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Iterative Divergent/Convergent Doubling Approach to Linear Conjugated Oligomers. A Rapid Route to a 128 Å Long Potential Molecular Wire and Molecular Alligator Clips.

by

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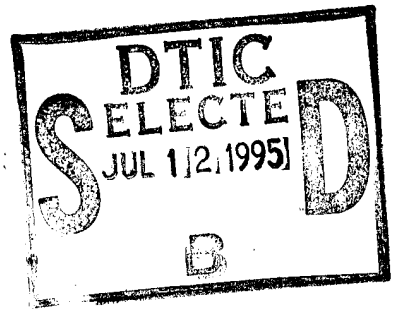

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13. ABSTRACT *(Maximum 200 words)*

The synthesis of a 128 Å long potential molecular wire will be described. Additionally, the synthesis and attachment of thiol-containing and isonitrile-containing end groups will be presented.

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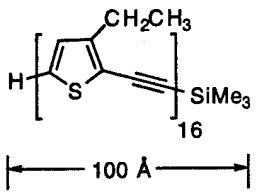
Iterative Divergent/Convergent Doubling Approach to Linear Conjugated Oligomers. A Rapid Route to a 128 Å Long Potential Molecular Wire and Molecular Alligator Clips

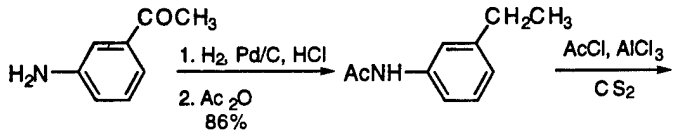
Jeffry S. Schumm, LeRoy Jones II, Darren L. Pearson, Ryuichiro Hara and James M. Tour*

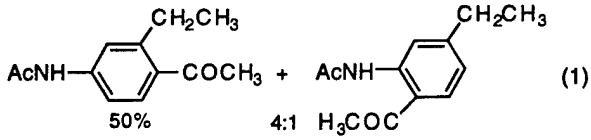
The ultimate computational system would consist of logic devices that are ultra dense, ultra fast, and molecular-sized.[1] Even though state-of-the-art nanopatterning techniques allow lithographic probe assemblies to be engineered down to the 100 Å gap regime,[2] the issue of electronic conduction based upon single or small packets of molecules has not been addressed and the feasibility of molecular electronics remains theoretically controversial.[1,3] In an attempt to assess the possibility of molecular wire[4] conduction by spanning the 100 Å probe gaps with small packets of molecules, we describe here the synthesis of phenylene-alkynylene oligomers that remain in a near-linear conformation due to 1,4-phenylene-substitution patterns and alkyne linearity. This linear arrangement should minimize undesired conformational movement during adhesion and testing between nanofabricated probes. Our approach to such a molecular framework involves a rapid iterative method that doubles molecular length at each iteration[5] to provide an air and light-stable linear conjugated oligomer that is 128 Å long that could also serve as a useful model for understanding bulk polymeric material properties.[4i,j,6] Moreover, the product could easily permit independent functionalization of the ends to serve as "molecular alligator clips" that might be required for surface contacts to metal probes for molecular electronics studies.[7]

We recently described the synthesis of a thiophene-ethynylene oligomer by an iterative divergent/convergent approach. In its extended zig-zag form, it was 100 Å

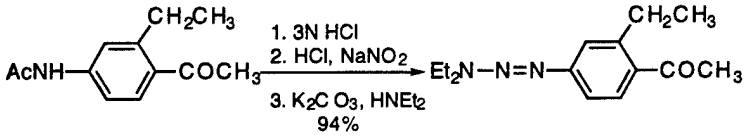


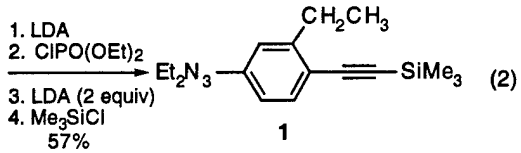
long.[8] Thus the linear system described here is complementary. The synthesis of the ethyl-containing monomer **1** is shown in eqs 1 and 2. The iterative





(1)



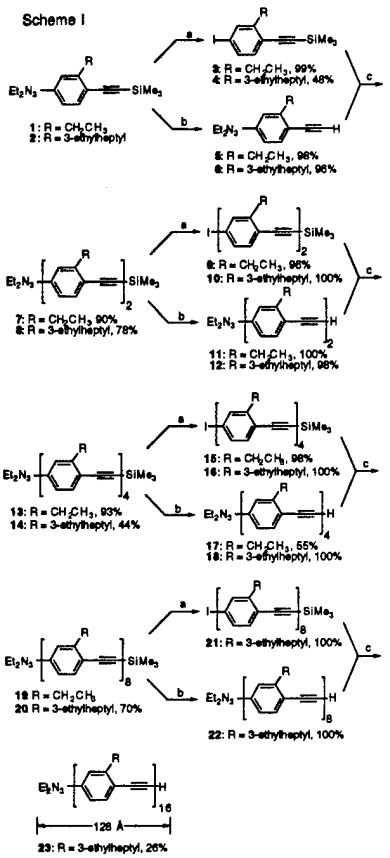


(2)

1

divergent/convergent approach to molecular length doubling is shown in Scheme I. Notice how just three

Scheme I

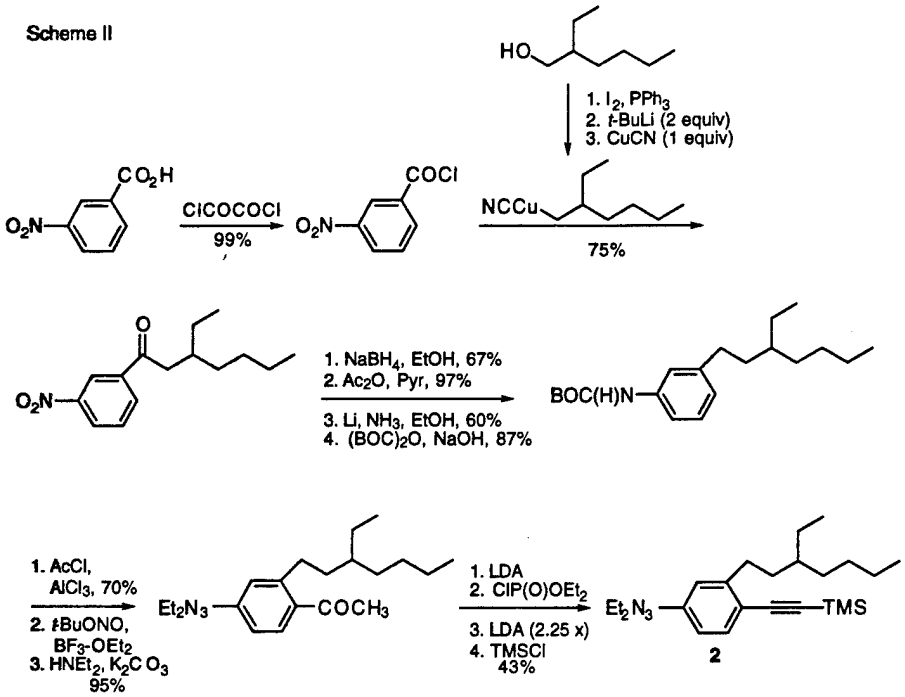


Reagents: a. MeI as solvent, 120°C in a screw cap tube. b. K_2CO_3, MeOH, 23°C or n-Bu_4NF, THF, 23°C c. $Pd(dba)_2$(5 mol %), CuI (10 mol %), PPh_3(20 mol %), iPr_2NH/THF (1:5), 23°C.

different reactions are needed at each stage to double the molecular length.[5c,d,9] We initially conducted the synthesis starting from monomer **1** with the notion that the ethyl group would provide sufficient solubility to permit formation of a 16-mer that has a length sufficiently long to bridge between lithographically-derived probe gaps. Unfortunately, the octamer **19** was nearly insoluble. Therefore, we were only able to obtain a UV-visible spectrum and a direct exposure mass spectrum (MS) (Table 1).

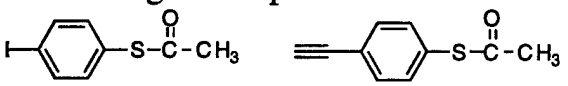
In an effort to insure the solubility of the linear rigid rod oligomer through to the 16-mer, we prepared monomer **2** as shown in Scheme II.[10] In addition to

Scheme II



possessing a longer alkyl chain than **1**, **2** also has a stereogenic center which, upon successive dimerization, will afford numerous diastereomers that will retard crystallization and thereby increase the likelihood of solubility. Indeed, we were delighted to discover that both the octamer **20** as well as the 16-mer **23** (Scheme I) were quite soluble and they could both be adequately spectroscopically characterizated. While **1**, **2**, **7**, **8**, **13**, **14**, and **19** were characterized by direct exposure via electron impact MS, in order to obtain MS data on **20** and **23**, it was necessary to use matrix assisted laser desorption/ionization (MALDI) MS (Table 1). **23** was 128 Å long as determined by a conformational minimization using MMX with extended π-Hückel and multiconformational parameters.

With the phenylene-ethynylene and thiophene-ethynylene oligomers now in hand, we have begun to synthesize and attach end groups that could serve as "molecular-sized alligator clips". The thioacetates, upon



hydrolysis, will form thiols. The thiols form gold-thiolates on exposure to gold surfaces.[7] We have also synthesized arylformamides which, after coupling to the oligomers, can be converted to isonitriles with PPh_3, CCl_4, $CHCl_3$, and

NEt_3. These can serve as good adhesion units to tungsten surfaces. We hope to use self-assembly methods to affix single or small packets of molecules between nanolithographically-derived probes or two STM tips.

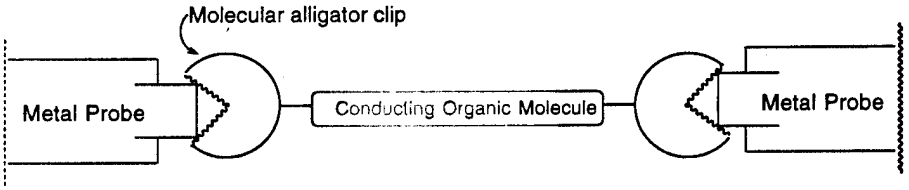


Table 1. Characterization Data.

19: Direct exposure MS statistical isotopic range calculated for $C_{87}H_{83}N_3Si$: 1198 (95%), 1199 (100%), 1200 (55%). Found: 1098.6 (signifying loss of the triazene moiety at 100 amu). λ_{max} (CH_2Cl_2) = 364 nm. UV 10% edge value = 500 nm.

20: IR (neat) 2952, 2198, 2147, 1464, 827 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.48 - 7.27 (m, 24 H), 3.77 (q, J = 7.1 Hz, 4 H), 2.98 - 2.63 (m, 16 H), 1.84 - 1.58 (m, 8 H), 1.58 - 1.10 (m, 86 H), 1.10 - 0.78 (m, 48 H), 0.27 (9 H). λ_{max} (CH_2Cl_2) = 376. UV 10% edge value = 422 nm. M_n = 2800, M_w = 2960, M_w/M_n = 1.05. MALDI MS (sinapinic acid matrix, positive ion mode) average molecular weight calculated for $C_{143}H_{195}N_3Si$: 1984. Found peak maximum (M + 1): 1791±9 (large error due to broad signal), (loss of -$SiMe_3$ at 73 amu, -N_3Et_2 at 100 amu, -C≡C at 24 amu which a common phenyl-alkynyl cleavage route).[11]

23: IR (neat) 2956, 2927, 2360, 2340, 1506, 1458 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.47 - 7.24 (m, 48 H), 3.77 (q, J = 7.1 Hz, 4 H), 2.95 - 2.65 (m, 32 H), 1.82 - 1.58 (m, 16 H), 1.58 - 1.10 (m, 166 H), 1.10 - 0.70 (m, 96 H), 0.26 (s, 9 H). λ_{max} (CH_2Cl_2) = 376 nm. UV 10% edge value = 422 nm. M_n = 6649, M_w =7114, M_w/M_n = 1.07. MALDI MS (sinapinic acid matrix, positive ion mode) average molecular weight calculated for **23** with $C_{279}H_{371}N_3Si$: 3795. Found (M + 1): 3486±14 (large error due to broad signal), (signifying loss in the MS of the -$SiMe_3$ at 73 amu, -N_3Et_2 at 100 amu, -C≡C at 24 amu which a common phenyl-alkynyl cleavage route, and a -C_8H_{17} fragment at 113 amu which represents a typical benzylic methylene-ethylene cleavage site.)[11]

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