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Nanoscale Aryleneethynylene Molecular Wires with Reversible Fluorenone Electrochemistry for Self-Assembly onto Metal Surfaces

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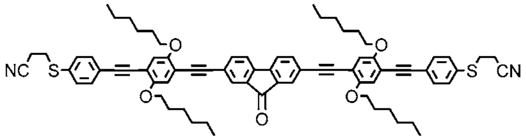
ABSTRACT



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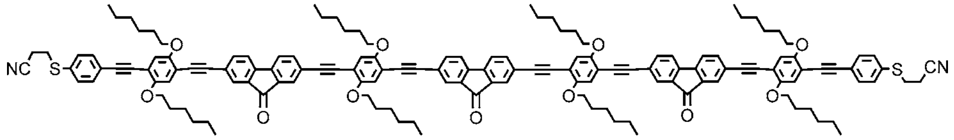

12

Two rigid-rod conjugated molecules (11 and 12) of ca. 4 and 7 nm length, respectively, bearing protected terminal thiol groups have been synthesized via multistep Sonogashira coupling reactions and shown to possess reversible cathodic solution electrochemistry arising from reduction of the fluorenone units.

Single molecular (SM) electronics is attracting great attention due to the potential applications in future computing technology and related fields.[1] The current molecular device fabrication technique is de facto the preparation of metal−molecule−metal junctions between macroscopic electrodes and an individual organic molecule or a monolayer array of molecules. Reliable molecular junctions require a bespoke gap distance between the electrodes that is close to the length of an active molecule. Due to the intrinsic roughness of noble metal electrode surfaces, fabrication of devices with use of small molecules[2] has proved difficult and low yielding. Scanning probe,[3] break-junction,[4] and electromigration[5] methodologies are more reliable in terms of testing molecular junctions. However, they are less likely to be industrialized for large-scale production. Many issues still need to be addressed as it becomes apparent that the behavior of electrically active molecules in experimental devices is critically dependent upon their immediate environment, e.g.

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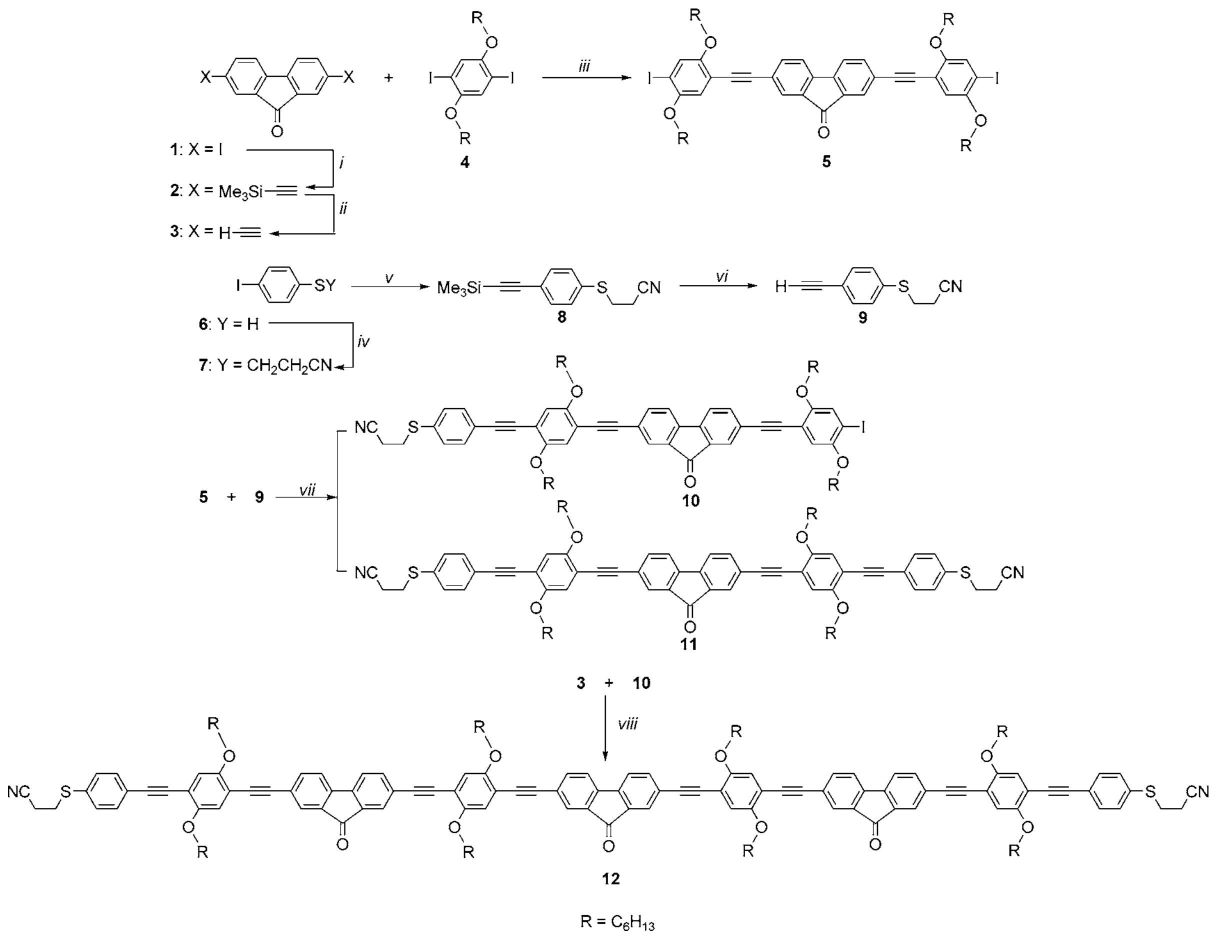
Scheme 1 *a*



a Reagents and conditions: (i) (trimethylsilylacetylene) (TMSA) (4 equiv.), THF, Pd[PPh$_3$]$_2$Cl$_2$ (3%), CuI, TEA, rt, 2 h, then 50 °C, 2 h, 98%; (ii) 1:1 (v/v) DCM−methanol, K$_2$CO$_3$, rt, 12 h, 76%; (iii) **3** and **4** (5 equiv), THF, Pd[PPh$_3$]$_2$Cl$_2$ (3%), CuI, TEA, rt, 12 h, then 50 °C, 2 h, 43%; (iv) **6**, 3-bromopropionitrile, dry DMF, K$_2$CO$_3$, 100 °C, 24 h, 93%; (v) **7**, TMSA (1.5 equiv), THF, Pd[PPh$_3$]$_2$Cl$_2$ (3%), CuI, TEA, rt, 3 h, 88%; (vi) HOAc, Ac$_2$O, TBAF, rt, 0.5 h, 76%; (vii) **5**, **9**, THF, Pd[PPh$_3$]$_2$Cl$_2$, CuI, TEA, rt, 12 h, 50 °C, 2 h, 44% (for **10**) and 29% (for **11**); (viii) **3**, **10**, THF, Pd[PPh$_3$]$_4$, CuI, TEA, rt, 0.5 h, then 50 °C, 3 h, 54%.

electrodes or other organic molecules. Earlier results on conductivity changes and switching behavior are being reappraised.[1f] Nevertheless, synthesizing functional molecules with lengths of at least several nanometers, which will self-assemble on metal electrodes, will no doubt permit easier and more reliable fabrication (due to the larger gaps required) and be of fundamental importance.

Monodisperse, π-conjugated oligomers based on rodlike aryleneethynylene backbones are of considerable current interest as optoelectronic materials and as model compounds for related polymers.[6] The arylene units in aryleneethynylene structures include 2,5-dialkyl-*p*-phenylene,[7] 2,5-dialkoxy-*p*-phenylene,[8] 2,6-diphenyl-*p*-phenylene,[9] 1,5-naphthalene,[10] and 9,9-dihexylfluorene.[11] Herein we report the first such extended systems containing fluorenone units.[12] The special features of these new oligomers **11** and **12** are their reversible solution electrochemistry and the presence of terminal protected thiol groups. These molecular wires **11** and **12** are designed for SM device fabrication.

The synthesis (Scheme 1) comprises an iterative Pd-mediated Sonogashira strategy. The high degree of purity of compounds **11** and **12** has been established by CHN analysis, ^{1}H and ^{13}C NMR, and MALDI-TOF mass spectrometry (see Supporting Information). The molecules incorporate 2-cyanoethyl as the terminal thiol protecting group. This protecting group is known for tetrathiafulvalene thiolates but the original deprotection conditions[13] are not suitable for

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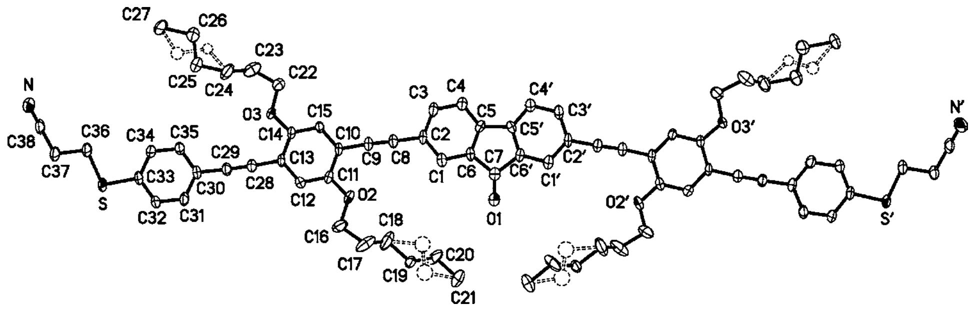

Figure 1. Molecular structure of **11** determined by X-ray diffraction.

self-assembly. However, cyanoethyl-protected thiophenol derivatives (such as **12**) can be easily deprotected under much milder conditions by either sodium methoxide or tetrabutylammonium fluoride (TBAF) in THF solutions at room temperature.[14] A disadvantage of using an acetyl protecting group for thiophenol derivatives is that it is too easily removed, resulting in side reactions and difficult product purification. The increased stability of the 2-cyanoethyl group is advantageous for our Sonogashira reactions, enabling the use of higher temperatures, longer reaction times, and an increased amount of amines. In addition, the stability of the final products is increased compared to that of acetyl analogues.[15] Starting from 4-iodothiophenol,[15] the new terminal phenylethynyl building block **9** bearing a protected thiolate group was prepared in multigram quantities. This compound provides an ideal substitute for 4-acetylthiophenylacetylene developed by Tour and co-workers[12,16] and the (*N*,*N*-dimethylcarbamoyl)thio analogue synthesized by Müllen and co-workers.[7] THF solutions of **11** and **12** were stored at room temperature for a week without detectable decomposition.

The crystal structures of **5** and **11** have been determined by X-ray diffraction.[18] Molecule **11** (Figure 1) has crystallographic C_2 symmetry and an almost planar conformation, with the average deviation of all non-H atoms of ca. 0.2 Å and all ring planes parallel within 13°. The intramolecular S···S′ distance of 37.4 Å in **11** was in good agreement with the MM^+ calculated value of 36 Å.[17] Considering the additional Au···S bonds in a Au···**11**···Au junction, a gap of ca. 4 nm will be required for fabrication. Similarly, the S···S′ distance in **12** was predicted to be 69 Å,[17] which allows an electrode gap of ca. 7 nm.

Reversible cathodic solution electrochemistry was brought about by reduction of the fluorene group(s) in **11** and **12** (Figure 2). As the irreversibility of a redox process means either decomposition or subsequent chemical reactions of the molecules under bias, it is likely that a molecular junction could be more easily broken when a charge is injected into an irreversible molecule, hence leading to failure of the device, compared with those derived from reversible molecules. We note that at least two functioning SM transistors[5a,b] were fabricated by using electrochemically reversible mol-

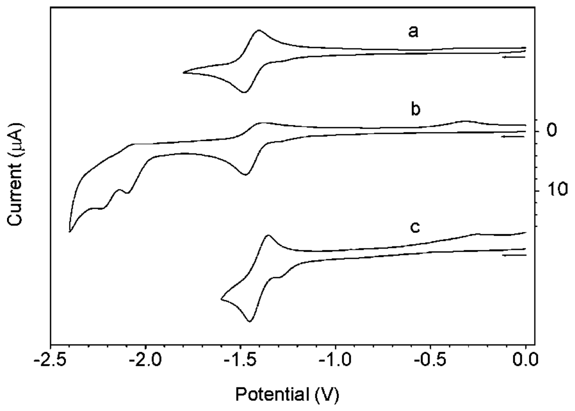

Figure 2. Cyclic voltamograms of **11** (a and b) and **12** (c). Traces a and b were recorded in dry DMF, and trace c in dry THF. Supporting electrolyte: 0.1 M $TBAPF_6$. Electrodes: working, Pt disk (Φ = 1.8 mm); counter, Pt wire; reference, $Ag/AgNO_3$–acetonitrile. Scan rate: (a, b) 100 mV/s; (c) 500 mV/s.

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(14) Typical deprotection conditions are as follows: to methyl 4-[2-cyanoethyl)thio]benzoate (0.221 g, 1 mmol) (see Supporting Information for its preparation) in THF (40 mL) was added sodium methoxide–methanol solution (0.5 M, 2.1 mL, 1.05 mmol) at 20 °C and the mixture was stirred for 15 min. Iodomethane (0.2 mL, 3.2 mmol) was syringed in followed by an additional 1 h of stirring, yielding methyl 4-methylthiobenzoate in 91% yield after column chromatographic purification (silica, chloroform). For the same reactions with tetrabutylammonium fluoride (1.0 M THF solution, 1.1 mmol) as deprotecting reagent, 2 h of stirring yielded methyl 4-methylthiobenzoate in 80% isolated yield.

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(18) Crystal data: $C_{53}H_{62}I_2O_5$ (**5**), $M = 1032.83$, triclinic, space group $P\bar{1}$ (no. 2), $T = 120$ K, $a = 9.986(1)$ Å, $b = 15.134(3)$ Å, $c = 17.310(4)$ Å, $\alpha = 102.56(3)°$, $\beta = 94.34(2)°$, $\gamma = 107.62(2)°$, $U = 2405.4(8)$ Å^3, $Z = 2$, systematic twinning, $R = 0.065$ on 13154 unique data with $I > 2\sigma(I)$; CCDC-231672. $C_{75}H_{78}N_2O_5S_2$ **(11)** $M = 1151.51$, monoclinic, space group $C2/c$ (no. 15), $T = 120$ K, $a = 8.541(1)$ Å, $b = 21.607(5)$ Å, $c = 34.169(8)$ Å, $\beta = 95.17(2)°$, $U = 6280(2)$ Å^3, $Z = 4$, $R = 0.056$ on 2930 unique data with $I > 2\sigma(I)$; CCDC-231673.

ecules. As shown in Figure 2a, when the cathodic scan was limited to −1.8 V, **11** had one reversible redox wave at $E_{1/2} = -1.44$ V, which was due to the reduction of the fluorenone unit. The compound also showed two irreversible waves at $E_{red} = -2.10$ and −2.23 V, associated with the reduction of the triple bonds. However, the current intensity on the reverse anodic scan at −1.4 V (Figure 2b) was reduced, indicating that at such negative potentials an electrochemical reaction changed the molecular structure. In THF (it is poorly soluble in DMF), **12** also showed a reversible wave at −1.40 V. However, its acetylenic reductions could not be observed with certainty in this solvent.

In summary, we have synthesized a new series of soluble fluorenone-based molecular wires suitable for single molecular device fabrication. The methodology provides efficient access to versatile aryleneethynylene derivatives which should serve as valuable building blocks for the construction of other functional molecular wires of precise conjugation lengths.

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Supporting Information Available: Characterization data for **12** including copies of the ^{1}H NMR, MALDI-TOF mass spectra, and HPLC trace; molecular structure of **5** and packing diagram for **11**; preparation of methyl 4-[2-cyanoethyl)thio]benzoate; cyclic voltamograms of fluorenone and two model 2,7-diethynylfluoren-9-one derivatives. This material is available free of charge via the Internet at http://pubs.acs.org.

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