through the silicon oxide layer. All molecules were directly bound to the Si surface via a Si−C bond; there was no intervening oxide. Use of this structure with $\pi$-conjugated organic molecules resulted in a hysteresis loop with $I(V)$ measurements that are useful for an electronic memory device. The memory is nonvolatile over >3 days, nondestructive over >1000 reading operations, and capable of >1000 write−erase cycles before device breakdown. Devices without $\pi$-conjugated molecules (Si−H surface only) or with long-chain alkyl-bearing molecules produced no hysteresis, indicating that the observed memory effect is molecularly relevant. Temperature-independent $I(V)$ behavior was observed.

Notice that in the molepore embodiment, the electrical current is through the molecules, much like what was done in the metal−molecule−metal sandwich structures. Later, in the hybrid architectures, molecules as a complement to the silicon will be considered wherein the molecules are simply enhancing the silicon's current carrying ability. But in all the cases shown here, an active nanostructure is required wherein the nanoscale entity needs to switch its state or store an electronic charge for its function. And this is a far greater requirement than what was previously expected of the nano entitites in the passive applications. This can be further seen in the construction of nanocars.

**Nanocars.** Further exemplifying active nanosystems where the nano entity has complex requirements of function,[45] our work on nanocars is highlighted here. The goal of the nanocar project is to realize a nanomachine that can convert energy-inputs (such as heat or electric fields) into controlled motion on a surface and transport of nanocargo (materials or information) from one place to another on the surface. This will be an important step toward future nanomachine development because the bottom-up construction will, in part, take place on the surface

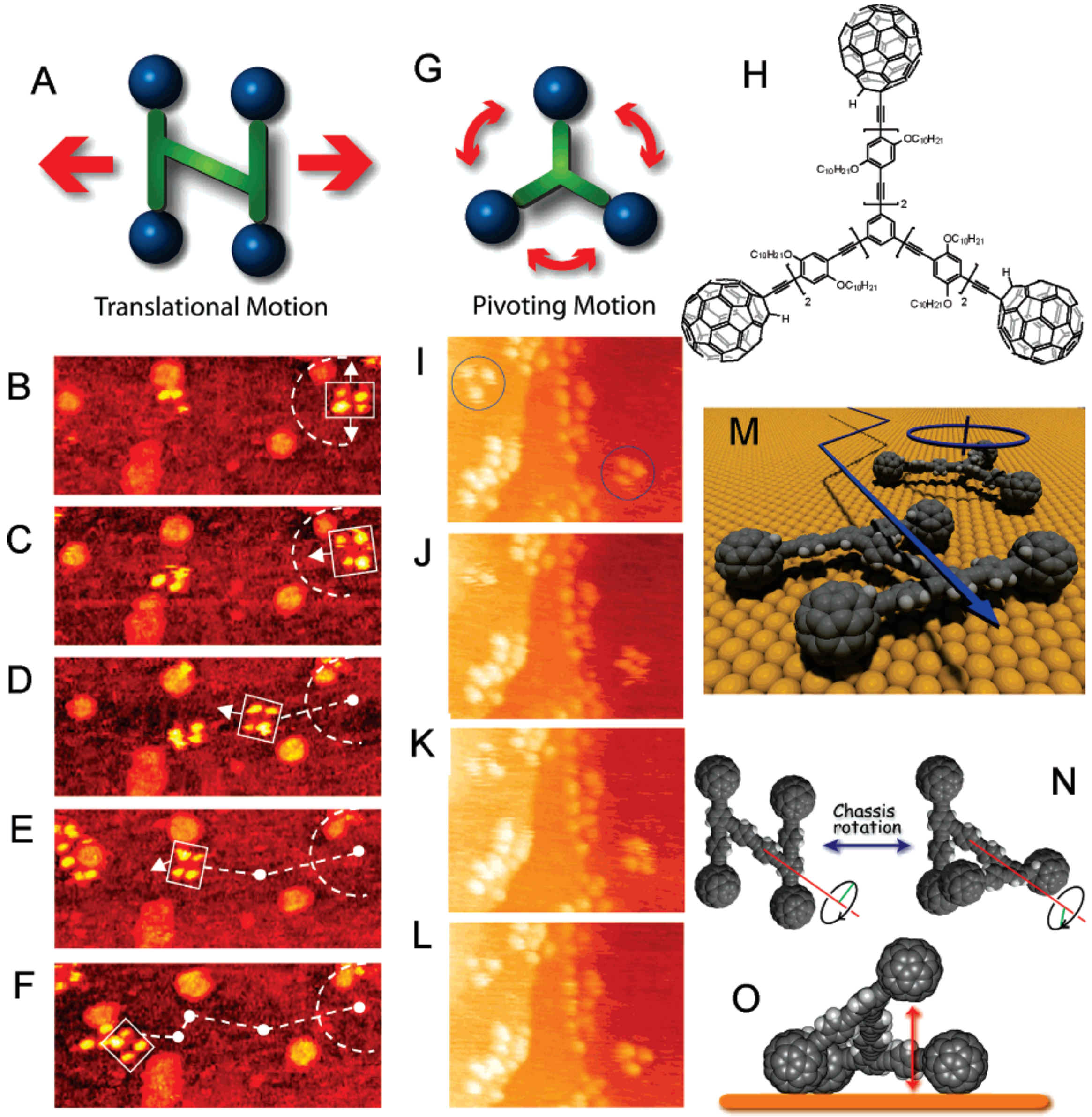


**FIGURE 6.** Comparison of thermally induced motions of (A) four-wheeled **1** and (B−F) its STM-imaged motions and (G, H) a three-wheeled version and its STM-imaged motions (I−L). (B−F) Sequence images were taken during annealing at ~200 °C (bias voltage $V_b = -0.95$ V, tunneling current $I_t = 200$ pA. Image size is 51 × 23 nm). The orientation of the nanocar is easily determined by the fullerene wheel separation, with motion occurring perpendicular to the axles. Acquisition time for each image is approximately 1 min, with (B−F) selected from a series spanning 10 min, which shows ~80° pivot (C) followed by translation interrupted by small-angle pivot perturbations (D−F). (I−L) A sequence of STM images acquired approximately 1 min apart during annealing at ~225 °C show the pivoting motion and lack of translation of the three-wheeled molecules. ($V_b = -0.7$ V, $I_t = 200$ pA. Image size is 34 × 27 nm.) For video files of nanocar motions, see: http://tourserver.rice.edu/movies/. These figures and experimental text were adapted from our earlier publications.[46] (M) Depiction of the differences of motion observed for the four-wheeled vs the three-wheeled versions, underscoring the directional control based on the design. (N, O) The flexibility of the semirigid chassis structure (nanocar derivative, devoid of alkoxy groups for clarity). (N) The triple bonds in the OPE structure can rotate until the fullerene wheels touch one another, which gives the nanocar flexibility orthogonal to the surface plane. (O) One fullerene wheel is elevated while the other wheels remain on the surface to illustrate the suspension concept.[47] These STM images were obtained by K. Kelly and A. Osgood of Rice University.

of semiconductors, metals, or artificial membranes. Thus, gaining better data regarding the chemistry and physics acting on molecular scale transporters on a surface is critical, and the surface-rolling nanovehicles (nanocars and nanotrucks) give us opportunities to learn some basic rules for their design and operation. The synthesis of one of the nanocars is outlined in Scheme 11.[46]

Figure 6A−F shows the range of motion of the nanocar, pivoting followed by translation, on a surface by STM analysis. This is further compared to the pivoting but no translation observed in the three-wheeled versions (Figure 6G−L), thereby underscoring that the design dictates the range of motion (Figure 6M). The power source for the motion could be either heat to the substrate surface or an electric field placed along the rolling axis of the nanocar.[46] The flexibility that was built into the chassis of the nanocar (Figure 6N,O) aided in the ability of the nanocar to traverse 1-atom high atomic steps on the surface.[47]

The achievement with the nanocar was significant because it demonstrated for the first time structurally controlled direc-

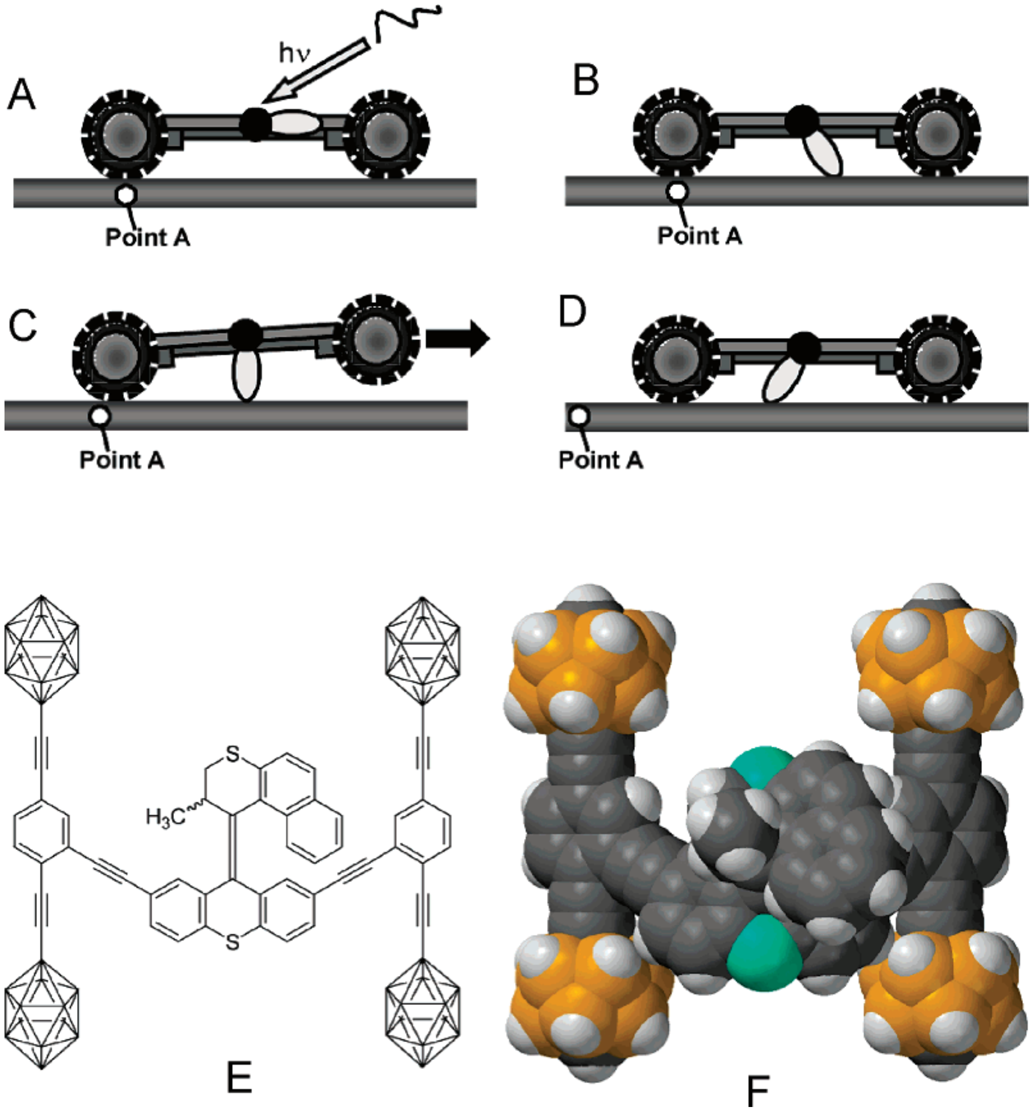


**FIGURE 7.** Propulsion scheme for the motorized nanocar where (A) 365 nm light would impinge upon the motor which (B) affords motor rotation and (C) sweeping across the surface to (D) propel the nanocar forward. (E) The structure of motorized nanocar that was synthesized and (F) its space-filling analogue. The *p*-carborane wheels have BH at every vertices except at the top and bottom vertices which represent C and CH positions, ipso and para, respectively, relative to the alkynes.[49]

tional movement on a surface due to rolling of the wheels rather than the common nondirectional stick−slip motion of molecules on a substrate surface. The next goal of our project was to construct a nanomachine that could convert energy-inputs into controlled motion on a surface. The motorized nanocar bears a light-powered molecular motor in its central portion for an eventual paddlewheel-like propulsion action along a substrate surface for motion of the nanomachine (Figure 7A−D). We opted to utilize the unidirectional molecular motor developed by Feringa and co-workers as the engine for our motorized nanocar because it can (1) perform repetitive rotary movement, (2) use light and mild heating (35−65 °C) as the power input, (3) precisely perform unidirectional rotation, (4) be functionalized without disturbing rotation, allowing the motor substructure to be introduced into more complex structures, and (5) operate even when assembled atop metal surfaces.[48] We first sought to incorporate the motor into the fullerene-wheeled nanocar; however, the model study with the fullerene−motor hybrid revealed the incompatibility of the two molecular components, the fullerene wheel and light-powered motor moieties. The rapid intramolecular quenching of the photoexcited state of the motor moiety by the fullerene wheels mitigated motor operation. Thus, photochemically inert molecular wheels were needed for the development of motorized nanocars. After a survey for alternative molecular wheels, we arrived at the *p*-carborane structure. Using the *p*-carborane wheels, we successfully completed the synthesis of the first motorized nanocar (Figure 7E,F).[49]

A variety of other carborane-wheeled nanocars and three-wheeled analogues were rapidly synthesized, and they are shown in Figure 8. The arrows indicate the expected direction of rolling motion on surfaces.[50] We are now attempting to prove the rolling vs sliding movement of the *p*-carborane-wheel based vehicles on surfaces using a variety of microscopy and spectroscopy methods, and this is demonstrating to be the bottleneck of our current research. This highlights the deficiency in present-day nanoscale imaging probes and should encourage the development of these needed tools.

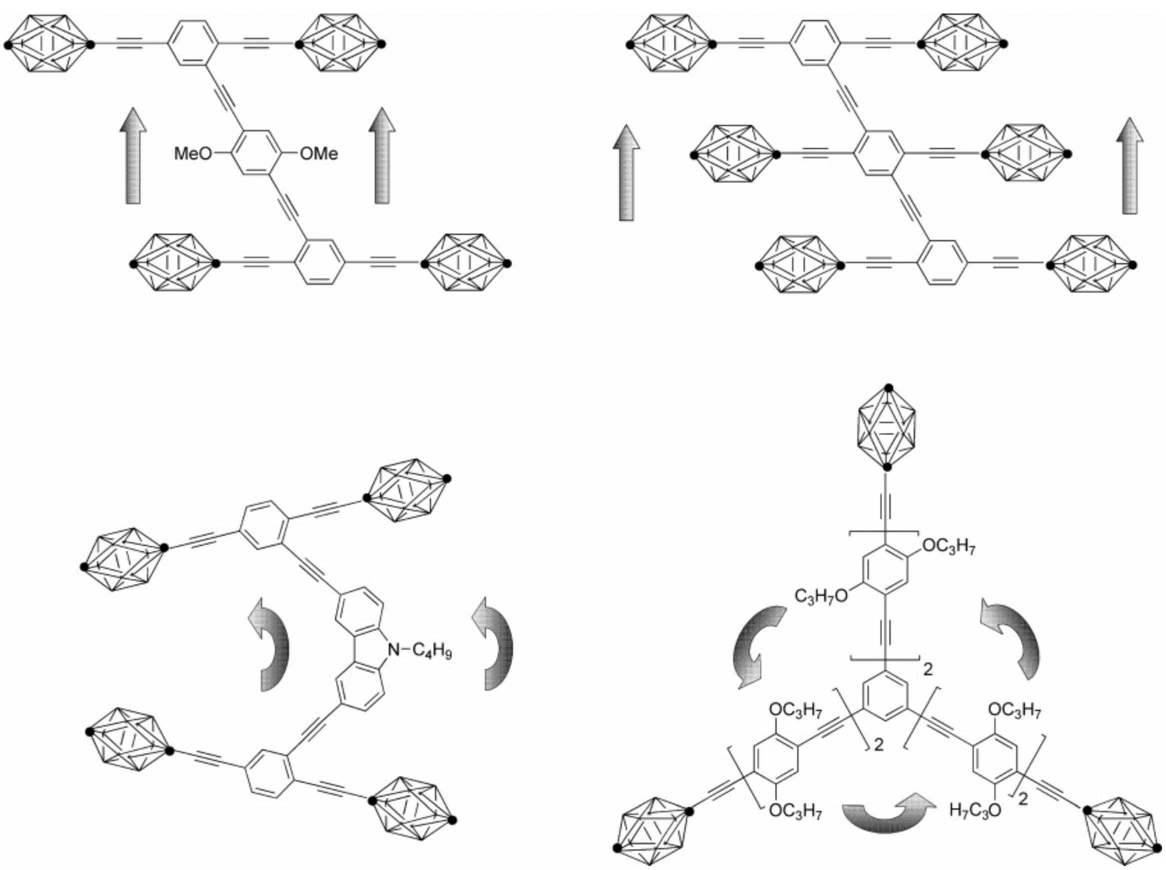


**FIGURE 8.** Molecular structures of some *p*-carborane-wheeled nanocars that we have prepared.

**Active Nanotechnology Conclusions.** Through active nanotechnology, as exemplified here in molecular electronics and nanocars, we are taking nano entities and demanding complex behavior from each individual structure: electric switching or controlled motion, for example. The laboratory demonstrations of these active systems are here today, but their realization in any commercial systems, which require a high degree of resiliency and control, are many years away.

## Hybrid Nanotechnology: Silicon/Molecule Hybrid Systems

Hybrid nanotechnology is defined here as complementing a known platform through the attachment of a nanosized entity but where the platform carries the bulk of the burden. Considered here is a silicon platform to carry out electronics, but making the silicon work with higher performance through the attachment of a surface layer of organic molecules that add or accept charge though a $\pi$-donation or accepting, respectively. Therefore, silicon is still performing "the heavy lifting" by carrying the current—no current need pass through the molecule—but the molecules are complementing and enhancing the behavior of this active silicon platform.

Although a number of alternatives to silicon-based materials have been proposed,[33a,51] silicon remains the stalwart of the electronics industry. As scaling to the sub-20 nm-size region is pursued, routine impurity doping becomes problematic due to its resultant uncertainty of distribution.[52] Taking advantage of the dramatic increase in the surface-area-to-volume-ratios of small features, it is attractive to seek controllable modulation of device performance through surface modifications. Furthermore, obviating what is called "body biasing" could be possible through the attachment of molecules to specific transistors. In body biasing, a voltage is applied to the backside of a transistor to minimize the leakage in that transistor. Presently, about 50% of the energy used on a chip is lost due to leakage, so minimization of this effect without having to incorporate body bias wiring would be welcomed by the industry, and molecules might provide a solution.

The device testbeds constructed for this hybrid study are shown in Figure 9A, which form the basis for the pseudo metal−oxide−semiconductor field-effect transistor (MOSFET) devices demonstrated here that we term a moleFET for molecular-FET.[53] The molecules used in the molecular grafting are shown in Figure 9B. We demonstrated that by grafting a monolayer of molecules atop oxide-free H-passivated silicon surfaces (channel region), the drain current and threshold voltage in pseudo MOSFETs can be systematically modulated over a 2.5 V range in accordance with the electron-donating ability of the grafted molecules (Figure 9C). This effect is ascribed to the charge transfer between the device channel and the molecules. This could serve as an excellent method to controllably tune electronic performance in nanoscale devices (large surface-area-to-volume ratios) through surface grafting where consistent impurity doping becomes hard to achieve due to doping profile inhomogeneities between devices.

**Hybrid Nanotechnology Conclusions.** Through hybrid nanotechnology, as exemplified here in transistors that have molecular layers grafted atop their channel surfaces, profound

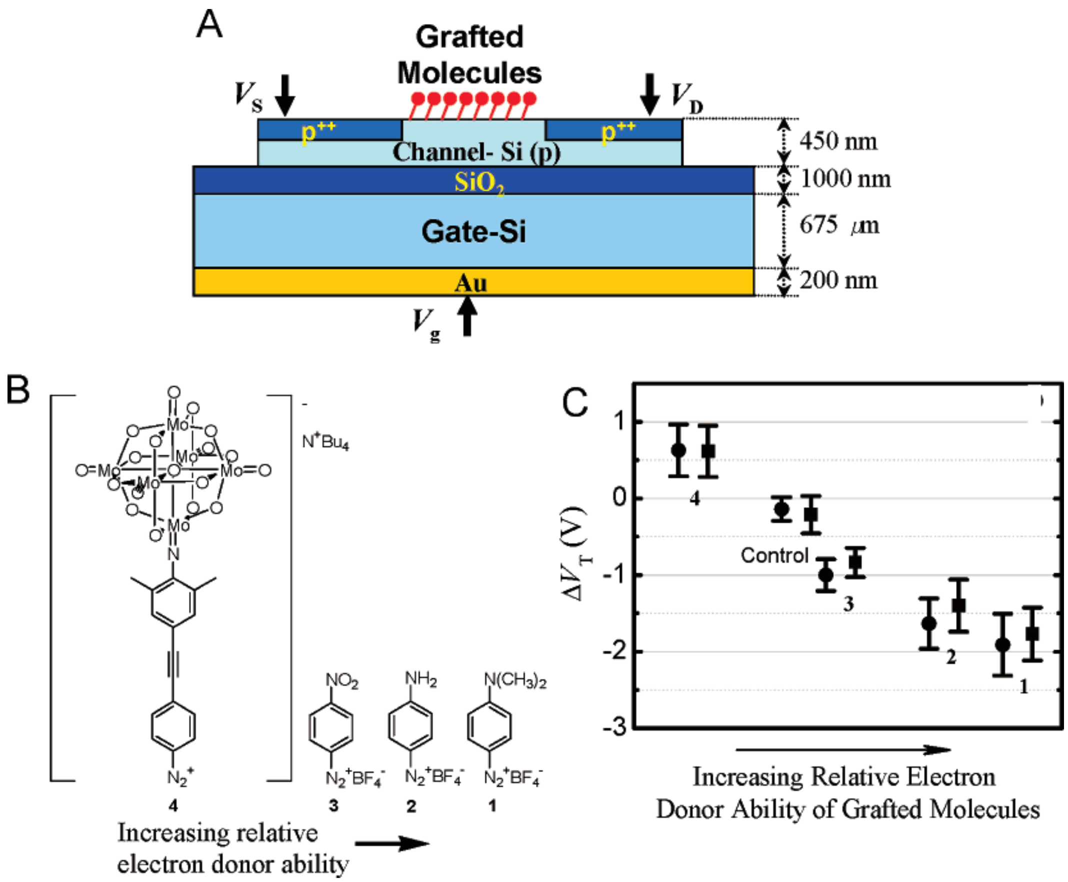


**FIGURE 9.** (A) Schematic side-view representation (not to scale) of the moleFET device. The molecules were grafted between source and drain electrodes. $V_S$, $V_D$, and $V_g$ refer to the bias applied on the source, drain, and gate, respectively. (B) The molecular structures used for grafting (as in Scheme 9) atop the pseudo-MOSFET channel. (C) Electrical output results of the moleFET devices. Representative $\Delta V_T$ ($= V_{T(\text{with molecules})} - V_{T(\text{without molecules})}$) of the devices under test extracted from both the forward (solid circle) and back (solid square) scans after the grafting of different molecular monolayers (**1**−**4**), as well as on the control samples. Data shown here is the average value for 14 devices. The vertical bars indicate standard deviations for each of the 14 devices tested.[53]

effects on the behavior of these active silicon devices can be realized through the electrical donation properties of the grafted system. Although no current is being passed across the molecules, as was done in the active molecular electronics, the inherent donor or acceptor ability of the molecules is being exploited to enhance the functionality of silicon-based transistors. Although the laboratory demonstration is upon us, due to the complex requirements of semiconductor fabrication, which includes temperature extremes in excess of 400 °C even for late-stage processing, and specific area placements through patterning, realization of these hybrid systems in commercial devices is likely many years away.

## Summary

Our research in the area of passive nanotechnology has shown that the simple addition of a nanomaterial to a host matrix can have a profound effect on the behavior of the overall composite structure. The active nanotechnological components, which require far greater control, afford exciting laboratory demonstrations, but their utility is generally far off. The hydrid systems, which enhance known complex platforms, are also demonstrated here through the complement of silicon transistor electronics. The journey from small molecule synthesis to organic materials and nanotechnology was partially by intent, ignited initially by simple yet directed conversations, and fanned by several others who were willing to invest themselves into my life. And the journey was partially by fate or providence, as manifested by withering funding in one locale and fruitful pasture in another. The application of synthetic chemistry methods to materials science in general, and nanotechnology in particular, has proven to be exciting and rewarding. It has served its primary purpose of educating scores of students and post docs in my labs. But is has also provided a setting for the exploitation of modern synthetic organic chemical techniques for the advancement of these new interdisciplinary topics.

## Closing Remarks

When I was in graduate school, our training was narrow but exceedingly deep. Students nowadays are much broader in their trainings and understandings, able to take their work into realms that I could never have fathomed as a graduate student. Much of this is likely due to nanotechnology's influence on collaborative studies and the need to take one's research to ever expanding phases. The aspect that is lost, however, is depth. At least my students seem to not be as deeply trained in organic synthesis as I was trained, or as I trained my first few generations of students. But their breadth is far greater. We probably need both types, and organic materials science and nanotechnology is ensuring that the breadth of science is taught to a generation of researchers. And it is to these wonderful students, post docs, and collaborators with whom I have had the good fortune to work that I extend my thanks upon receipt of the 2007 Cope Scholar Award.

**Acknowledgment.** Our program has been generously supported throughout the years by the following agencies and companies: ONR, DARPA, ARO, AFOSR, NSF, FAA, NASA, DOE, Battelle, Honda, Shell, Albemarle, Ethyl, Hercules, IBM, Welch Foundation, Zyvex, PRF, FAR Research, Petra Research, the states of South Carolina and Texas, the University of South Carolina and Rice University. And my deepest thanks to the many graduate students, post docs, undergraduates, and high school students and our collaborators and colleagues, some of whom, but not all, are named in the cited publications, and particularly to my close associate, Dr. Dustin James, who graciously aids all aspects of my program.

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JO070543S