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13. ABSTRACT (Maximum 200 words)

Described is the synthesis of oligo(3-ethylthiophene-ethynylene)s via an iterative divergent convergent approach starting from 3-ethyl-2-(trimethylsilylethynyl)thiophene. Synthesized were the monomer, dimer, tetramer, octamer and 16-mer. The 16-mer is approximately 100 Å long in its minimum energy conformational form. At each stage in the iteration, the length of the framework doubles. Only three sets of reaction conditions are needed for the entire iterative synthetic sequence; an iodination, a protodesilylation, and a Pd/Cu-catalyzed cross coupling. The oligomers were characterized spectroscopically and the mass spectrometry data are discussed. The optical properties are presented which show that at the octamer stage, the optical absorbance maximum is nearly saturated. The size exclusion chromatography values for the number average weights, relative to polystyrene, illustrate the tremendous differences in the hydrodynamic volume of these rigid rod oligomers versus the random coils of polystyrene. These differences become quite apparent at the octamer stage. The rigid rod conjugated oligomers may act as molecular wires in molecular electronic devices and they also serve as useful models for understanding analogous bulk polymers.

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**Iterative Divergent/Convergent Approach to Conjugated Oligomers by a Doubling of Molecular Length at Each Iteration. A Rapid Route to Potential Molecular Wires**

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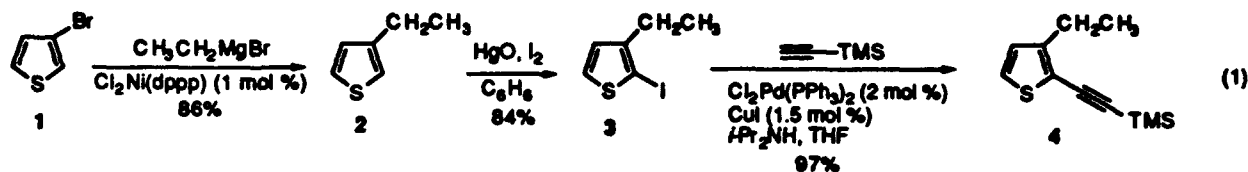
Columbia, South Carolina 29208

**Abst. act**

Described is the synthesis of oligo(3-ethylthiophene-ethynylene)s via an iterative divergent convergent approach starting from 3-ethyl-2-(trimethylsilylethynyl)thiophene. Synthesized were the monomer, dimer, tetramer, octamer and 16-mer. The 16-mer is approximately 100 Å long in its minimum energy conformational form. At each stage in the iteration, the length of the framework doubles. Only three sets of reaction conditions are needed for the entire iterative synthetic sequence; an iodination, a protodesilylation, and a Pd/Cu-catalyzed cross coupling. The oligomers were characterized spectroscopically and the mass spectrometry data are discussed. The optical properties are presented which show that at the octamer stage, the optical absorbance maximum is nearly saturated. The size exclusion chromatography values for the number average weights, relative to polystyrene, illustrate the tremendous differences in the hydrodynamic volume of these rigid rod oligomers verses the random coils of polystyrene. These differences become quite apparent at the octamer stage. The rigid rod conjugated oligomers may act as molecular wires in molecular electronic devices and they also serve as useful models for understanding analogous bulk polymers.

The ultimate computational system would consist of logic devices that are ultra dense, ultra fast, and molecular-sized.<sup>1</sup> Though bulk conjugated organic materials can indeed be semiconducting or even conducting,<sup>2</sup> electronic conduction based upon single or small packets of molecules has not been demonstrated and it is theoretically controversial.<sup>1,3</sup> Present nanopatterning techniques allow lithographic probe assemblies to be engineered down to the 100 Å gap regime.<sup>4</sup> In an attempt to span this 100 Å gap with molecules and to assess the feasibility of molecular wire conduction, we describe here a rapid synthetic approach to potential molecular wires based on an oligo(thiophene-ethynylene) derivative.<sup>5,6</sup> Additionally, these compounds possess properties that could make them useful for understanding bulk polymeric materials properties.<sup>7</sup>

The synthesis of the key monomer **4**, whose length will double at each stage, is outlined in eq 1.<sup>8</sup> The iterative divergent/convergent synthetic approach is outlined in Scheme I. The



sequence involves partitioning **4** into two portions; iodinating the 5-position in one of the portions to form **5** and protodesilylating the alkynyl end of the second portion to form **6**. Bringing the two portions back together in the presence of a Pd/Cu catalyst<sup>8c-f</sup> couples the aryl iodide to the terminal alkyne, thus generating the dimer **7**. Iteration of this reaction sequence doubles the length of the dimer **7** to afford the tetramer **10**, and so on to the octamer **13**, and finally the 16-mer **16**. The 16-mer, in its minimum energy conformational form, has a molecular length of approximately 100 Å.<sup>9</sup>

The monomer through 16-mer, **4**, **7**, **10**, **13**, and **16**, have been characterized spectroscopically. While the tetramer **10** and octamer **13** afforded molecular ions by direct exposure via electron impact mass spectrometry (MS), neither this method nor FAB or electrospray MS sufficed for obtaining a molecular ion of **16**. However, matrix assisted laser

desorption MS did afford an  $M+1$  peak for 16 (sinapinic acid matrix, positive ion mode,  $M+1$  calc'd for  $C_{131}H_{106}S_{16}Si + 1 = 2222.32$ . Found  $2219.98 \pm 1.20$ ).

The optical spectra are interesting in that a near saturation of the systems appears to have occurred by the octamer stage so that doubling the conjugation length to the 16-mer caused little change in the absorbance maximum (Figure 1). The results of the size exclusion chromatography (SEC) are also quite intriguing (Figure 2). SEC is not a direct measure of molecular weight but a measure of the hydrodynamic volume. Thus, by SEC using randomly coiled polystyrene standards, the number average molecular weights ( $M_n$ ) of rigid rod polymers are usually greatly inflated relative to the actual molecular weights (MW). Accordingly, the SEC recorded  $M_n$  values of the octamer (13) ( $M_n = 1610$ , actual MW = 1146) and 16-mer (16) ( $M_n = 3950$ , actual MW = 2218) were much greater than the actual MWs. Conversely, the monomer (4) through tetramer (10) had  $M_n$  values that were very close to the actual MWs (slope  $-1.0$  in Figure 2) because they are in the low MW region, prior to significant polystyrene coiling. Therefore Figure 2 could serve as a useful calibration chart for determining the MW of rigid rod polymers. In all cases, the SEC-determined values of  $M_w/M_n \approx 1.02-1.05$  were within the detectable range limits.

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### References

- (1) (a) *Molecular Electronics: Science and Technology*, Aviram, A., Ed.; Confer. Proc. No. 262, American Institute of Physics: New York, 1992. (b) *Molecular Electronic Devices II*; Carter, F. L., Ed.; Marcel Dekker: New York, 1984. (c) Hammeroff, S. R. *Ultimate Computing. Biomolecular Consciousness and Nano Technology*; North Holland: Amsterdam, 1987. (d)

Miller, J. S. *Adv. Mater.* 1990, 2, 378. (e) Aviram, A. *J. Am. Chem. Soc.* 1988, 110, 5687. (f) Hush, N. S.; Wong, A. T.; Bacskay, G. B.; Reimers, J. R. *J. Am. Chem. Soc.* 1990, 112, 4192. (g) Farazdel, A.; Dupuis, M.; Clementi, E.; Aviram, A. *J. Am. Chem. Soc.* 1990, 112, 4206. (h) Waldeck, D. H.; Beratan, D. N. *Science* 1993, 261, 576. (i) Ball, P.; Garwin, L. *Nature* 1992, 355, 761. (j) Tour, J. M.; Wu, R.; Schumm, J. S. *J. Am. Chem. Soc.* 1991, 113, 7064.

(2) *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Dekker: New York, 1986.

(3) (a) Miller, J. S. *Adv. Mater.* 1990, 2, 495, 601. (b) Chjatterji, P. K.; Yang, P. Schichijo, H. *Proc. IEEE* 1983, 130, 105. (c) Bate, R. T. In *VSLI Electronics*, Einspruch, N. G., Ed.; Academic: San Diego, 1982; Vol 5.

(4) (a) Reed, M. A., Yale University, personal communication, 1993. (b) *Nanostructure Physics and Fabrication*, Reed, M. A.; Kirk, W. P., Eds.; Academic Press: San Diego, 1989. (c) *Nanostructures and Mesoscopic Systems*, Kirk, W. P.; Reed, M. A., Eds.; Academic: San Diego, 1992.

(5) An iterative doubling approach was first described by Whiting and then later used by Moore to prepare oligo(1,3-phenylene-ethynylenes). See: (a) E. Ignier, O. I. Paynter, D. J. Simmonds, M. C. Whiting, *J. Chem. Soc., Perkin Trans. 1*, 1987, 2447. (b) I. Bidd, D. J. Kelly, P. M. Otley, O. I. Paynter, D. J. Simmonds, M. C. Whiting, *J. Chem. Soc., Perkin Trans. 1*, 1983, 1369. (c) J. Zhang, J. S. Moore, Z. Xu, R. A. Aguirre, *J. Am. Chem. Soc.* 1992, 114, 2273. (d) Z. Xu, J. S. Moore, *Angew. Chem. Int. Ed. Engl.* 1993, 32, 1354. For related oligomers and polymers, see: (e) Grubbs, R. H.; Kratz, D. *Chem. Ber.* 1993, 126, 149. (f) U. Scherf, K. Müllen, *Synthesis* 1992, 23.

(6) For a presentation of some foundational work in the area of "molecular wires," see: (a) Kenny, P. W.; Miller, L. L. *J. Chem. Soc., Chem. Commun.* 1988, 85. (b) Kugimiya, S.-i.; Lazrak, T.; Blanchard-Desce, M.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* 1991, 1179. (c) Crossley, M. J.; Burn, P. L. *J. Chem. Soc., Chem. Commun.* 1991, 1569. (d) Zecevic, S.; Simic-Glavaski, B.; Yeager, E. *J. Electroanal. Chem.* 1985, 196, 339. (e) Yoshimura, T.; Tatsuura, S.; Sotoyama, W.; Matsuura, A.; Hayano, T. *Appl. Phys. Lett.* 1992, 60, 268. (f) Sessler, J. L.;

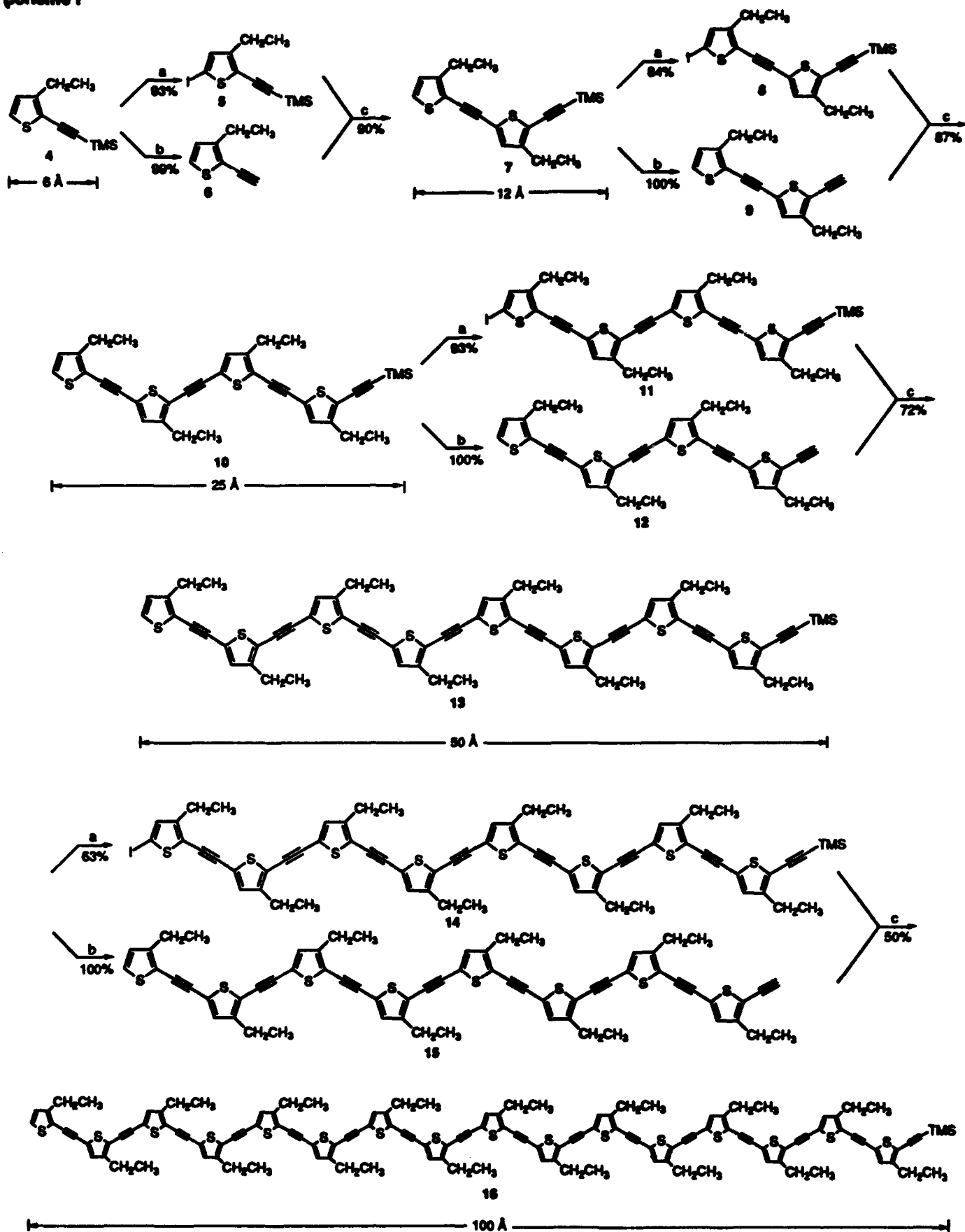
Capuano, V. L.; Harriman, A. *J. Am. Chem. Soc.* **1993**, *115*, 4618. (g) Tachibana, H.; Azumi, R.; Nakamura, T.; Matsumoto, M.; Kawabata, Y. *Chem. Lett.* **1992**, 173. (h) O'Neil, M. P.; Niemczyk, M. P.; Svec, W. A.; Gosztola, D.; Gaines, G. L., III; Wasielewski, M. R. *Science* **1992**, *257*, 63. (i) Wudl, F.; Bitler, S. P. *J. Am. Chem. Soc.* **1986**, *108*, 4685. (j) Lu, F.-L.; Wudl, F.; Nowak, M.; Heeger, A. J. *J. Am. Chem. Soc.* **1986**, *108*, 8311.

(7) (a) Guay, J.; Diaz, A.; Wu, R.; Tour, J. M.; Dao, L. H. *Chem. Mater.* **1992**, *4*, 254. (b) Tour, J. M.; Wu, R. *Macromolecules* **1992**, *25*, 1901. (c) Guay, J.; Kasai, P.; Diaz, A.; Wu, R.; Tour, J. M.; Dao, L. H. *Chem. Mater.* **1992**, *4*, 1097.

(8) (a) Tamao, K.; Kodama, S.; Nakajima, I.; Kumada, M.; Minato, A.; Suzuki, K. *Tetrahedron* **1982**, *38*, 3347. (b) Uhlenbroeck, J. H.; Bijloo, J. D. *Rec. Trav. Chim.* **1960**, *79*, 1181. (c) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467. (d) Stephens, R. D.; Castro, C. E. *J. Org. Chem.* **1963**, *28*, 3313. (e) Suffert, J.; Ziessel, R. *Tetrahedron Lett.* **1991**, *32*, 757. (f) Xu, Z.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1354.

(9) The minimization was done using MMX with extended  $\pi$ -Hückel and multiconformational parameters ( $10^\circ$  aryl-alkynyl bond rotational steps).

**Scheme 1**



Reagents: (a) LDA, Et<sub>2</sub>O, -78° to 0°C then I<sub>2</sub>, -78°. (b) K<sub>2</sub>CO<sub>3</sub>, MeOH, 23°C. (c) Cl<sub>2</sub>Pd(PPh<sub>3</sub>)<sub>2</sub> (2 mol %), CuI (1.5 mol %), THF, tPr<sub>2</sub>NH, 23 °C.



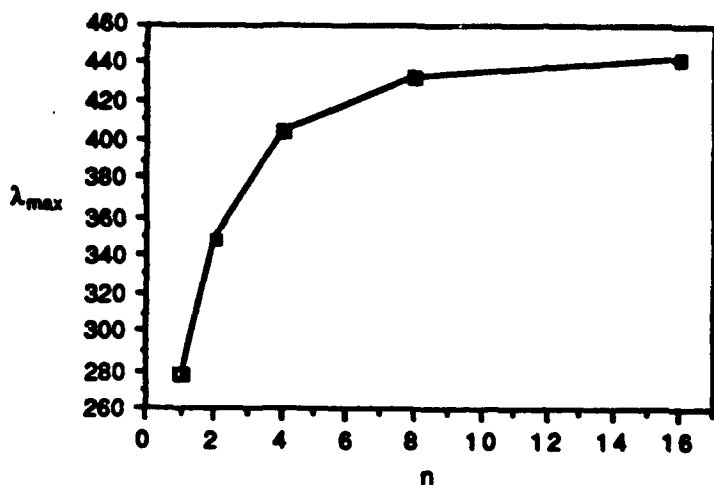


Figure 1. The optical absorbance maximum ( $\lambda_{max}$ ) in  $\text{CH}_2\text{Cl}_2$  versus the number of units in the oligomer (n) for 4, 7, 10, 13, and 16.

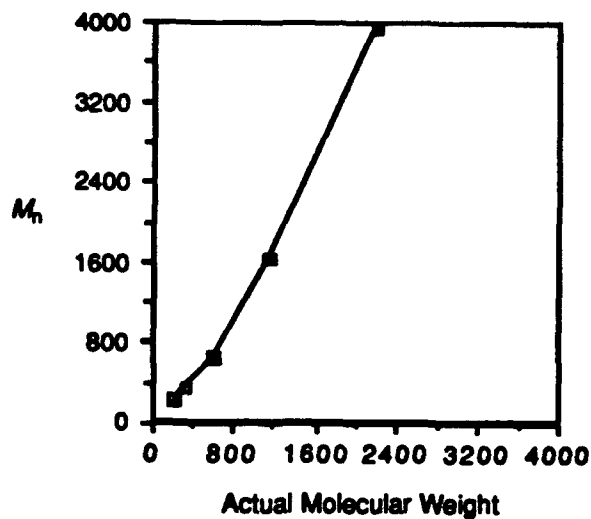


Figure 2. The values of  $M_n$  determined by SEC in THF (relative to polystyrene standards) versus the actual molecular weights of the monomer through 16-mer, 4, 7, 10, 13, and 16, respectively.