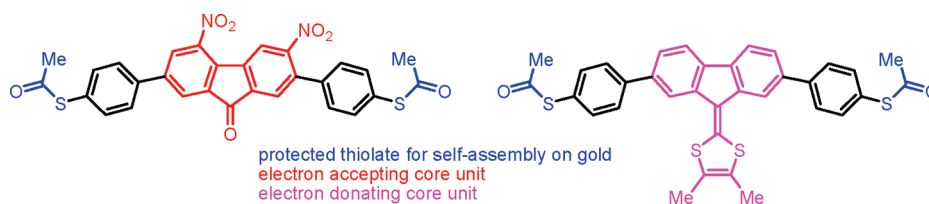# Synthesis and Properties of Functionalized Oligo(arylene) Molecular Wires with Thiolated Termini: Competing Thiol-Au and Nitro-Au Assembly

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protected thiolate for self-assembly on gold
electron accepting core unit
electron donating core unit

We report the synthesis by Suzuki cross-coupling methodology of oligo(arylene) molecular wires with protected thiolates at both termini and a central electron-acceptor unit (3,5-dinitrofluorenone, compounds **10**−**12**) or an electron-donor unit [9-(1,3-dithiol-2-ylidene)fluorene, compounds **14**−**17**] in the backbone. Core reagents are 2,7-dibromo-3,5-dinitrofluorenone **7** (obtained by nitration of 2,7-dibromofluorenone) and 2,7-dibromo-9-(4,5-dimethyl-1,3-dithiol-2-ylidene)fluorene **13**. The solution electrochemical redox properties of these oligo(arylene) derivatives have been studied. The reduction CVs of the dinitrofluorenone-containing molecules display three reversible/quasireversible couples yielding, sequentially, radical anion, dianion, and radical trianion species, e.g., for **11** E^{1red} −1.02 V (vs. Ag/Ag$^+$ in THF). The 1,3-dithiol-2-ylidene unit imparts good electron donor properties to molecules **14**, **15**, and **16** with radical cation formation observed at E^{ox} ca. 0.65 V (vs. Ag/Ag$^+$ in DCM). We also report studies on the assembly of **11** and **15** on gold substrates. Current−voltage (I−V) characteristics and X-ray photoelectron spectra of the monolayers reveal that **11** assembles via competing S−Au and NO$_2$−Au interactions. This unusual phenomenon is ascribed to the very electron deficient dinitrofluorenone core of **11** weakening the S−Au interaction. An important conclusion is that thiolated molecules which possess strongly electron-withdrawing core units, especially those containing nitro groups, may not be suitable for controlled assembly in junctions. In contrast, **15** assembles via conventional S−Au interactions.

The synthesis and electronic behavior of organic conjugated molecules is a rapidly expanding field of study. A long-term aim is to utilize an individual molecule, or small assemblies of molecules, as active components in molecular electronic devices[1]

to overcome the impending miniaturization threshold of silicon devices.[2] Currently, the most promising way to interconnect an organic molecule into electronic circuitry is by thiol−gold bonds.[3] For this purpose the organic molecule is functionalized with terminal thiol groups, or protected thiols which hydrolyze during the assembly protocol to liberate thiol functionalities.[4]

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Alternative terminal groups such as amines[5] and isocyanides[6] are also promising candidates. For electrical characterization of the resulting hybrid nanostructures, scanning probe microscopy (SPM), mechanically controllable break-junction (MCBJ), and electromigration techniques have been developed.[7]

To test the scope and limitations of these contacting techniques and to probe basic structure—property relationships in molecular electronics, there is a requirement for new thiol-terminated organic molecules, e.g., molecules which possess tailored conformations, conjugation lengths, and/or tunable carrier transport properties at nanometer length scales. In this regard, the incorporation of redox-active groups into molecular wires can impart a basic electrical function to the system. However, integrating such molecules, with their added structural complexity, into electrode|molecule|electrode architectures can be experimentally very demanding, especially at the single-molecule level. Nonetheless, for a few systems this has been achieved.[8]

The rationale behind the present work is to study new oligo(arylene)s with thiolated groups at both termini designed to bridge a gap between two gold surfaces and thereby create an electrode|molecule|electrode junction. Redox-active units are incorporated into the backbone. Self-assembled molecules which can be reduced or oxidized are expected to play a key role in molecular electronics. A major goal is to modulate conductance by an electrochemical or chemical process involving the molecules within a molecular junction, thereby providing molecular switches or sensors at the level of single molecules or small ensembles.[8] Oligo(arylene)s are an important family of compounds within the field of molecular electronics. For example, 1,4-benzenedithiol continues to be a benchmark compound for single-molecule devices[9] and recent experimental and theoretical studies have focused on 4,4′-biphenyldithiol and its derivatives.[5,10] Thiol-terminated oligo(thiophenes)[11] and benzene—furan co-oligoaryls with up to nine aryl rings and terminal −C_6H_4-CH_2-S units have been synthesized recently.[12] In this article we describe synthetic protocols for new thiol-terminated oligo(arylene) wires with redox-active building blocks in the backbone. The synthesis of compounds **10−12** and **14−17** and the solution electrochemical properties of **11**, **12**, and **14−16** are presented. The key molecular subunits are the following: (i) for **10−12**, 3,5-dinitrofluorenone, which has enhanced electron-acceptor properties (compared to fluorenone),[13,14] and (ii) for **14−17**, 9-(1,3-dithiol-2-ylidene)fluorene, which has good electron-donor properties.[15] The assembly of **11** and **15** on gold substrates is described. The monolayers are characterized by XPS data and scanning tunneling microscopy (STM) with a gold probe to create Au|molecule|Au junctions.

Results and Discussion

Synthesis. For the synthesis of thiol-terminated oligo(arylenes) we required the boronic acid derivatives **2** and **5**, whose syntheses are shown in Scheme 1. 4-Bromo(*tert*-butylsulfanyl)benzene **1** was converted into the corresponding boronic acid derivative **2** by lithium—halogen exchange, followed by addition of trimethylborate and an aqueous acid workup. Reaction of 2,5-bis(2-ethylhexyloxy)-1,4-dibromobenzene **3**[16] with 1 equiv of **2** under standard Suzuki—Miyaura cross-coupling conditions[17] gave the bromobiphenyl derivative **4** in 85% yield, which was converted to the biphenyl boronic acid derivative **5** in high yield, by analogy with the synthesis of **2**. The alkoxy substituents in **5** were present to ensure good solubility of the subsequent oligo(arylene) products.

Nitro substituents were attached to fluorenone to enhance its electron affinity (Scheme 2).[18] Nitration of 2,7-dibromofluorenone with a mixture of sulfuric acid and fuming nitric

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(18) For a different approach to 2,7-dibromo-4-nitrofluorenone, viz. by nitration of 2,7-dibromofluorene followed by oxidation, see ref 14a. Two-fold Sonogashira cross-coupling of 2,7-dibromo-4-nitrofluorenone with trimethylsilylacetylene was reported.

SCHEME 1. Synthesis of Reagents 2 and 5
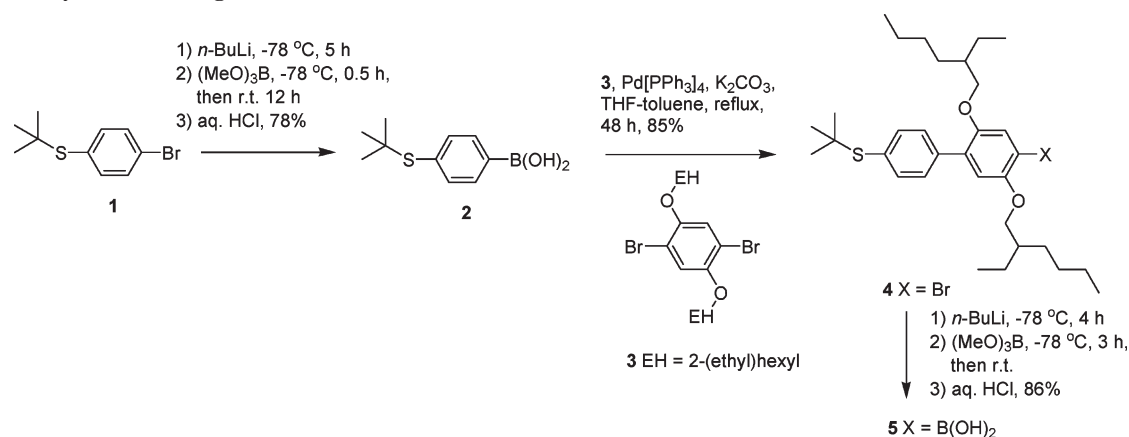
SCHEME 2. Synthesis of 11 and 12
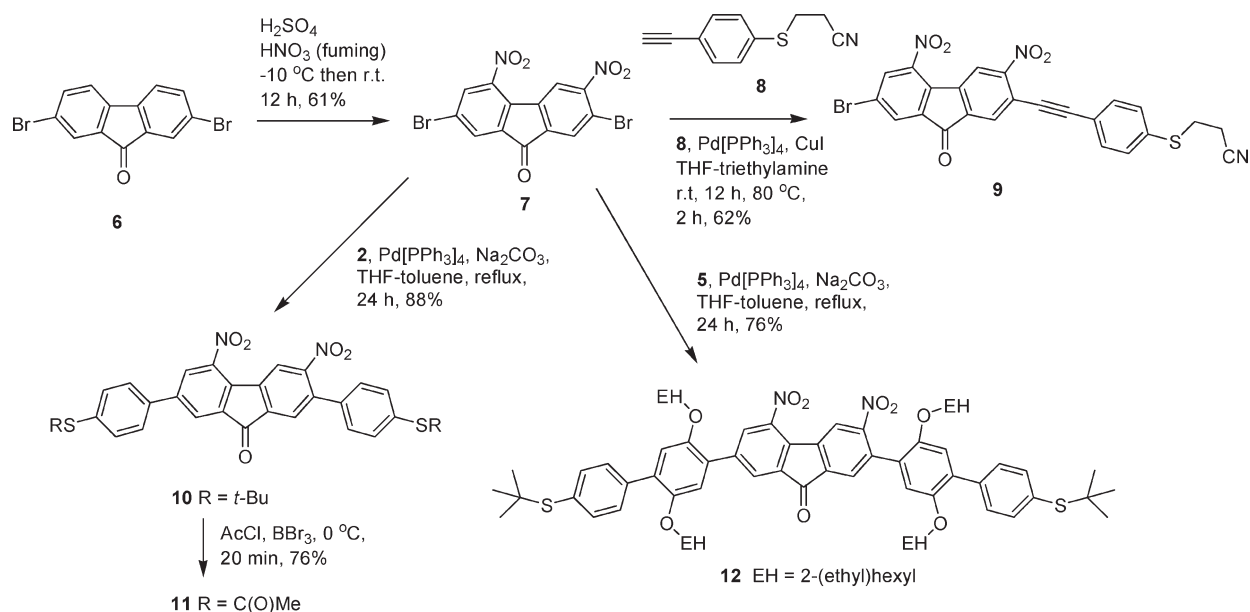
acid gave a dinitro product in 61% yield, which had only limited solubility. Initially its structure could not be assigned unambiguously from NMR data. Reaction of the product with reagent **8**[14b] (2.2 equiv) under Sonogashira conditions[19] gave an interesting result. A monosubstituted derivative was obtained as the major product (62% yield). X-ray crystal analysis revealed structure **9** (see the Supporting Information), which, in turn, established that the 3,5-dinitro isomer **7** had been produced in the nitration of **6**. Nitration at the 3,5-positions is unusual and contrasts with the nitration of 2,7-diX-fluorenone (X = NO₂, CO₂H), which yields initially 2,4,7 (mononitration)- and then 2,4,5,7 (dinitration)-substitution patterns.[13] The formation of compound **7**, in preference to the 4,5-isomer, can be explained as follows. The first nitration occurs at C(4) of compound **6** as with other fluorenone derivatives (i.e., the meta directing effect of the carbonyl group plus the ortho directing effect of the other phenyl ring dominate over the ortho/para directing effect of

bromine). Electronic and steric factors then combine to favor the second nitration ortho to the other bromine atom to give product **7**. Steric hindrance is thereby avoided between the two nitro groups. The increased reactivity of the 2-bromo substituent of **7** (compared to the 7-bromo substituent) is due to an enhanced activating effect of the *o*-nitro substituent at C(3).[20]

In contrast to the Sonogashira reaction, both the 2- and 7-bromo substituents of **7** were readily replaced upon Suzuki−Miyaura reaction with **2** or **5** (2.0−2.1 equivs) to afford the disubstituted oligo(arylene) derivatives **10** and **12**, respectively. The *t*-Bu group is a useful protecting group for thiols because it increases solubility and *t*-Bu-S-Ar species are resistant to both strongly basic and acidic conditions.[21]

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(20) Attempts to replace both the 2- and 7-bromo substituents in **7** by using an increased molar ratio of **8** and triethylamine and/or elevating the reaction temperature led to an inseparable mixture of the 2,7-disubstituted product and the butadiyne derivative obtained by oxidative self-coupling of **8**.

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SCHEME 3. Synthesis of **15** and **17**
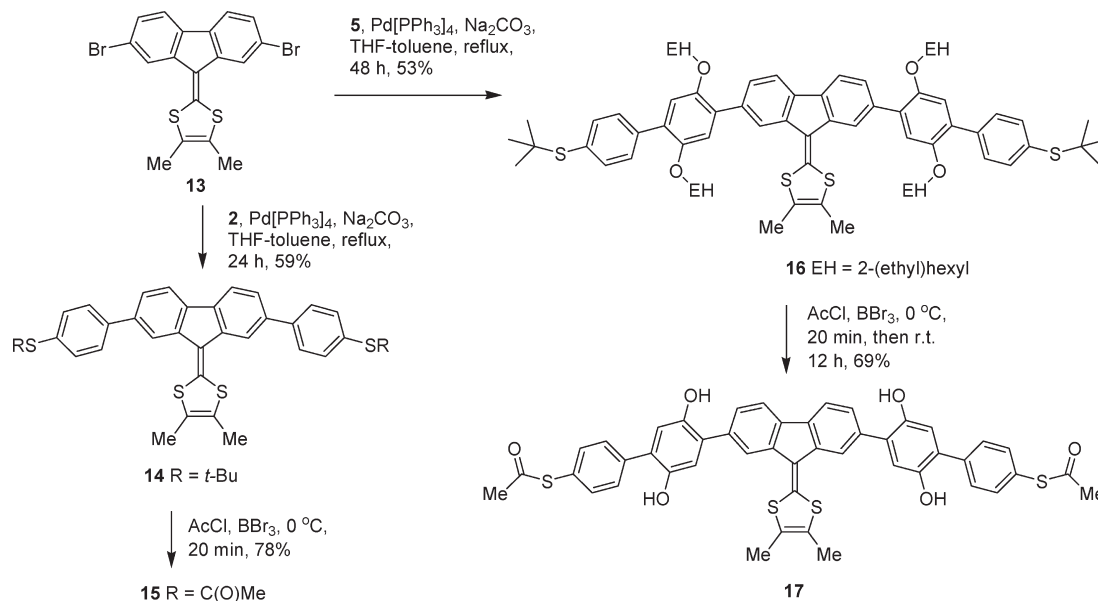
Conversion of the *t*-BuS groups of **10** into the more labile acetylthio groups was achieved by a bromine-catalyzed deprotection protocol.[22] We have found that 2-(ethyl)hexyloxy side chains are cleaved under these conditions (see Scheme 3), so the comparable reaction was not attempted for **12**.

To incorporate an electron donor unit into the backbones, the 9-(1,3-dithiol-2-ylidene)fluorene reagent **13**[15] was treated with compounds **2** and **5**, as above, to give the oligo(arylene)s **14** and **16**, respectively. Compound **14** was cleanly converted into the bis(acetylthio) analogue **15**. The comparable reaction of **16** resulted in concomitant removal of the 2-(ethyl)-hexyl chains to give the bis(acetylthio) derivative **17** (Scheme 3). Nonetheless, compounds **12** and **16** may be useful for molecular electronics applications as *t*-BuS-terminated wires can be physisorbed onto electrodes by a weak van der Waals contact.[23] The X-ray crystal structure of **16** is reported in the Supporting Information.

Solution Electrochemical Properties. Cyclic votammetry (CV) studies have probed the solution redox properties of the oligo(arylene) wire molecules. The reduction CVs of the dinitrofluorenone-containing molecules **11** and **12**, shown in Figure 1, display three reversible/quasireversible couples yielding, sequentially, radical anion, dianion, and radical trianion species (peak potentials are given in Figure 1). The electron-donating dialkoxyphenyl rings in **12** lead to a negative shift (i.e., reduced electron affinity) for all three waves compared with **11**.

The 1,3-dithiol-2-ylidene unit imparts good electron donor properties to molecules **14**, **15**, and **16** with radical cation formation observed at E^{ox} ca. 0.65 V (vs. Ag/Ag+). The CVs are shown in Figure 2. No oxidative features were observed for **12** (scanning to +2.0 V); no reductive features were observed for **16** (scanning to −2.0 V).

Self-Assembly, XPS, and Electrical Characterization. We have investigated self-assembled monolayer (SAM) formation

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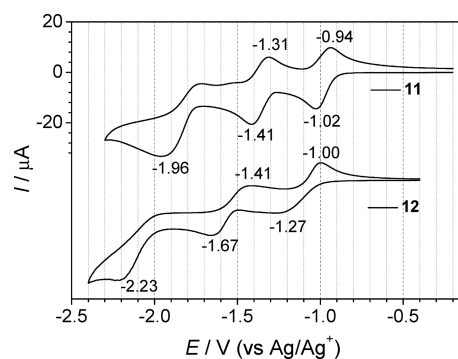

FIGURE 1. Cyclic voltammograms of compounds **11** and **12** in THF solution containing Bu4NPF6 (0.1 M) as supporting electrolyte, scan rate 100 mV s⁻¹. The peak potentials are shown for the redox waves.

of **11** and **15** and performed STM experiments on the resulting structures. Gold-coated substrates were plasma cleaned prior to use and then immersed in dilute THF solutions of the molecules (0.1 mg cm⁻³, 20 cm³) and in solutions to which ammonium hydroxide solution (0.1 cm³) was added to facilitate cleavage of the acetyl groups. They were repeatedly immersed for 20 min intervals and washed with THF to remove physisorbed material. The process was monitored from the frequency change following assembly on the gold electrodes of 10 MHz quartz crystals and the chemisorption was verified by X-ray photoelectron spectroscopy (XPS).

Self-assembly of **15** occurs in the absence of the deprotecting agent and a Sauerbrey analysis[24] of the frequency data yielded a limiting area of 0.72−0.76 nm² molecule⁻¹ after ca. 600 min compared with 200 min when self-assembled in the presence of NH4OH. X-ray photoelectron spectra (XPS) confirm chemisorption and show an S 2p peak at 162 eV characteristic of the Au−S link and another at 164 eV that relates to the 1,3-dithiol-2-ylidene unit and unbound terminal group.

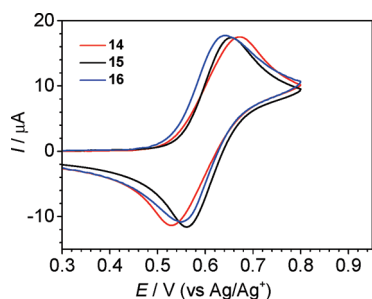(24) Sauerbrey, G. *Z. Phys.* **1959**, *155*, 206–222.

FIGURE 2. Cyclic voltammograms of compounds **14**, **15**, and **16** in dichloromethane solution containing Bu_4NPF_6 (0.1 M) as supporting electrolyte, scan rate 100 mV s^{-1}.

In contrast, **11** exhibits a limiting area of 1.0−1.1 nm^2 molecule^{-1} after ca. 150 min when assembled both with and without the deprotecting agent. The larger area of this less bulky analogue may be explained by an alternative type of packing that involves assembly of some of the molecules of **11** via one, or both, of the nitro substituents. This explanation is consistent with a report that electron-withdrawing substituents on aromatic thiols decrease the rate of conventional adsorption[25] and thereby weaken the interaction between sulfur and gold.[26] XPS data obtained for **11** also suggest that the gold−thiolate link is not necessarily the dominant adsorption in the SAM. The sulfur core-level spectra, fitted with a Gaussian−Lorentzian function, exhibit the characteristic Au−S doublet for an assembled aromatic thiol[27] at 161.9 (S 2p$_{3/2}$) and 163.1 eV (S 2p$_{1/2}$), as well as a second, considerably stronger doublet at 163.4 and 164.6 eV (cf. 163.7 and 164.9 eV for a powdered sample of **11**) that corresponds to the unbound sulfur-containing groups. Quantitative analysis of the areas under the curves suggests that only ca. 40% of molecules assemble via an Au−S link (thus, ca. 60% via NO$_2$) in the absence of a deprotecting agent (Figure 3). The relative areas for SAMs formed under basic conditions suggest that 40−65% of molecules assemble via Au−S links with the remainder attached via their nitro substituents (Figure 4).[28]

SAMs of **11** formed in the presence and absence of the deprotecting agent exhibit similar N 1s core-level spectra (Figure 5). A single peak at 405.6 eV is characteristic of the NO$_2$ groups and the ratio of areas under the N 1s and S 2p peaks, when corrected for atomic sensitivity factors, is ca. 1:1 and consistent with the molecular formula. The XPS data provide no evidence of the chemical instability reported by Stapleton et al.[29] These authors reported that nitro-substituted oligo(phenyleneethynylene) thiolate molecules assembled in the presence of NH$_4$OH reveal the expected NO$_2$ peak at 405.6 eV as well as others at 402.1 and 399.3 eV

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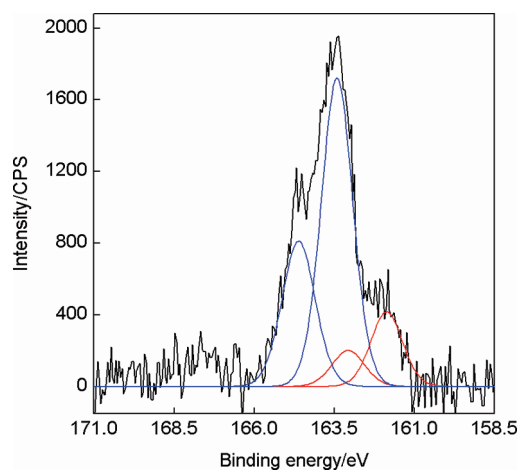
FIGURE 3. S 2p$_{3/2}$ and S 2p$_{1/2}$ spectra of a SAM of **11** prepared without the deprotecting agent where the red doublet corresponds to the Au−S link and the blue doublet to S−C(O)CH$_3$. The area ratio, corrected for atomic sensitivity factors, is ca. 1:4, whereas if self-assembled only via Au−S, this ratio should be 1:1.
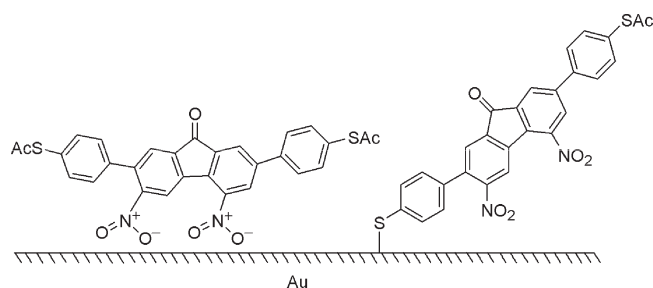

FIGURE 4. Diagrammatic representation of the assembly of **11** on a gold substrate showing competing nitro and thiol group attachment.

which were assigned to NH(OH) and NH$_2$ arising from thiolate−nitro redox processes. We observed a broadened N 1s peak in the same range but only from some monolayer samples. Moreover, its occurrence each time coincided with a higher than expected N:S ratio (as high as 2:1) whereas the ratio calculated with the area of the NO$_2$ peak at 405.6 eV was 1:1. Thus, from this study, we attribute the anomalous lower energy peak, when observed (see the Supporting Information, Figure S3), to a contaminant derived from NH$_4$OH and note that its range is consistent with the binding energies of NH$_3$ (399 eV)[30] and NH$_4^+$ (399−402 eV).[31−33]

Current−voltage ($I−V$) curves of self-assembled monolayers (SAMs) formed from **11** and **15** on gold-coated highly oriented pyrolytic graphite were obtained by scanning tunneling spectroscopy. The gold probe was landed at several locations across each of the SAMs: $I−V$ data were recorded for different set-point currents and voltages and averaged each time for ten scans at each of the sites. Typical $I−V$

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(31) Grunert, W.; Feldhaus, R.; Anders, K.; Shpiro, E. S.; Antoshin, G. V.; Minachev, K. M. *J. Electron Spectrosc. Relat. Phenom.* **1986**, *40*, 187−192.
(32) Swartz, W. E.; Alfonso, R. A. *J. Electron Spectrosc. Relat. Phenom.* **1974**, *4*, 351−354.
(33) Escard, J.; Mavel, G.; Guerchais, J. E.; Kergoat, R. *Inorg. Chem.* **1974**, *13*, 695−701.
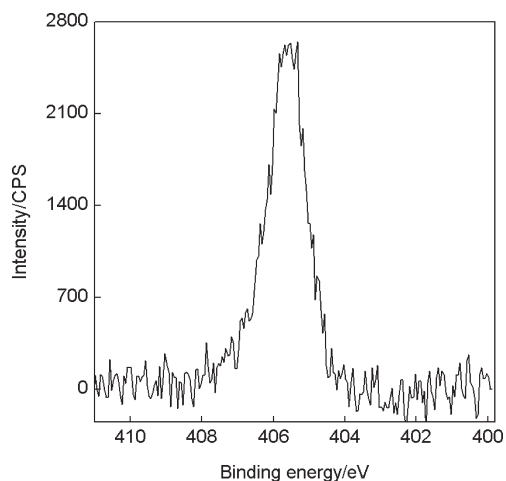
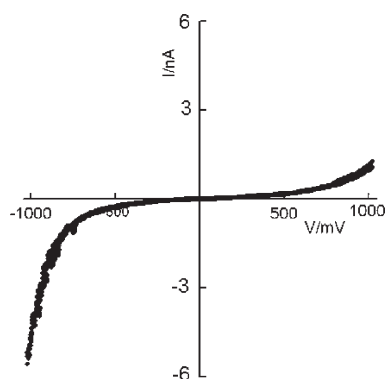**FIGURE 5.** N 1s spectrum of a SAM of **11** where the peak at 405.6 eV is characteristic of NO_2.

FIGURE 6. $I-V$ characteristics of SAMs of **11** formed under basic conditions on gold contacted by a gold probe. The data were obtained by averaging 10 scans on the same site for a set point current of 200 pA and bias of +0.2 V where the polarity is defined by the sign of the substrate electrode.

characteristics are shown in Figures 6 (**11**) and 7 (**15**) and, for the most part, their profiles are unaffected by the set point conditions and the method of assembly (i.e., with or without the deprotecting reagent). Both systems exhibit slight electrical asymmetry. This is more pronounced for **11** where the higher negative-quadrant current corresponds to electron flow from the gold substrate (cathode) to gold probe (anode) and this behavior can be explained by some of the molecules being aligned parallel to the substrate and the electron-accepting nitro groups of the central core being adsorbed to gold. The considerably weaker asymmetry exhibited by **15** with the same preferred direction of electron flow can be explained by an upright alignment with all molecules assembled via Au−S links and with the electron-donating 1,3-dithiol-2-ylidene unit in this case being tilted toward the gold probe. We further note that an analogue without the redox-active dithiole unit (namely, a 9,9-dimethylfluorene core)[10e] exhibits symmetrical $I-V$ characteristics.

These data establish that **11** forms a disordered assembly on gold, which means the compound is unlikely to find an application in molecular electronics. However, **15** forms an ordered monolayer and functions as a molecular wire in an electrode|molecule|electrode junction.
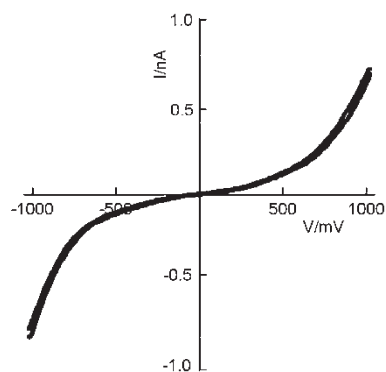

FIGURE 7. $I-V$ characteristics of SAMs of **15** formed under basic conditions on gold contacted by a gold probe. The data were obtained by averaging 10 scans on the same site for a set point current of 200 pA and bias of +0.2 V where the polarity is defined by the sign of the substrate electrode.

Conclusions

New oligo(arylene) molecular wires endowed with functional groups at their cores and thiolated anchor groups at both terminal positions have been obtained via efficient synthetic transformations. 4-(*tert*-Butylsulfanyl)phenylboronic acid **2**, 2,7-dibromo-3,5-dinitrofluorenone **7**, and 2,7-dibromo-9-(1,3-dithiol-2-ylidene)fluorene **13** serve as key reagents in these procedures. The solution redox properties of the oligo-(arylene)s have been studied by cyclic voltammetry, which reveals reduction waves for the dinitrofluorenone compounds **11** and **12**, and oxidation processes for the 9-(1,3-dithiol-2-ylidene)fluorene derivatives **15** and **16**. Compounds **11** and **15** form self-assembled monolayers on gold substrates and their current−voltage ($I-V$) characteristics have been probed by a gold STM tip. Electrical studies and XPS data reveal very different modes of assembly of **11** and **15**. Evidence has been presented that **11** forms a disordered monolayer due to assembly via competing S−Au and NO_2−Au interactions as a consequence of the very electron deficient dinitrofluorenone core, which is in conjugation with the thiolate group, thereby weakening the S−Au interaction. This is consistent with previous evidence that electron-withdrawing substituents decrease the rate of conventional S−Au adsorption.[25] In contrast, **15** assembles via conventional S−Au interactions. One of the goals of molecular electronics is to understand the factors that govern the assembly of specifically functionalized molecules. The work described in this paper is informative in probing functional group compatibility in electroactive molecular wires and molecular electronic circuitry. An important conclusion is that thiolated molecules which possess strongly electron-withdrawing core units, especially those containing nitro groups in conjugation with the thiolate group, may not be suitable for controlled assembly in junctions.

Experimental Section

4-(*tert*-Butylsulfanyl)phenylboronic Acid (2). A solution of 4-*tert*-(butylsulfanyl)bromobenzene (12.26 g, 50 mmol) in THF (200 mL) was cooled to −78 °C and *n*-BuLi (2.5 M in hexane, 25 mL, 62.5 mmol) was added. The solution was stirred for 5 h at −78 °C and then trimethylborate (20 mL, excess) was added slowly. The mixture was stirred for 30 min at −78 °C and then slowly warmed to room temperature and stirred for 12 h at room temperature. The mixture was concentrated in vacuo and the

residue was dissolved in dichloromethane (50 mL) and stirred with HCl (5% aq, 200 mL) for 2 h. The organic phase was separated and the aqueous phase was extracted with dichloromethane. The combined organic phases were dried over MgSO$_4$. The solvent was removed under reduced pressure. The residue was triturated with hexane (30 mL) and the solid product was filtered, washed with hexane, and dried to give **2** as a white powder (8.26 g, 78% yield): mp 172−174 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.15 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.0 Hz, 2H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 138.7, 136.7, 135.7, 46.9, 31.3. Anal. Calcd for C$_{10}$H$_{15}$BO$_2$S: C, 57.17; H, 7.20. Found: C, 57.28; H, 7.16.

2,7-Dibromo-3,5-dinitro-9-fluorenone (7). 2,7-Dibromo-9-fluorenone **6**[34] (10.14 g, 30 mmol) was dissolved in sulfuric acid (200 mL) at room temperature with stirring and sonication. The viscous solution was cooled to −10 °C followed by the dropwise addition of fuming nitric acid (100%, 150 mL) with cooling and stirring. During the addition, the temperature was maintained between −15 and −10 °C to afford a yellow viscous suspension. The cooling bath was removed and the mixture was stirred for 12 h at room temperature then poured onto crushed ice (∼500 g). A yellow solid was obtained by suction filtration and washed with a large volume of water. Crystallization of the solid from DMF yielded **7** as yellow crystals (7.78 g, 61% yield): ^{1}H NMR (200 MHz, DMSO-d_6) δ 8.47 (d, J = 1.8 Hz, 1H), 8.30 (s, 1H), 8.21 (d, J = 1.8 Hz, 1H), 8.18 (s, 1H); ^{13}C NMR (100 Hz, DMSO-d_6) δ 186.7, 153.3, 144.7, 139.3, 136.8, 136.4, 133.0, 131.6, 131.4, 129.9, 123.9, 122.2, 116.3; MS (EI) (m/z, %) 427.7 (M[+], 86), 149 (100).

Compound 10. To a mixture of compound **7** (428 mg, 1.0 mmol), **2** (441 mg, 2.1 mmol), THF (30 mL), toluene (30 mL), and aqueous sodium carbonate (1 M, 3.0 mL, 3 mmol) was added Pd(PPh$_3$)$_4$ (46 mg, 0.04 mmol) in one portion, then the mixture was heated at reflux for 24 h. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane (40 mL) and washed with water (40 mL). The red organic phase was separated and dried over MgSO$_4$. The solvent was removed and the residue was purified by column chromatography (SiO$_2$, eluent DCM) to give **10** as a yellow powder (525 mg, 88% yield): mp 241−242 °C dec;

ES-MS 598.3 (M[+]); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.53 (s, 1H), 8.45 (d, J = 2.0 Hz, 1H), 8.26 (d, J = 2.0 Hz, 1H), 7.88 (s, 1H), 7.68 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 1.34 (s, 9H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 189.0, 153.5, 145.0, 144.1, 140.0, 138.2, 138.0, 137.8, 137.1, 136.8, 136.3, 135.7, 135.3, 134.8, 133.7, 128.7, 127.6, 127.5, 127.1, 126.8, 122.0, 46.7, 46.6, 31.1, 30.9. Anal. Calcd for C$_{33}$H$_{30}$N$_2$O$_5$S$_2$: C, 66.20; H, 5.05; N, 4.68. Found: C, 66.18; H, 5.10; N, 4.56.

Compound 11. A suspension of **10** (120 mg, 0.20 mmol), dichloromethane (15 mL), and acetyl chloride (4 mL) was cooled to 0 °C and then BBr$_3$ (1.8 mL, 1.8 mmol) solution in dichloromethane (10 mL) was added in one portion. The resulting clear orange solution was stirred for 20 min at 0 °C then poured into ice. The organic layer was separated, dried over MgSO$_4$, and concentrated, then the residue was chromatographed (silica, eluent DCM) to give **11** as a yellow powder (87 mg, 76% yield): mp 205−206 °C; ES-MS: 570.1 (M[+]); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.56 (s, 1H), 8.45 (d, J = 1.2 Hz, 1H), 8.26 (d, J = 1.6 Hz, 1H), 7.90 (s, 1H), 7.73 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 2.48 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 193.1, 193.0, 188.8, 153.4, 145.0, 143.8, 140.1, 137.7, 137.4, 137.1, 136.39, 136.36, 135.2, 134.8, 133.8, 130.1, 129.8, 128.8, 128.4, 128.3, 128.0, 127.54, 127.49, 127.1, 122.0, 30.38, 30.35. Anal. Calcd for C$_{29}$H$_{18}$N$_2$O$_7$S$_2$: C, 61.04; H, 3.18; N, 4.91. Found: C, 61.12; H, 3.13; N, 4.87.

Supporting Information Available: Additional experimental details, including synthesis, characterization, electrical data, X-ray crystal structures of **9** and **16**, and copies of NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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