

Synthesis and Preliminary Testing of Molecular Wires and Devices

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Abstract: Presented here are several convergent synthetic routes to conjugated oligo(phenylene ethynylene)s. Some of these oligomers are free of functional groups, while others possess donor groups, acceptor groups, porphyrin interiors, and other heterocyclic interiors for various potential transmission and digital device applications. The syntheses of oligo(phenylene ethynylene)s with a variety of end groups for attachment to

numerous metal probes and surfaces are presented. Some of the functionalized molecular systems showed linear, wire-like, current versus voltage ($I(V)$) responses, while others exhibited nonlinear $I(V)$ curves for negative differential resistance (NDR) and molecular ran-

dom access memory effects. Finally, the syntheses of functionalized oligomers are described that can form self-assembled monolayers on metallic electrodes that reduce the Schottky barriers. Information from the Schottky barrier studies can provide useful insight into molecular alligator clip optimizations for molecular electronics.

Keywords: cross-coupling • molecular devices • self-assembly

Introduction

With the miniaturization of transistors on silicon semiconductor chips come faster processing speeds and more powerful computational systems. However, these progressions in size reduction are placing a heavy financial burden on the silicon industry.^[1–7] Gordon Moore, one of the founders of Intel, predicted in 1968 that the minimum device feature size

on a semiconductor chip would decrease by a factor of two every 18–24 months. Moore's prediction has held true over the past 33 years; the routine commercial feature size of microchips has dramatically declined to almost 0.1 μm . Although a further decrease is likely, once the line size on integrated circuits becomes $<0.01 \mu\text{m}$, several quantum limitations will likely limit the performance of solid state devices. Moreover, the high cost of the more complex semiconductor fabrication facilities, and the inability to create ever-smaller semiconductor devices due to inherent fundamental physical constraints, could severely retard the industry in the next decade.

Therefore, new paradigms of computer architecture should be considered. Molecular electronics is a field of study that proposes the use of single or small packets of molecules to function as the key components in future computational devices.^[1–9] The use of a single molecule has the advantage of being about 10^6 times smaller in area than current silicon devices.^[1] Molecular-based systems can offer distinct advantages in uniformity and potential fabrication costs. Additionally, these molecular systems offer the advantage of ease of synthesis and the ability to create large varieties of structures by the use of facile chemical transformations.^[1, 2]

Discrete conjugated oligo(phenylene ethynylene)s can respond as wires, devices (nonlinear $I(V)$ curves) or dynamic random access memory components.^[10–14] We focus here primarily upon the synthetic chemistry used to make the active molecular components while touching upon the wire and device characteristics obtained. The use of these molec-

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 Supporting information (full experimental details of all compounds synthesized) for this article is available on the WWW under <http://www.wiley-vch.de/home/chemistry/> or from the author.

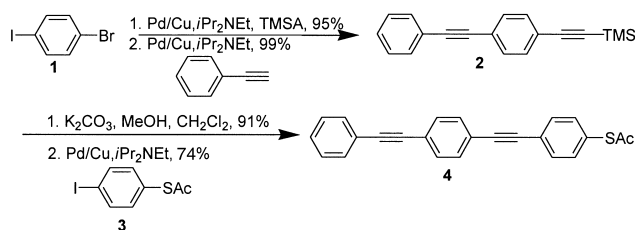
ular scale electronic devices should allow for a plethora of new and exciting computing architectures. Although numerous obstacles remain, such as addressing large molecular arrays, dealing with heat dissipation, and designing defect-tolerant architectures, molecular electronics offers an exciting incentive to consider molecular systems for future computing.

Results and Discussion

Synthesis of molecular-scale wires

The syntheses of molecular wires that exhibit nearly linear $I(V)$ curves are described in this section. Many of the molecular wires have previously been tested. In each case, the molecular wires bear one or more thioacetyl end groups that can be deprotected, during the self-assembled monolayer (SAM) formation step, to afford the free thiols for attachment to metallic probes.

Synthesis of one-terminal oligo(phenylene ethynylene) molecular wires: The synthesis of a simple wire, **4**, from readily available 1-bromo-4-iodobenzene (**1**) is shown in Scheme 1. The starting material was monocoupled to trimeth-



Scheme 1. Synthesis of unfunctionalized wire **4**. TMSA = trimethylsilylacetylene.

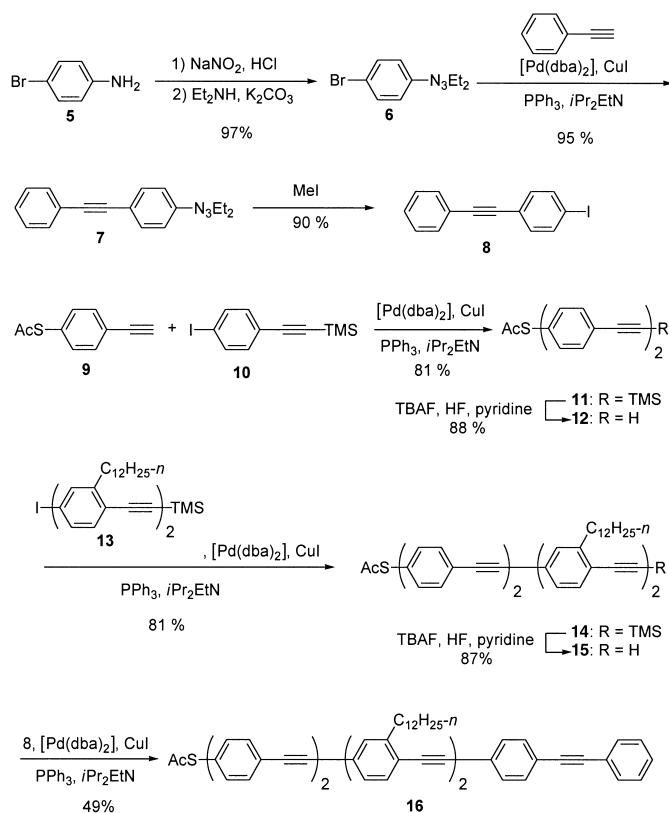
ylsilylacetylene using typical Sonogashira coupling procedures.^[15] The reaction proceeded with good chemoselectivity due to the greater reactivity of the aryl iodide. The resulting aryl bromide was then coupled to phenylacetylene using similar conditions yet higher temperatures to enhance coupling to the aryl bromide. The terminal alkyne **2** was deprotected using potassium carbonate and methanol and then coupled to 1-iodo-4-thioacetylbenzene^[16] (**3**) to form molecular wire **4**.

X-ray diffraction crystallography of a thiol derived from **4** attached to an Os cluster has shown that this oligo(phenylene ethynylene) exists predominantly in a planarized form; the phenyl rings being nearly parallel.^[17] It is hypothesized that the conductivity of these systems arise through the extended π -orbital overlap which is maximized while the molecule is planar. If the phenyl rings are skewed from planarity, the π -orbital overlap is diminished, and then conduction is decreased.^[18]

The solubility of unsubstituted **4** is moderately low in most organic solvents; therefore, it was necessary to place n -alkyl side chain moieties on the phenylene ethynylene oligomers when there are more than three phenyl units. Although a long alkyl chain is important to retain solubility of a molecular wire in common organic solvents, it could sterically retard self-

assembly or inhibit formation of a well-ordered and densely packed monolayer.

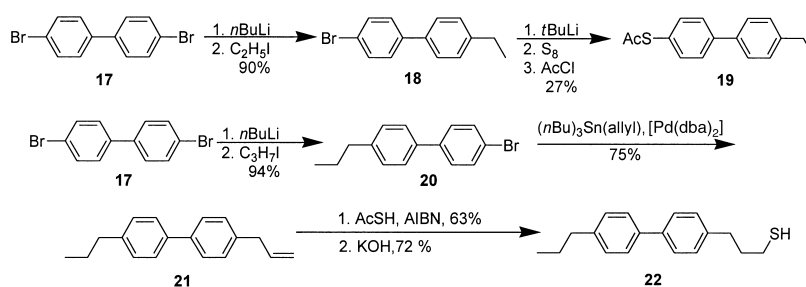
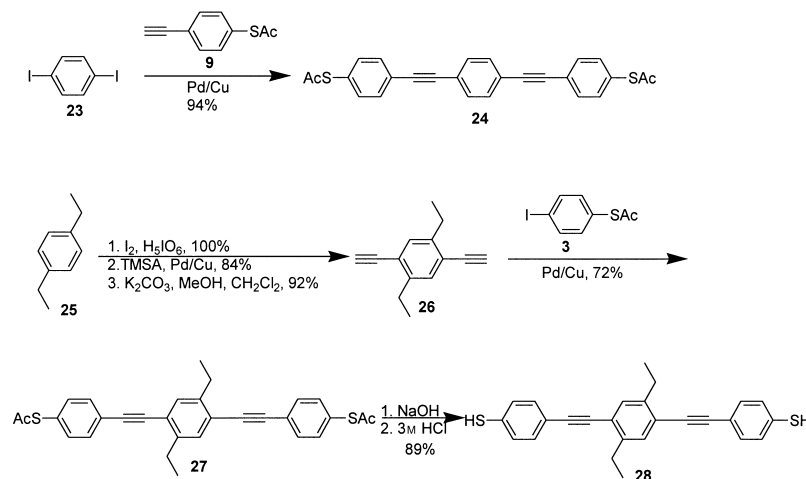
To make more soluble systems, we prepared molecular wire **16** by Pd/Cu-catalyzed coupling reactions of **8**, **12**, and **13** (Scheme 2). Compound **8** was synthesized by the coupling



Scheme 2. Synthesis of molecular wire **16**. dba = *trans,trans*-dibenzylideneacetone; TBAF = tetrabutylammonium fluoride.

reaction of **6**^[19] with phenylacetylene followed by an iodination with iodomethane. Compound **9**^[16] was coupled with **10** to afford dimer **11**. Deprotection of the terminal alkyne with TBAF provided intermediate **12** that was coupled with **13**^[20] to afford tetramer **14** which, upon deprotection and coupling with aryl iodide **8**, afforded **16**. Compound **16** has dodecyl chains on the two central units that allow this system to be soluble in many organic solvents but the chains point in the opposite direction of thiol group that serves as a molecular alligator clip; therefore, it does not impede the formation of the SAM.^[21]

The synthesis of wires with central conduction units and terminal conducting barrier units is shown in Scheme 3. These were prepared to study the effects of imbedding the molecular system in a mildly insulation terminal framework. Monolithiation on 4,4'-dibromobiphenyl (**17**) followed by treatment with iodoethane afforded **18** that was then converted to the alligator clip-bearing molecular-scale wire **19** with one ethyl end group barrier. The two-barrier system **22** was synthesized by conversion of 4-bromo-4'-propylbiphenyl (**20**) to 4-allyl-4'-propylbiphenyl (**21**). Radical thioacetyl formation^[22] afforded the thiol-protected molecular scale wire with an imbedded

Scheme 3. Synthesis of two-terminal system **22**. AIBN = 2,2'-azobisisobutronitrile.Scheme 4. Syntheses of two-terminal molecular wires **24** and **28**.

conductive portion that could be further converted to the alkythiol **22**.

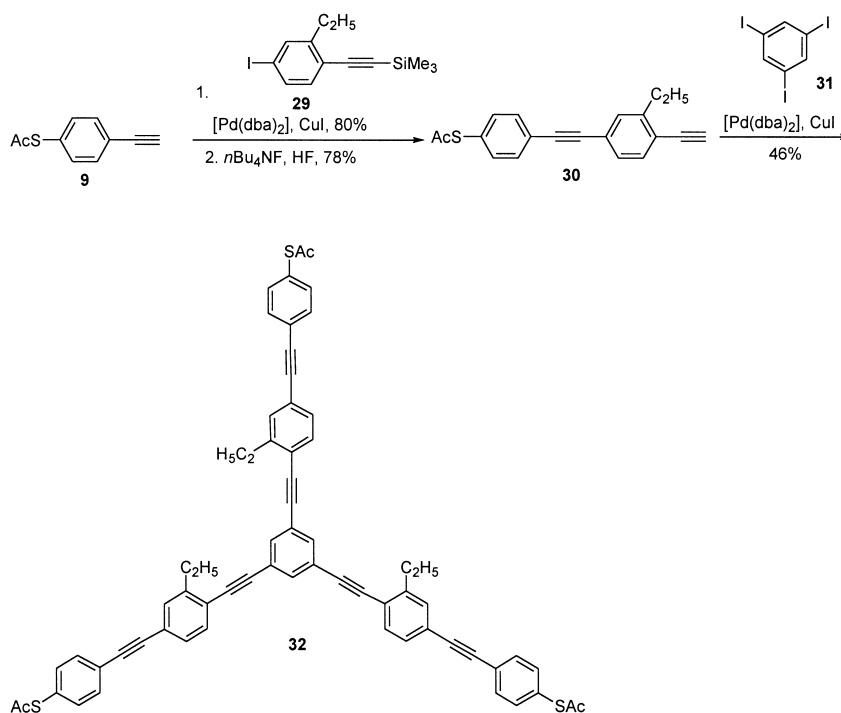
Synthesis of two-terminal oligo(phenylene ethynylene) molecular wires: Several syntheses of oligo(phenylene ethynylene)s with α,ω -dithioacetyl moieties, used as protected alligator clips, have been executed. These compounds will permit molecular scale wires to perform as interconnects between metallic probes (Scheme 4). Specifically, Pd/Cu-catalyzed cross couplings of 1,4-diiodobenzene (**23**) with two equivalents of alligator clip **9**^[16] afforded the rigid rod molecular scale wire **24**. Due to the poor solubility of the deprotected dithiol made from **24**, the more soluble diethyl-containing wire, **28**, was synthesized. Iodination of 1,4-diethylbenzene followed by a series of Pd/Cu-catalyzed couplings led to the formation of **27**. Removal of the acetyl protecting groups with sodium hydroxide in THF/H₂O and rapid workup produced soluble **28** with free thiol end groups.

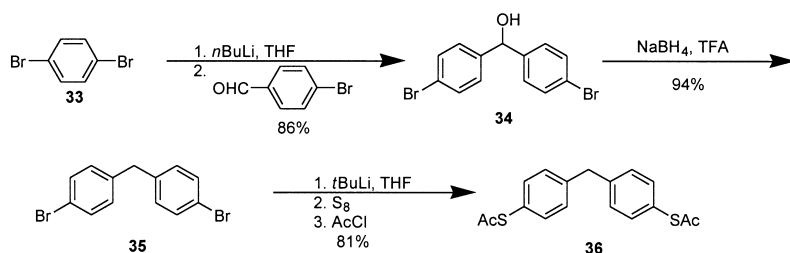
However, it is recommended that the end groups remain protected until the SAM formation step. In this way, oligomerization through oxidative disulfide formation is inhibited.

Syntheses of three-terminal molecular-scale wires: Three-terminal interconnects were prepared for branched interconnect locations (Scheme 5).^[23] Alligator clip **9**^[16] was cross-coupled with **29**^[20] followed by subsequent deprotection of the terminal alkyne to afford **30**. Three equivalents of intermediate **30** were coupled with 1,3,5-triiodobenzene (**31**) to afford the desired **32**.

Molecular wires with internal methylene and ethylene transport barriers: Molecular-scale wires with internal methylene and ethylene conduction barriers have been synthesized. These alkyl conduction barriers are positioned in the rigid-rod

phenylene ethynylene backbone to disrupt the electronic characteristics of the wires. It was hoped that the use of these methylene and ethylene conduction barriers in molecular wires might allow the development of nanoscale molecular devices, that is resonant tunneling diodes (RTDs). Mono-

Scheme 5. Synthesis of three-terminal molecular wire **32**.



Scheme 6. Synthesis of two-terminal wire with a methylene barrier. TFA = trifluoroacetic acid.

lithiation of 1,4-dibromobenzene and subsequent quenching with *p*-bromobenzaldehyde gave diarylmethanol **34** that was then converted to the diarylmethane **35** by reduction with sodium borohydride.^[24] Compound **36**, with one central methylene conduction barrier, was easily synthesized from **35** by lithium–halogen exchange followed by quenching with sulfur and subsequent addition of acetyl chloride (Scheme 6).

Compounds **41** and **45** (see Schemes 7 and 8) are molecular wires with a tunnel barrier to study the effects of asymmetric and symmetric barrier placement on the electronic properties. The synthesis of **41**, a 3-phenyl ring molecular scale wire with a methylene conduction barrier, is described in Scheme 7. 1,4-Diiodobenzene was monolithiated and quenched with 4-bromobenzaldehyde to form intermediate **38** followed by reduction of the secondary alcohol to form **39** in high yield. Coupling to the more labile aryl iodide gave compound **40**. Lithium–halogen exchange followed by quenching with sulfur and subsequent addition of acetyl chloride afforded the molecular-scale wire **41** containing a methylene conduction barrier.

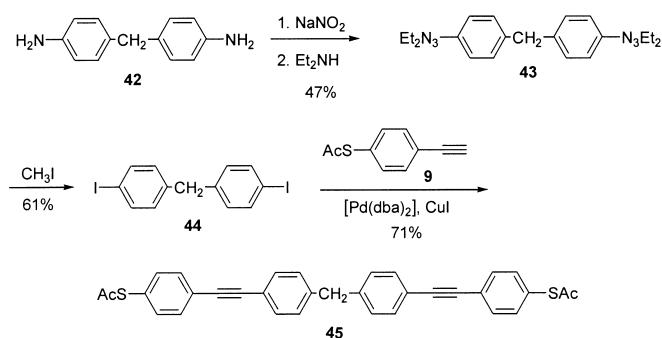
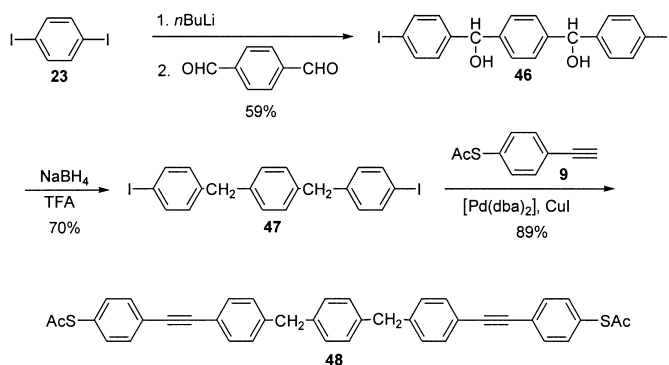
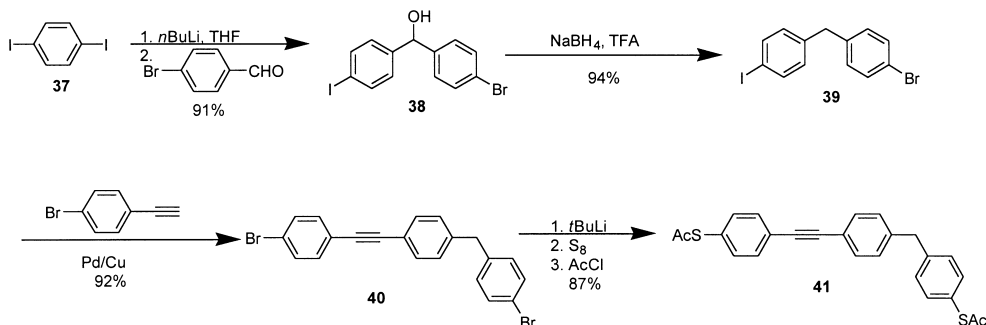
The synthesis of a symmetric molecular wire with a methylene conduction barrier is described in Scheme 8. Conversion of 4,4'-diaminodiphenylmethane (**42**) to the diiodide **44** through the formation of the bistriazene **43** proceeded in moderate yields. Intermediate **44** was coupled with the molecular alligator clip **9**^[16] to afford molecular wire **45** with the desired central methylene transport barrier.^[23]

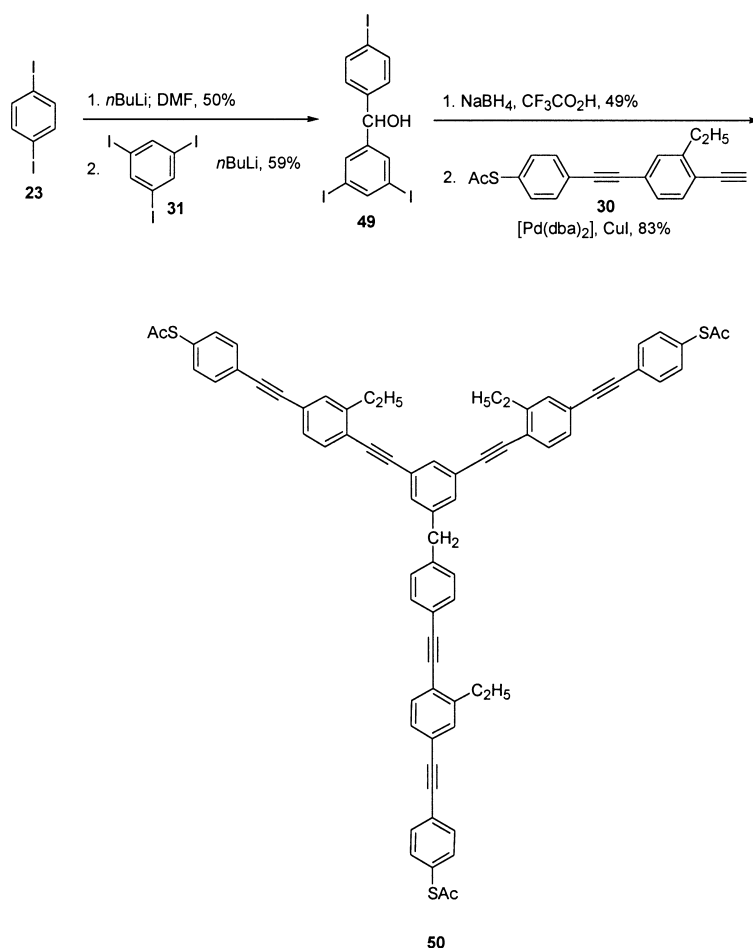
Compound **48** is a more sophisticated device with two barriers that resembles a linear quantum dot or a RTD.^[23] Compound **46** was synthesized from terephthalaldehyde and 1-iodo-4-lithiobenzene (Scheme 9). Reduction of the two hydroxyl moieties on **46** afforded **47** that was further coupled

with two equivalents of alligator clip **9** to afford the desired **48**. This compound did indeed respond as a room temperature RTD when placed in the nanopore configuration.^[25]

A three-terminal system with one barrier could be reminiscent of a molecular-sized field effect transistor (FET) or switch in which there is a

source, drain and gate (Scheme 10).^[23] 4-Iodobenzaldehyde was treated with 1,3-diiodo-5-lithiobenzene to afford the alcohol **49**. Reduction and Pd/Cu-catalyzed coupling with **30** yielded **50**, the desired three-terminal system with one methylene transport barrier.

Scheme 8. Synthesis of two-terminal molecular wire **45** with one methylene barrier.Scheme 9. Synthesis of two-terminal wire **48** with two methylene barriers.Scheme 7. Synthesis of molecular-scale wire **41** with one methylene barrier.



Scheme 10. Synthesis of three-terminal molecular wire **50** with one methylene barrier.

Four-terminal systems were synthesized according to Scheme 11. 4,4'-Diaminodiphenylmethane was treated with bromine followed by removal of the amino groups to afford 3,3',5,5'-tetrabromodiphenylmethane (**51**). Compound **51** proved to be too unreactive toward Pd/Cu coupling; therefore, conversion of the bromides to the iodides was necessary. Lithium–halogen exchanges on **51** followed by quenching with molecular iodine resulted in monoiodination on each ring. Complete halogen exchange on **51** was achieved by conversion to the tetra(trimethylsilyl) system by addition of *n*-butyllithium and chlorotrimethylsilane followed by treatment with iodine monochloride. The Pd/Cu-catalyzed coupling reaction of **9** or **30** with the tetraiodide intermediate afforded the four-terminal systems **52** and **53**, respectively. Compounds **52** and **53** could be viewed as molecular logic devices as described previously.^[23]

The synthesis of two four-terminal systems with two methylene conduction barriers is shown in Scheme 12. The dibromoxylene was oxidized and converted to the di(acid chloride) **54**. Friedel–Crafts acylation of **54** with bromobenzene was sluggish and low yielding. However, the tetrabromobis(arylketone) **56** was conveniently prepared by treatment of **54** with 1-bromo-4-trimethylsilylbenzene.^[26] The reduction of **56** was successfully carried out using triethylsilane and trifluoromethanesulfonic acid.^[27] Conversion of the bromides to the iodides was achieved by lithium–halogen

exchange with *t*BuLi followed by quenching with iodine. Pd/Cu couplings of **57** with the alligator clip **9** or **30** afforded the four-terminal systems **58** and **59**, respectively.

A two-terminal system with a lengthened resistive section was sought. Conversion of 1,2-(4,4'-dinitrodiphenyl)ethane (**60**) to the diiodide **62** followed by Pd/Cu-catalyzed coupling with alligator clip **9** afforded **63** with the desired central ethylene transport barrier (Scheme 13).

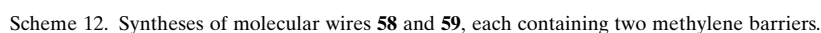
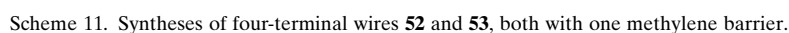
The syntheses of two ethylene-barrier containing systems, **66** and **67**, are described in Scheme 14. Compound **64** was synthesized in three steps from 1,4-diiodobenzene. Hydrogenation of **64** was achieved over Pd/C in the presence of a small amount of hydrochloric acid. Without an acid additive, no reduced products were isolated in a range of solvents and temperatures. The intermediate was then converted to **65** by treating with ICl in carbon tetrachloride. Pd/Cu couplings of **65** with two equivalents of the alligator clip **9** produced

wire **66**. Alternatively, coupling with one equivalent of phenylacetylene followed by one equivalent of the alligator clip **9** afforded **67** with one thioacetyl terminal group.

Synthesis of molecular-scale devices with heteroatomic functionalities

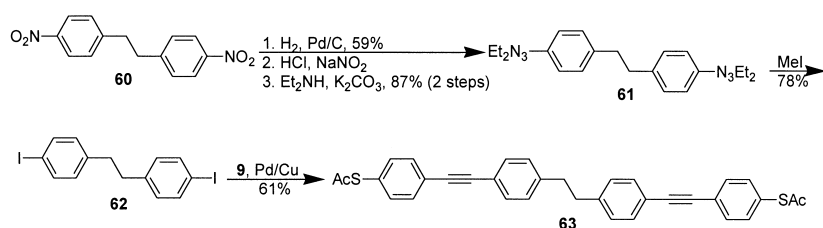
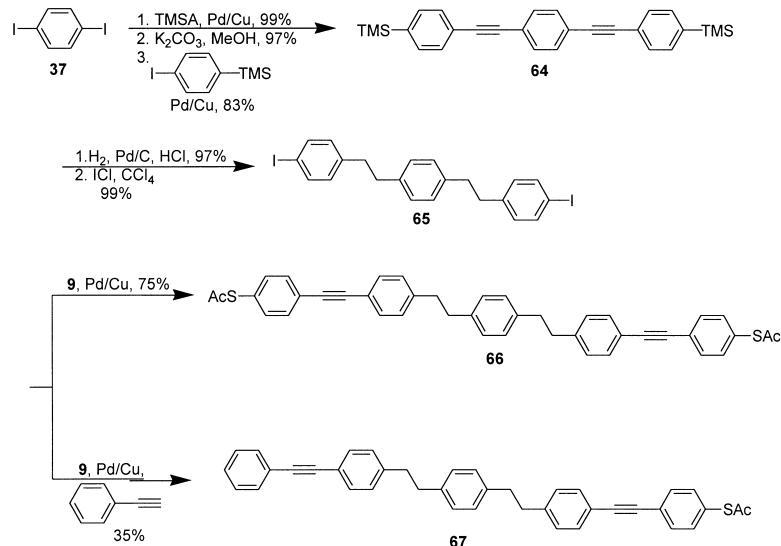
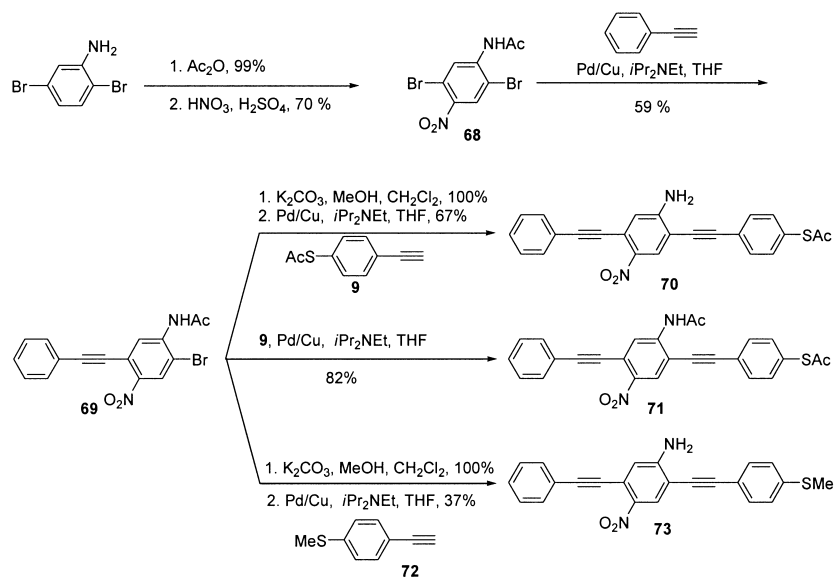
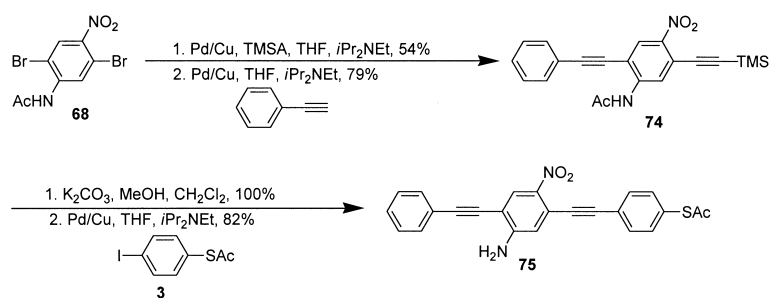
Described here are the syntheses of functionalized molecular-scale devices which are designed to have nonlinear $I(V)$ responses by adding heterofunctionalities to modulate the π -electron system. Some of the systems have been shown to possess NDR and memory properties. The majority of these molecules are based on functionalized oligo(phenylene ethynylene)s which are substituted with electron withdrawing and donating groups and are terminated with thioacetyl alligator clips.^[16, 20]

The synthesis of a molecular-scale device with amino and nitro moieties is described in Scheme 15. The formation of 2,5-dibromo-4-nitroacetanilide (**68**) proceeded according to a literature procedure.^[26b, 28] Caution must be used during the synthesis of **68** due to the possibility of multiple nitrations on the phenyl ring which could generate polynitrated compounds; on one occasion the compound exploded violently upon drying.^[26b] The Pd/Cu-catalyzed coupling of phenylacetylene to the substituted dibromobenzene gave a moderate



Compound **71** differs from **70** in that it possesses an acetamide rather than an amine moiety. The Pd/Cu-catalyzed coupling reaction to form **71** proceeded at a faster rate than the coupling to the amine/nitro compound due to the diminished electron-donating potential of the acetamide allowing faster Pd oxidative addition across the aryl bromide bond. The overall net dipole moment of this compound has been calculated to be 2.7 Debye, substantially lower than that for **70**.^[29]

The cyclic voltammetry char-

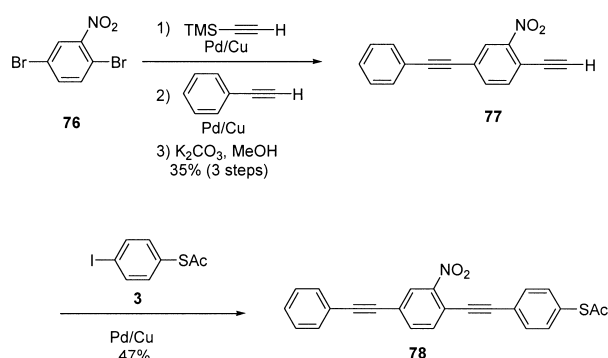
Scheme 13. Synthesis of molecular wire **63** with an ethylene barrier.Scheme 14. Syntheses of one-terminal and two-terminal molecular wires **66** and **67**, both containing two ethylene barriers.Scheme 15. Synthesis of molecular-scale device **70** and **71** and compound **73** for cyclic voltammetry experiments.Scheme 16. Synthesis of molecular device **75**.

containing molecular-scale devices were determined to help elucidate the transport mechanism. It was therefore necessary to synthesize thioether **73**, which is more stable to hydrolysis and subsequent oxidation than the thioacetate-terminated system (Scheme 15). For the synthesis of thioether **73**, intermediate **69** was deprotected and Pd/Cu-catalyzed coupled to **72** to form thioether terminated **73**. This compound was subjected to cyclic voltammetry that confirmed that the compound was being reduced at -1.7 V and again reduced at -2.3 V (Ag/AgNO₃ reference electrode, 1.0 M *n*-tetrabutylammonium tetrafluoroborate in DMF at a scan rate of 100 mV s⁻¹). Of course, there can be no correlation of absolute reduction potentials between the solution-phase and SAM experiments since the environments are grossly different. However, that **73** could undergo a reversible two-electron reduction was useful in the development of a hypothesis of a mechanism of the transport effect.^[29]

To determine the effect of the direction, if any, of the dipole moment on *I(V)* properties, compound **75** was synthesized, according to Scheme 16. It possesses a dipole that is directed toward the thioacetyl terminus, a direction opposite that of the dipole in **70**. With a deficient amount of trimethylsilylacetylene, the coupling with intermediate **68** proceeded at the more labile bromide α to the nitro group (vide supra). Subsequent coupling to phenylacetylene provided **74**. Deprotection of the amine and the terminal alkyne, followed by coupling to **3** afforded **75**.

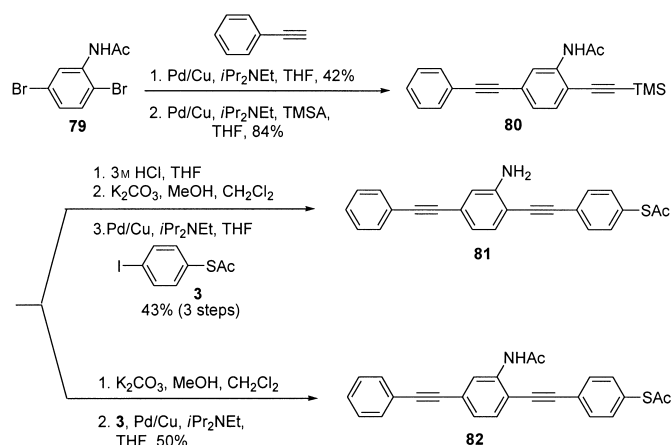
To determine the effects of an electron-withdrawing or -donating moiety on the electrical properties of these compounds, materials with solely an amine, nitro, or acetamide

A two-terminal molecular-scale device that is similar to compound **70** has been synthesized according to Scheme 19 although this bears α,ω -alligator clips.



Scheme 17. Synthesis of mononitro molecular device **78**.

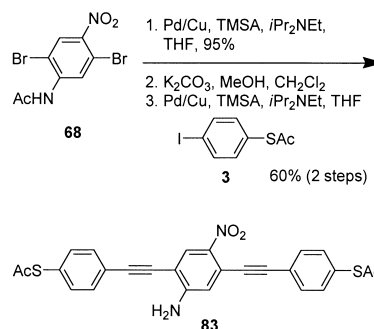
The system, which possessed an amino moiety, was synthesized according to Scheme 18 allowing the couplings of phenylacetylene and trimethylsilylacetylene to **79**, and the deprotection of compound **80** with 3M HCl afforded two



Scheme 18. Synthesis of monoamino compound **81** and molecular wire **82**.

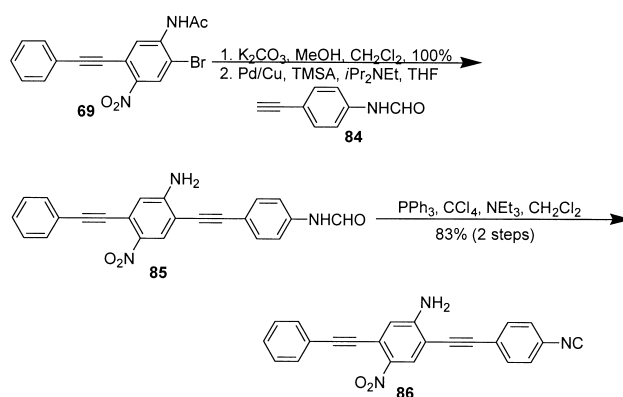
compounds: the desired amine product and the amine-cyclized bicyclic indole product.^[30] The separation of these compounds was not attempted due to similar retention factors on silica gel in most eluents. The terminal alkyne was revealed by using potassium carbonate and methanol followed by Pd/Cu-catalyzed coupling to **3** to form **81** which, at this stage, could be separated from the other products. The sequence of couplings to the bromo moieties on **79** was inferred based upon the electron donation of the acetamide; however, no crystallographic confirmation of the regioselectivity was obtained.

Similar to **81**, the acetamide adduct was synthesized according to Scheme 18. In this case, the deprotection of the terminal alkyne with potassium carbonate and methanol did not remove the acetyl-protecting group.



Scheme 19. Synthesis of two-terminal molecular device **83**.

To study the effects of other alligator clips on the impedance of molecular/metal junctions,^[1] compounds with isonitrile end groups were synthesized. The nitroaniline with an isonitrile terminus, **86**, was synthesized according to Scheme 20. The amine moiety in intermediate **69** was

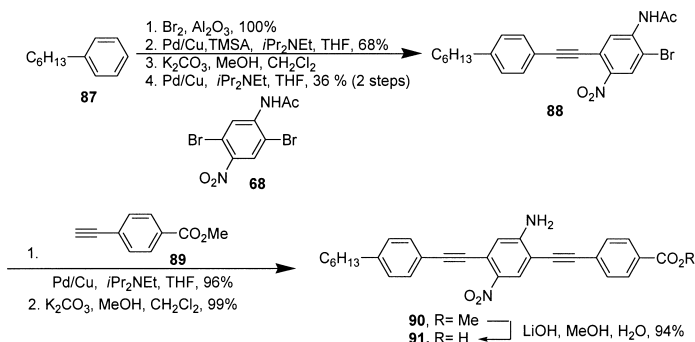


Scheme 20. Synthesis of molecular device **86** with an isonitrile alligator clip.

unmasked with potassium carbonate and methanol followed by Pd/Cu-catalyzed cross coupling with the formanilide-bearing end-group (**84**) to afford compound **85**. Although **85** had limited solubility, it was dehydrated in the presence of triphenylphosphine and triethylamine to afford the isonitrile **86**.^[31]

Currently, these molecular systems are studied as SAMs on a metal surface. An additional method of preparing ordered monolayers of molecular devices is the use of Langmuir–Blodgett (LB) films.^[32] Therefore, a compound with hydrophilic and hydrophobic subunits with the central nitroaniline core similar to **70** was synthesized as in Scheme 21.^[32] *n*-Hexylbenzene was easily brominated on neutral alumina^[33] and coupled to trimethylsilylacetylene followed by silyl removal and coupling to the nitroacetanilide core intermediate **68** to afford **88**. The methyl ester, intermediate **90**, was synthesized by the coupling of methyl 4-ethynylbenzoate (**89**) to **88**. The amine was unmasked and the methyl ester was saponified with lithium hydroxide to afford molecular-scale

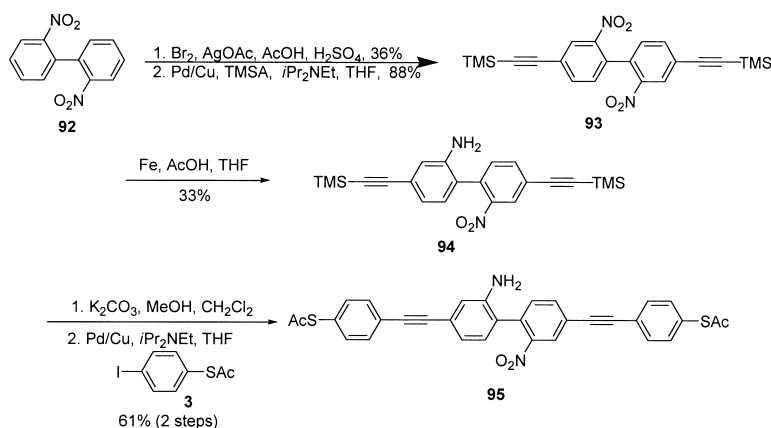
device **91**.^[34] Compound **91** is suitable for the formation of a LB film due to its hydrophilic carboxylic acid end-group and the hydrophobic *n*-hexyl end-group.



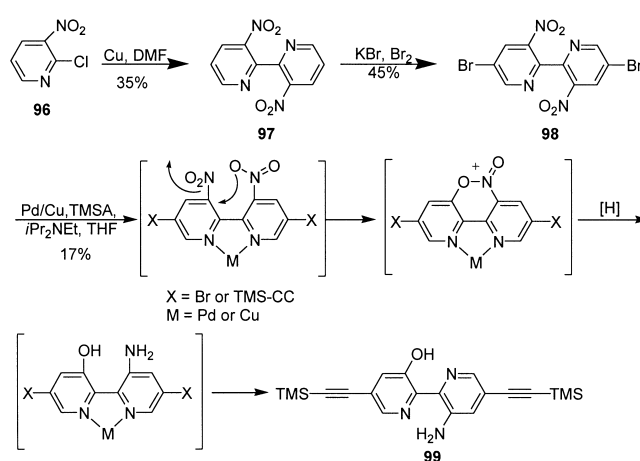
Scheme 21. Synthesis of compound **91**.

Other compounds with substituted biphenyl and bipyridyl core units have been sought (Scheme 22 and Scheme 23). 2,2'-Dinitrobiphenyl (**92**) was brominated at the 4 and 4'-positions on the biphenyl core using bromine, silver acetate, and acid.^[35] The brominated biphenyl was coupled to trimethylsilylacetylene to afford **93** that was then mono-reduced to the nitroamine **94** in the presence of iron and acetic acid.^[36] Finally, the terminal alkynes were revealed and coupled to two equivalents of alligator clip **3** to afford compound **95**.

A similar compound with a bipyridyl central core was sought according to Scheme 23. In this manner, a greater degree of planarity could be achieved due to reduced interactions in the absence of 2- and 2'-steric interactions. To that end, 2-chloro-3-nitropyridine was homocoupled in the presence of copper/bronze and dimethylformamide.^[37] The bipyridine ring system was brominated at the 5- and 5'-position under harsh conditions^[38] (due to its electrophilicity) to afford intermediate **98** that was then coupled with two equivalents of trimethylsilylacetylene. These coupling conditions unfortunately afforded the hydroxyamine and a very small amount of the dinitro-coupled product. The electron-deficient **98** presumably underwent nitro loss and Pd-catalyzed reduction by the hydridopalladium species that are present in the coupling catalytic cycle to afford the undesired **99** (Scheme 23).^[38b]

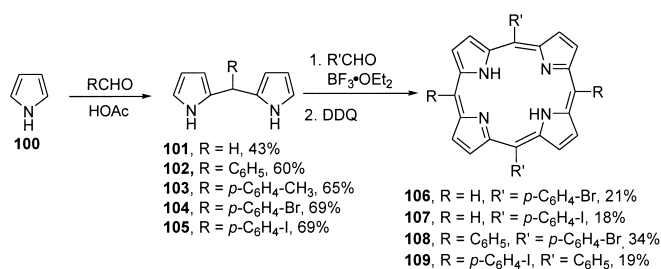


Scheme 22. Synthesis of nitro-amine biphenyl compound **95**.



Scheme 23. Synthesis of bipyridyl compound **99**.

Porphyrin-containing molecular-scale wires: Initial efforts directed toward the porphyrin targets involved the preparation of dipyrromethane or aryl-substituted-dipyrromethanes with the intent of subsequent Pd/Cu-catalyzed coupling^[39] to the aryl halides for preparation of the final compounds.^[40] The porphyrin syntheses are shown in Scheme 24.



Scheme 24. Syntheses of various porphyrin compounds.

The dipyrromethanes could be prepared in reasonable yield, and further condensed with the complementary benzaldehyde component to generate the *trans*-(halophenyl)porphyrins.^[41] Unfortunately, further attempts to elaborate the halogenated positions by Pd/Cu-catalyzed cross coupling or lithium-halogen exchange and subsequent conversion directly to thioacetyl moieties (excess BuLi, sequential quenching with S_8 and AcCl)^[16] were unsuccessful; all reactions afforded only small amounts of mono-substituted products, if any. Additionally, complexing the porphyrin with zinc did not change the unsuccessful course of the subsequent derivatizations of **106–109**.

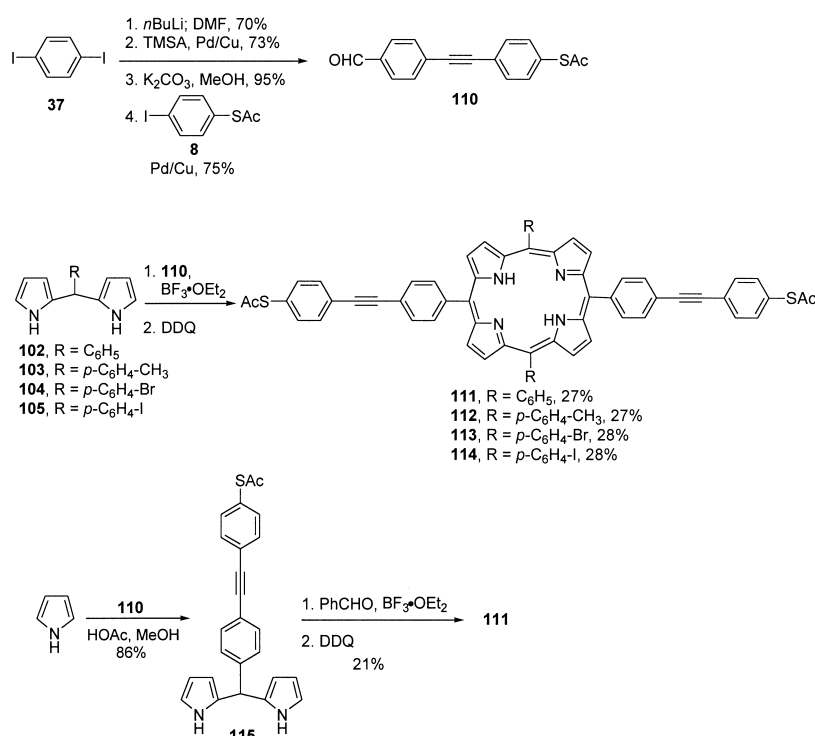
The strategy was therefore modified by preparing the aldehyde-bearing protected thiol using Pd/Cu-catalyzed coupling of 4-iodobenzaldehyde with trimethylsilylacetylene, subsequent deprotection, and another

er Pd/Cu-catalyzed coupling with 4-iodo-1-thioacetylbenzene (**8**) to afford aldehyde **110** (Scheme 25).^[42] Protected thiol **110** was then condensed with the substituted dipyrromethanes (**102**–**105**) and oxidized to form porphyrins **111**–**114**, respectively (Scheme 25). Likewise, **110** was condensed with pyrrole to form **115** and then further condensed with benzaldehyde and oxidized to form **111**. Accordingly, no further functionalization of the porphyrin was needed. Furthermore, the thioacetyl moieties did not inhibit the reaction neither were they affected to a significant extent; the yields were similar to those obtained in reactions that did not have these thioacetyl functionalities. In a less controlled manner, the three-component system involving pyrrole, benzaldehyde, and **110** could be used to prepare **111** in 8% yield after oxidation with *p*-chloranil. Similarly, the tetra(alligator clip) substituted system **116** could be prepared from **110** and pyrrole (Scheme 26).^[39–41]

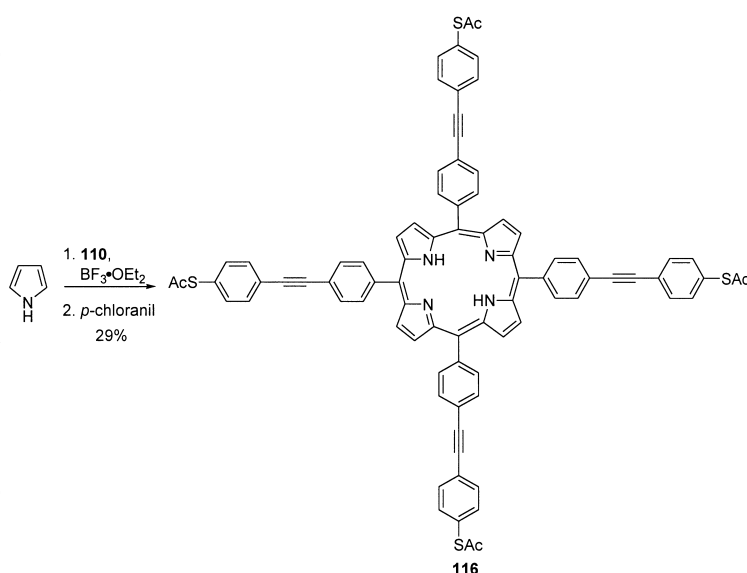
Finally, we have demonstrated efficient removal of the acetyl groups in **111** using ammonium hydroxide.^[43] Metal incorporation into **111**, specifically Zn (91%), Cu (95%), and Co (90%), using the corresponding hydrated metal acetates, followed by ammonium hydroxide-promoted thiol generation,^[43] proceeded without metal loss as indicated by ¹H NMR analysis.

Synthesis of dipole-possessing molecular wire SAMs to control Schottky barriers in organic electronic devices

Concurrent with our efforts to build molecules for SAMs that will be used for molecular electronic devices, we are considering compounds that would form SAMs at metal interfaces in organic polymer-based LEDs. Similar issues that affect the efficiency of the metal's Fermi level overlap with the



Scheme 25. Syntheses of porphyrin intermediate **110**, and porphyrins **111**, **112**, **113**, and **114**.



Scheme 26. Synthesis of four-terminal porphyrin **116**.

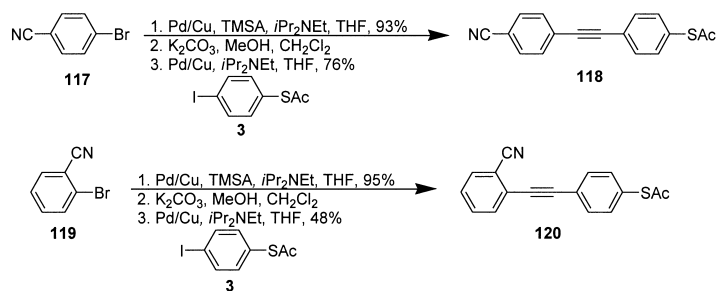
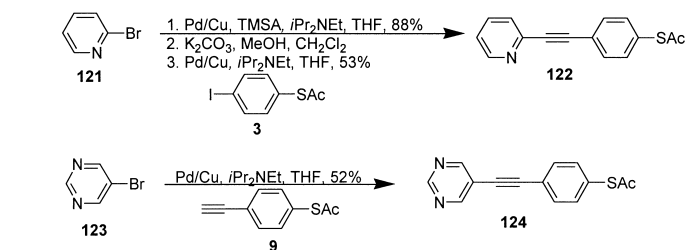
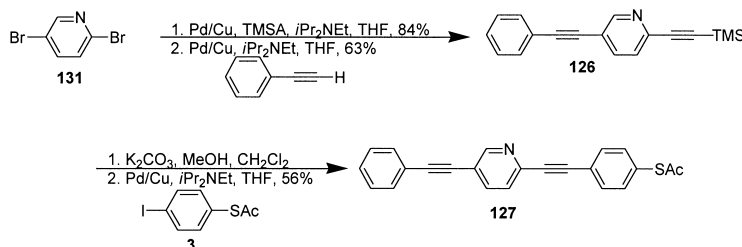
molecule's LUMO in molecular electronics will affect the electron injection at LED interfaces. Therefore, we are currently synthesizing molecules to act as SAM interfaces between the metal contacts and the organic substrates in LEDs. By tailoring the Schottky barrier of the metal/organic interface, we are hoping to improve the efficiency of the LEDs. The Cu/SAM injection of holes at low voltage could also improve ohmic contact.

We envisioned conjugated phenylene–ethynylene compounds that possess electron-deficient units or electron-rich units to be good candidates for lowering or raising the LUMO energies, respectively, as needed for the electron or hole injecting interfaces. Again, these compounds need alligator clips to provide the SAM formation.

Compounds **118** and **120** were synthesized by Pd/Cu-catalyzed cross couplings reactions (Scheme 27). Surprisingly, each of these compounds were extremely difficult to separate by column chromatography and recrystallizations. They were finally purified by multiple cold hexanes washes.

Likewise, compounds **122** and **124** were synthesized (Scheme 28). Again, these compounds were produced in a straightforward fashion by Pd/Cu-catalyzed cross couplings.

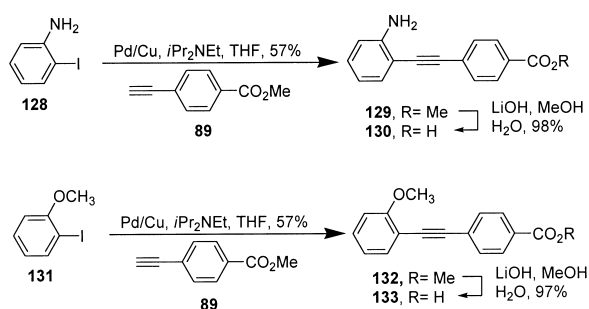
A three-aryl system with a pyridine interior was synthesized for the LED interfaces (Scheme 29). 2,5-Dibromopyridine was coupled to trimethylsilylacetylene followed by phe-

Scheme 27. Syntheses of cyano-containing systems **118** and **120**.Scheme 28. Syntheses of pyridine system **122** and pyrimidine system **124**.Scheme 29. Synthesis of pyridine system **127**.

nylacetylene under Pd/Cu-catalyzed conditions. The first coupling reaction occurred at the more labile bromide at the 2-position in the pyridine ring. The alkyne in intermediate **126** was unmasked and then was coupled to alligator clip **3** to form the desired **127**.

To decrease the Schottky barrier for electron injection in LEDs, compounds with electron-donating moieties and carboxylic acid alligator clips were synthesized for the formation of SAMs on aluminum oxide contacts.^[44]

In separate reactions, compounds **128** and **131** were coupled to **89** to afford methyl ester intermediates, **129** and **132**, respectively. The methyl ester moieties were saponified in the presence of lithium hydroxide to afford compounds **130** and **133** (Scheme 30).^[34] These compounds are currently being

Scheme 30. Syntheses of compounds **130** and **133**.

tested for their ability to lower the electron injection barrier between the aluminum oxide contact and the organic polymer in organic LEDs and provide corroborating evidence for impedance lowering in molecular electronic devices.

Testing of molecular-scale wires and devices

Electronic measurements on molecular scale wires and devices were performed in the nanopore testing assembly. The nanopore system consists of a small (30–50 nm diameter) surface of evaporated metal (which can vary, but most often gold or palladium) on which a SAM of the molecular wires or devices is permitted to form. An upper metal (usually gold or titanium) contact is then evaporated onto the top of the SAM layer making a sandwich of metal-SAM-metal through which $I(V)$ measurements are recorded.^[45] By using such a small area for the SAM (~1000 molecules), we can probably achieve SAMs that are defect-free since the entire areas are smaller than the typical defect density of a SAM, thereby eliminating electrical shorts that can occur if one evaporates metal atop a SAM that is larger, for example, micron-sized. Note that metals have been deposited by evaporation atop micron-sized LB monolayers when the lower metal was an oxide, specifically aluminum oxide. The oxide inhibits the short circuits of the system.^[32]

The first device curve we recorded from a molecular system was one that is reminiscent of a RTD. A classical solid-state RTD device has a two-barrier system between conducting segments. An RTD shows negative differential resistance (NDR), which is a deflection in the $I(V)$ curve. Indeed, the two-barrier compound, **48**, when assembled in the nanopore, exhibited the RTD-like NDR response shown in Figure 1.^[25]

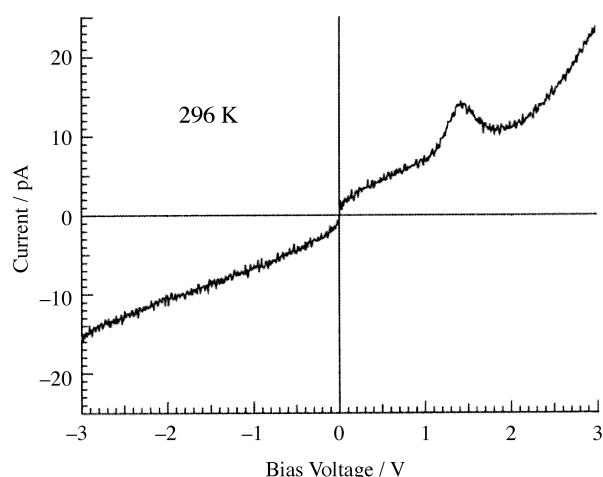


Figure 1. $I(V)$ plot of **48** at 296 K, which shows NDR. The non-symmetric NDR effect may be due to the differences in the self-assembled versus metal-evaporated contacts on either side of the nanopore.

Conductivity of these oligo(phenylene ethynylene) molecular-scale wires and devices is hypothesized to arise from transfer of electrons through the π -orbital backbone that extends over the entire molecule. When the phenyl rings of the phenylene ethynylene oligomers are planar, the π -orbital

overlap of the molecule is continuous. Thus transfer over the entire molecule is achieved; electrons can freely flow between the two metal contacts, and conductivity is maximized. But if the phenyl rings become perpendicular with respect to each other, the π -orbitals between the phenyl rings become orthogonal. The discontinuity of the π -orbital network in the perpendicular arrangement minimizes free flow of electrons through the molecular systems, thus conductivity is greatly decreased.^[18, 46]

There is experimental evidence for this result as well. As seen in Figure 2, **134** and **135** show a sharp decrease in conductance between 20 and 40 K in the temperature–cur-

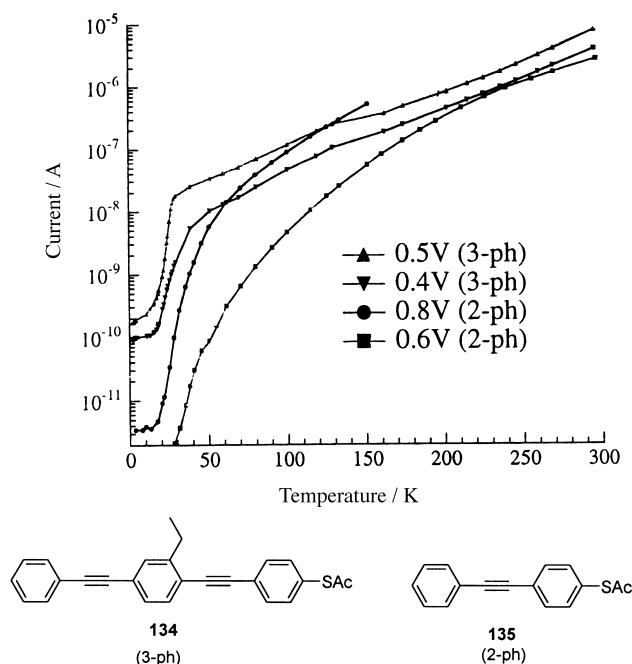


Figure 2. Plot of current versus temperature of compounds **134**^[20] (3-ph) and **135**^[43] (2-ph) in the nanopore with a bottom contact (SAM-contact side) of gold and a top contact of titanium. Each nanopore contains approximately 1000 molecules.

rent plots.^[47] At these lower temperatures, phenylene ethynylenes have the tendency to fishbone pack on crystallization in the SAM.^[46] The phenyl rings are therefore in perpendicular arrangements with respect to each other along each molecule, causing a decrease in the π -orbital overlap. This results in the sudden decline in current at lower temperatures whereupon crystallization in the SAM restricts conformational rotation.^[46] As the SAM is permitted to warm above 40 K, the system has enough energy to permit conformational rotation. This rotational movement permits the phenyl subunits to attain some conformations with near planarity, and conduction thus occurs.

Since modulation of temperature is an inefficient and impractical way to modulate a structure's conformation and hence conductance, we sought another structural element that would permit altering the degree of a molecule's π -orbital overlap through the use of a third electrode (gate). Thus molecules that have net dipoles that are orthogonal (or simply out of plane from the long molecular axis), could be

controlled by use of a third electrode in the nanopore to modulate the conformation, and hence the current through the system.

However, since nanopore devices with an electrode perpendicular to the SAM axis had not yet been fabricated, we simply began with the control experiments. Namely, to study the two-electrode nanopore made with molecules bearing dipolar groups.

Accordingly, **70** was tested in the nanopore, in the absence of an orthogonal external electric field, to determine its electronic characteristics. A series of control experiments were performed with alkanethiol-derived SAMs and systems containing no molecules. Both the Au-alkanethiolate-Au junctions and the Au-silicon nitride membrane-Au junctions showed current levels at the noise limit of the apparatus (<1 pA) for both bias polarities at both room and low temperatures. The Au–Au junctions gave ohmic $I(V)$ characteristics with very low resistances. A device containing a SAM of conjugated molecules similar to **70** but not bearing the nitroaniline functionalities, namely **134**, was fabricated and measured in nearly identical conditions^[47] and it exhibited essentially linear $I(V)$ behavior (Figure 2) within its non-crystalline temperature range (vide supra).

Remarkably, typical $I(V)$ characteristics of an Au-(**70**)-Au device at 60 K are shown in Figure 3.^[13] Positive bias corresponds to hole injection from the chemisorbed thiol-

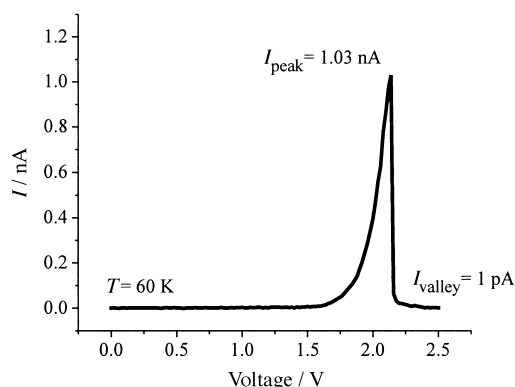


Figure 3. $I(V)$ characteristics of a Au-(**70**)-Au device at 60 K in the nanopore.

–Au contact and electron injection from the evaporated contact. Unlike previous devices that also used molecules to form the active region, this device exhibits a robust and large negative differential resistance (NDR) with a valley-to-peak ratio (PVR) of 1030:1.^[13] The NDR effect from the system containing **70** was observed up to 260 K. Beyond that temperature, however, no NDR was observed. More recently room temperature NDR has been seen in the nanopores containing **78**.^[48]

Additionally, we demonstrated charge storage in a self-assembled nanoscale molecular device that operated as a molecular dynamic random access memory (mDRAM) with practical thresholds and output under ambient operation.^[14] The memory device operates by the storage of a high or low conductivity state. Hence, we need not address the nanopore and attempt detection of a small number of additional

electrons; a problematic feature of typical solid state single electron devices. Conversely, the added electrons dramatically affect the conductivity of the molecular system thus a conductivity check notes the presence of the information state. Figure 4 shows the write, read, and erase sequence for

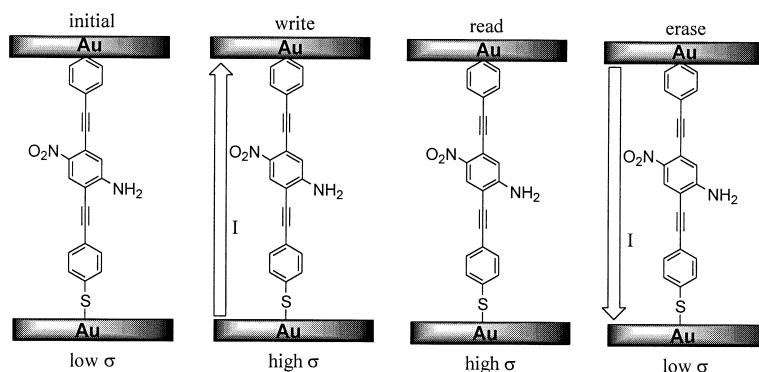


Figure 4. Write, read, and erase sequences for **70** in the nanopore and its use as a one-bit random access memory.

70. An initially low-conductivity state (low σ) is changed (written) into a high-conductivity state (high σ) upon application of a voltage pulse. The direction of current that flows during this “write” pulse is diagrammed. The high σ state persists as a stored “bit”, which is read in the low-voltage region. Again, this effect persisted up to 260 K.^[13]

To further explore the mechanism of this mNDR and mDRAM phenomenon, several related compounds have been synthesized. Compound **71** differs from NDR molecule **70** in that it possesses an acetamide rather than a free amine moiety. After testing in the nanopore, compound **71** exhibited the NDR effect, however, a smaller peak-to-valley ratio of 200:1 was observed at 60 K.

To determine if the orientation of the dipole moment relative to the SAM surface affected the electronic characteristics, **75** was synthesized. This compound possesses a dipole that is directed towards the thioacetyl terminus that is opposite of the dipole in compound **70**. To date, however, no comparative nanopore tests have been performed on **75**.

Several other compounds were tested that had either neutral, electron-donating or electron-withdrawing groups. The amine-only compound **81** and an unfunctionalized oligo(phenylene ethynylene) **4** do not exhibit storage; the latter two systems possess nearly linear $I(V)$ curves with no switching states. The nitro only containing compound **78** remarkably showed both NDR (4:1 PVR at 300 K)^[48] and mDRAM capabilities even at 300 K.^[14]

Figure 5 is a measured logic diagram demonstrating the mDRAM cell using **78** in the nanopore. To convert the stored conductivity to standard voltage conventions, the output of the device was dropped across a resistor, sent to a comparator and inverted and gated with the “read” pulse. The upper trace shown in Figure 5 is an input waveform applied to the device, and the lower is the mDRAM cell output. The first positive pulse configures the state of the cell by writing a bit, and the second and third positive pulses read the cell. The third pulse (and subsequent read pulses, not shown here for simplicity) demonstrates that the cell is robust and continues to hold the

state (up to the limit of the bit retention time). The negative pulse erases the bit, resetting the cell. The second set of four pulses repeats this pattern, and one year of continuous operation (10^9 cycles) have been observed with no degradation in performance. This effect can be rationalized based

upon conduction channels that change upon charge injection that studied by density functional theory (DFT).^[29, 49] These DFT studies further corroborate with the experimental results in that compounds **4** and **81** would be inactive as devices (having linear $I(V)$ curves) while **70** and **78** would both have switching states (exhibited by sharp nonlinear $I(V)$ characteristics) due to the accepting of electrons during voltage application. Furthermore, the DFT calculations showed that **70**

would need to receive one electron in order to become conductive whereas **78** would be initially conductive (“on” in the mDRAM) and then become less conductive, “off”, upon receipt of one electron.^[49] This is precisely the effect observed in the experiment. The four compounds on which we have

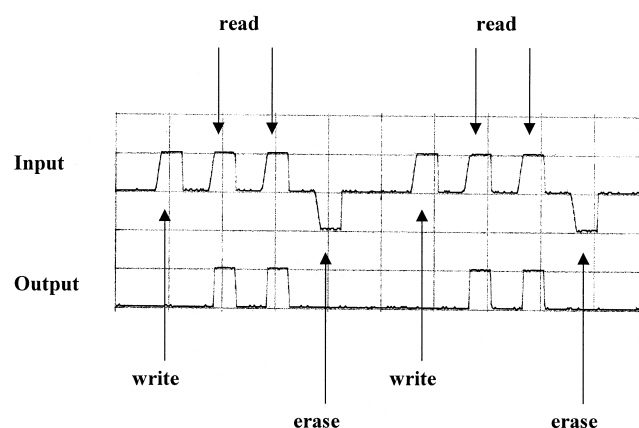


Figure 5. The mDRAM cell input and output that is constructed from **78** in the nanopore. The mDRAM was built into a circuit that had a transistor and a comparator (as do most commercial solid state DRAMs) and operation was at 300 K.

mNDR and mDRAM experimental results are summarized in Figure 6.

A two-terminal molecular-scale device **83** that is similar to mNDR compound **70** has been synthesized, however, no device tests have yet been performed on this compound.

A problem that persists in molecular electronics is the impedance mismatch between the molecule and the metal contact and we have been studying this resistance barrier over the last few years.^[1, 50] To reduce this impedance mismatch, the sulfur in our alligator clips has been replaced with more metallic Se and Te termini to allow for greater overlap of the compound's LUMO and the gold's Fermi levels. Nonetheless, it was determined that neither the selenium nor tellurium alligator clip significantly reduced the barrier height.^[51, 52]

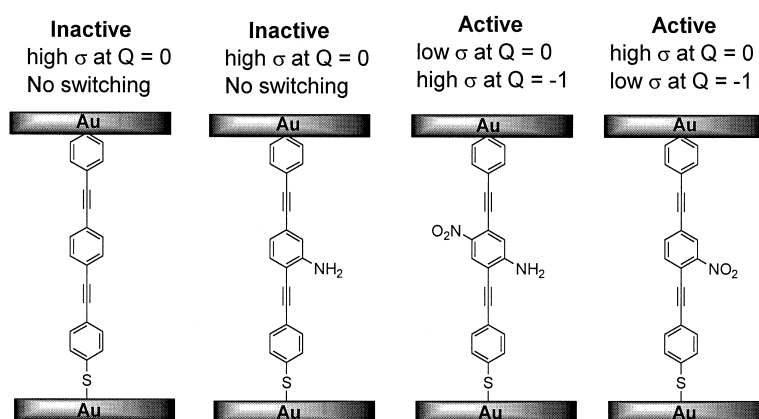


Figure 6. Summary of the mNDR and mDRAM results obtained to date in the nanopore cell where σ is the conductance and Q is charge. “Inactive” and “Active” refer to the device properties wherein a large nonlinearity in the $I(V)$ curve results upon application of a voltage.

Recently it has been discovered that the use of an isonitrile as the contact between the organic molecular-scale wire and a palladium probe would significantly reduce the conduction barrier,^[53] and would allow an increase in the conductivity of the molecular-scale wires. Therefore molecular-scale device **86** with an isonitrile attachment moiety was synthesized. Compound **86** is currently being tested for mNDR and mDRAM properties as well.

We have primarily used self-assembly as the initial attachment method to affix these molecular-scale wires to the metal probe and devices. An additional method of preparing ordered monolayers of molecular devices is the use of LB films.^[32] Therefore, **91** was synthesized, which is a compound with hydrophilic and hydrophobic subunits with the central core similar to that in **70**. Electrical conductivity tests are currently being performed on **91**.

Furthermore, we envisioned a nanopore cell containing **95** could act as a molecular controller wherein the molecular system would have greater contiguous overlap in the presence of an applied orthogonal (gate) field as described in the Figure 7. In the ground state, the biphenyl ring system will be nonplanar due to steric interactions. This will cause the π -overlap of the molecular device to be noncontiguous thus decreasing the electrical conductivity. In an applied electric field that is perpendicular to the molecular axis gate, the more planar zwitterionic resonance form will be a greater contributor to the overall structure. Hence, gated control of the current through the system might be permitted. It is not essential that the molecule be entirely planar when the gate electrode is activated. It is simply necessary that the applied field lessens the twist angle between the two central rings; hence, current modulation between the top and bottom electrodes could be maintained. The increased conductivity in the perturbed state (gate voltage applied), compared to the ground state, will allow this material to function as a molecular-scale switch. Therefore, compound **95** was synthesized.

As described previously, we also sought to prepare the bipyridyl-containing version rather than the biphenyl version, so as to permit a greater degree of planarity in the zwitterionic form. However, this target has proven to be elusive (Scheme 23).

Due to the difficulties in fabrication of the nanopore with an electrical field line perpendicular to upper and lower address electrodes, conductivity and switching studies on compound **95** have not yet been performed. If the gate-control effects in **95** are realized, we will revisit the synthesis of related systems (vide supra).

Several of the porphyrin-containing systems bearing alligator clips did not possess significantly nonlinear $I(V)$ characteristics in both the forward and reverse bias modes. But we have yet to test the metal-containing porphyrins.

Although our device studies on the porphyrins have not afforded positive results, these observations were specifically found in the nanopore using a specific set of symmetric structures and should not be used to exclude the search for other porphyrin-based molecular electronic devices.^[54]

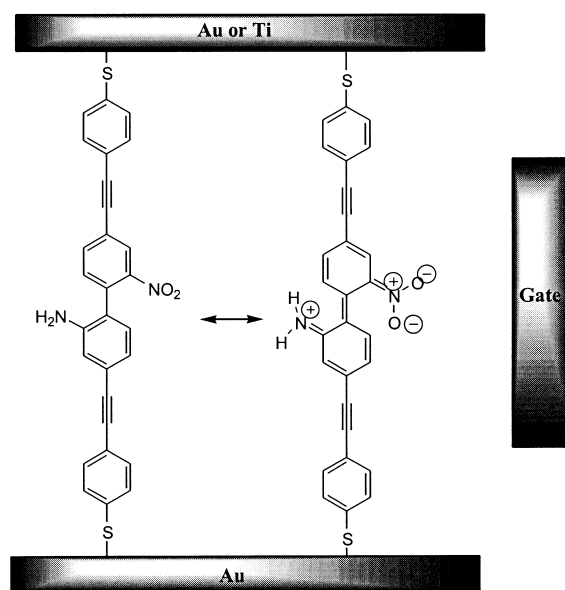


Figure 7. Schematic of a molecular device controller where a gate electrode could modulate the overlap in a molecule by preferring the more planar zwitterionic form.

The use of dipole-possessing molecular-scale systems to control Schottky barriers in organic electronic devices

Recently, the use of organic molecules in electronic devices has found great utility. Conductive organic compounds have several advantages over traditional inorganic materials including ease of fabrication, mechanical flexibility, and cost effectiveness.^[55] A few of the areas of promise include LEDs,^[56–58] transistors,^[59] and photodetectors.^[60] Large electronic energy barriers have been evident at the contact point

between metal and organic materials and they have been a source of limitation and instability in these systems.^[60] The metal/organic interface in LEDs have been shown to follow ideal Schottky behavior, that is, the electron Schottky barrier is determined by the energy difference between the metal work function and the electron affinity of the organic material.^[61] These effects are also apparent in the metal/organic interface of molecular electronic systems, hence the studies here shed light on some of the key parameters in question for our molecular electronic research.

We have been experimenting with SAMs as a controlled method to modify the metal surface and produce ordered dipole layers that change the effective work function of the metals. The useful range of metal work functions is from Ca and Sm (about 3 eV) to Pt (about 5.6 eV). It would be desirable to make useful metal contacts with both larger and smaller work functions (i.e. < 3 eV or > 5.6 eV) by attaching stable, ordered dipole layers to metals for example. The larger the dipole moment and surface potential shift, the better. In some monolayers, surface potential shifts of about 0.7 V have been observed.^[62]

The lowering of the Schottky barrier, with functionalized molecular-scale systems assembled as a SAM on the metallic interface, would permit better transport of an electron or hole from the metal contact to the organic LED (Figure 8). It has been demonstrated that electronically conductive SAMs, that

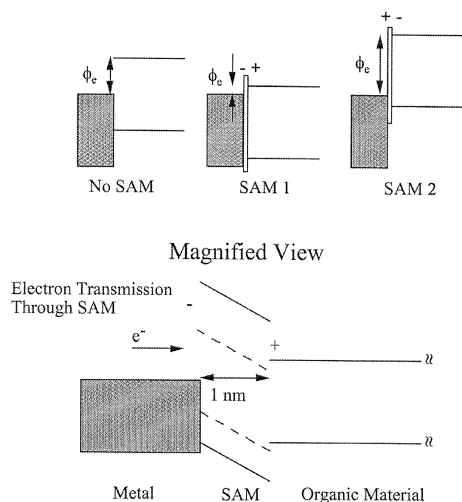


Figure 8. Illustration of the effect of incorporating a SAM (with a significant dipole moment) between a metal electrode and an organic material used in an organic electronic device (e.g. diode or transistor). The dipole of the monolayer can be used to manipulate the energy separation between the metal Fermi level and the electron polaron levels of the organic (ϕ_e). If it is oriented appropriately as in SAM 1, the decrease in the energy barrier, relative to the electron polaron levels, will increase electron injection into the device.

are composed of oligo(phenylene ethynylene)s, lower the barrier for injection of an electron from a metal contact to the organic substrate and therefore tune the Schottky energy barrier between metal and organic surfaces.^[63] We synthesized electron deficient compounds to act as interfaces between the metal contacts and the organic substrates in LEDs by enhancing hole injection from the metal, through the SAM

(the HOMO of the molecules), and into the polymer layer. The Cu/SAM injection of holes at low voltage could also improve the contact. We envisioned electron deficient conjugated phenylene ethynylenes, such as **118**, **120**, **122**, **124**, **127**, and 4'-nitro-1-thiitolane (**136**)^[64] as good candidates which also bear thiol end-groups, after deprotection, for attachment to the Cu surface. Figure 9 illustrates the efficiency of these approaches in a SAM of **136** on Cu that was further coated by the standard MEH-PPV system.

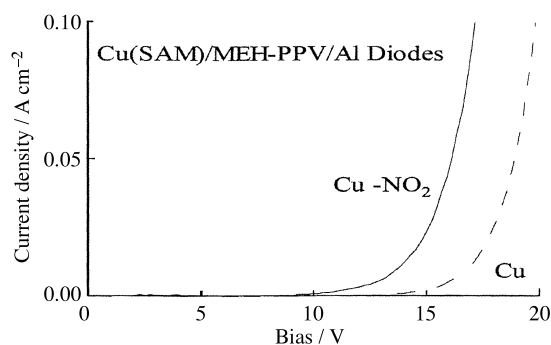


Figure 9. Copper (SAM)/MEH-PPV/Al diodes demonstrating improvement of charge injection from Cu using the NO₂ terminated SAM, **136**. The current in the devices is dominated by hole injection from the Cu contact (the Al electrode is a poor electron injector) so the increased current from the Cu/SAM electrode (compared to the Cu electrode that does not bear a SAM) indicates improved injection from that contact. The MEH-PPV film thickness is 100 nm in both cases.

The Kelvin probe results of Au compared to Au/SAMs of **118**, **122**, **124**, and **136** are shown in Figure 10. Kelvin probe is a standard surface potential measurement technique.^[61] These results show that the SAMs increase the work function and thus make the contact a better hole injector, as expected.

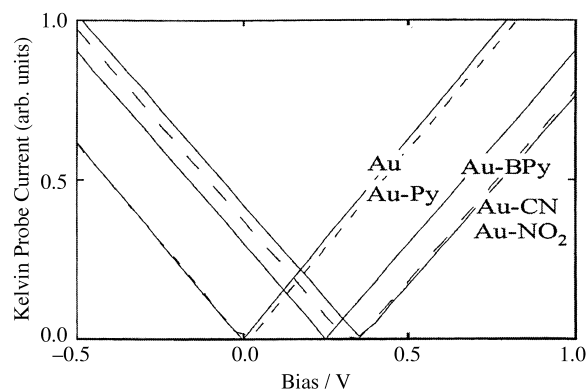


Figure 10. Kelvin Probe current vs. substrate bias for a series of Au/SAM electrodes. The zero point of the current is significant. The shift of the zero current to positive bias indicates an increase in the effective work function of the metal electrode by that voltage, i. e. the effective work function of the Au-CN electrode is about 0.35 eV higher than Au. This increase in the work function leads to improved hole injection. Py = **122**, Bpy = **124**, CN = **118**, and NO₂ = **136**.

To decrease the Schottky barrier for electron injection in a LED, compounds with electron donating moieties and carboxylic groups, **130** and **133** were synthesized for the formation of SAMs to aluminum oxide contact.^[44] These

remain to be tested for their ability to lower the electron injection barrier between the aluminum oxide contact and organic LEDs. Hence these studies on metal/organic/polymer interfaces will also feed information to our molecular electronics program wherein we are seeking methods to lower the metal/organic interface barrier.

Concluding Remarks

In an effort to extend the continued pace of electronic chip capacity and performance, new paradigms of computer architecture are being considered that are based upon molecules acting as discrete wires and devices.^[1–9] We described several synthetic routes to conjugated oligo(phenylene ethynylene)s with and without functionalities such as donor groups, acceptor groups, porphyrin interiors, and heterocycle interiors for various potential wire and digital device applications. Additionally, we discussed the synthesis of functionalized oligomers with a variety of end groups for attachment to numerous metal probes and surfaces. Some of the functionalized molecular systems showed nonlinear current voltage characteristics, such as NDR and molecular DRAM properties. Additionally, the synthesis of functionalized systems were described that can be used in hybrid SAM/polymer systems to reduced Schottky barriers.

Experimental Section

Full details and spectroscopic data for all the new compounds described are given in the Supporting Information.

General: All reactions were performed under an atmosphere of nitrogen unless stated otherwise. Alkyl lithium reagents were obtained from FMC. Pyridine, methyl iodide, triethylamine, and *N,N*-dimethylformamide (DMF) were distilled over calcium hydride, and stored over 4 Å molecular sieves. Toluene and benzene were distilled over CaH₂. Dichloromethane and hexanes were distilled. Ethyl ether and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl. Triethylamine and diisopropylethylamine (Hünig's base) were distilled over CaH₂. MeOH was dried over oven dried 3 Å molecular sieves. Gravity column chromatography, silica gel plugs, and flash chromatography were performed using 230–400 mesh silica gel from EM Science. Thin-layer chromatography was performed by using glass plates precoated with silica gel 60 F₂₅₄ with a layer thickness of 0.25 mm purchased from EM Science. Combustion analyses were obtained from Atlantic Microlab, Inc., P. O. Box 2288, Norcross, GA 30091.

General procedure for the coupling of a terminal alkyne with an aryl halide by using the palladium–copper cross-coupling (Castro–Stephens/Sonogashira Protocol):^[15] To an oven-dried round-bottom flask equipped with a water cooled West condenser and magnetic stir bar or to a screw cap pressure tube with a magnetic stir bar were added the aryl halide, a palladium catalyst such as bis(triphenylphosphine)palladium(II) dichloride (3–5 mol % per halide), and copper(I) iodide (6–10 mol % per halide). Triphenylphosphine was used in some reactions to keep the palladium in solution. The vessel was then sealed with a rubber septum (flask) or capped (tube) under a N₂ atmosphere. A solvent system of THF and/or benzene and/or methylene chloride was added depending on the solubility of the aryl halide. Then base, triethylamine or diisopropylethylamine, was added. Finally, the terminal alkyne (1–1.5 mol % per halide) was added and the reaction was heated until complete. Upon completion of the reaction, the reaction mixture was quenched with water, a saturated solution of NH₄Cl, or brine. The organic layer was diluted with dichloromethane or Et₂O and washed with water, a saturated solution of NH₄Cl, or brine (3 ×). The combined aqueous layers were extracted with dichloromethane or Et₂O (2 ×). The combined organic layers were dried over MgSO₄ and the solvent

removed in vacuo to afford the crude product that was purified by column chromatography (silica gel). Eluents and other slight modifications are described for each material in the Supporting Information.

General procedure for the iodination of triazenes:^[65] To an oven-dried screw cap tube was added the corresponding triazene and iodomethane. The mixture was degassed by slowly bubbling nitrogen for more than 15 min. After flushing with nitrogen, the tube was capped and heated at 120 °C overnight. The reaction mixture was cooled and diluted with hexane. The mixture was passed through a plug of silica gel. After evaporation of the solvent in vacuo, purified product was obtained by chromatography. Eluents and other slight modifications are described for each material in the Supporting Information.

General procedure for the deprotection of trimethylsilyl-protected alkynes (Method A): The silylated alkyne was dissolved in methanol and often a cosolvent, and potassium carbonate was added. The mixture was stirred at room temperature before being poured into water. The solution was extracted with ether or ethyl acetate and washed with brine. After drying over magnesium sulfate, the solvent was evaporated in vacuo to afford the products that generally required no purification. (Method B) The silylated alkyne was dissolved in pyridine in a plastic vessel. A mixed solution of 49% hydrofluoric acid and 1.0M tetrabutylammonium fluoride (TBAF) in THF was added at room temperature. The solution was stirred for 15 min and quenched with silica gel. The mixture was poured into water and extracted with diethyl ether. The extract was washed with brine and dried over magnesium sulfate. After filtration the solvent was evaporated in vacuo. The crude product was purified by a flash chromatography on silica gel. Eluents and other slight modifications are described for each material in the Supporting Information.

General procedure for the conversion of aryl halides to arylthioacetates: To *t*-BuLi (2 equiv per halide) in diethyl ether or THF at –78 °C was added a solution of the aryl halide in THF. After the mixture had been stirred for 40 min, sulfur powder was added as a solid or via cannula as a slurry in THF. The resulting green slurry was stirred for 1 h and then warmed to 0 °C. The mixture was re-cooled to –78 °C and acetyl chloride (1.2 equiv per halide) was added. The resultant yellow solution was allowed to warm to room temperature and stirred for 1 h before quenching with water. The mixture was extracted with diethyl ether (3 ×). The combined organic fractions were washed with water (2 ×) and dried over magnesium sulfate. Removal of solvents in vacuo followed by flash chromatography afforded the desired material. Eluents and other slight modifications are described for each material in the Supporting Information.

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