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Synthesis of High Carbon Materials from Acetylenic Precursors. Preparation of Aromatic Monomers Bearing Multiple Ethynyl Groups[1]

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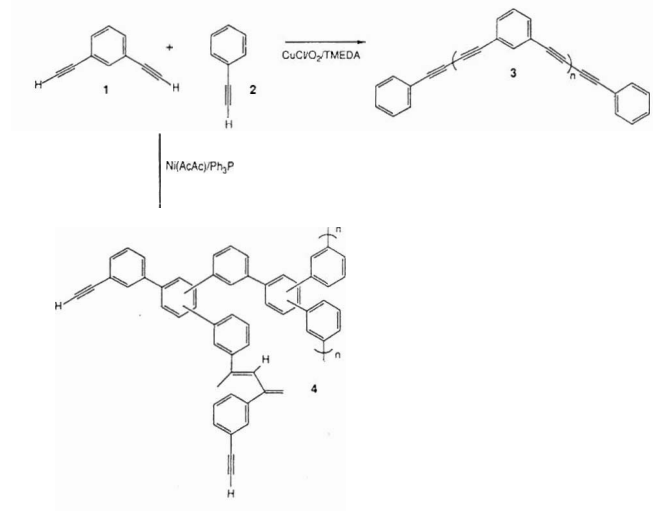
The synthesis of polyethynyl aromatics as starting materials for the preparation of highly cross-linked organic solids containing high atom fractions of carbon is described. Treatment of bromo- and iodoaromatic compounds with (trimethylsilyl)acetylene (TMSA) in the presence of palladium(0) and copper(I) in amine solvents yields (trimethylsilyl)ethynyl-substituted aromatics. The TMS protecting groups can be removed by hydrolysis with mild base. Compounds prepared by using this technique include 1,3-diethynylbenzene, 2,5-diethynylthiophene, 1,3-diethynyltetrafluorobenzene, 1,4-diethynyltetrafluorobenzene, 2-ethynylthiazole, 2,4-diethynylthiazole, 2,7-diethynylnaphthalene, hexakis((trimethylsilyl)ethynyl)benzene, tetraethynylthiophene, 2,5-bis((trimethylsilyl)ethynyl)-3,4-bis(3-hydroxy-3-methyl-1-butynyl)thiophene, 2,5-diethynyl-3,4-bis(3-hydroxy-3-methyl-1-butynyl)thiophene, 2,5-bis(4-(2-thienyl)butadiynyl)-3,4-bis(3-hydroxy-3-methyl-1-butynyl)thiophene, and 2,5-bis-(4-(2-thienyl)butadiynyl)-3,4-diethynylthiophene.

Introduction

We are engaged in a project aimed at the preparation of organic solids containing a high density of strong, directed carbon–carbon bonds. Our objective in this project is to relate the molecular-level structure of the solids to their macroscopic physical properties and to determine if it is possible to replicate in these materials some of the remarkable range of properties exhibited by pure allotropes of carbon (diamond: hardness, high thermal conductivity) (graphite: electrical conductivity, lubricity).[3] We expect high-carbon, densely cross-linked organic solids to display high thermal stability and a high degree of hardness. Our strategy for the preparation of these materials involves the initial syntheses of low molecular weight poly(diacetylenes); these polymers are then molded into desired shapes and processed thermally, photochemically, and/or catalytically to yield the final, highly cross-linked organic solids.

This paper details the preparation of several monomeric polyacetylenic aromatic compounds. Certain of these monomers are the precursors to the intermediate polymers; others were too reactive and unstable to be useful in polymerizations but are of interest in their own right as unusual ethynylated compounds. We will discuss the polymerization of these monomers and materials processing of the resulting polymers in later papers.[4]

The commercial development of organic solids from acetylenic precursors dates from the 1960s when Hay showed that the oxidative coupling of 1,3-diethynylbenzene (1) yielded a soluble polymer.[5] The molecular weight and solubility of this polymer could be controlled by using mixtures of 1 and phenylacetylene (2) (as an end-capping group) in the polymerization. This procedure yielded phenyl-terminated poly(diethynylbenzene) oligomers 3 that could be further processed at high temperatures to form carbon films and fibers. Research at General Electric expanded this type of chemistry to include a wide range of acetylenic aromatic monomers.[6] More recently, research at IBM has developed related materials based upon the oxidative coupling of 1,3,5-triethynylbenzene.[7]



A separate effort directed toward high-carbon solids at Hercules concentrated on the polymerization of diethynylbenzenes by a route involving cyclotrimerization of the ethynyl groups.[8] This procedure yielded polymers ostensibly containing polyphenylene units, residual acetylenic residues, and a small fraction of olefinic units. These olefinic groups resulted from a process in which the acetylenes underwent a linear rather than a cyclotrimerization polymerization. The Hercules process also used suitable end-capping groups such as 2 to limit molecular weight. Soviet workers have also extensively developed the cyclotrimerization polymerization of diethynyl aromatics.[9] Commercialization of materials derived from diethynylbenzene and other acetylenic precursors was explored at both General Electric and Hercules. The absence of an inexpensive route to the monomers, together with the limitation of a low elongation-to-break of the finished materials, discouraged their full development.

A parallel effort to develop acetylene-containing polymers as thermoset resins resulted in the development of

(1) This work was supported by the National Science Foundation, Grant CHE 85-08702.

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(8) Cessna, L. C., Jr. U.S. Pat. 3882073, 1975. Jabloner, H. U.S. Pat. 4070333, 1978. Jabloner, H. U.S. Pat. 4097460, 1978.

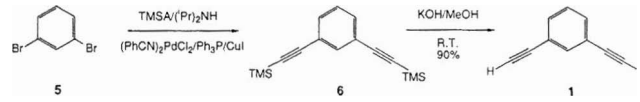
(9) Korshak, V. V.; Volpin, M. E.; Sergeev, V. A.; Shitikov, V. K.; Kolomnikov, I. S. U.S. Pat. 3705131, 1972. Korshak, V. V.; Gribova, I. A.; Krasnov, A. P.; Sergeev, V. A.; Shitikov, V. K.; Elerdashvili, G. V. U.S. Pat. 3756982, 1973.

acetylene-terminated imide oligomers such as the Thermid-600 series.[10] These materials have excellent thermal stability but their high cost and difficulty in curing have restricted their development.

Classical methods for the synthesis of terminal arylacetylenes involve the manipulation of preformed two-carbon units.[11] Most useful among these are the Vilsmeier reaction,[12] the halogenation–dehydrohalogenation of vinyl aromatics and ketones,[13,14] and the dehydrohalogenation of β,β-dihalo olefins.[15] This latter reaction was employed for the preparation of diethynylbenzene in the research of both General Electric and Hercules. A number of reactions also introduce ethynyl moieties directly into aromatic rings. The most widely accepted of these methods has been the Stephens–Castro[16,17] reaction between an aromatic halide and a protected cuprous acetylide in refluxing pyridine. Difficulty in removing protective groups has been a limitation of this method. An alternative to the Stephens–Castro method—the coupling between arylcopper reagents and (iodoethynyl)trimethylsilane at low temperatures[18]—is limited by the necessity to form the organocopper reagents. The palladium-catalyzed reaction of alkynylzinc reagents with aryl halides[19] yields terminal and internal ethynyl aromatic compounds and does not require protection of the alkynyl groups but does require as reactant an aryl iodide or activated aryl bromide. A system of palladium(0) and copper(I) catalytically couples acetylenes and aryl iodides.[20,21] Hagihara and Lau improved this reaction by using (trimethylsilyl)acetylene (TMSA).[22] This improvement yields stable, readily manipulated trimethylsilyl-protected ethynyl aromatics as intermediates; mild basic hydrolysis removes the TMS group. Electron-withdrawing groups on the aryl ring facilitate the reaction; electron-donating groups are detrimental. This method offers the advantages of simplicity, ease of workup, and high yields. Vollhardt and co-workers first demonstrated multiple replacement of halogens on the same molecule by using this reaction.[23] We chose this route to polyethynyl aromatics for these reasons and because of the wide range of suitably substituted haloaromatics available as starting materials. TMSA is expensive[24] and 2-methyl-3-butyn-2-ol has been proposed[25] as an alternative, but deprotection requires hydroxide base in high boiling solvent.

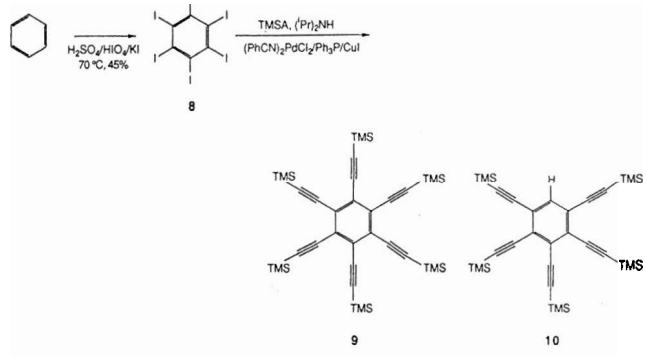
Results and Discussion

Ethynylbenzenes. We prepared 1,3-diethynylbenzene (1) by the reaction of 1,3-dibromobenzene with TMSA using dichlorobis(benzonitrile)palladium, triphenylphosphine, and copper(I) iodide as catalyst. The TMS-protected intermediate (6) is an air- and moisture-stable



solid. Treatment of compound 6 with a catalytic amount of base in methanol removes the protecting groups. Compound 1 is a clear colorless liquid that discolors upon prolonged standing. Compound 1 may be purified by distillation at moderate temperatures and under high vacuum. (*Note: Our initial attempt to distill 1 at temperatures of up to 110 °C and at aspirator pressures resulted in an exothermic reaction followed by an explosion. Compound 1 and all other volatile polyethynyl aromatics should be distilled at high vacuum and at temperatures of less than 60 °C in well-shielded equipment. Only limited quantities should be distilled, stored, or manipulated as pure (undiluted) material. All of the deprotected ethynyl aromatics mentioned in this paper should be treated as potentially explosive materials.*)[26]

The same chemistry can be extended to the preparation of higher poly- and persubstituted acetylenic aromatic compounds. Reaction of hexaiodobenzene (8) with TMSA



yielded 9 in 1% isolated yield and the related 10 in 14% yield. Compound 9 is only produced after prolonged reflux of the reaction mixture, and these conditions result in competitive reduction of the halogens and formation of 10. The reaction yields other mixed substituted and reduced products (of higher R_f). These compounds were not characterized. Vollhardt has previously reported a synthesis of 9 from hexabromobenzene in 27% yield.[2]

Derivatives of Tetrafluorobenzene. We expect polymers prepared from (fluorophenyl)acetylenes to have lower water permeability, and perhaps greater thermal stability, than polymers from analogous phenylacetylenes. The preparation of 1,4-diethynyltetrafluorobenzene by the coupling of the lithium salt of TMSA with hexafluorobenzene followed by basic hydrolysis of the protecting groups has been described by Walton.[27] Application of the same palladium/copper chemistry described above to commercially available 1,4-dibromotetrafluorobenzene (11)

(10) For a review of the development of Thermid-600 and of other acetylene terminated oligomers, see: Hergenrother, P. M. In *Reactive Oligomers*; ACS Symposium Series 282; American Chemical Society: Washington, DC, 1986; p 1–16.
(11) *The Chemistry of the Carbon–Carbon Triple Bond*; Patai, S., Ed.; Wiley: New York, 1978.
(12) Staab, H. A.; Neunhoffer, K. *Synthesis* **1974**, 424.
(13) Collier, W. L.; Macomber, R. S. *J. Org. Chem.* **1973**, *38*, 1367–1369.
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(15) Villieras, J.; Pierrot, P.; Normant, J. F. *Synthesis* **1975**, 458–461. Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 3769–3772.
(16) Castro, C. E.; Stephens, R. D. *J. Org. Chem.* **1963**, *28*, 3313–3315.
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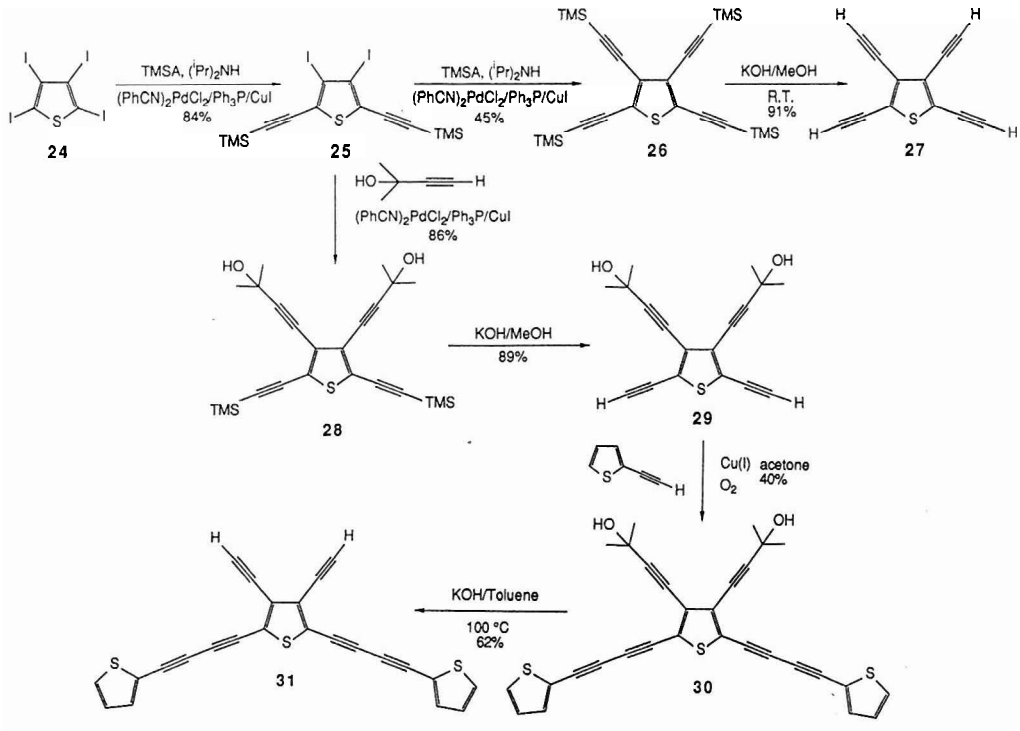
(23) Berris, B. C.; Hovakeemian, G.; Lai, Y. H.; Mestdagh, H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1985**, *107*, 5670–5687. Diercks, R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 266–268.
(24) A new and inexpensive synthesis of TMSA has been described: Jones, G. E.; Kendrick, D. A.; Holmes, A. B.; Sporikou, C. N. *Org. Synth.* **1987**, *65*, 61–67.
(25) Oponchenko, A.; Sabouin, E. T.; Selwitz, C. M. *J. Org. Chem.* **1979**, *44*, 1233–1236.
(26) For advice on the safe handling of acetylenic compounds, see: Rutledge, T. F. *Acetylenic Compounds. Preparation and Substitution Reactions*; Reinhold: New York, 1968.
(27) Waugh, F.; Walton, D. R. M. *J. Organomet. Chem.* **1972**, *39*, 275–278.

Scheme I



followed by deprotection of **12** yields 1,4-diethynyltetrafluorobenzene (**13**) in >90% overall yield.

Since we were aware that para-substituted diethynyl monomers might yield rigid rod polymers with limited solubility, we were particularly interested in preparing monomers in which the two ethynyl groups were meta. Several attempts to brominate 1,2,3,5-tetrafluorobenzene yielded only starting material, but 1,2,3,5-tetrafluorobenzene (**14**) reacted cleanly with periodic acid and KI in hot concentrated sulfuric acid when a variation of the method of Mattern[28] was used and yielded 1,3-diiodo-2,4,5,6-tetrafluorobenzene (**15**). The conversion of **15** to 1,3-bis((trimethylsilyl)ethynyl)tetrafluorobenzene (**16**) then proceeded smoothly by using the palladium/copper catalyst system. Removal of the TMS protecting groups with KOH in methanol yielded 1,3-diethynyl-2,4,5,6-tetrafluorobenzene (**17**) as a colorless liquid. Compound **17** could be purified by vacuum transfer, but attempts to distill it at aspirator pressure resulted in an explosive decomposition.

Ethynylpentafluorobenzene (20) (an end-capping agent in the polymerization) was prepared by using a similar procedure from bromopentafluorobenzene (**18**).

Derivatives of Thiophene. The synthesis of simple diethynylthiophenes such as 2,5-diethynylthiophene[29] (**23**) could be accomplished by using procedures analogous to those described for the phenyl derivatives.

The reaction of tetraiodothiophene[30] (**24**) with a 2 equiv of TMSA at room temperature resulted in the clean formation of 2,5-bis((trimethylsilyl)ethynyl)-3,4-diiodothiophene (**25**) in 84% isolated yield (Scheme I). Attempts to derivatize **25** further by, for example, treatment with CuCN in DMF resulted in decomposition. Reaction of **25** with 2 equiv of TMSA did, however, yield tetrakis((trimethylsilyl)ethynyl)thiophene (**26**) in 45% yield. Compound **26** could also be prepared directly from **24** by treatment with 4.5–6 equiv of TMSA. Compound **26** was isolated as stable but slightly light-sensitive white crystals. Deprotection of the four acetylene groups could be accomplished by treatment with dilute KOH in degassed methanol. Tetraethynylthiophene (**27**) was isolated in 91% yield after rapid chromatography on silica with hexanes. Compound **27** is a white crystalline material which rapidly turns black upon standing in air. (*Note: Compound 27 is sensitive to heat and shock and attempts to sublime it under high vacuum resulted in an explosive decomposition. Compound 27 is the least stable compound described in this work and great caution is advised in its preparation and handling.*) Solutions of **27** in chlorinated solvents deposit insoluble black crystals upon standing. These crystals were not examined further.

More complicated ethynyl monomers are also accessible by the same general route. For example, reaction of 2,5-bis((trimethylsilyl)ethynyl)-3,4-diiodothiophene (**25**) with an excess of 2-methyl-3-butyn-2-ol[25] in the presence of the same palladium/copper catalyst system resulted in the isolation of the doubly protected tetraethynylthiophene (**28**) (as light-sensitive crystals in 86% yield). The presence of the two different protecting groups allows for selective deprotection. Thus, treatment of **28** with a catalytic amount of KOH in methanol at room temperature permits the essentially quantitative isolation of compound **29**, in which the TMS protecting groups alone have been removed. Coupling of **29** with an excess of 2-ethynylthiophene[31] using standard Glaser coupling conditions followed by chromatography allowed the isolation of the end-capped derivative **30** together with higher oligomers, from which **30** could be easily separated by chromatography. The removal of the acetone protecting groups has been described previously.[32] This reaction is less effective than the removal of TMS protecting groups and requires

(28) Mattern, D. L. *J. Org. Chem.* **1980**, *45*, 4772–4773.
(29) Okuhara, K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2045–2052.
(30) Steinkopf, W.; Schmitt, H. F.; Fiedler, H. *Ann.* **1937**, *527*, 237–263.
(31) 2-Ethynylthiophene may be prepared by the route described in this paper for 2,5-diethynylthiophene and using 2-bromothiophene or 2-iodothiophene as the starting material. For alternative routes, see ref 29.
(32) Trumbo, D. L.; Marvel, C. S. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 2231–2238.

prolonged reflux in the presence of solid KOH and a high boiling solvent. Nevertheless, the deprotection could be accomplished in good yield by following the evolution of acetone (by GC) from the reaction. Compound **31** was recovered as orange air-stable crystals.

Derivatives of Thiazole. The thermal stability of the thiazole nucleus has been exploited in the preparation of the well-known poly(benzothiazole) engineering plastics.[33] These materials are stable at temperatures up to 400 °C. For this reason and to provide a comparison with the diethynylthiophene case, we attempted the preparation of several acetylenic thiazoles. Although a great variety of halogenated thiazoles have been reported,[34] the number of useful commercially available examples is limited. Freshly distilled 2-bromothiazole (**32**) reacted quickly with TMSA under palladium/copper catalysis to yield 2-((trimethylsilyl)ethynyl)thiazole (**33**) in 68% isolated yield. Compound **33** was isolated as a pale yellow oil that darkened upon standing in air or in light. Removal of the protecting group was accomplished as before by treatment of **33** with a catalytic amount of base in methanol. 2-Ethynylthiazole (**34**) was recovered as a volatile unstable oil. An alternative route to **34** was devised starting from 2-iodothiazole.[35]

The preparation of a diethynylthiazole derivative was complicated by the low reactivity of both the 4 and 5 positions of the ring toward halogen replacement.[34] Thus, attempted reaction of 2,5-dibromothiazole with TMSA in the presence of catalyst resulted primarily in decomposition with production of only small quantities of monosubstituted (probably in the 2 position) product. We did find, however, that 2,4-dibromothiazole (**38**) (prepared from the corresponding diol (**37**) by reaction with $POBr_3$)[36] reacted rapidly with TMSA and yielded quantitatively a monosubstituted product (presumably 2-((trimethylsilyl)ethynyl)-4-bromothiazole). Prolonged reflux of the reaction mixture (>36 h) yielded the desired protected 2,4-disubstituted derivative (**39**). The later stages of the reaction were complicated by decomposition and the protected diethynylated thiazole was only recoverable in ~20% yield after chromatography on alumina. The product could neither be crystallized or distilled. Deprotection of the TMS groups was accomplished as before and the desired 2,4-diethynylthiazole (**40**) was isolated as a yellow oil (which rapidly turned dark upon standing) in 62% yield.

Ethynylnaphthalenes. The synthesis of 1-ethynylnaphthalene is summarized in Table I. The preparation of a suitable diethynylnaphthalene proved to be more troublesome. Although 1,4-dibromonaphthalene is commercially available, we felt that the rigid rod-like character of any polymer prepared from a monomer having the two ethynyl groups in this configuration would result in poor solubility. We therefore settled upon the preparation of the 2,7 derivative. We prepared 2,7-dibromonaphthalene (**41**) by treatment of the commercially available 2,7-dihydroxynaphthalene (**40**) with triphenylphosphine/Br_2 complex.[37] This reaction was complicated by the contamination of the product by triphenylphosphine oxide. We therefore give a reliable procedure for this synthesis in the Experimental Section. The syntheses of the protected (**42**) and deprotected 2,7-diethynylnaphthalene (**43**) are summarized in Table I.

Conclusions

This work describes a simple route to poly- and peracetylenic aromatics through the palladium/copper-catalyzed reaction between an activated aromatic halide and a protected acetylene. The intermediate protected acetylenic aromatics were then deprotected by basic hydrolysis. We have found that any combination of reagents that generates a bis(triphenylphosphine)palladium(0) complex in solution (palladium chloride plus 2 equiv of triphenylphosphine or bis(benzonitrile)palladium chloride plus 2 equiv of triphenylphosphine) works equally well as the catalytic species. Copper(I) iodide or copper(II) acetate is the most suitable choice for the copper reagent.

We have examined both TMSA and 2-methyl-3-butyn-2-ol as protected acetylenes for the reaction. Despite its high cost, TMSA is the most suitable choice as the protected acetylene because it forms stable crystalline TMS-protected intermediates and the TMS groups may be removed by very mild basic hydrolysis.

Both aromatic bromides and iodides are suitable as precursors to the aromatic acetylenes. In certain cases (as in the attempted preparation of hexakis((trimethylsilyl)ethynyl)benzene (**9**)), we found that iodo-substituted aromatics underwent a side reaction in which reduction rather than substitution of the iodines occurred. Electron-withdrawing groups on the ring facilitated substitution of both bromo and iodo substituents, whereas electron-donating groups were detrimental. In certain cases (as in the preparation of compounds **25** and **28**), we were able to take advantage of the variations in reactivity between halogens in the same molecule to selectively substitute at certain positions.

We isolated acetylenic substituted molecules by mild basic hydrolysis of the protected intermediates. We found that attempted distillation of many of the free acetylenes even at moderate temperatures resulted in an explosive decomposition. All of the liquid acetylenes, however, could be purified by vacuum transfer at room temperatures, and the solid materials could be purified by recrystallization or sublimation.

Experimental Section

General. Melting points were determined on a Thomas Hoover melting point apparatus and are uncorrected. Infrared spectra were recorded as KBr disks or as thin films on NaCl plates. UV spectra were recorded as 10^{-5} M solutions in heptane. ^1H NMR spectra were recorded at 80 MHz or 300 MHz and ^{13}C NMR spectra were recorded at 75 MHz. Mass spectra were recorded at 70 eV or by GC/MS on a HP 5990A spectrometer. Elemental analyses were obtained by Galbraith Laboratories, Nashville, TN. (Trimethylsilyl)acetylene (TMSA), copper(I) iodide, dichlorobis(benzonitrile)palladium(II), 2,5-dibromothiophene, 1,2,3,5-tetrafluorobenzene, 2-aminothiazole, 2-bromothiazole, and 2,7-dihydroxynaphthalene were obtained from Aldrich and were used without further purification. Silica gel (70–320 mesh) was obtained from Fluka. Diisopropylamine (Aldrich) and piperidine (Aldrich) were distilled from KOH before use. Diethyl ether and tetrahydrofuran (THF) were distilled from purple sodium benzophenone dianion solutions before use. Hexaiodobenzene (**8**) was prepared from benzene by the method of Mattern[28] in 45% yield. Tetraiodothiophene (**24**) was prepared from thiophene by the

(33) Cassidy, P. E. *Thermally Stable Polymers. Syntheses and Properties*; Marcel Dekker: New York, 1980.

(34) Herkes, F. E.; Blazer, T. A. *J. Heterocycl. Chem.* **1976**, *13*, 1297–1304.

(35) The synthesis of 2-iodothiazole (**36**) from 2-aminothiazole (**35**) has been reported by Travagli (Travagli, G. *Gazz. Chim. Ital.* **1948**, *78*, 592–599). The conversion of 2-aminothiazole to 2-iodothiazole is low and in our hands was never greater than 40%. Nevertheless the low cost of 2-aminothiazole, together with the enhanced reactivity of the iodo derivative, make this route attractive. We therefore give a procedure for the preparation of 2-iodothiazole in the Experimental Section.

(36) Reynaud, P.; Robba, M.; Moreau, R. C. *Bull. Soc. Chim. Fr.* **1962**, 1735–1738.

(37) Porizi, G.; Concilli, C. *J. Organomet. Chem.* **1977**, *128*, 95–98.

method of Steinkopf[30] in 75% yield. All reactions, except where indicated, were carried out under an atmosphere of argon.

General Procedure for the Synthesis of TMS Acetylene Derivatives. Synthesis of 1,3-Bis((trimethylsilyl)-ethynyl)benzene (6). To a solution of 1,3-dibromobenzene (5) (15.0 g, 48 mmol) in freshly distilled diisopropylamine (50 mL) were added dichlorobis(benzonitrile)palladium (1.68 g, 2.4 mmol), triphenylphosphine (1.26 g, 4.8 mmol), and copper(II) acetate hydrate (0.47 g, 2.4 mmol).[38] The solution was degassed by passing a rapid stream of argon through it. TMSA (10.4 g, 14.6 mL, 2.2 equiv) was added over 1 h at room temperature to the clear yellow-green solution. The solution changed color rapidly to a yellow-brown with the formation of a heavy precipitate. The solution was heated at reflux until GC analysis indicated that all starting material had disappeared (~3 h). (In some cases the solution eventually changed to a very dark brown color, but this change did not appear to correlate with a decrease in yield.) The solution was allowed to cool to room temperature and was filtered to remove the precipitate of diisopropylamine hydrobromide salts. The solvent was removed at reduced pressure and the residue was taken up in methylene chloride. Extraction with 5% HCl followed by extraction with water (twice), drying of the organic layer, and removal of the solvent yielded the crude product as a dark oil. The oil was taken up in the minimum amount of hexanes (10 mL) and applied to a silica gel column (200 g) packed in hexanes. Elution with hexanes removed first 1,4-bis(trimethylsilyl)butadiyne (0.44 g) followed by the desired 1,3-bis((trimethylsilyl)-ethynyl)benzene as colorless crystals (15.3 g, 89%), mp 57–59 °C (lit.[39] 57–59 °C): ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.2–6.8 (m, 4 H), 0.26 (s, 18 H); mass spectrum (EI), m/z (rel intensity) 270 (M^+, 23.6), 255 (100). Anal. Calcd for $C_{16}H_{22}Si_2$: C, 71.11; H, 8.11. Found: C, 70.99; H, 8.22.

Synthesis of 1,3-Diethynylbenzene (1). To a solution of 1,3-bis((trimethylsilyl)ethynyl)benzene (6) (10 g, 37 mmol) in degassed methanol (200 mL) was added KOH (28 mg, 0.5 mmol) in 1 mL of water. The solution was stirred at room temperature for 20 min until GC analysis indicated that the reaction was complete. The reaction mixture was diluted with water (200 mL) and extracted with *n*-pentane until the extracting solvent was free of product (by GC analysis). The combined organic layers were dried over magnesium sulfate and the solvent was removed at reduced pressure at room temperature. The residue was distilled to yield 1 as a colorless liquid which turned yellow upon standing. The yield was 4.2 g, 90.1%, bp 37 °C (0.05 torr) (lit.[40] bp 78 °C at 15 Torr): IR (NaCl) 3300, 3090, 2120, 1600, 1250 cm^{-1}; ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.55 (m, 4 H), 3.05 (s, 2 H); mass spectrum (EI), m/z (rel intensity) 126 (M^+, 100), 98 (9.2).

Hexakis((trimethylsilyl)ethynyl)benzene (9) and Pentakis((trimethylsilyl)ethynyl)benzene (10). Hexaiodobenzene (8) (0.5 g, 0.6 mmol) was dissolved in freshly distilled piperidine (20 mL), and the clear yellow solution was diluted to 40 mL with diisopropylamine. The solution was flushed with argon, and dichlorobis(benzonitrile)palladium(II) (0.13 g, 0.3 mmol), triphenylphosphine (0.16 g, 0.6 mmol), and CuI (68 mg, 0.3 mmol) were added. The solution was cooled to 0 °C and TMSA (0.52 mL, 3.7 mmol) was added dropwise over 10 min. The solution turned bright yellow, then green, and finally brown, with the formation of a heavy precipitate. The solution was allowed to warm to room temperature and was then heated at reflux for 3 h. TLC analysis (hexanes, silica) of the reaction at this point showed complete loss of the starting material and the formation of at least eight new compounds. An additional 0.1 mL of TMSA was added, and the solution was refluxed for a further 24 h. TLC showed evidence of extensive decomposition (dark material at the origin) with the same complicated mixture of products. The solution was cooled to room temperature and filtered to remove salts. The solvent was removed at reduced pressure and the residue dissolved in methylene chloride, washed first with dilute HCl, followed by water, and finally dried with $MgSO_4$, and the solvent was removed. The residue was chromatographed on silica gel with hexanes. After the elution of several lower substituted ethynyl compounds, a pale yellow band was removed from the column that yielded **10** (54 mg, 14%). Further elution yielded 9 (5 mg, 1%) as a pale yellow solid.

Compound **9**: mp >300 °C; IR (KBr) 2980, 2920, 2150, 1400, 1250, 940, 850, 760 cm^{-1}; ^{1}H NMR (80 MHz, $CDCl_3$) δ 0.23 (s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 128, 105.2, 101, 0.03; mass spectrum (EI, exact mass), calcd for $C_{36}H_{54}Si_6$ m/z 654.2841, found 654.2796; UV max (log ϵ) 285 (4.72), 290 (4.90), 298 (5.15), 307 (4.86), 320 (4.93) nm. Compound **10**: pale yellow crystals, mp 155–157 °C; IR (KBr) 2975, 2895, 2140, 1420, 1390, 1250, 1210, 1010, 915, 835, 760, 700, 635 cm^{-1}; ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.50 (s, 1 H), 0.28 (s, 45 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.2, 128.9, 127.9, 125.6, 105.1, 103.9, 101.9, 100.9, 1.53, 1.40; mass spectrum (EI), m/z (rel intensity) 558 (M^+, 83.5), 543 (3.7), 455 (6.2), 425 (2.34), 397 (2.2), 381 (2.3), 73 (100); UV max (log ϵ) 270 (4.73), 286 (4.98), 298 (4.56), 308 (4.53), 322 (4.49) nm. Anal. Calcd for $C_{31}H_{46}Si_5$: C, 66.66; H, 8.24. Found: C, 66.58; H, 8.21.

1,3-Diiodotetrafluorobenzene (15). To a cooled solution of concentrated H_2SO_4 (50 mL) was added in portions periodic acid (HIO_4) (7.5 g, 33 mmol). To this clear solution was added in portions finely ground KI (16.4 g, 100 mmol). An exothermic reaction took place with the evolution of iodine vapor and the formation of a dark solution. 1,2,3,5-tetrafluorobenzene (14) (5 g, 33 mmol) was added dropwise and the reaction mixture was heated at 70 °C for 4 h. Upon cooling, the solution was poured carefully onto crushed ice (200 g) and filtered to remove excess iodine. The filtrate consisted of an orange aqueous layer and a heavy dark oil. Diethyl ether (200 mL) was added to dissolve the oil and the organic layer was separated, washed with 10% sodium thiosulfate solution and water, and dried over magnesium sulfate. The solvent was removed, leaving an orange oil that was further purified by passing it through a short column of silica gel, using hexanes as the eluting solvent. Removal of the solvent yielded 1,3-diiodotetrafluorobenzene (7.1 g) as a colorless liquid in 61% yield (based on 85% pure starting material from Aldrich), bp 140 °C (13 Torr): mass spectrum (EI), m/z (rel intensity) 402 (M^+, 37), 275 (72), 254 (5.4), 148 (100), 129 (9.3), 127 (54.8), 110 (6.0). Anal. Calcd for $C_6F_4I_2$: C, 17.91; I, 63.18. Found: C, 17.52; I, 63.18.

1,3-Bis((trimethylsilyl)ethynyl)tetrafluorobenzene (16) and 1,4-bis((trimethylsilyl)ethynyl)tetrafluorobenzene (12) were synthesized as described for 1,3-bis((trimethylsilyl)-ethynyl)benzene (6) above. Compound **12** was sublimed at 90 °C and 0.1 Torr; white crystals, mp 97–99 °C; IR (KBr) 2985, 2920, 2085, 1500, 1250, 990 cm^{-1}; ^{1}H NMR (80 MHz, $CDCl_3$) δ 0.28; mass spectrum (EI), m/z (rel intensity) 342 (18.2), 329 (10.1), 328 (26.4), 327 (100), 156 (9.0). Anal. Calcd for $C_{16}H_{18}F_4Si_2$: C, 56.14; H, 5.26. Found: C, 56.11; H, 5.36. Compound **16** was purified by chromatography with hexanes on silica. It formed white needles in 92% yield, mp 55–57 °C: IR (KBr), 2980, 2920, 2080, 1505, 1260, 990, 850 cm^{-1}; ^{1}H NMR (80 MHz, $CDCl_3$) δ 0.28 (s); mass spectrum (EI), m/z (rel intensity) 342 (M^+, 22.4), 327 (100), 156 (10.7). Anal. Calcd for $C_{16}H_{18}F_4Si_2$: C, 56.14; H, 5.26. Found: C, 56.34; H, 5.34.

1,4-Diethynyltetrafluorobenzene (13). Removal of the TMS protecting groups was accomplished as for the synthesis of 1,3-diethynylbenzene described above. The yield of compound **13** (as white crystals after chromatography on silica with hexanes) was 95%: mp 132–134 °C (lit.[27] mp 132–133 °C); IR (KBr), 3295, 2120, 1480 cm^{-1}; ^{1}H NMR (80 MHz, $CDCl_3$) δ 3.43 (s); mass spectrum (EI), m/z (rel intensity) 198 (M^+, 100), 167 (5.5), 148 (8.6), 129 (11.0), 99 (8.4).

1,3-Diethynyltetrafluorobenzene (17): yield 91% after purification by vacuum distillation at 55 °C and 1.0 Torr; IR (film on NaCl) 3300, 2130, 1480 cm^{-1}; ^{1}H NMR (80 MHz, $CDCl_3$) δ 3.50 (s). Anal. Calcd for $C_{10}H_2F_4$: C, 60.60; H, 1.01. Found: C, 60.68; H, 0.94.

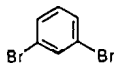
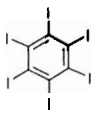
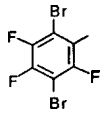
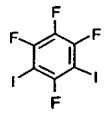
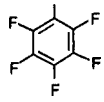
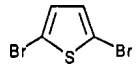
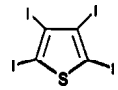
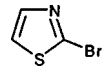
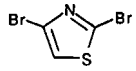
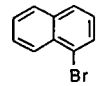
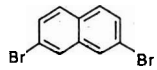
((Trimethylsilyl)ethynyl)pentafluorobenzene (19) was prepared by treatment of pentafluorobromobenzene (18) with 1.1

(38) It appears that any combination of reagents that generates a bis(triphenylphosphine)palladium(0) complex in solution works equally well as the catalytic species. We have used palladium(II) chloride plus 2 equiv of triphenylphosphine, bis(benzonitrile)palladium(II) chloride plus 2 equiv of triphenylphosphine, or bis(triphenylphosphine)palladium(0) dichloride. The choice of copper reagent is also flexible. The original reports describe the use of copper iodide. Economy and coworkers, however, report that the use of copper(II) acetate hydrate lessens the amount of colloidal palladium formed.[7] We have found this variation to be useful.

(39) White, D. M.; Levy, G. C. *Macromolecules* **1972**, *5*, 526–531.

(40) Deluchat, M. *C.R. Hebd. Seances Acad. Sci.* **1931**, *192*, 1387–1389.

Table I. Preparation of TMS-Protected and Deprotected Polyethynyl Aromatics

aryl halide	equiv TMSA	conditions	reactn time (h)	protected	yield,[b] %	deprotected[e]	yield, %
 **5**	2.2	A[a]	3	6	89	1	90
 **8**	14	B[a]	27	9 10	1 14		
 **11**[c]	2.2	C[a]	6	12	94	13	95
 **15**[d]	2.2	C	5	16	92	17	91
 **18**[c]	1.1	A	2	19	20	20	95
 **21**	2.2	A	1	22	98	23	92
 **24**	2.0	A	13	25	84		
	6.0	A	6	26	45	27	91
 **32**	1.2	A	8	33	68	34	74
 **38**	2.2	C	9	39	20	40	62
 **41**	1.1	A	1	42	71	43	95
 **45**	2.2	A	5	46	82	47	91

[a] The following conditions were used for the substitution reactions: A. The concentrations of palladium(0) and of copper(I) were 2 mol % with respect to replaceable halogen. The solvent was diisopropylamine. The TMSA was added at 0 °C. The reaction time included 1 h of heating at reflux (84 °C) at the end of the reaction period. B. The concentrations of palladium(0) and of copper(I) were 8% with respect to the available halogen. TMSA was added at 0 °C. A mixture of diisopropylamine and piperidine (1:1) at reflux was used as the solvent. C. The concentrations of palladium(0) and of copper(I) were 2 mol % with respect to replaceable halogen. The solvent was diisopropylamine. The reaction time included 1 h at room temperature and the remainder at reflux. [b] The reported yields are isolated yields. [c] Only bromine atoms are replaced. [d] Only iodine atoms are replaced. [e] Removal of the TMS groups was carried out by stirring the protected derivatives with 1% KOH in methanol for 25 min at room temperature.

equiv of TMSA under the same conditions described for **12** and **16**: bp 97 °C (13 Torr); ^{1}H NMR (80 MHz, $CDCl_3$) δ 0.14 (s); mass spectrum (EI), m/z (rel intensity) 264 (M^+, 31.0), 249 (100). Anal. Calcd for $C_{11}H_9F_5Si$: C, 50.00; H, 3.41. Found: C, 50.22; H, 3.48.

Ethynylpentafluorobenzene (20). Basic hydrolysis of **19** yielded **20** in 95% yield: bp 129–131 °C (lit.[23] bp 50–52 °C, 37 Torr); IR (NaCl) 3310, 2135 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.55.

2,5-Bis((trimethylsilyl)ethynyl)thiophene (22). The synthesis of **22** from 2,5-dibromothiophene (**21**) was carried out as for the synthesis of 1,3-diethynylbenzene described above: yield 98%; mp 80–81 °C (lit.[29] mp 82.5–83.5 °C); ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.02 (s, 2 H), 0.17 (s, 18 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.2, 124.8, 99.9, 97.1, 0.38. Anal. Calcd for $C_{14}H_{20}SSi_2$: C, 60.80; H, 7.29; S, 11.59. Found: C, 60.23; H, 7.25; S, 11.35.

2,5-Diethynylthiophene (23) was prepared by the basic hydrolysis of **22** and purified by vacuum distillation at 40 °C and approx. 0.1 Torr: IR (NaCl) 3290, 2107 cm^{-1}; ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.09 (s, 2 H), 3.33 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$)

δ 132.6, 121.9, 81.9, 76.3. Anal. Calcd for C_8H_4S: C, 72.72; H, 3.03. Found: C, 72.52; H, 3.19.

2,5-Bis((trimethylsilyl)ethynyl)-3,4-diiodothiophene (25). To a solution of tetraiodothiophene (**24**) (0.85 g, 1.45 mmol) in diisopropylamine (50 mL) were added dichlorobis(benzonitrile)palladium(II) (27 mg, 0.07 mmol), triphenylphosphine (37 mg, 0.14 mmol), and CuI (14 mg, 0.07 mmol). The clear yellow solution was cooled in ice and the flask was flushed with argon. TMSA (0.44 mL, 3.19 mmol, 2.2 equiv) was added dropwise via a syringe. The color of the solution changed from yellow to green and finally to black with the formation of a heavy white precipitate. The solution was stirred at 0 °C for 1 h and was then allowed to warm to room temperature. After 12 h at room temperature the solution was heated at reflux for 1 h, cooled, and filtered. The solvent was removed at reduced pressure. The residue was dissolved in methylene chloride and extracted with dilute aqueous HCl and then with water. Drying the organic phase with $MgSO_4$ followed by removal of the solvent yielded the crude product as a dark brown solid. Chromatography on silica with hexanes yielded 640 mg (84%) of **25** as white needles, mp 148–150 °C: IR (KBr) 2965, 2895, 2140, 1460, 1410, 1250, 1200, 1170, 835, 760 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 0.27 (s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 126.5, 104.7, 101, 97.9, –0.3; mass spectrum (EI), m/z (rel intensity) 528 (M^+, 66.4), 513 (100), 341 (8.3), 259 (14.1), 248 (13); UV (max, log ε) (heptane) 235 (4.4), 243 (4.2), 318 (4.3), 325 (4.37), 340 (4.34) nm. Anal. Calcd for $C_{14}H_{18}I_2SSi_2$: C, 31.81; H, 3.40. Found: C, 31.36; H, 3.61.

Tetrakis((trimethylsilyl)ethynyl)thiophene (26). To a solution of **25** (2 g, 2.9 mmol) in diisopropylamine (120 mL) were added dichlorobis(benzonitrile)palladium(II) (108 mg, 0.28 mmol), triphenylphosphine (146 mg, 0.56 mmol), and CuI (54 mg, 0.28 mmol). The solution was cooled to 0 °C in an ice bath and the flask was flushed with argon. TMSA (2.64 mL, 17.4 mmol, 6 equiv) was added by syringe and the solution allowed to warm to room temperature. After being stirred for 3 h, the solution was heated at reflux until the reaction was judged to be complete by TLC (hexanes, silica). The solution was cooled and filtered to remove the heavy precipitate of diisopropylammonium iodide, and the solvent was removed at reduced pressure. The residue was dissolved in methylene chloride and washed in succession with dilute HCl and water. After drying with $MgSO_4$, the solvent was removed and the residue was chromatographed on silica gel (100 g) with hexanes. A trace of **25** was removed first from the column followed by the desired compound **26** as off-white and slightly light-sensitive crystals. The yield of **26** was 45%: mp 104–106 °C; IR (KBr) 2970, 2895, 2150, 1500, 1420, 1370, 1250, 1100, 960, 950, 840, 760 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 0.36 (s, 18 H), 0.28 (s, 18 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 129.3, 125.7, 104.8, 101.4, 97.2, 95.8, –0.05, –0.2; mass spectrum (EI), m/z (rel intensity) 468 (39.2), 415 (7.2), 396 (7.9), 374 (14.2), 351 (23.7), 297 (14.0), 272 (8.0), 73 (100); UV max (log ε) 260 (4.46), 273 (4.55), 285 (4.58), 328 (4.06), 345 (4.02) nm. Anal. Calcd for $C_{24}H_{36}SSi_4$: C, 61.53; H, 7.69. Found: C, 61.41; H, 7.83.

Tetraethynylthiophene (27). To a suspension of **26** (1 g, 2.13 mmol) in deoxygenated methanol (50 mL) was added 1.0 mL of 0.1 M aqueous KOH. The mixture was stirred at room temperature under an atmosphere of argon for 25 min, gradually forming a clear solution. The solution was diluted with water (100 mL) and extracted with *n*-pentane (3 × 50 mL). The combined organic fractions were dried over $MgSO_4$ and the solvent was removed at reduced pressure to yield **27** as an unstable white solid which darkened upon standing. The yield of isolated **27** was 91%: ^1H NMR (80 MHz, $CDCl_3$) δ 3.61 (s, 2 H), 3.45 (s, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 130.1, 128.9, 128.2, 125.9, 86.6, 83.8; mass spectrum (EI), m/z (rel intensity) 180 (M^+, 100); UV max (log ε) 245 (4.2), 254 (4.23), 264 (4.11), 308 (3.93) nm.

2,5-Bis((trimethylsilyl)ethynyl)-3,4-bis(3-hydroxy-3-methyl-1-butynyl)thiophene (28). To a solution of **25** (5 g, 9.4 mmol) in diisopropylamine (150 mL) were added dichlorobis(benzonitrile)palladium (36 mg, 0.09 mmol), triphenylphosphine (47 mg, 0.18 mmol), and CuI (18 mg, 0.09 mmol). The solution was degassed with a stream of argon and 2-methyl-3-butyn-2-ol (2.3 g, 28 mmol, 3 equiv) was added dropwise at room temperature. The solution was heated at reflux for 4 h, and the disappearance of starting material was followed by TLC. After the reaction was complete, the solution was cooled and filtered to remove salts. The solvent was removed at reduced pressure and the residue dissolved in the minimum amount (~15 mL) of 10% THF/methylene chloride. This solution was applied to a column of neutral alumina (Brockman Activity I 180–200 mesh) packed in methylene chloride. The column was eluted first with methylene chloride to remove traces of starting material and then the product was removed from the column by eluting with 10% THF/methylene chloride. Compound **28** was recovered as colorless cubic crystals that darkened upon standing. The yield was 3.59 g (86%). An analytical sample was obtained as white crystals by recrystallization from methanol/benzene (1:1): mp 153–155 °C; IR (KBr) 3320, 2950, 2120, 1365, 1242, 1205, 1155, 1060, 935, 835 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 2.17 (br, 2 H, OH), 1.61 (s, 12 H, CH_3), 0.25 (s, 18 H, TMS); mass spectrum (EI), m/z (rel intensity) 441 (35.1), 440.14 (100), 407.1 (42.3), 73 (92). Anal. Calcd for $C_{24}H_{32}O_2SSi_2$: C, 65.45; H, 7.27. Found: C, 65.55; H, 7.36.

Synthesis of 2,5-Diethynyl-3,4-bis(3-hydroxy-3-methyl-1-butynyl)thiophene (29). To a solution of **28** (1.62 g, 3.7 mmol) in degassed methanol (80 mL) was added KOH (2 mg, 0.037 mmol) in 1 mL of water. The solution was stirred at room temperature for 25 min. The solvent was removed at reduced pressure, and the residue was taken up in 100 mL of diethyl ether, washed with water, and dried with magnesium sulfate. The ether was removed to yield compound **29** in quantitative yield. The compound could be further purified by rapid chromatography on neutral alumina using 10% THF in methylene chloride as the eluting solvent. The purified compound was obtained as pale yellow crystals: ^1H NMR (80 MHz, $CDCl_3$) δ 3.55 (s, 2 H, ethynyl), 1.60 (s, 12 H, CH_3), OH proton not observed; mass spectrum (EI), m/z (rel intensity) 264 (M^+, 100), 231 (43.7). Anal. Calcd for $C_{18}H_{16}O_2S$: C, 72.97; H, 5.40. Found: C, 73.08; H, 5.63.

2,5-Bis(4-(2-thienyl)butadiynyl)-3,4-bis(3-hydroxy-3-methyl-1-butynyl)thiophene (30). A solution was prepared of CuCl (100 mg, 10 mmol) and TMEDA (0.2 mL) in reagent-grade acetone. A steady stream of oxygen was bubbled through the solution for 10 min. A mixture of **29** (0.3 g, 1 mmol) and 2-ethynylthiophene[27] (0.87 g, 8 mmol) in acetone (3 mL) was added and the reaction was allowed to proceed for 4 h, while a steady stream of dioxygen was bubbled through it. The solution was filtered and the solvent removed under reduced pressure. The residue was dissolved in methylene chloride and applied to a silica gel column packed in methylene chloride. Elution with methylene chloride removed first 1,4-bis(2-thienyl)butadiyne as a pale yellow band. Changing the solvent to 5% THF in methylene chloride removed the desired compound **30** as a orange oil that solidified upon standing: yield 0.20 g (40%); IR (KBr) 3400, 3020, 2020, 1240, 1160, 850 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 7.39–7.05 (m, 6 H), 2.15 (s, 2 H), 1.64 (s, 12 H); mass spectrum (EI), m/z (rel intensity) 508 (65.4), 484 (12.2), 450 (6.0), 368 (13.3), 296 (100), 129 (13.6). Anal. Calcd for $C_{30}H_{20}O_2S_3$: C, 70.86; H, 3.93. Found: C, 70.80; H, 3.99.

2,5-Bis(4-(2-thienyl)butadiynyl)-3,4-diethynylthiophene (31). To a sample of **30** (75 mg, 0.15 mmol) in toluene (30 mL) was added KOH (75 mg, 1.33 mmol). The reaction flask was fitted with a Dean–Stark trap and heating was begun. A mixture of toluene and acetone was removed by distillation and the toluene was replaced by degassed toluene when necessary. After 2 h, heating was discontinued and the organic solution was extracted with water and dried with magnesium sulfate and the toluene removed. The bright yellow product was chromatographed on silica gel with methylene chloride as the solvent to yield **31** as light-sensitive yellow crystals. The yield was 38 mg (62%): IR (KBr) 3300, 2950, 2120, 1050, 870 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 7.41–7.00 (m, 6 H), 3.52 (s, 2 H); mass spectrum (EI), m/z (rel intensity) 392 (M^+, 36.2), 277 (64.2), 169 (100), 147 (29.1), 69 (45.6). Anal. Calcd for $C_{24}H_8S_3$: C, 73.66; H, 2.04. Found: C, 73.52; H, 1.73.

2-Iodothiazole[41] (36). To a mixture of concentrated H_2SO_4 (20 mL) and water (50 mL) cooled to –5 °C was added 2-aminothiazole (**35**) (10 g, 0.1 mol). To the dark red solution was added $NaNO_2$ (7.3 g, 0.1 mol) (dissolved in the minimum amount of chilled water) dropwise over a period of 1 h. The rate of

(41) For alternative syntheses of 2-iodothiazole, see: Iversen, P. E. *Acta Chem. Scand.* **1968**, *22*, 1690–1692. Vincent, E. J.; Phan Tan Luu, R.; Metzger, J.; Surzur, J. M. *Bull. Soc. Chim. Fr.* **1966**, *11*, 3524–3530.

addition was such that the temperature did not rise above −2 °C. The solution was stirred for 1 h. A solution of KI (20 g, 0.12 mol) in water (50 mL) was added and the solution was allowed to stir for 1 h at 0 °C, for 3 h at room temperature, and finally at 70 °C for 30 min. The dark solution was filtered. To the filtrate was added enough dilute sodium bicarbonate to make the solution basic. The solution was extracted with diethyl ether (three 200-mL portions), and the organic layers were combined, washed with water, and dried over $MgSO_4$. The solvent was removed to yield the crude product as a dark oil. The material was purified by distillation at reduced pressure (bp 117 °C at 40 Torr): yield 8.4 g (40%); IR (film on NaCl), 3100 (s), 2720 (m), 1600 (w), 1570 (s), 1360 (s), 1290 (s), 1260 (w), 1140 (m), 1040 (s), 965 (s), 860 (m), 620 (s) cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 7.60 (d, J_{HH} = 3.5 Hz, 1 H), 7.32 (d, J_{HH} = 3.5 Hz, 1 H); mass spectrum (EI), m/z (rel intensity) 211 (M^+, 100), 127 (48.7), 84 (3.3), 83 (5.2), 59 (3.1), 58 (58.3), 57 (21.5).

2-((Trimethylsilyl)ethynyl)thiazole (33). To a solution of freshly distilled 2-bromothiazole (5 g, 30 mmol) were added dichlorobis(benzonitrile)palladium (1.05 g, 1.5 mmol), triphenylphosphine (1.89 g, 3.0 mmol), and copper(II) acetate hydrate (0.3 g, 1.5 mmol). The solution was degassed by means of a rapid stream of argon and to the solution was added TMSA (3.9 g, 1.2 equiv). The solution was heated gently (45 °C) and heating was continued until TLC analysis (silica) indicated that the reaction had gone to completion. The solution was filtered to remove the heavy precipitate of diisopropylamine hydrobromide and the solvent was removed at reduced pressure. The residue was chromatographed on silica gel by using methylene chloride as the eluting solvent. A dark band of an unidentified tarry byproduct was removed first from the column followed by the desired product as a yellow oil. A total of 3.8 g (68%) was recovered. The material darkens if allowed to sit in air for any period of time. **33**: IR (NaCl) 2950, 2220, cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 7.75 (d, J_{HH} = 3.2 Hz, 1 H), 7.32 (d, J_{HH} = 3.2 Hz, 1 H), 0.27 (s, 9 H); mass spectrum (EI), m/z (rel intensity) 181 (34.6), 166 (100), 151 (5.1), 108 (6.4), 75.1 (17.9), 58 (18.3). Anal. Calcd for $C_8H_{11}NSSi$: C, 53.04; H, 5.52. Found: C, 53.34; H, 5.66.

2,4-Bis((trimethylsilyl)ethynyl)thiazole (39) was prepared from the corresponding 2,4-dibromothiazole and isolated in 20% yield as a dark oil after chromatography with methylene chloride on neutral alumina. The yield was 20%: IR (KBr) 3050, 2950, 2230, 1500, 1240, 1050, 970, 840 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 7.4 (s, 1 H), 0.28 (s, 18 H); mass spectrum (EI), m/z (rel intensity) 277 (M^+, 32.8), 262 (100), 207 (24.8), 139 (12.8), 127 (14.8), 73.1 (9.8). Anal. Calcd for $C_{13}H_{19}NSSi_2$: C, 61.01; H, 6.86. Found: C, 61.34; H, 6.94.

2-Ethynylthiazole (34). Deprotection of the TMS derivatives of the thiazole series was carried out as for the corresponding thiophenes. The deprotected thiazoles are considerably less stable than their thiophene analogues, turning dark even when stored at low temperatures. Compound **34** was a colorless oil that discolored upon standing: IR (film on NaCl) 3290 (s), 3100 (w), 2100 (w), 1470 (s), 1385 (m), 1315 (w), 1180 (m), 1100 (vs), 1050 (m), 875 (w) cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 7.9 (d, J_{HH} = 2.0 Hz, 1 H), 7.35 (d, J_{HH} = 3.0 Hz, 1 H), 3.45 (s, 1 H); mass spectrum (EI), m/z (rel intensity) 109 (M^+, 44.9), 82 (15.5), 69 (44.7), 58 (26.7).

2,4-Diethynylthiazole (40) was prepared from **39** as a colorless oil using a similar procedure: ^1H NMR (80 MHz, $CDCl_3$) δ 7.4 (s, 1 H), 3.55 (s, 1 H), 3.49 (s, 1 H); mass spectrum (EI), m/z (rel intensity) 133 (M^+, 100), 108 (34), 94 (45.5), 53 (23.8). This compound was too sensitive to be submitted for elemental analysis.

2,7-Dibromonaphthalene (45). A 1000-mL round-bottomed flask was charged with triphenylphosphine (144 g, 0.55 mol) and 200 mL of dry acetonitrile. The suspension was cooled to 0 °C and to this mixture was added bromine (88 g, 28.2 mL, 0.55 mol) dropwise such that the temperature remained below 5 °C. A heavy white precipitate was formed (an overhead stirrer was necessary at this point to ensure efficient mixing). To this mixture was added dropwise 2,7-dihydroxynaphthalene (**44**) (40 g, 0.25 mol) as a solution in acetonitrile (200 mL). The precipitate became even thicker and stirring was maintained only with difficulty. The mixture was heated to 70 °C at which point the precipitate dissolved and heating was continued for 30 min. The flask was fitted with an air-cooled distillation head and the acetonitrile was removed at atmospheric pressure. The temperature was then gradually raised to 250 °C. Evolution of HBr appeared to begin at about 190 °C and the HBr was trapped by means of a beaker filled with cold NaOH solution. The temperature was maintained at 250 °C for 50 min, and the dark oil was allowed to cool to approximately 100 °C, at which point it was poured into a flask containing 500 mL of absolute ethanol. The flask was stoppered and allowed to sit overnight. A dark crystalline mass of crude 2,7-dibromonaphthalene (**45**) was formed (scratching of the inside of the flask was necessary to induce crystallization). The product was isolated by filtration and washed with small amounts of cold ethanol. Final purification was achieved by recrystallization from ethanol: yield 62%, mp 140–142 °C (lit.[37] mp 140–141 °C).

1-((Trimethylsilyl)ethynyl)naphthalene (42) and 2,7-Bis((trimethylsilyl)ethynyl)naphthalene (46). The syntheses of these compounds were analogous to the preparation of the protected diethynylbenzene reported above. The monosubstituted product was formed at room temperature from 1-bromonaphthalene (**41**), while the disubstituted compound (prepared from 2,7-dibromonaphthalene) (**45**) required gentle heating. **1-((Trimethylsilyl)ethynyl)naphthalene (42)** was prepared in 71% yield as white needles after recrystallization from absolute ethanol: mp 41–43 °C; IR (KBr) 3060 (w), 2955 (m), 2895 (w), 2140 (vs), 1585 (s), 1505 (m), 1390 (vs), 1340 (w), 1248 (vs), 1075 (s), 1040 (m), 1010 (m), 880 (vs), 840 (vs), 800 (s), 765 (s), 730 (m), 700 (w), 640 (s) cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 8.45–8.25 (m, 1 H), 7.9–7.25 (m, 6 H), 0.39 (s, 9 H). Anal. Calcd for $C_{15}H_{16}Si$: C, 80.00; H, 7.11. Found: C, 80.05; H, 7.40. **2,7-Bis((trimethylsilyl)ethynyl)naphthalene (46)** was obtained in 82% yield after recrystallization from absolute ethanol: mp 133–134.5 °C; IR (KBr) 3050 (w), 2950 (s), 2890 (w), 2145 (vs), 1575 (s), 1390 (s), 1250 (vs), 1070 (m), 1040 (w), 1030 (w), 830 (vs) cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 8.10–7.50 (m, 6 H), 0.31 (s, 18 H). Anal. Calcd for $C_{20}H_{24}Si_2$: C, 75.00; H, 7.50. Found: C, 74.77; H, 7.57.

1-Ethynylnaphthalene (43). Deprotections of the naphthalene derivatives were carried out as described for 1,3-diethynylbenzene. Compound **43** was obtained as a colorless oil in 95% yield: IR (film on NaCl) 3295 (vs), 3050 (s), 2090 (vw), 1590 (m), 1500 (m), 1390 (m), 1200 (s), 1020 (m), 790 (s), 770 (vs) cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 8.44–8.25 (m, 1 H), 7.9–7.25 (m, 6 H), 3.55 (s, 1 H). **2,7-Diethynylnaphthalene (47)** was obtained as colorless crystals from methanol in 91% yield: mp 135–137 °C; IR (KBr) 3300 (vs), 3030 (s), 2085 (w), 1590 (m), 1010 (s), 770 (br, s) cm^{-1}; ^1H NMR (80 MHz, acetone-d_6) δ 8.08–7.59 (m, 6 H), 3.73 (s, 2 H). Anal. Calcd for $C_{14}H_8$: C, 95.46; H, 4.54. Found: C, 95.68; H, 4.29.

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