

An 11 nm Molecular Wire that Switches Electrochemically between an Insulating and a Fully Conjugated Conducting State

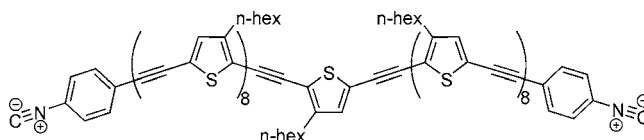
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ABSTRACT



Molecular wires consisting of oligothiophenes and oligothiophenylethyne, ranging in length from 2 to 11 nm, are synthesized and examined by spectroscopy and electrochemistry. UV spectroscopy shows that the longest wires are not fully conjugated, but twisted. However, cyclic voltammetry indicates that their monocations are now flattened and conjugated over the entire length range. In appropriate systems, the wires will link to two electrodes across a nanoscale gap and conduct current.

For the construction of a molecular field effect transistor (FET), it is important to have molecular wires that can switch between an insulating and a conducting state. In pursuit of this goal, we have examined a family of oligothiophenes (OT) **1a–d** and seen that, when terminated with an isocyanide group, such molecules could bind to a platinum surface (Figure 1).¹ This is a more desirable linkage between an organic wire and a metal contact than the often-used thiol–gold bond² since high-melting platinum is less easily distorted than gold and the isocyanide group is not as oxidizable as the thiol group.³ The relatively small shifts in spectroscopic and electrochemical data in the OT series **1a–d** with increasing molecular length (Table 1) suggested that there could be sterically induced twisting of the direct thiophene-to-thiophene linkage.

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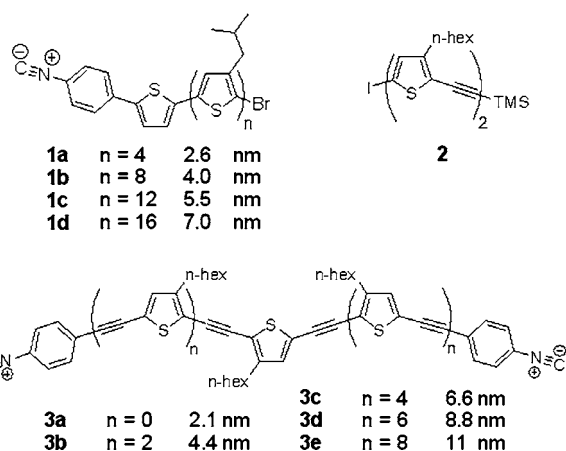


Figure 1. Structures of OT monoisocyanide **1a–d** and OTE diisocyanides **3a–e**, along with their respective calculated end-to-end lengths, and bithiophenyl–ethynylene building unit **2**.

We have now examined a series of oligomeric thiophenyl–ethynylenes (OTE) **3a–e** terminated with isocyanide

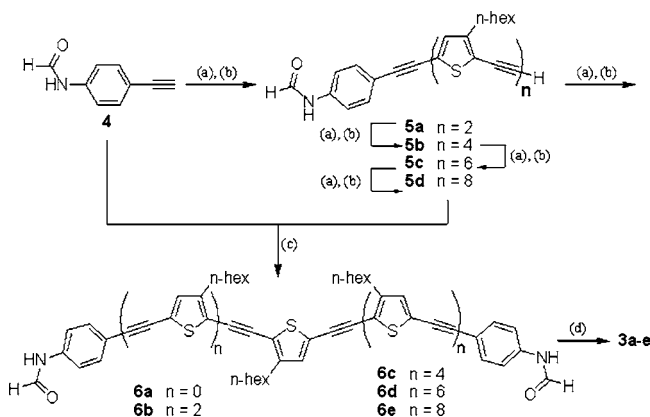
Table 1. Absorption and Emission Maxima and First and Observed (see text) Second Oxidation Potentials of **1a–d** and **6a–e** in Solution^a

	UV-vis (nm)	Fl (nm)	E_{pa} (mV)	E_{pa} (mV)
	λ_{max}	λ_{max}	(soln) ^b	(soln) ^c
1a ¹	409	542	450	380
1b ¹	419	551	420	340
1c ¹	423	555	410	290
1d ¹	430	555	400	265
6a	364	536	810	830 ^d
6b	425	539	665	655, 790
6c	431	542	605	625, 880
6d	442	544	590	525, 840
6e	444	544	530	470, 745

^a UV and Fl maxima were acquired in CH₂Cl₂. ^b CV was measured at a scan rate of 100 mV·s⁻¹ in CH₂Cl₂ with 0.1 M Bu₄NPF₆ using a Pt working electrode and referenced to the F₄/F₄⁺ couple. ^c CV was measured at a scan rate of 100 mV·s⁻¹ in CH₂Cl₂ with 0.1 M Bu₄N[B(C₆F₅)₄] using a Pt working electrode and referenced to the F₄/F₄⁺ couple. ^d Irreversible oxidation. For details, see Supporting Information.

groups (Figure 1) and synthesized, via intermediates **4** and **5**, their precursor formamides **6a–e** (Scheme 1). Because

Scheme 1^a



^a Reagents and conditions: (a) **2**, Pd(PPh₃)₂Cl₂, DIEA, THF; (b) K₂CO₃, CH₂Cl₂/MeOH; (c) 3 equiv of **4** or **5a–d**, Pd(PPh₃)₂Cl₂, 2,5-diiodo-3-hexylthiophene, DIEA, THF; (d) triphosgene, CH₂Cl₂.

of their greater chemical stability, we have done our extensive studies on the bis-amide series **6** rather than the isonitriles **3**, and we list the results for **1** in Table 1.

The ethynyl units diminish the steric crowding that can lead to twisting in the OT series **1**.⁴ Even so, our studies reveal that the longest of these molecules are twisted, so they are not fully conjugated in their neutral states. However, they become fully conjugated when electrochemically oxidized

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to cations. Most interestingly, the result is an electrochemical ECE process, in which removal of the first electron from the long wires induces a geometric change to full conjugation that permits the second electron to be removed at the same potential, overcoming the normal Coulombic repulsion in a polycation. Thus the OTEs **3**, including the longest molecule **3e**, will apparently have the desired on/off switching properties that can be induced by a potential gap between source and drain and perhaps modulated by the potential of the gate in an FET.

Initial Sonagashira coupling of alkyne **4** to iodide **2** was followed by iterative deprotection and coupling cycles to yield a series of monoformamides **5a–d** (Scheme 1).⁵ Subsequent dicoupling to 2,5-diiodo-3-hexylthiophene gave diformamide intermediates **6a–e**, which were readily dehydrated to the diisocyanide products **3a–e**.⁶ The β -functionality on each thiophene ring was changed from isobutyl in the OT series to *n*-hexyl in the OTE series to confer better solubility for the long oligomers in organic solvents.⁷

Even with the addition of the acetylene spacers, OTEs **6a–e** showed less than full conjugation in the longer wires (Table 1). While the UV maxima exhibit a continuous red-shift up to 16 subunits (7 nm) in the OT series **1**, the UV red-shift becomes saturated between 13 and 17 subunits (8.8–11 nm) in the OTE series **6** (comparable to literature values).^{4a,5a,8} Perhaps there is a less effective electronic conjugation between thiophenes and triple bonds that counteracts any π -conjugation improvement gained from the decrease in steric interaction in **6a–e**.^{4b,c,9}

One interesting finding is that the emission spectra in both the OT and OTE series are almost independent of the lengths of the wires. It is striking that lengthening the conjugated systems moves the absorption maxima, at least until the molecules are very long, but that this extra conjugation is not reflected in the fluorescence maxima.

In contrast to the UV data for the neutral molecules, cyclic voltammetry (CV) results indicate that OTEs **6a–e** are better able to extend the conjugation upon oxidation to the first and higher cationic states. As the OTEs become longer, they are oxidized more readily, as evident by the observed steady decrease in the first oxidation potentials (E_{pa}) in both solutions with **6a–e** (Table 1) and as a self-assembled monolayer (SAM) of **3a–e** (1040, 610, 565, 540, and 520 mV, respectively). The relative positions of the first E_{pa} of OTEs **6a–e** are higher than OTs **1a–d**, implying that the acetylene spacers are slightly insulating electronically be-

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tween the thiophene subunits. In-depth inspection of further oxidation processes involving the removal of additional electrons required the use of $\text{Bu}_4\text{N}[\text{B}(\text{C}_6\text{F}_5)_4]$, owing to its enhanced ability to solubilize positively charged oligomers produced during anodic reactions in CH_2Cl_2 .¹⁰

A striking finding concerns the second oxidation wave observed in the **6a–e** series. The ΔE_p (>60 mV) of the first oxidation potential indicates only quasi-reversible behavior—hence, the number of electrons transferred in each process is not securely deducible. However, the position of the second E_{pa} of **6c** is *more positive* than that of the shorter oligomer **6b**, even though the shift of the first oxidation wave indicates that **6c** is more easily oxidized at its first wave than **6b**, as expected. Indeed, the second oxidation wave for **6c** comes between the second and third wave for the oxidation of **6b**.

The only reasonable interpretation of this is that the second oxidation wave of **6b** involves its conversion to a dication—the normal process—but the second wave for **6c** corresponds to its conversion from a dication to a trication. That is, the first oxidation wave for **6c** involves an ECE process: (1) the first electron is removed; (2) the molecule then flattens to induce better conjugation and delocalize the first positive charge; and (3) the increased conjugation then permits a second electron to be abstracted at the same potential, producing a delocalized dication. This better delocalization overcomes the Coulombic repulsion of the two charges, and the same process must occur with all the longer wires. However, in the short **6b**, Coulombic repulsion wins, and the second electron is abstracted only at a higher potential than the first.

The ability to form a self-assembled monolayer (SAM) via chemisorption on the Pt working electrode confirms the binding of the isocyanide group to Pt. SAM coverage was determined to be $>95\%$ for **3a–e** by comparing the oxidation of $\text{K}_3[\text{Fe}(\text{CN})_6]$ by the Pt working electrode before and after exposure to the diisocyanides.¹¹ Ellipsometry measurements

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of **3a–e** deposited on Pt films provided a positive correlation between molecular length and SAM thickness. Assuming a constant angle for all molecules, the OTEs deposit on Pt at a tilt angle of $\sim 40^\circ$ from the surface normal, similar to our previous report with the OTs.¹ Additionally, solution IR spectroscopy of **3a–e** provided unequivocal evidence for the formation of isocyanide–platinum bonds upon treatment of diisocyanides with Pt nanoparticles. The characteristic free CN stretch at 2120 cm^{-1} was shifted to higher wave numbers (2186 cm^{-1}), indicating the formation of a Pt–CN bond.¹²

We have recently used the diamines derived by hydrolysis of the **6** series to couple across a gap in a nanotube by direct covalent formation of amide linkages.¹³ We saw that, indeed, there is direct electrical conduction through the molecular wires, not seen with saturated control molecules.

The next step is to use our wires in the construction of molecular field effect transistors in suitable molecules with three attached leads. This is underway.

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Supporting Information Available: Experimental details for the synthesis of **2–6**; UV, emission, solution, and SAM CV, and nanoparticle IR experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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