

# Conjugated Macromolecules of Precise Length and Constitution. Organic Synthesis for the Construction of Nanoarchitectures

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James M. Tour received his B.S. degree in chemistry from Syracuse University (1981) and his Ph.D. from Purdue University (1986) for work on synthetic organometallic methodology and natural product synthesis carried out under the supervision of Professor E. Negishi. He served as a National Institutes of Health postdoctoral fellow, under the guidance of Professor Barry M. Trost at the University of Wisconsin–Madison and Stanford University, developing new transition metal catalyst systems for organic transformations. He then joined the faculty at the University of South Carolina in 1988, Department of Chemistry and Biochemistry, where he is presently a Professor. His current research involves the synthesis of new well-defined conjugated oligomers and polymers for electronic, photonic, and high-performance materials applications. He is also involved in the development of fullerene chemistry and new halogen-free flame-retarding polymer additives.

## I. Introduction

### A. Coverage

Outlined here are recent synthetic approaches to conjugated step growth<sup>1</sup> oligomers and polymers that possess precisely controlled lengths and molecular constitutions. The current and potential applications of these new compounds are briefly presented. Coverage of the titled topic is illustrative of current work in the field, and it is not intended to be comprehensive. Extended structures prepared by Langmuir Blodgett or self-assembly techniques, usually resulting in noncovalently linked arrays, will not be discussed.<sup>2</sup> Note that the point at which one refers to a homologous series as an oligomer as opposed to a polymer has been controversial. In fact, different authors have designated values of 20 monomer units, 1000, 6000, or 10 000 Da, as the oligomer/polymer distinction point.<sup>3</sup> The reasons for such demarcations are synthesis or property related, and no definitive segregation points will be inferred in this coverage of the topic.

### B. Historical Perspective

Over the past several decades, few synthetic organic chemists showed interest in polymer synthesis.

Polymers were those undesirable byproducts that coated the bottom of reaction flasks or remained adsorbed to the top of silica gel purification columns. University chemistry programs in the United States were often devoid of courses relating to polymer synthesis, characterization, physical properties, and processing. At the undergraduate level, instructors often omitted the sparse organic chemistry text coverage on polymers in view of both the time constraints placed upon such courses, and the lack of instructor interest. The academic instruction of polymer science was left to a few select polymer programs around the country. For the most part, a polarization had occurred between the mainstream synthetic organic chemistry and polymer chemistry communities. This is disconcerting when we realize that the polymer industry has been a heavy recruiter of graduates in organic chemistry and that synthetic polymers permeate our daily lives. Educating the organic chemist with the basic tools of the polymer trade, a formidable task if done properly, was left to the industry and the individual scientist. This separation between modern synthetic organic chemistry and polymer chemistry also caused a lack of information transfer of new synthetic methodology,

which exploded during the past two decades, to infuse those teaching polymer chemistry. Thus polymer chemists often used only classical reactions for both monomer and polymer preparations.

What was the cause of this separation between mainstream organic chemistry and polymer chemistry? One reason may be that as synthetic procedures became more exacting for the synthesis of naturally occurring compounds of medicinal interest, synthetic chemists viewed the commonly obtained statistical distributions of polymers as less precise, therefore outside their realm of study. Recently, however, there has been a revival of interest in the construction of well-defined macromolecules.<sup>4-6</sup> As a result, modern synthetic chemistry has been finding widespread utility for the construction of these classes of compounds. Not only have new synthetic methods been used for synthesizing these macromolecular targets, but convergent and rapid growth methodologies have been utilized for the construction of these materials. This renewed interest, bridging the disciplines of both synthetic organic chemistry and polymer chemistry, is most welcomed.

### C. Why Synthesize Precisely Defined Oligomers and Polymers?

Due to the statistical nature of polymerization processes, most synthetic reactions that afford polymeric compounds generate polydisperse materials, namely, mixtures of polymer chains of varying molecular weights.<sup>1</sup> Such heterogeneity is often of little consequence when the polymer is used for a bulk application. Prior to the high polymer limit, such heterogeneity can even be beneficial since it can serve to retard crystallization. Then why study precisely defined systems? First, such oligomers and polymers serve as excellent models for their corresponding polydisperse macromolecular analogs.<sup>5,6</sup> These precise models often provide specific information concerning the solution, electronic, photonic, thermal, and morphological properties of their higher homologs. They also serve as useful models for interpreting structural and conformational properties of a polymer. When does an oligomer begin responding like a polymer for a specific function? For example, at what degree of polymerization does a conjugated polymer start responding like a conducting polymer? By building a series of oligomers and determining their linear optical ( $\lambda_{\text{max}}$  and band gap) or nonlinear optical response trends, can we assess the required minimum degree of polymerization needed to attain a desired optical response from a polymer? Can we learn about polymer conformations in solution by studying the responses of a family of well-defined, spectroscopically simple, smaller structures? Is there detailed X-ray structural data of well-defined oligomeric systems that can be used to predict morphological patterns of bulk polymeric materials? The answer to these questions, and far more, can indeed come from analysis of precisely defined oligomers and polymers. Therefore, exact data can be obtained that relates chain length and conformation to physical, electronic, and optical phenomena.

The detailed characterization of precisely defined materials is often far easier than characterization of

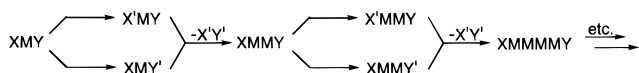
the polydisperse homologs. NMR spectroscopic details are more easily resolved than with randomly distributed polymer samples; however, even on the well-defined systems, the ability to make an exact assignment becomes increasingly difficult with larger structures. With the advances in matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS), molecular ions of synthetic polymers up to the 200 000 Da range can be obtained.<sup>7</sup> This data has proved invaluable for the characterization of large well-defined structures.

In addition to these well-defined systems serving as models for higher homologs, there exists distinct advantages to utilizing precisely controlled length, size, and shaped compounds. Inhomogeneities can be detrimental in applications where the individual polymer chains are used for molecular functions, for example, in catalysis (including enzymatic catalysis), host-guest interactions, and related molecular recognition processes. Future nanoelectronic or nanophotonic processes will likely require monodisperse materials. Also, the design of large-pocketed organic crystals will likely require the construction of large monodisperse frameworks. Therefore, specific objectives are arising for many specialty oligomer and polymer syntheses, namely, precise control of molecular weight, composition, sequence, and stereochemistry. Additionally, one would like to construct macromolecular architectures rapidly and efficiently with the ability to use a wide variety of monomer substrates. Thus, versatility and efficiency in macromolecular construction are also key components to be considered. Consequently, these precisely controlled length compounds are of great significance in their own right and their utility is on the increase.

### D. General Methods of Preparation

Although the specific systems covered in the review will be conjugated molecules, the general methods of preparation described in this section are applicable to the synthesis of either conjugated or nonconjugated systems. The major obstacle in studying precisely defined oligomers and polymers lies in the difficulty of their isolation in pure form. Early work often focused on fractionation methods for obtaining oligomers or small polymers. One would start with a difunctional monomer and carry out standard polymerization reactions; however, the reaction times were shortened and the reaction temperatures were lowered to maximize the formation of the lower molecular weight species. The yield of a desired product was often low while separation methods usually proved to be inadequate for the preparative fractionations required. Similarly, one could start with polymeric materials and carry out a degradation process to generate oligomeric compounds. As before, the inadequacy of the requisite fractionation processes can inhibit the utility of this approach.

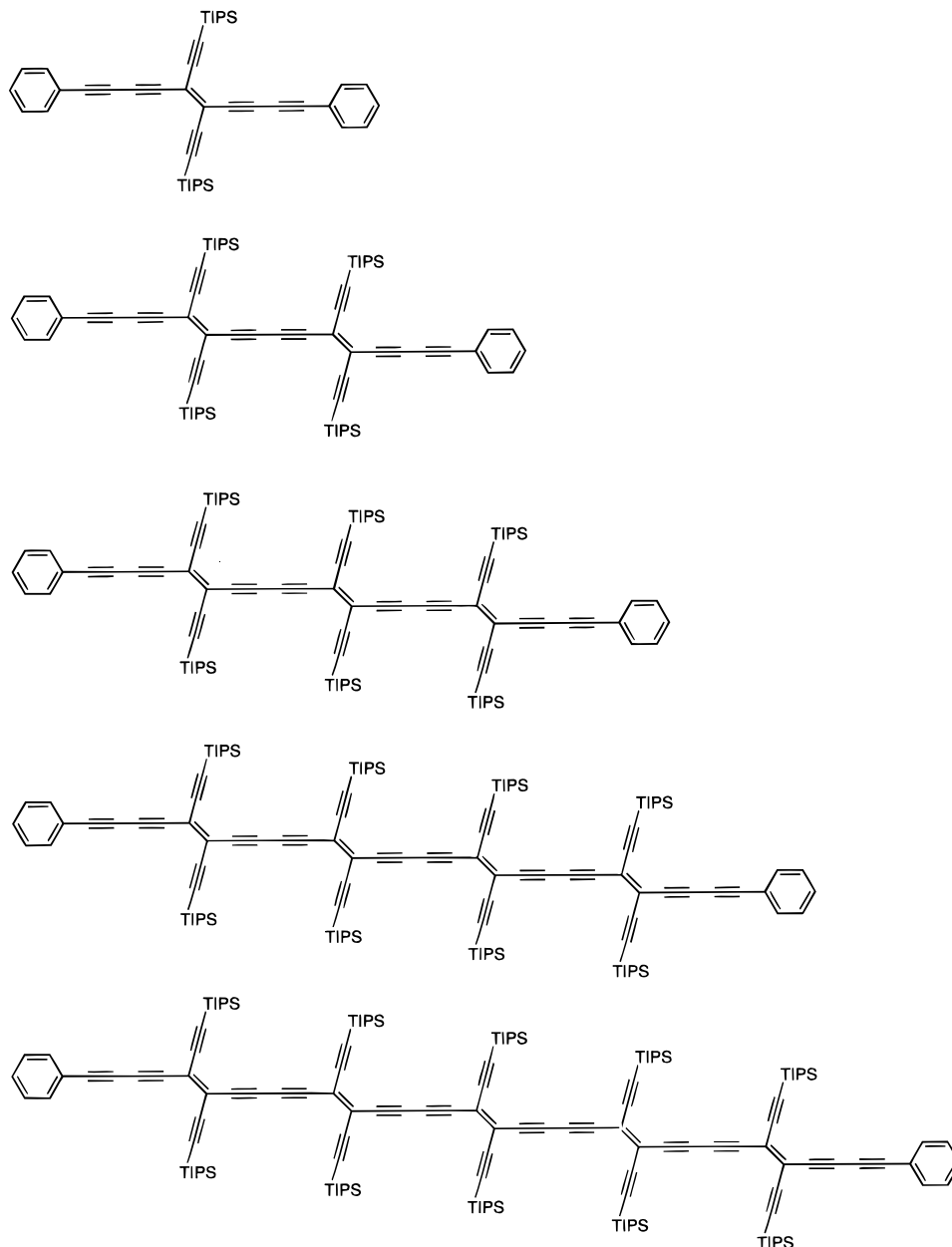
More recently, modern synthetic organic and organometallic methodologies are proving to be extremely powerful for the direct acquisition of the desired compounds by stepwise approaches. The stepwise approaches can take several forms. A



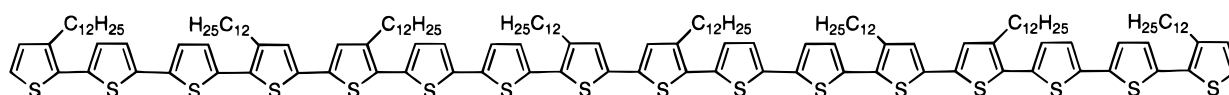
**Figure 1.** Scheme showing the iterative divergent/convergent approach to molecular length doubling.

monofunctional monomer can be added, successively, to the end of a growing chain. After the addition of each monomer unit, the material is usually purified, the new end refunctionalized, and another monomer unit attached to the end of the chain. An analogous segmented synthetic procedure can be utilized where oligomers of known length are added to the end or ends of a chain with the same purification and end group refunctionalization being needed after each

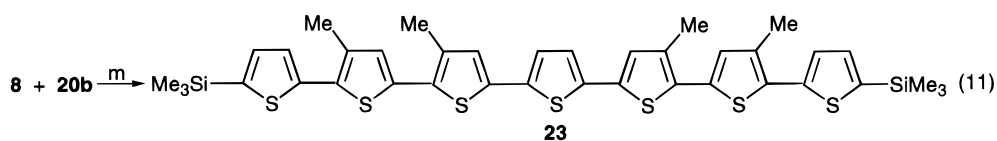
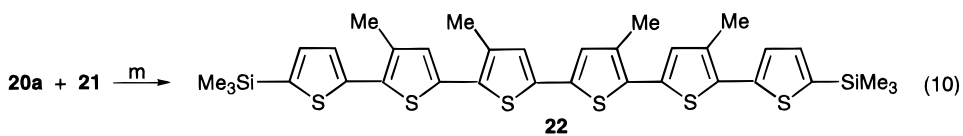
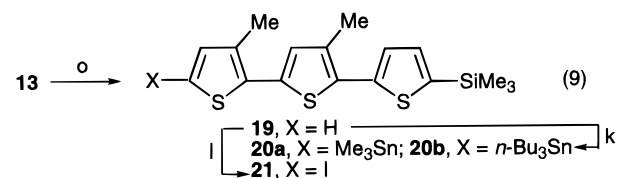
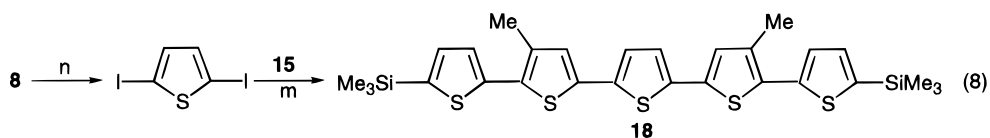
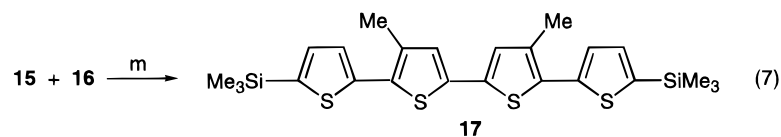
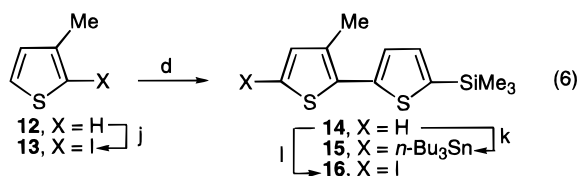
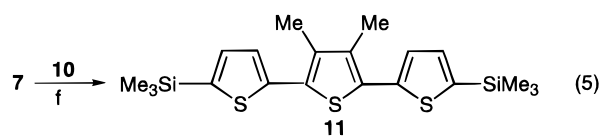
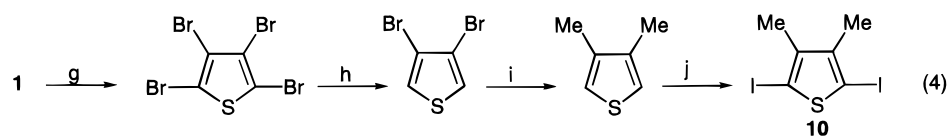
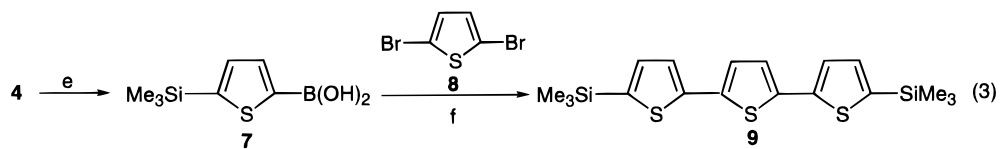
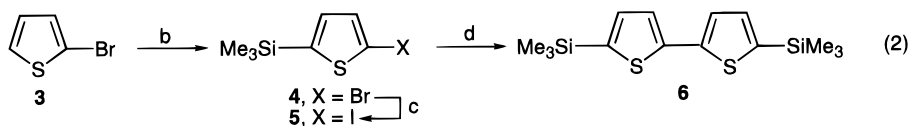
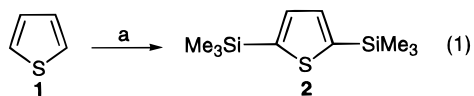
step.<sup>5,6</sup> In this segmented procedure, rather than having only one unit growth per iteration, the oligomeric chain can grow by several monomer units per iteration. Purifications can also be simpler here since the differences in size between the reacted segments and the unreacted segments are often several monomer units in length. Even with this approach, however, there reaches a point where the differences in the polymeric homologs are not sufficient to permit facile separation from each other. Moreover, low solubility of the larger intermediates is often a problem. As expected, the solubility problem often manifests itself at very early stages during the preparation of the rigid conjugated macromolecules.

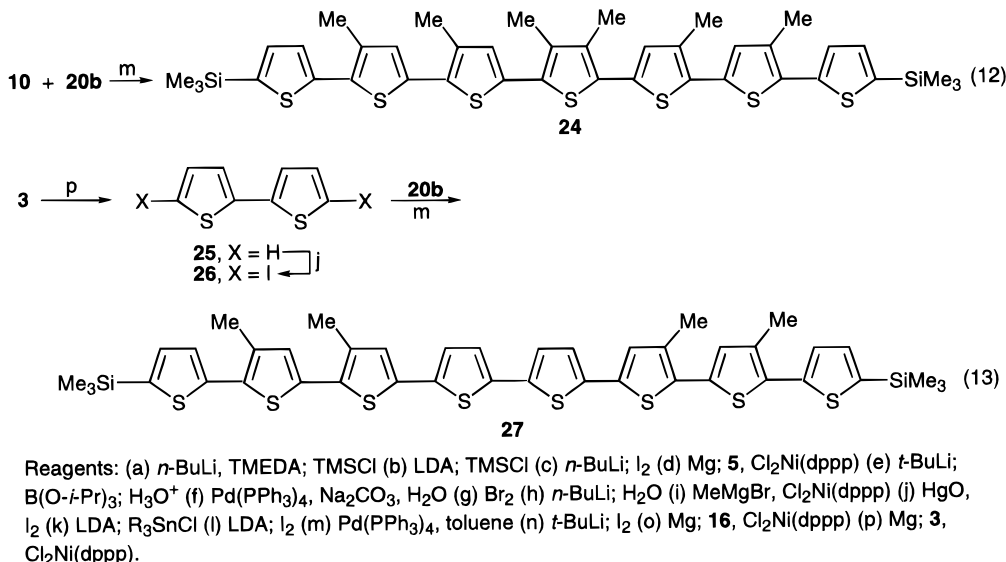


**Figure 2.** A family of chromatographically separable polytriacetylenes prepared using Cu-promoted oxidative couplings of alkynes.

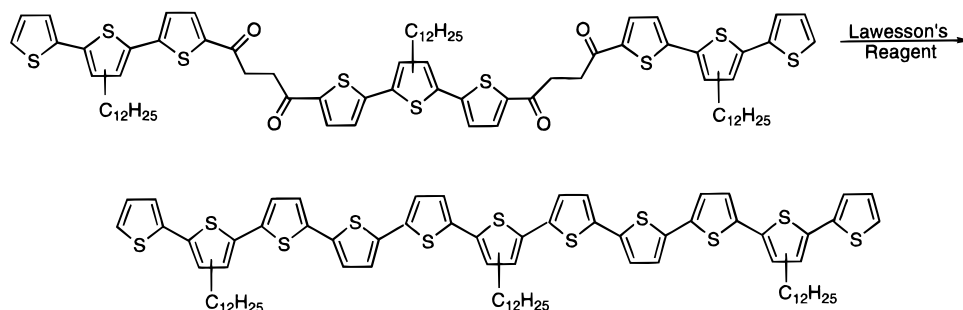


**Figure 3.** The longest homogeneous oligothiophene that has been obtained by a random coupling of oligomers followed by repeated chromatographic separations.





**Figure 4.** Modern synthetic organometallic coupling reactions used to synthesize families of homogeneous, soluble, substituted  $\alpha$ -oligothiophenes.

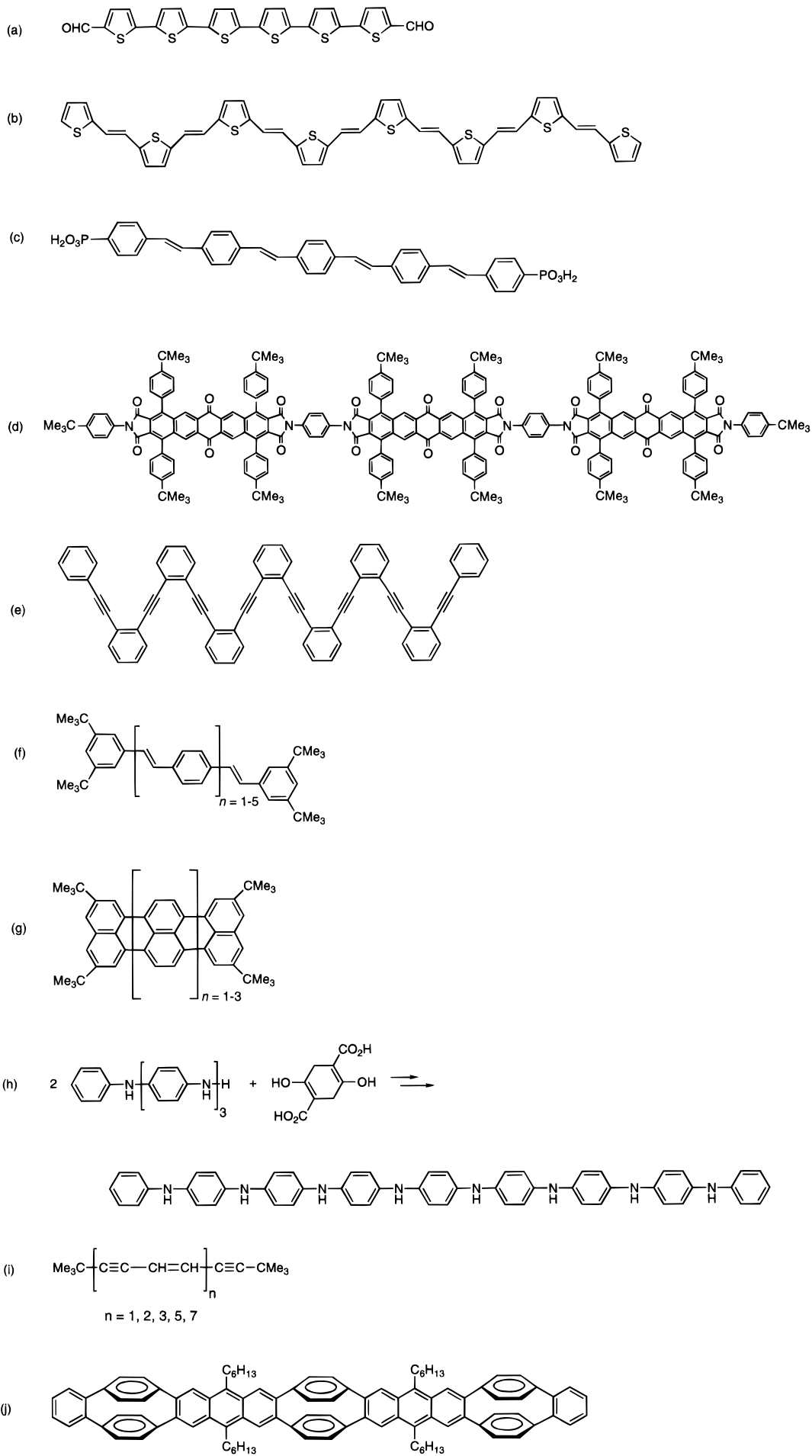


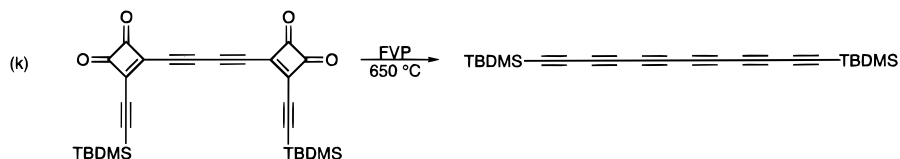
**Figure 5.** An  $\alpha$ -oligothiophene of precisely controlled length that has been synthesized utilizing Lawesson's reagent for the thiophene ring formations.

An extrapolation of this stepwise approach has been in the development of solid-phase support-based oligomer synthesis, a method pioneered by Merrifield for the preparation of oligopeptides.<sup>8</sup> In this approach, monomer units are bound, via a covalent linkage, to an insoluble polymer support such as poly(*p*-chloromethylstyrene). The free end of the polymer-supported unit is then activated and coupled to a new unit that is dissolved in a suspension of the polymer-supported material. After reactivation, new units are successively added to the ends of the previous unit. Complete reaction growth emanating from all oligomeric chains is critical, or else some of the growing chains will be shorter than the others. One of the major advantages of this solid-phase supported method is that vast excesses of monomeric reagents can be added to help insure that nearly all chain ends properly activate and affix a new unit. The excess reagents are easily removed by filtration and washing of the solid phase. The solid-phase method can easily be applied to a continuous flow system with automation. Although solid-phase synthesis has been applied to conjugated macromolecule synthesis, automation has not yet been demonstrated for these classes of compounds. Another method to insure that nearly all growing chains will have the same length and sequence is to use a second reagent as a capping agent that will irreversibly block the end of the chains that did not affix the new end group. In this way, one will not continue to grow off a chain end that is deficient in chain length. This is useful since,

ultimately, it is far easier to separate two compounds of large size differences. For example, a tetramer is easily separated from an 18-mer while a 17-mer can be very difficult to separate from an 18-mer. Once the desired oligomeric sequence has been synthesized, the chains are cleaved from the support by some chemical or photochemical method to afford the desired, near uniform oligomers. If possible, purification at this point is needed to remove the irreversibly blocked shorter chains. Segmental growth has also been applied to solid-phase synthetic methods.

Another rapid approach involves the use of an iterative divergent/convergent approach (Figure 1).<sup>9</sup> A monomer *M*, with inactive end groups *X* and *Y*, is divided into two portions. In one portion, the end group *X* is activated by conversion to *X'*. In the second portion, *Y* is activated by conversion to *Y'*. The two portions are then brought back together to form the dimer *XMMY* with loss of *X'Y'*. Since the same end groups that were present in the monomer are now present in the dimer, the procedure can be repeated with a doubling of molecular length at each iteration. The advantages of this approach are that the molecular length grows very rapidly and incomplete reactions yield unreacted material that is half the size of the desired material. Hence, purification at each step is far simpler since separation involves, for example, an octamer from a 16-mer. This iterative divergent/convergent approach is, therefore, particularly attractive, and it has been adapted to use with solid phase synthesis.<sup>10</sup>





**Figure 6.** (a) An  $\alpha$ -oligothiophene that possesses aldehydic termini to serve as a functional oligomer in further polymerization processes. (b) An oligo(thiophene vinylene) of precise length that has been prepared using controlled Wittig–Horner coupling reactions and low-valent titanium coupling reagents. (c) An oligo(phenylene vinylene) with heterofunctional end caps for use in the synthesis of multilayer structures. (d) A linear semiladder rigid rod molecule prepared by stepwise repetitive Diels–Alder reactions. (e) Oligo(*o*-phenylene ethynylene)s prepared by Pd/Cu-mediated couplings of aryl iodides and terminal alkynes. (f) A family of precisely controlled oligo(arylene vinylene)s. (g) A family of precisely controlled oligorylenes. (h) Synthesis of phenyl-copper octaaniline. (i) End-capped oligo(ene-yne)s for optical studies related to polydiacetylenes. (j) Oligomeric structure of precise length with alternating orthogonal subunits that was prepared by a Diels–Alder route. (k) An extended oligomeric carbyne-like structure that was prepared using a combination of metal-promoted couplings and solution spray flash vacuum pyrolysis.

## II. Noncontrolled Synthetic Approaches to Conjugated Oligomers

Although the classical method for obtaining oligomers of discrete length involved random oligomerizations and subsequent fractionations, such processes are still being used to generate a series of linear conjugated oligomers.<sup>11,12</sup> For example, a family of chromatographically separable polytriacetylenes have been prepared using a Cu-promoted oxidative coupling of alkynes with phenylacetylene capping groups to terminate oligomer growth (Figure 2).<sup>13</sup> The authors suggest using these intermediates as models for intermediates between polyacetylene, polydiacetylene, and carbyne. Additionally, they will be evaluated for their use in nonlinear optical materials and molecular wire studies. The longest homogeneous oligothiophenes have been obtained by a random coupling of oligomers followed by repeated chromatographic separations (Figure 3).<sup>14</sup> Metathesis using Mo catalysts has been used to prepare oligo(phenylene vinylene)s to form, after ethylene extrusion, predominantly the tetramer which could be isolated by fractionation.<sup>15</sup> Thus the classical approaches for obtaining precisely defined oligomers by random synthesis and subsequent fractionation are still being utilized for obtaining conjugated oligomers.

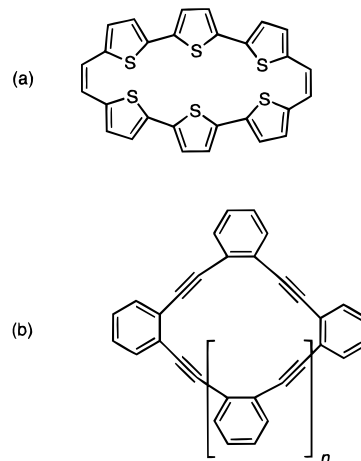
## III. Controlled Synthetic Approaches to Macromolecules

### A. Stepwise Methods

#### 1. Acyclic Systems

Controlled growth methods can be used to prepare a number of conjugated macromolecular structures. This involves the repetitive addition of monomer or longer units to a growing chain. We have used modern synthetic organometallic coupling reactions to synthesize families of homogeneous, soluble, substituted  $\alpha$ -oligothiophenes (Figure 4).<sup>16</sup> Notice that in some cases, one unit at a time is added per reaction while, in other cases, several monomer units (a segmented approach) were added in a single pot. Palladium- and nickel-catalyzed aryl–aryl coupling methods have proved to be invaluable for the synthesis of these and related conjugated oligomers.

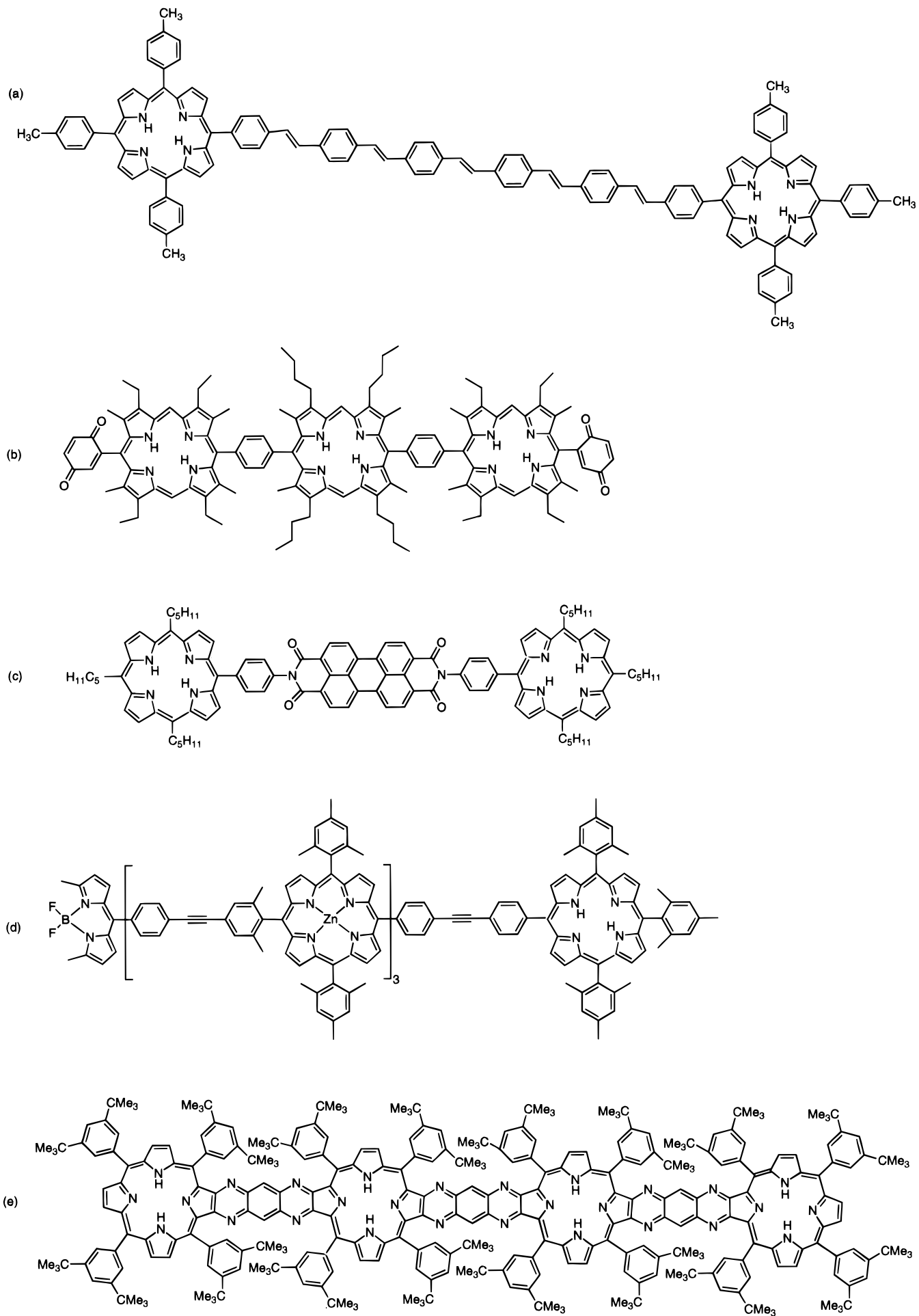
We studied the linear optical,<sup>16</sup> nonlinear optical,<sup>17</sup> and electronic properties<sup>18</sup> of the thiophene oligomers. By comparison of the UV–visible spectroscopic char-



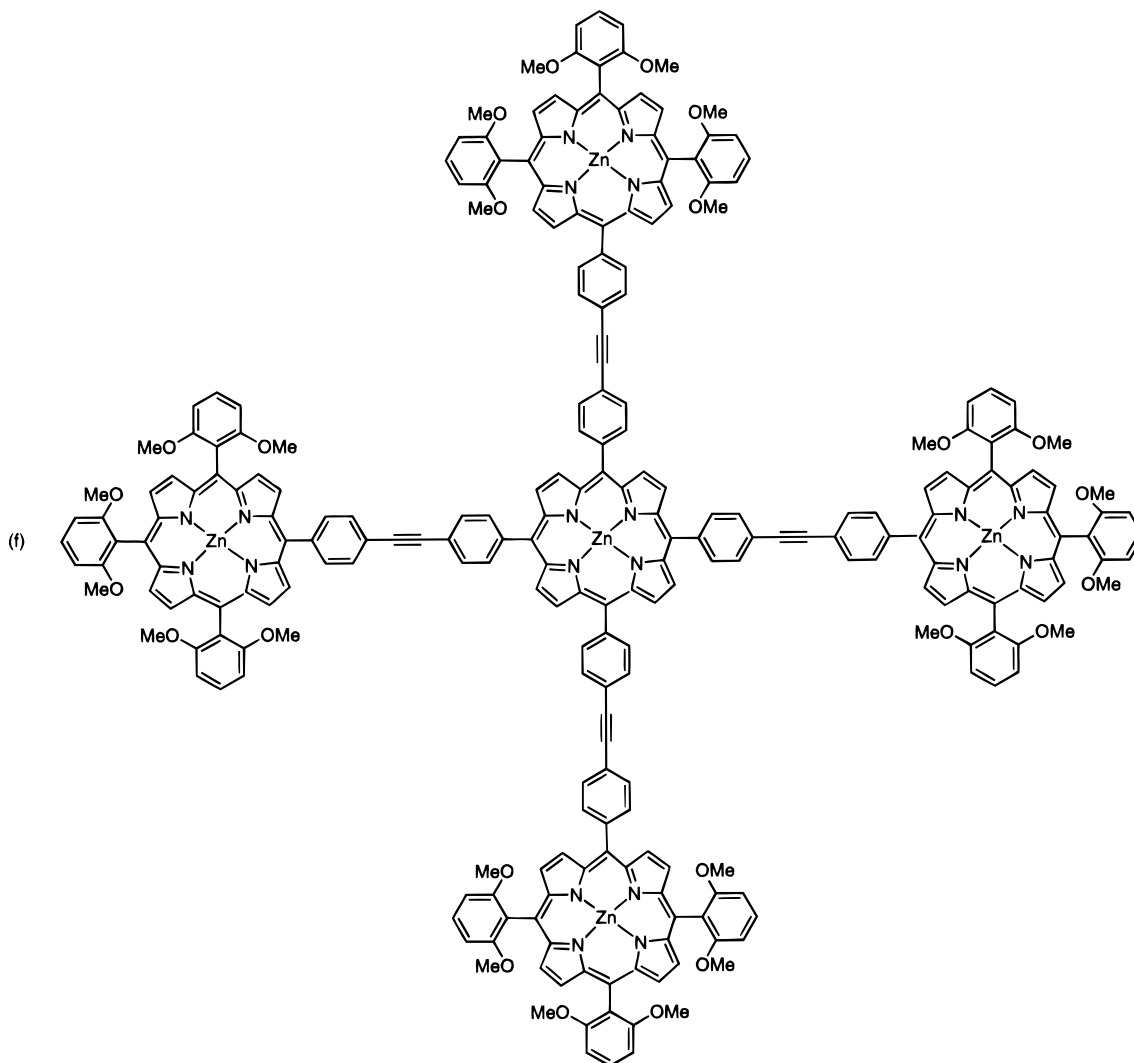
**Figure 7.** (a) Thiophene-containing annulenes prepared by the McMurray coupling of carbonyl functions and (b) a family of cyclic oligo(*o*-phenylene ethynylene)s.

acteristics of the oligomers with the spectra of the analogous polymers, it was determined that, in solution, electrochemically prepared poly(3-alkyl- $\alpha$ -thiophene) effectively has only 6–7 contiguous conjugated  $\alpha$ -thiophene units. However, in the solid state, the conjugation path in the polymer is much longer, probably due to crystalline ordering.<sup>16</sup> The third-order nonlinear optical studies, by third-harmonic generation, on the family of soluble  $\alpha$ -oligothiophenes corroborated well with the results obtained on the polymeric systems while refluxing data that had been obtained on the less soluble unsubstituted oligothiophenes.<sup>17</sup> The electronic properties of the soluble thiophenes were most informative. These soluble thiophene oligomers with three or more units can be electrooxidized stepwise at room temperature to give, sequentially, both the radical cation and dication forms. This was in contrast to the previous conclusion that conducting and conjugated polymers were expected to be oxidized in one broad single step.<sup>18</sup> Moreover, the study demonstrated that previous assignments of electronic transitions were inappropriate. Correlation of the energy of the electronic transitions of the oxidized oligomers permitted us to estimate the delocalization length of the radical cation (12 units) and the dication (10 units) in the corresponding polymer.<sup>18</sup> There have been numerous other electrical, optical, and nonlinear optical studies on precisely defined oligothiophene systems prepared by organometallic couplings.<sup>19</sup>

Analogous  $\alpha$ -oligothiophenes of precisely controlled length have been synthesized up to the 11-mer







**Figure 8.** (a) Porphyrin-terminated oligo(phenylene vinylene)s prepared by the Ramberg–Backlund reaction; (b) quinone-terminated oligoporphyrins; (c) “picosecond optical switches”; (d) “molecular photonic wires”; (e) linear tetraporphyrin-containing systems; and (f) “light harvesting arrays”.

utilizing Lawesson’s reagent for the thiophene ring formations (Figure 5).<sup>20</sup> The values of  $\lambda_{\max}$  increase along the oligomeric series, and even between the nonamer and 11-mer, the values of  $\lambda_{\max}$  continued to rise. Additionally, the doped conductivity of the 11-mer was similar to that of the doped polythiophenes, inferring that the effective conjugation length in the polymer is not much more than 11 units. However, doping-induced coupling of the oligomer was not ruled out. Others have used stepwise approaches to shorter oligothiophene-based systems that bear aldehydic termini to serve as functional oligomers, or telechelic systems, to be used in further polymerization processes (Figure 6a).<sup>21</sup>

Oligo(thiophene vinylene)s of precise length have been prepared using controlled Wittig–Horner coupling reactions and low-valent titanium coupling reagents (Figure 6b).<sup>22</sup> Oligo(phenylene vinylene)s have been prepared with various end caps. In the case where the ends were functionalized with phosphonates (Figure 6c), the compounds have been used for the synthesis of multilayer structures.<sup>23</sup> Stepwise repetitive Diels–Alder reactions have been used to prepare linear semiladder rigid rod molecules that are 75 Å long (Figure 6d).<sup>24</sup> Stepwise approaches have been used to make interesting families of oligo-

(*o*-phenylene ethynylene)s by Pd/Cu-mediated couplings of aryl iodides and terminal alkynes (Figure 6e).<sup>25</sup> Thermolysis of these compounds yielded oligo-(acene)s while the spectroscopic study of the family of compounds provided insight into the electronic conjugation length of the extended  $\pi$ -systems. Several studies on precisely controlled oligo(arylene vinylene)s (Figure 6f) and oligorylenes (Figure 6g) and related structures have been carried out to better understand the interplay between  $\pi$ -conjugation and the electronic and optical properties in polymers.<sup>26,27</sup> The extraordinary proton-doped conducting properties of polyaniline have been probed utilizing phenyl-capped octaaniline, prepared by a segmental approach, from tetraaniline and dihydroxydihydroterephthalic acid (Figure 6h).<sup>28</sup> Remarkably, upon doping, the monodisperse octaaniline exhibited the same conductivity as polyaniline. This suggests that the charge carriers on polyaniline are localized on just a few aniline units and that an intermolecular mechanism must be operating for charge transport. The nonlinear optical, chromotropic (color changing), and dichroic properties of polydiacetylenes, that is conjugated polyene structures, have been of considerable interest. A stepwise synthesis of the series of well-defined structures shown in Figure 6i permit-

ted both a direct comparison between typical nondegenerate ground state conducting polymers with a polyeneyne and an analysis of the polydiacetylene's electronic and photonic properties intrinsic to the polyeneyne backbone.<sup>29</sup> Unconventional oligomeric structures of precise length with alternating orthogonal subunits have been prepared by Diels–Alder routes (Figure 6j).<sup>30</sup> The cyclic voltammetry studies suggest unusual behavior possibly due to the unique orthogonal arrangements of the aryl units. Finally, extended oligomeric carbyne-like structures have been prepared using a combination of metal-promoted couplings and solution spray flash vacuum pyrolysis (Figure 6k).<sup>31</sup>

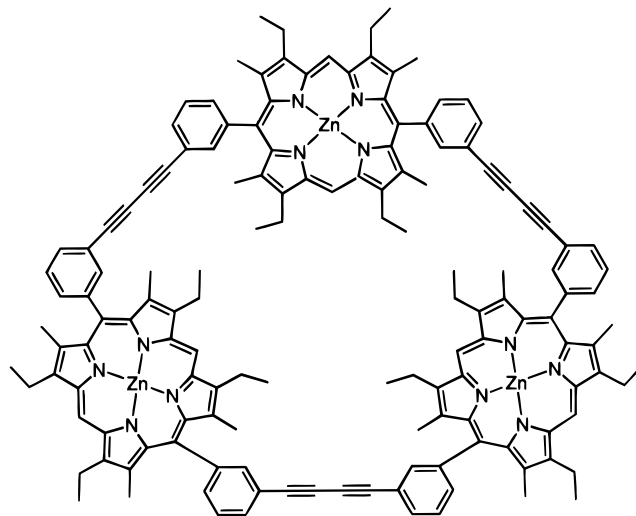
## 2. Cyclic Systems

Controlled stepwise routes to thiophene-containing annulenes have been explored for the preparation of peripherally aromatic neutral and cationic compounds. The synthetic coupling procedure utilized the McMurray coupling of carbonyl functions (Figure 7a).<sup>32</sup> Stepwise syntheses have been explored for the preparation of intermediates that were used in the synthesis of numerous cyclic oligo(*o*-phenylene ethynylene)s containing up to the 200-membered ring (C<sub>400</sub>H<sub>200</sub>) (Figure 7b).<sup>33</sup> Note that although the acyclic oligomers were prepared in a controlled fashion, the cyclization step, involving two components, was affected in a random fashion. The lower molecular weight cyclic oligomer (C<sub>80</sub>H<sub>40</sub>, *n* = 7) could be isolated by chromatographic separation while the higher oligomers (*n* = 17, 27, 37, and 47) were detected as a mixture using time of flight mass spectrometry. These cyclic systems were prepared with the intent of designing conjugated helical  $\pi$ -systems or hydrocarbon tubules.

## 3. Porphyrin-Containing Systems

In an effort to exploit electronic and photonic-based cooperation between individual subunits of a molecular assembly, many have been using porphyrin containing conjugated oligomers of precise length. An approach to systems with such cooperative control is to mimic the essential features used by living systems for the light harvesting effect.<sup>34</sup> Specifically, one often desires photoinduced long-range electron transfer to occur between the input and output moieties. Modern synthetic approaches have permitted the preparation of numerous porphyrin-containing structures that afford this desired level of cooperative control. For example, porphyrin-terminated oligo(phenylene vinylene)s, prepared by the Ramberg–Backlund reaction, have been disclosed (Figure 8a).<sup>35</sup> Likewise, quinone-terminated systems (Figure 8b),<sup>34</sup> “picosecond optical switches” (Figure 8c),<sup>36</sup> molecular photonic wires” (Figure 8d),<sup>37</sup> linear tetraporphyrin-containing systems (Figure 8e),<sup>38</sup> and “light harvesting arrays” (Figure 8f).<sup>39</sup>

An interesting use of a porphyrin-containing cyclic conjugated oligomer has been described that promotes exo selectivity in an enzyme-like host-accelerated Diels–Alder reaction (Figure 9).<sup>40</sup> There are several competing effects that include the forward and reverse reactions of both the endo and exo adducts and the binding rates of the adducts inside



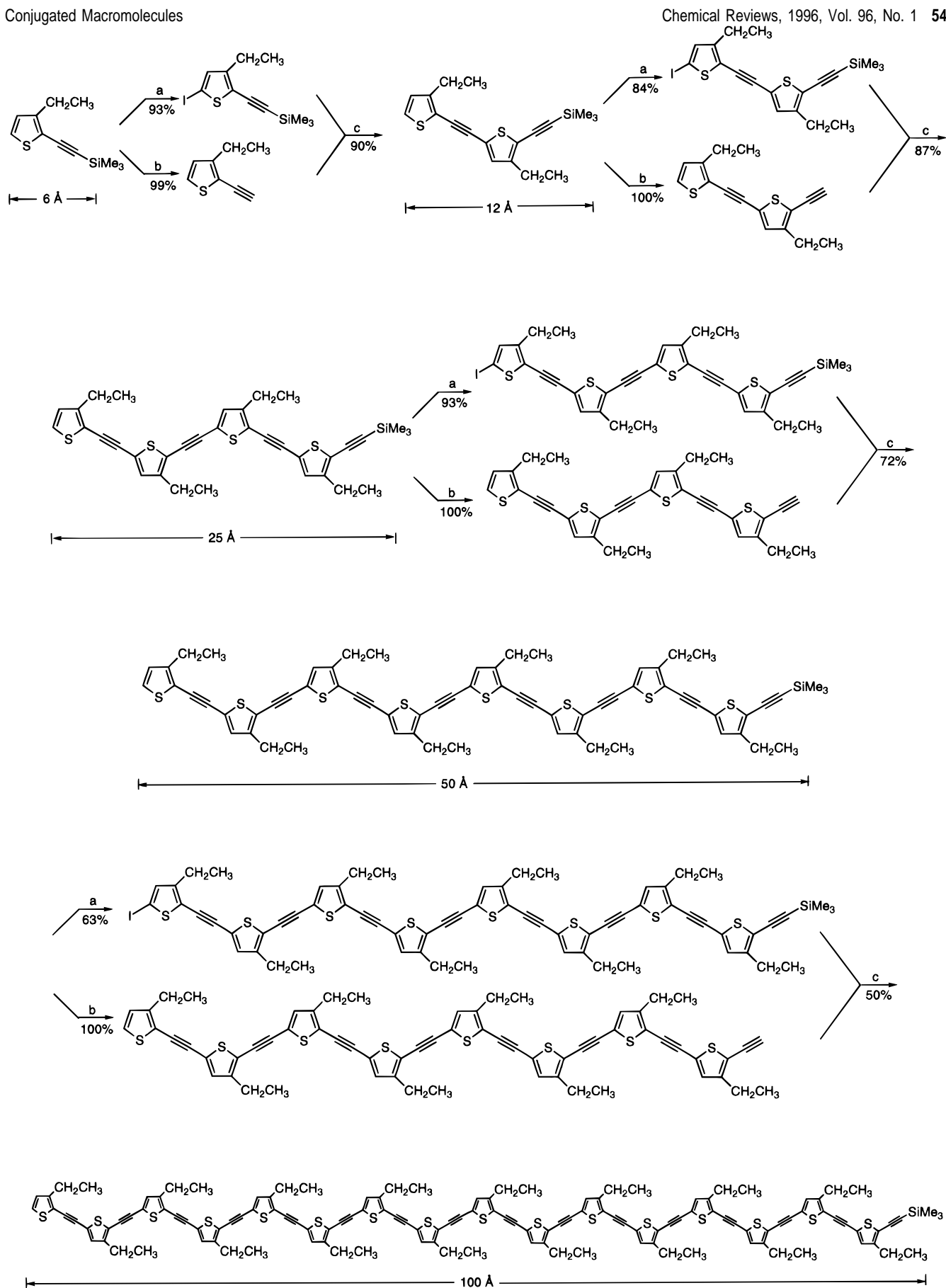
**Figure 9.** A porphyrin-containing cyclic conjugated oligomer that promotes exo selectivity in an enzyme-like host-accelerated Diels–Alder reaction.

the cavity. These culminate in an increase in the activation energy of the forward endo reaction and a decrease in activation energy for the forward exo reaction.

## B. Rapid Growth Methods

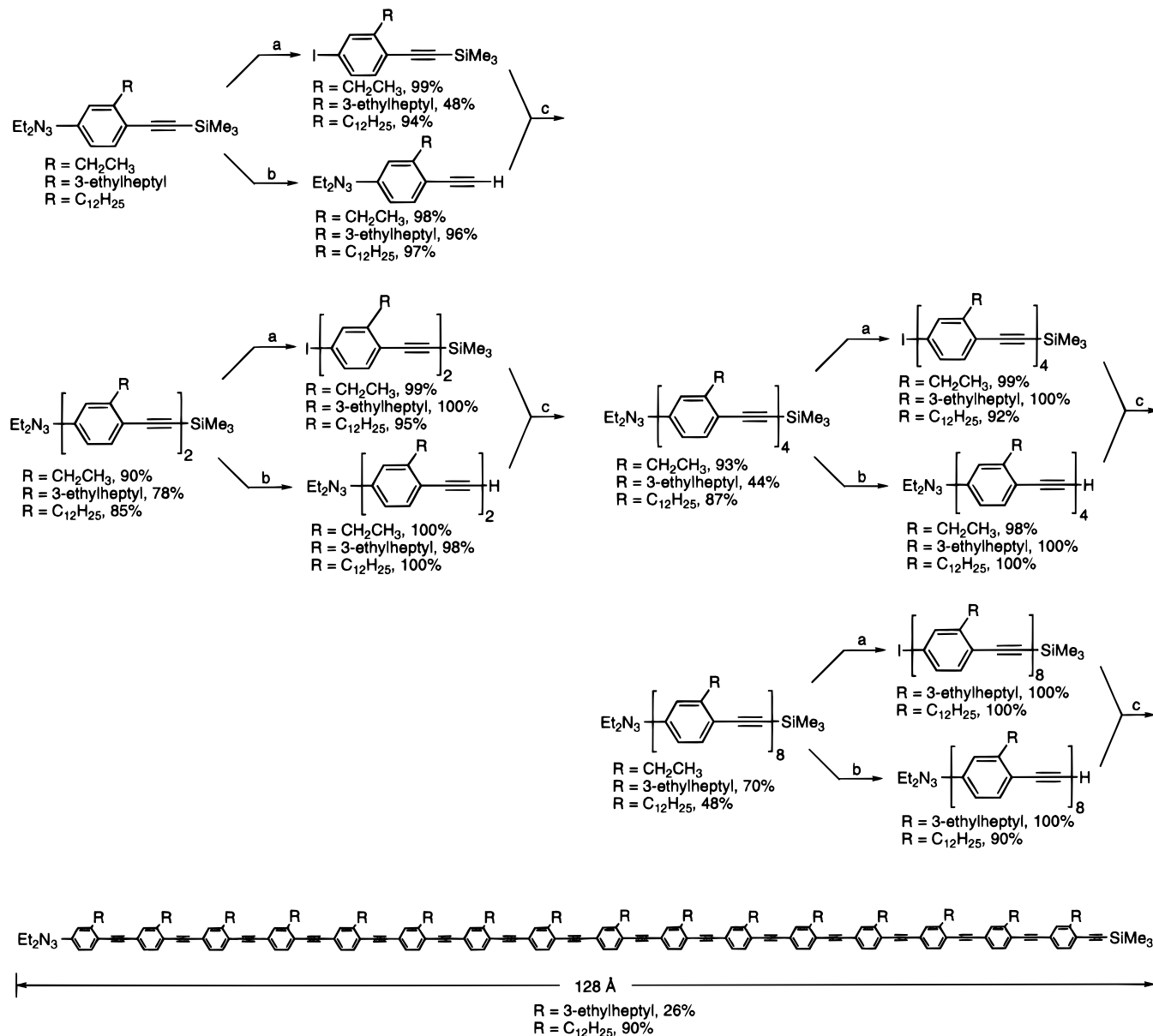
### 1. Acyclic Systems

In addition to the utilization of modern synthetic organic and organometallic reactions for the stepwise synthesis of conjugated oligomers and polymers, many have been using rapid controlled growth synthetic strategies for constructing large oligomers systems of precise length and constitution. A rapid growth method can be demonstrated by our preparation of oligo( $\alpha$ -thiophene ethynylene)s. But first, we desired the rapid construction of such a conjugated system for testing as potential molecular wires in molecular electronics-based nanofabricated arrays. Molecular electronics-based computation has attracted interest because the ultimate computational system would consist of logic devices that are ultra dense, ultra fast, and molecular sized. Even though state-of-the-art nanopatterning techniques allow lithographic probe assemblies to be engineered down to the 100 Å gap regime, 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.<sup>41,42</sup> In an attempt to assess the possibility of molecular wire conduction by spanning the 100 Å probe gaps with small packets of molecules, we recently synthesized the oligo( $\alpha$ -thiophene ethynylene)s by the rapid iterative divergent/convergent approach using, successively, the same three sets of reaction conditions (Figure 10).<sup>43</sup> The monomer through 16-mer have been characterized spectroscopically. While the tetramer and octamer afforded molecular ions by direct exposure via electron-impact mass spectrometry, neither this method nor fast-atom bombardment or electrospray mass spectrometry sufficed for obtaining a molecular ion of the final 16-mer. However, MALDI-MS did afford an *M* + 1 peak and this information proved to be most important for the definitive characterization.<sup>7,43</sup> We used



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, *i*-Pr<sub>2</sub>NH, 23 °C.

**Figure 10.** Iterative divergent/convergent synthesis of oligo(thiophene ethynylene)s.



Reagents: a. MeI as solvent, 120°C in a screw cap tube. b. K<sub>2</sub>CO<sub>3</sub>, MeOH, 23°C or *n*-Bu<sub>4</sub>NF, THF, 23°C c. Pd(dba)<sub>2</sub> (5 mol %), CuI (10 mol %), PPh<sub>3</sub> (20 mol %), *i*-Pr<sub>2</sub>NH/THF (1:5), 23°C.

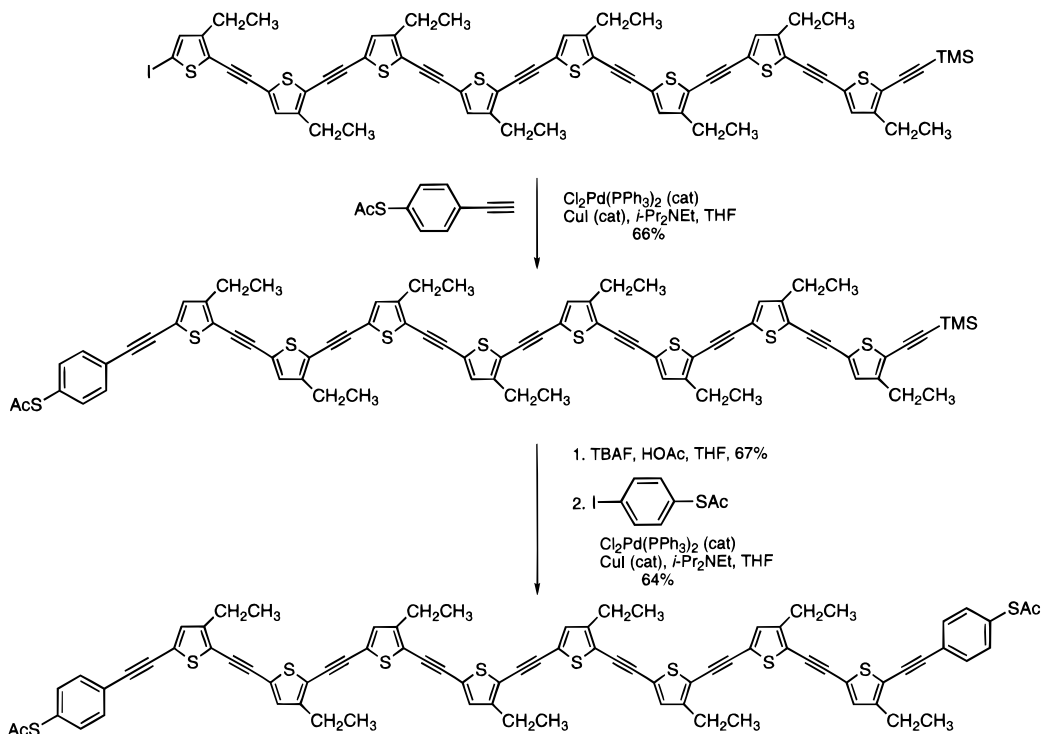
**Figure 11.** Iterative divergent/convergent synthesis of oligo(phenylene ethynylene)s.

a similar method to prepare oligo(*p*-phenylene ethynylene)s (Figure 11).<sup>44</sup> The linear oligo(phenylene ethynylene) arrangement should minimize undesired conformational movement during adhesion and testing between nanofabricated probes. Additionally, the oligo(arylene ethynylene)s can be functionalized at the ends to serve as “molecular alligator clips” that are required for surface contacts to metal probes for molecular electronics studies. For example, we have functionalized the ends of the octa( $\alpha$ -thiophene ethynylene) with thiol moieties, shown in protected form (Figure 12), for adhesion to gold probes by self-assembly methods.<sup>45</sup> We have also synthesized isonitrile end groups for adhesion to tungsten probes. Thus, the iterative divergent/convergent approach permitted both the facile construction of the potential molecular wires as well as providing compounds with ends that could be readily functionalized.

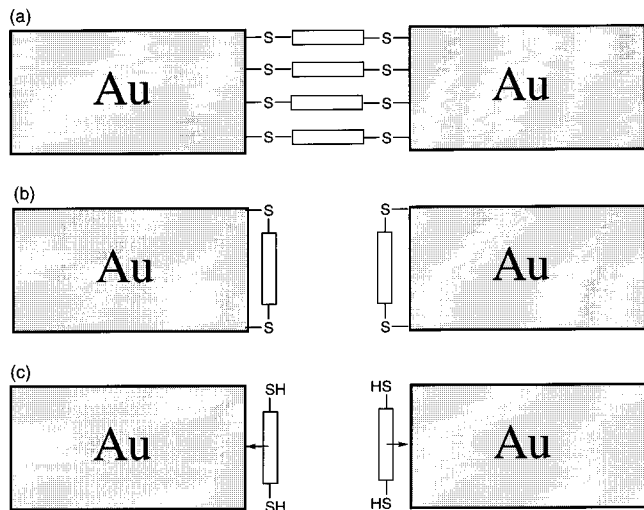
Since the potential molecular wires must bridge two gold electrodes, the question as to how these rigid

rod difunctional oligomers will order on gold surfaces comes into question. For example, will the oligomers bridge the gold–gold gap as in Figure 13a, or will they reside nearly parallel to the surface of the gold by either dithiol or aromatic adsorption to the gold surfaces as in Figures 13b and 13c, respectively? By making self-assembled monolayers on gold surfaces, we have demonstrated, using ellipsometry, XPS, and grazing angle IR measurements, that the rigid-rod systems predominantly stand perpendicular to the surface; the thiol groups dominating the adsorption sites on the gold. Even when the oligomers were  $\alpha,\omega$ -dithiol-substituted, the rigid molecules tended to stand on end as judged by the ellipsometric thickness of the adsorbate layer.<sup>46</sup>

In addition to these conjugated molecules serving as potential molecular wires, their optical and chromatographic properties proved to be most intriguing. An optical saturation or near saturation of the systems occurred by the octamer stage so that

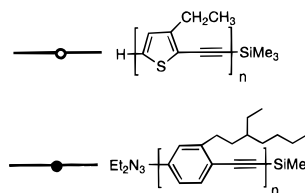
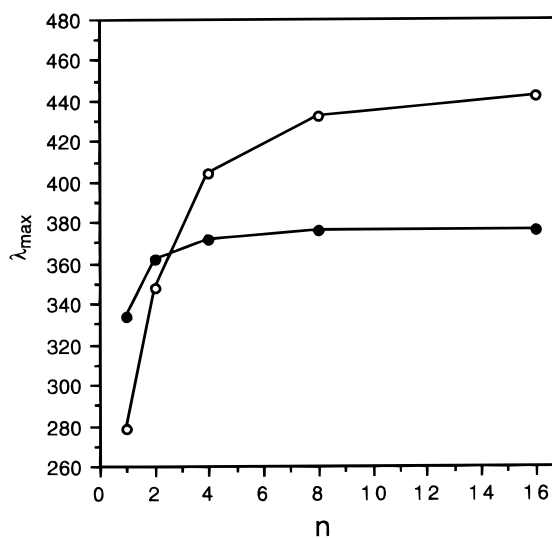


**Figure 12.** Functionalization of octa( $\alpha$ -thiophene ethynylene) with protected thiol moieties to act as molecular alligator clips for adhesion to gold probes by self-assembly methods.



**Figure 13.** (a–c) Three possible binding modes of thiol-terminated conjugated oligomers between gold probes.

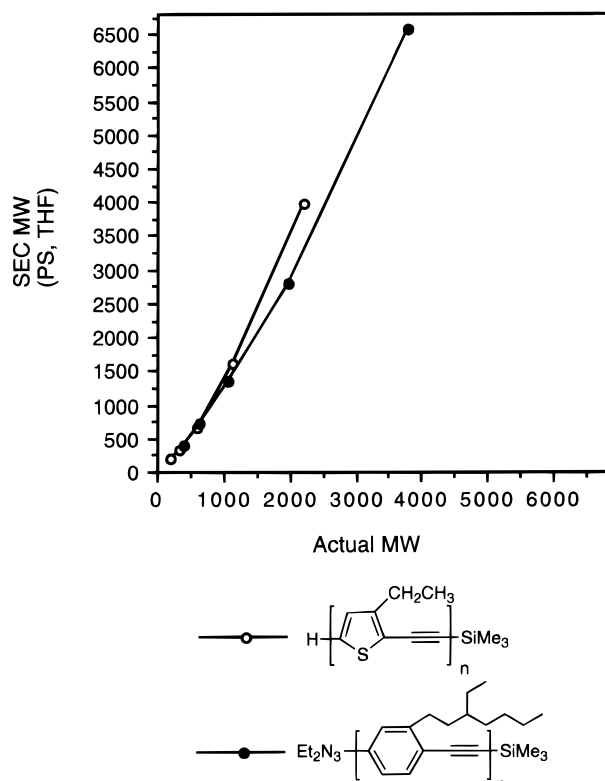
doubling the conjugation length to the 16-mer caused little or no change in the position of the absorbance maximum (Figure 14).<sup>43,44</sup> The results of the size exclusion chromatography (SEC) are shown in Figure 15 and compared with the actual molecular weights of the oligomers. SEC is not a direct measure of MW, 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. Accordingly, the SEC recorded  $M_n$  values of the octamers and 16-mers were much greater than the actual molecular weights. Also, as we would predict, the monomer, dimer, and tetramer had  $M_n$  values that were reasonably close to the actual molecular weights (slope  $\sim 1.0$  in Figure 15) because they are in the low MW region, prior to significant polystyrene coiling. In all cases, the SEC-determined values of  $M_w/M_n = 1.02\text{--}1.07$ . Thus this



**Figure 14.** Optical absorbance maximum ( $\lambda_{\max}$ ) in  $\text{CH}_2\text{-Cl}_2$  versus the number of units in the oligomer ( $n$ ) for families of precisely defined oligo(thiophene ethynylene)s and oligo(phenylene ethynylene)s.

plot can serve as a useful calibration chart for very rigid linear oligomers as they compare to polystyrene standards by SEC.<sup>43,44</sup>

In a related study directed toward the construction of molecular electronic devices,<sup>47</sup> we synthesized molecules with potentially addressable “on” and “off” states. The orthogonally fused conjugated oligomers are of precisely controlled length and molecular

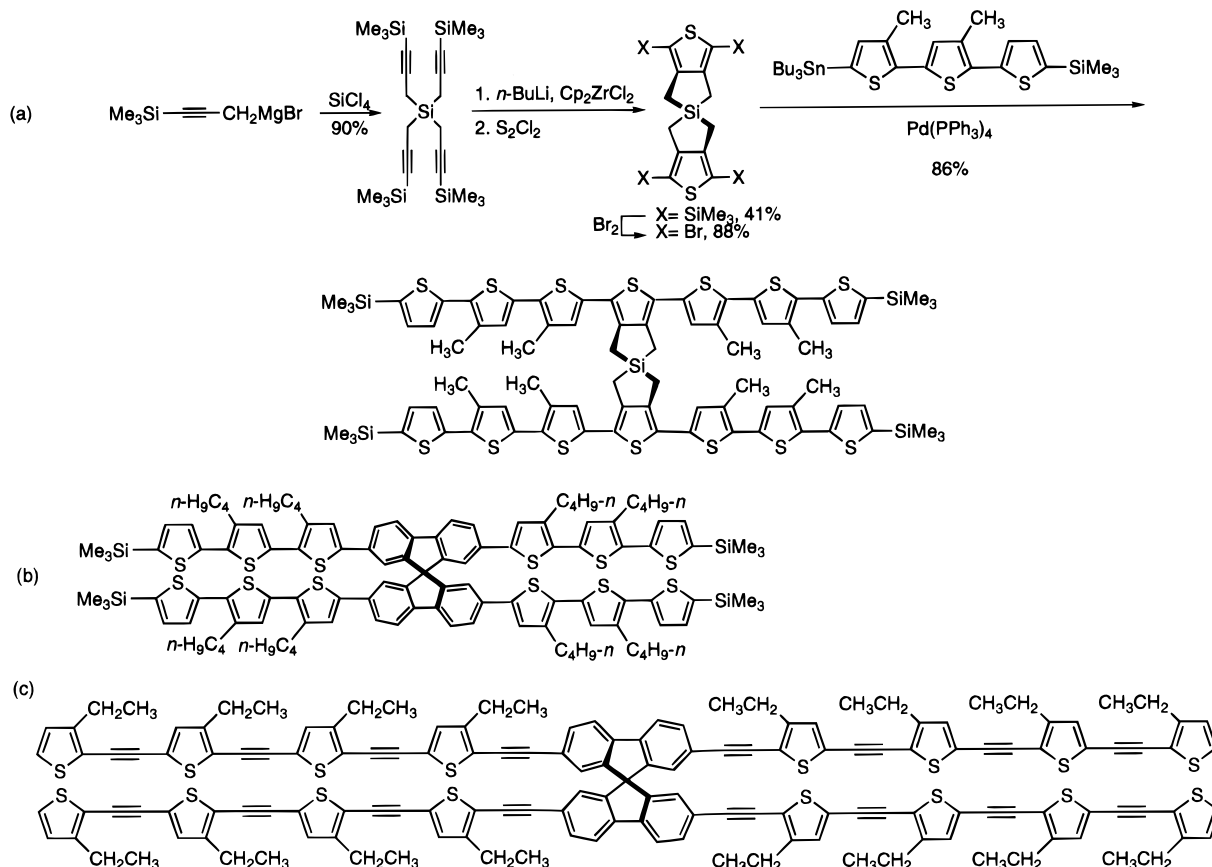


**Figure 15.** Values of  $M_n$  determined by SEC in THF (relative to polystyrene standards) versus the actual molecular weights for families of precisely defined oligo(thiophene ethynylene)s and oligo(phenylene ethynylene)s.

constitution for electronic testing. First, the spiro cores were constructed,<sup>48</sup> and then all four branching

arms were added in a single operation (Figure 16a).<sup>49</sup> The related systems in Figures 16b and 16c were also prepared. Electrochemically, we could independently observe the formation of the mono(radical cation), bis-(radical cation), radical-cation(dication), and bis-(dication) which indicates that, under unperturbed conditions, there is no cross-communication between the upper and lower segments, a prerequisite for the device capability.<sup>50,51</sup> Addressing is proposed by considering a six probe assembly; a probe at each of the four trimethylsilyl ends, a probe above the central spiro core moiety, and a probe below the central spiro moiety.<sup>47</sup> Instrument-induced electron removal (doping) from the top branch would permit facile conduction in the top segment while leaving the bottom segment unchanged (state 1). At a certain threshold potential (perturbation) across the spiro bridge, an electron would tunnel from the lower chain to upper chain, via the spiro core, to produce a doped (conducting) lower chain and a neutral upper chain (state 2). The two states would then be addressable based on the potential across the spiro bridge, thus creating a device. From such devices or simple two-state systems, logic gates could be formed.<sup>47</sup> Unfortunately, no such six probe array, at these dimensions, is presently available by nanopatterning techniques.<sup>41,42</sup>

Methods similar to those described in Figure 11 have been used to prepare oligo(*m*-phenylene ethynylene)s up to the 16-mer length.<sup>52</sup> Recently, the iterative divergent/convergent doubling approach was used in conjunction with solid-phase synthetic meth-

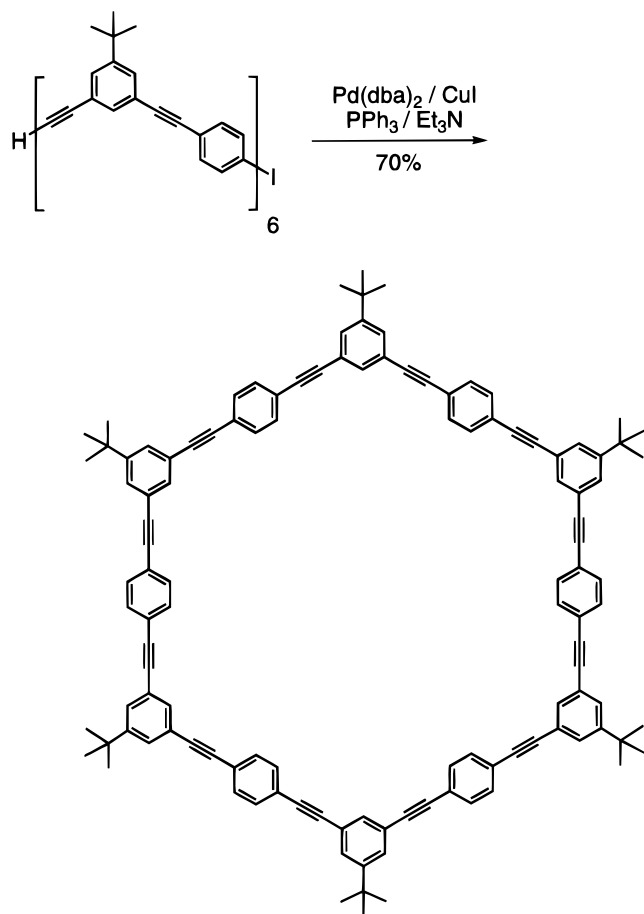


**Figure 16.** (a) Convergent synthesis of orthogonally fused oligomers for use as molecular electronic devices and (b and c) other related orthogonally fused systems that have been synthesized.

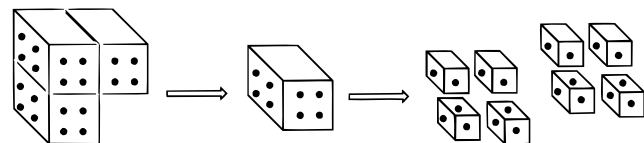
ods. Using this method, even the 64-mer was prepared.<sup>10</sup>

## 2. Cyclic Systems

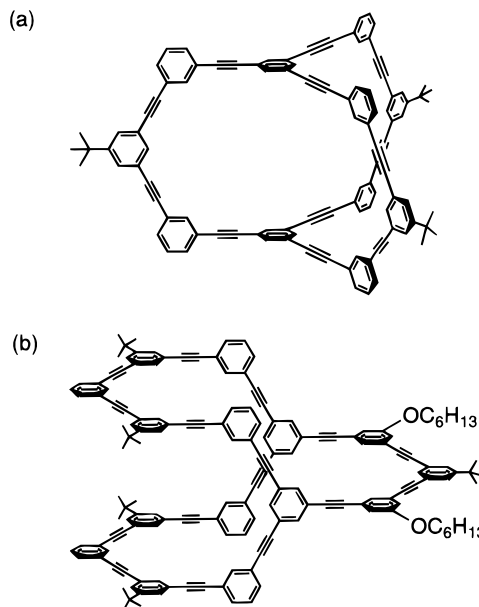
Acyclic conjugated oligomeric systems prepared by iterative divergent/convergent approaches have been cyclized into numerous sized phenylacetylene macrocycles systems for potential use in the construction of supramolecular assemblies.<sup>53</sup> Well-defined macromolecules of precise size and functionality are needed for the requisite electronically and sterically defined spatial and orientational arrangements in noncovalent supramolecular assemblies. One of several of the oligomers prepared is shown in Figure 17.<sup>53</sup> If we consider this macrocycle as a modular unit, there is the hope of using such units for the programmed assembly of molecular materials. This may be accomplished by utilizing the constitution of the individual fragments to control the condensed phase organization through the summation of non-covalent interactions, an approach analogous to the forming of structures using building blocks held together by frictional forces that are dependent upon good facial overlap (Figure 18).<sup>54</sup> Ultimately, the target is the rational design of new materials such



**Figure 17.** A well-defined cyclic oligomer prepared by rapid growth methods.



**Figure 18.** Conceptual approach to the condensed-phase organization of molecular materials.



**Figure 19.** Three-dimensional molecular-sized scaffolds have also been prepared from oligo(*m*-phenylene ethynylene)s using Sonogashira coupling methods.

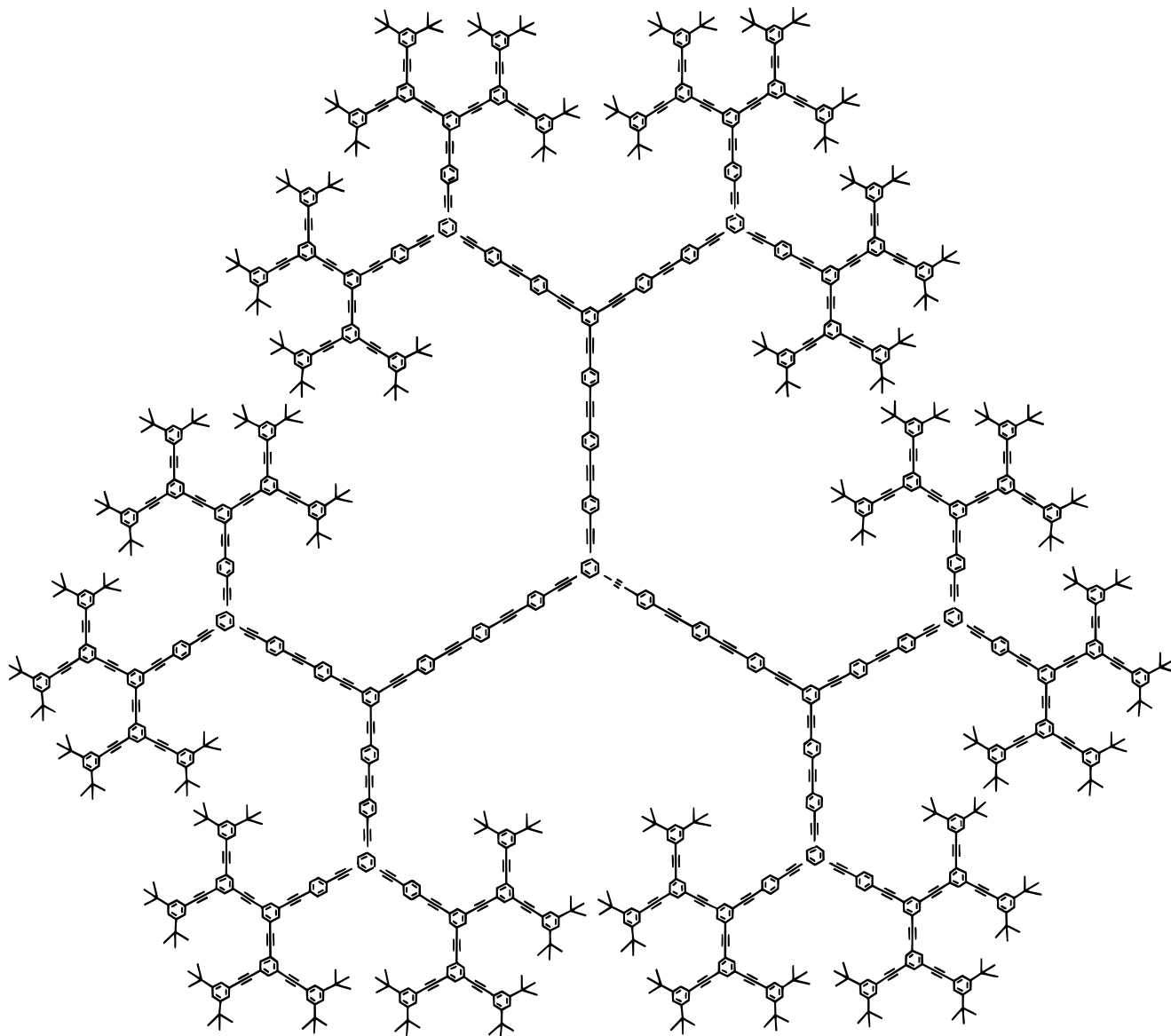
as organic crystals and tubular mesophases. Three-dimensional molecular-sized scaffolds have also been prepared from the oligo(*m*-phenylene ethynylene)s using the Sonogashira coupling methods (Figure 19, part a and b).<sup>55</sup> These arrays are of interest in fabrication of molecules with enzyme-like properties, modular nanosized construction components, and organic zeolite-like materials.

## 3. Dendritic Systems

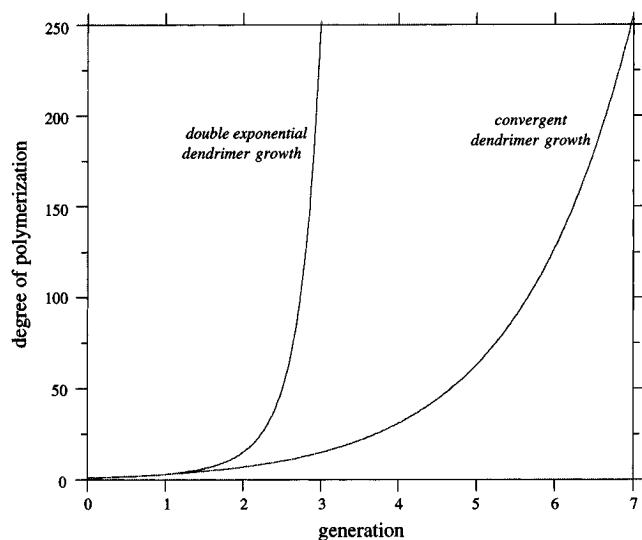
The synthesis of precisely defined globular macromolecules has grown dramatically in the last decade.<sup>56</sup> Dendrimers are structures that possess cores with successively increasing branches of precise length and constitution. Although this is a rich area of research, the construction of fully conjugated dendritic systems is strikingly limited. Dendritic oligo(phenylene ethynylene)s have been synthesized up to 125 Å in diameter using Sonogashira coupling methods (Figure 20).<sup>57</sup> Recently, more sophisticated methods of "double exponential growth" (Figure 21) involving the coupling of larger components have permitted the facile construction of related oligomeric systems.<sup>58</sup> Suzuki couplings have been used to prepare dendritic oligophenylene systems (Figure 22).<sup>59</sup> Although numerous applications of dendritic systems have been proposed, far fewer applications have actually developed. Recently, however, simple conjugated dendrimers of the type shown in Figure 23 have been used in stable multilayered organic electroluminescent devices.<sup>60</sup>

## IV. Summary and Future Directions

Precisely defined step growth oligomers and polymers will continue to be of interest as easy-to-study exact analogs of their higher polymeric forms. Families of oligomers and small polymers will be synthetic targets in order to predict and enhance the understanding of the physical, optical, and electronic properties in the corresponding polymers. In addition to serving as models, these oligomeric structures are becoming more important in their own right. The

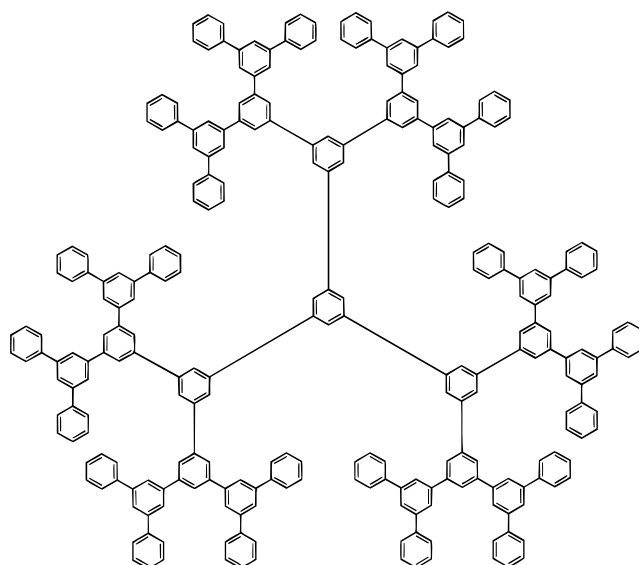


**Figure 20.** A dendritic oligo(phenylene ethynylene) of 125 Å in diameter prepared using Sonogashira coupling methods.



**Figure 21.** Plot illustrating the advantage of novel methods for "double exponential growth" as compared to traditional convergent approaches to dendritic macromolecules.

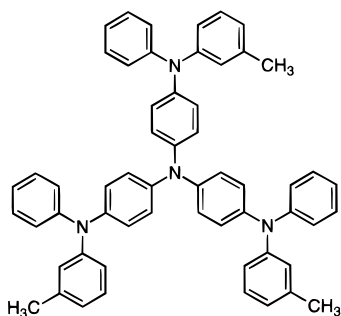
conjugated systems have the distinct advantages of contiguous  $\pi$ -overlap for electronic and photonic



**Figure 22.** A dendritic oligophenylene prepared by Suzuki couplings.

applications, for example, in nanoscale devices. The conjugated systems also exhibit enhanced rigidity for





**Figure 23.** A simple conjugated dendrimer used in stable multilayered organic electroluminescent devices.

the programmed assembly of molecular materials and supramolecular assemblies. As more applications of precisely defined structures become recognized, solid-phase automated methods may become the synthetic strategies of choice. This is especially true in light of the recent advances in combinatorial syntheses where large numbers of varying structures can be simultaneously constructed. However, if the large-scale production (multikilos) of these well-defined structures will be required, solid-phase methods may be limited due to the volumes of support-phase needed; a limitation that has been observed in the solid-phase-based commercial production of oligopeptides. Finally, the advances in the synthesis and utility of step growth oligomers and polymers of precisely controlled length and constitution are made possible by a rapid evolution and improvement in new synthetic organic and organometallic methodologies as well as in improved methods of chemical analysis. Therefore, synthesis has paved the way for the study of these unique classes of precisely defined conjugated macromolecular architectures. In the future, more rapid precise synthetic growth procedures need to be developed that tolerate a wide variety of chemical substrates with high versatility of monomer unit sequence control.

## V. Acknowledgments

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