Rapid Solution and Solid Phase Syntheses of Oligo(1,4-phenylene ethynylene)s with Thioester Termini: Molecular Scale Wires with Alligator Clips. Derivation of Iterative Reaction Efficiencies on a Polymer Support

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The syntheses of soluble oligo(2-alkyl-1,4-phenylene ethynylene)s via an iterative divergent/convergent approach starting from 1-(diethyltriazyl)-3-alkyl-4-[(trimethylsilyl)ethynyl]benzenes are described. When the solublizing alkyl group is an ethyl substituent, the monomer, dimer, tetramer, and octamer can be synthesized. The octamer, however, is only minimally soluble. When the alkyl substituent is 3-ethylheptyl or dodecyl, the compounds are easily dissolved even at the 16-mer stage. The 16-mer is 128 Å long in its near-linear extended conformation. At each stage in the iteration, the length of the framework doubles. Only three sets of reaction conditions are needed for the entire iterative synthetic sequence: an iodination, a protodesilylation, and a Pd/Cu-catalyzed cross coupling. Synthesis of the dodecyl-containing 16-mer was also achieved on Merrifield's resin using the iterative divergent/convergent approach. The oligomers were characterized spectroscopically and by mass spectrometry. The optical properties are presented which show that at the octamer stage, the optical absorbance maximum is nearly saturated. The size exclusion chromatography values for the number average weights, relative to polystyrene, illustrate the tremendous differences in the hydrodynamic volume of these rigid rod oligomers verses the random coils of polystyrene. These differences become quite apparent at the octamer stage. Equations were derived for assessing the efficiency of the polymer-supported reactions based on resin weight differences, molar concentration differences, and elemental analysis data. Each of these methods' limitations are discussed. Attachment of thiol end groups, protected as thioacetyl moieties, was achieved. These serve as binding sites for adhesion to gold surfaces. In some cases, one end of the oligomeric chains is capped with a thiol group so that the surface attachments to gold could be studied. In other cases, thiol groups are affixed to both ends of the molecular chains so that future conduction studies could be done between proximal metallic probes. The rigid rod conjugated oligomers may act as molecular wires in molecular scale electronic devices, and they also serve as useful models for understanding analogous bulk polymers.

Introduction

The expectation and potential of molecular-sized computational devices has attracted the interest of the synthetic chemist, and rapid synthetic architectural approaches to these and related structures have been dramatically increasing.[1] Here we describe the synthetic details for the formation of soluble oligo(2-alkyl-1,4-phenylene ethynylene)s, potential molecular scale wires, by a rapid iterative divergent/convergent doubling approach.[1−3] These 1,4-phenylene ethynylene compounds exhibit even further rigidity (no main-chain conformers that alter the molecular length) over the 2,5-thiophene ethynylene compounds described previously.[1] The syntheses and attachments of protected thiol moieties to one or both ends of the phenylene ethynylenes are presented. These thiols serve as molecular scale alligator clips for adhesion of the molecular scale wires to the gold probes.[1,4] Additionally, synthesis of the dodecyl-containing 16-mer was also achieved on Merrifield's resin (chloromethyl polystyrene) using the iterative divergent/convergent approach; a method which significantly streamlined the preparation.[5]

Results and Discussion

Monomer Syntheses for Solution-Based Oligomerizations. The syntheses of the monomers are described in Scheme 1. Initially, we thought an ethyl substituent would provide enough solubility for the conjugated oligomers up to the 16-mer, the size necessary for bridging patterned proximal gold probes.[1] We there-

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(1) See the preceding article (Pearson, D.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, xxx) and references therein for a description of molecular scale electronics, the synthetic organic challenges involved, the efficacy of the iterative divergent/convergent approach for the conjugated structures via the coupling approaches chosen here, and the utility of thiol end groups to act as alligator clips.

(2) Schumm, J. S.; Pearson, D. L.; Tour, J. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1360.

(3) An iterative divergent/convergent approach has been used to prepare the analogous oligo(1,3-phenylene ethynylenes): (a) Zhang, J.; Moore, J. S.; Xu, Z. F.; Aguirre, R. A. *J. Am. Chem. Soc.* **1992**, *114*, 2273. (b) Xu, Z. F.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1354. For related oligomers and polymers, see: (c) Grubbs, R. H.; Kratz, D. *Chem. Ber.* **1993**, *126*, 149. (d) Scherf, U.; Müllen, K. *Synthesis* **1992**, 23. For a recent review on the subject, see: (e) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537.

(4) Tour, J. M.; Jones, L., II; Pearson, D. L.; Lamba, J. S.; Burgin, T.; Whitesides, G. W.; Allara, D. L.; Parikh, A. N.; Atre, S. *J. Am. Chem. Soc.* **1995**, *117*, 9529. (b) Dhirani, A. A.; Zehner, R. W.; Hsung, R. P.; Guyot-Sionnest, P., Sita, L. R. *J. Am. Chem. Soc.* **1996**, *118*, 3319. (c) Bumm, L. A.; Arnold, J. J.; Cygan, M. T.; Dunbar, T. D.; Burgin, T. P.; Jones, L., II, Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **1996**, *271*, 1705.

(5) (a) Young, J. K.; Nelson, J. C.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 10841. (b) Bharathi, P.; Patel U.; Kawaguchi, T.; Pesak, D. J.; Moore, J. S. *Macromolecules* **1995**, *28*, 5955. (c) *Polymer-Supported Reactions in Organic Synthesis*; Hodge, P., Sherrington, D. C., Eds.; Wiley: New York, 1980. (d) Nelson, J. C.; Young, J. K.; Moore, J. S. *J. Org. Chem.* **1996**, *61*, 8160.

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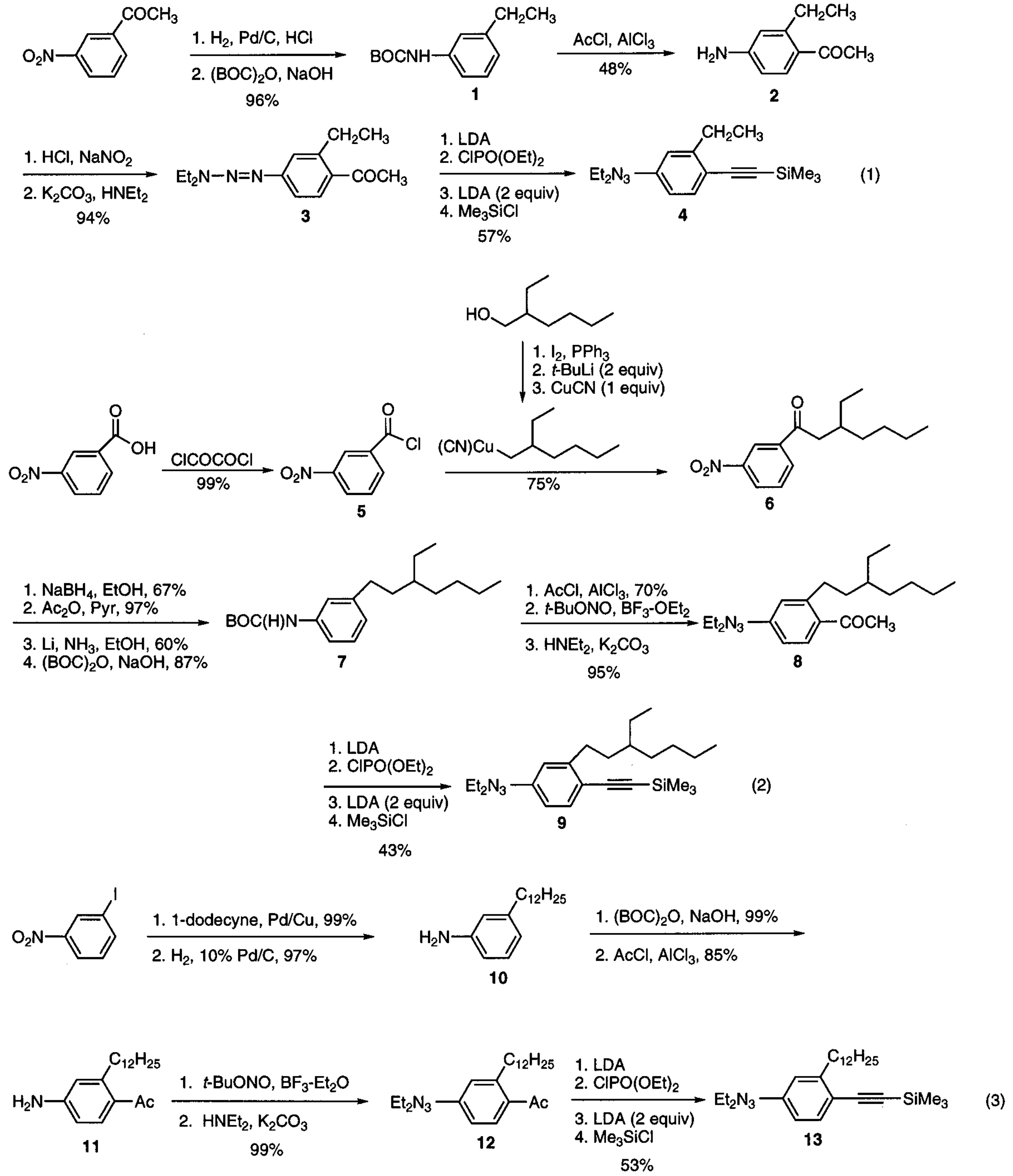
Scheme 1



fore started with 3-nitroacetophenone and easily formed the ethyl side chain by hydrogenation under acidic conditions. *N*-Acetyl protection and Friedel–Crafts acylation afforded a 4:1 mixture of the methyl ketones in which the desired 4-acylation product predominated.[2] However, *tert*-butoxycarbonyl (BOC) protection of the amine and Friedel–Crafts acylation afforded only the desired 4-acylation product **2**. The BOC protecting group was conveniently lost upon aqueous workup. Conversion of the amine to the diethyltriazene **3** followed by one-pot conversion of the methyl ketone to the (trimethylsilyl)-alkyne[6] afforded the desired monomer **4** for the iterative divergent/convergent oligomerization (Scheme 1, eq 1). Notice that the triazyl moiety was quite robust and able to survive the LDA treatment.

We subsequently discovered that the ethyl moiety did not provide sufficient solubility (*vide infra*), thus we prepared the analogous monomer bearing a 3-ethylheptyl substituent (Scheme 1, eq 2). It was surmised that a monomer bearing a stereogenic center would afford diastereomers on successive dimerizations, thereby retarding crystallization and increasing solubility. We started with 3-nitrobenzoic acid and treated the corresponding acid chloride **5** with the cyanocuprate to afford the desired ketone **6**. We tried numerous methods to concomitantly reduce both the ketone and the nitro moieties of **6**; however, all methods failed, including the Pd–C/H_2/HCl reduction that worked in the synthesis of **1**. Therefore, the multistep reaction sequence was used which involved reduction of the ketone to the alcohol, acetoxy formation, and finally reduction under dissolving metal conditions for both reductive removal of the acetoxy

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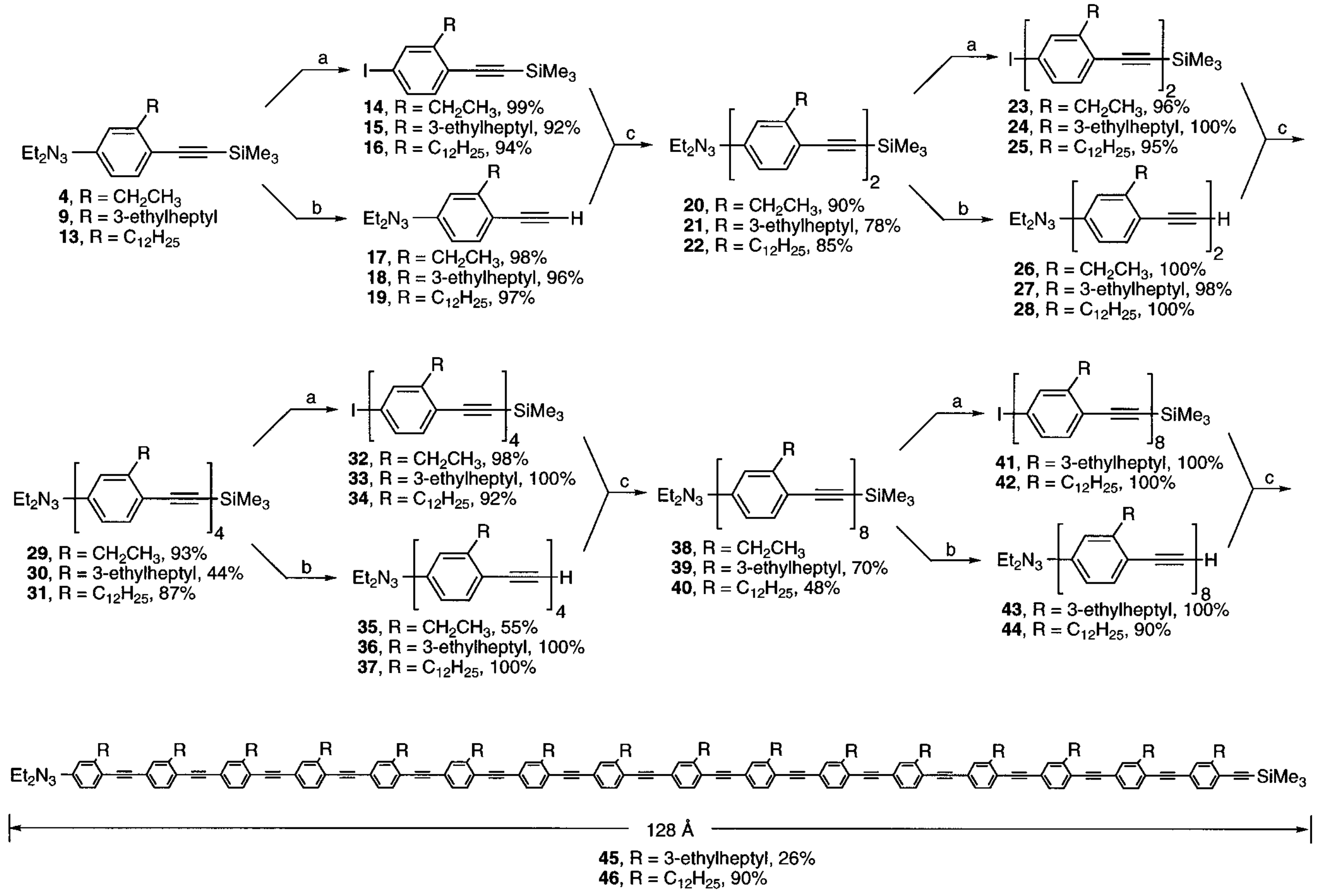
(6) Negishi, E.; King, A. O.; Tour, J. M. *Org. Synth.* **1985**, *64*, 44.

Scheme 2



Reagents: a. MeI. b. K_2CO_3, MeOH, or *n*-Bu_4NF, THF. c. $Pd(dba)_2$ (5 mol %), CuI (10 mol %), PPh_3 (20 mol %), *i*-Pr_2NH/THF (1:5).

moiety and amine formation. Additionally, the standard $NaNO_2$/HCl conditions that were used in eq 1 did not permit diazonium formation on this more lipophilic substrate; however, *tert*-BuONO permitted formation of the intermediate diazonium species which was followed by capture with diethylamine to form the triazene **8**.[7] Preparation of **9** then proceeded under the standard alkynylation conditions (Scheme 1, eq 2).[6]

After discovering that the 3-ethylheptyl substituent in **9** permitted solubility through to the 16-mer (*vide infra*), we desired to prepare an analogous version which would permit formation of soluble homogeneous material. Hexadecyl chains often cause side chain crystallization in polymers while dodecyl chains can impart solubility without the crystallization difficulties.[8] Thus a dodecyne moiety was affixed to 3-nitroiodobenzene, via a Pd/Cu-catalyzed coupling,[9] followed by reduction and conversion to the desired **13**, again via exclusive 4-acylation of the BOC-protected amine (Scheme 1, eq 3).

Oligomer Syntheses in Solution. The solution phase iterative divergent/convergent synthetic approach is outlined in Scheme 2. The sequence involved, for example, partitioning **4** into two portions, conversion of the triazene in one portion to the aryl iodide **14** with MeI,[10] and protodesilylation of the alkynyl end of the second portion to form **17**. Bringing the two portions back together in the presence of a soluble Pd/Cu catalyst mixture[9] coupled the aryl iodide to the terminal alkyne, thus generating the dimer **20**. Since the dimer had the same end groups as the monomer, the same process could be repeated. Iteration of this reaction sequence doubled the length of the dimer **20** to afford the tetramer **29** and so on to the octamer **38**. At that point, the octamer was nearly insoluble, and we were only able to obtain a UV-visible spectrum and a direct exposure mass spectrum (MS). However, carrying out the same sequence starting from 3-ethylhexyl or dodecyl bearing monomers **9** and **13**, respectively, we were able to achieve the syntheses of the 16-mers **45** and **46**, respectively. The silylated alkynes showed good oxidative stability; however, upon protodesilylation, the tetramers and octamers were air sensitive.

Monomer Syntheses for the Polymer Supported Approach. The monomers needed for the polymer support synthesis were prepared as depicted in Scheme 3. Compound **11** was converted to the diazonium intermediate which was captured with 2-(ethylamino)ethanol, to form the hydroxytriazene according to Moore's protocol.[5] Silylation to form **47** followed by acetyl conversion to the silylalkyne afforded **48**. Compound **48** was divided into two portions; the first portion was desilylated to form **49**, the anchor unit to be attached to the polymer support. The second portion was iodinated[10] to form the iodoarene **16**.

Oligomer Syntheses on the Polymer Support. Attachment of **49** to the polymer support resin and the

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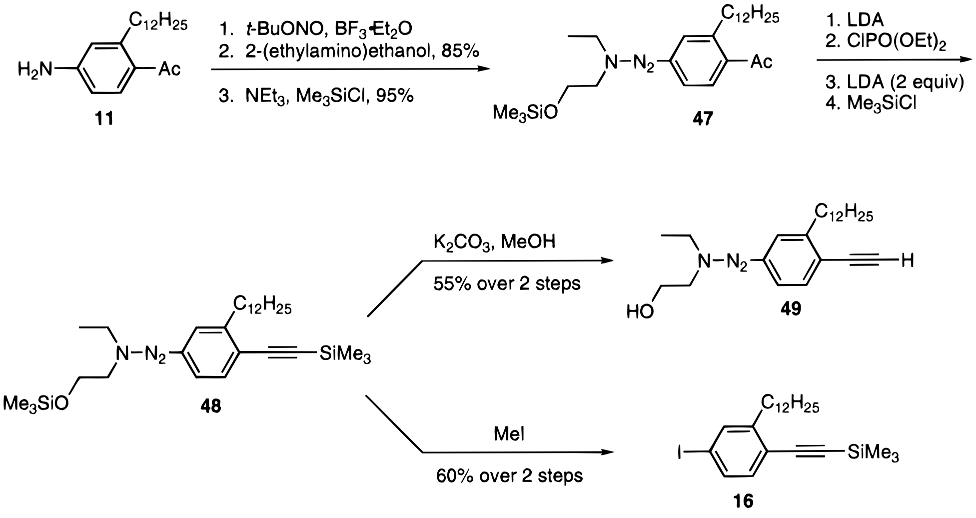
(7) Doyle, M. P.; Bryker, W. J. *J. Org. Chem.* **1979**, *44*, 1572.

(8) Lamba, J. S. S.; Tour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 11723.

(9) (a) Suffert, J.; Ziessel, R. *Tetrahedron Lett.* **1991**, *32*, 757. (b) Sonogashira, K; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467. (c) Stephens, R. D.; Castro, C. E. *J. Org. Chem.* **1963**, *28*, 3313.

(10) Moore, J. S.; Weinstein, E. J.; Wu, Z. Y. *Tetrahedron Lett.* **1991**, *32*, 2465.

Scheme 3



oligomer syntheses on the polymer support are depicted in Scheme 4. Etherification of Merrifield's resin with an excess of anchor **49** provided the polymer-supported monomer **50**. Unfortunately, it was difficult to determine the etherification reaction completion point by IR analysis (*vide infra*). Even though the reaction was allowed to stir over several days at elevated temperature with a 3-fold excess of anchor **49**, gel-phase ^{13}C NMR[11] on the supported material revealed a small resonance at δ 46.77 corresponding to benzylic chloride residues. This was further confirmed by elemental analysis. Fortunately, it was found that the unreacted benzylic chloride sites on the resin did not appear to hinder the oligomer synthesis on the polymer support.

The successive dimerization sequence was pursued as illustrated in Scheme 4. **50** was subjected to a Pd/Cu cross-coupling[9] with monomer **16** to afford the polymer-supported dimer **51**. Two-thirds of **51** was then treated with MeI, affording liberated dimer **25** in 86% yield over two steps. The remaining one-third of the polymer-supported dimer **51** underwent desilylation with tetra-*n*-butylammonium fluoride (TBAF) to afford the polymer-supported dimer **52**. **52** was then treated with all of the liberated iodide **25** under Pd/Cu cross coupling conditions to afford the polymer-supported tetramer **53**. The sequence was repeated to generate the tetramer **34**, octamer **42**, and 16-mer **58** in the yields indicated over three steps each. Remarkably, we found that the liberated oligomers were contaminated with only small amounts of impurities as assessed by chromatographic and spectroscopic analyses. These impurities were easily removed after passing the compounds through silica gel.

Spectroscopic Reaction Monitoring Techniques on the Resin. Since the aforementioned reactions were conducted on an insoluble support, conventional techniques such as TLC could not be used to monitor the progress of the reactions. Consequently, completion of each reaction was estimated by infrared analysis of the polymer bound substrate.[5,12] Polymer-supported material was placed on a NaCl plate. After the beads were swollen with 2−3 drops of CCl_4, a second NaCl plate was pressed onto the beads, and an FTIR spectrum was recorded. Absorptions at 3311 cm^{-1} (strong) and 2109 cm^{-1} (weak) are characteristic of the terminal alkynyl carbon−hydrogen and carbon−carbon stretches, respectively, and an absorption at 2156 cm^{-1} (strong) is characteristic of the carbon−carbon stretch of the trimethylsilyl-terminated alkyne.[5,13] As expected, we observed that the coupling reaction was accompanied by the disappearance of the 3311 cm^{-1} band and the appearance of the 2156 cm^{-1} absorption. In the reverse manner, the trimethylsilyl removal step was accompanied by the disappearance of the 2156 cm^{-1} band and the appearance of the 3311 cm^{-1} band. Suitability of this monitoring technique was confirmed by removal and characterization of the trimethylsilyl-protected product.[5]

Gel-phase ^{13}C NMR spectra were also recorded on the polymer-supported material at each step in the reaction sequence. Again, the loss or gain of the trimethylsilyl resonance at δ 0.3−0.5 was a diagnostic feature.

Assessing Solid Phase Reaction Yields. Though reaction progress was monitored by IR, and gel-phase NMR, these spectroscopic tools are of relatively low sensitivity when used for resin analysis. Yield estimation by these methods was difficult, especially for the longer oligomers. For these reasons, the approaches used for the calculation of yield are described.

The yield can be determined based on the weight difference of the resin.[14] The weight increase caused by chemical modification of the resin (ΔW) is related to the yield (Y) by the following relation:

$$Y = \Delta W / N_{\mathrm{si}} \Delta M \qquad (4)$$

where N_{si} is the moles of starting functionality in 1 g of initial resin, and ΔM is the change in molecular weight upon reaction. If mass is lost over the course of the reaction, both ΔW and ΔM should be negative. The results of these calculations for the formation of compounds **50**−**58** are given in Table 1. Unfortunately, the yields determined by this method were found to be

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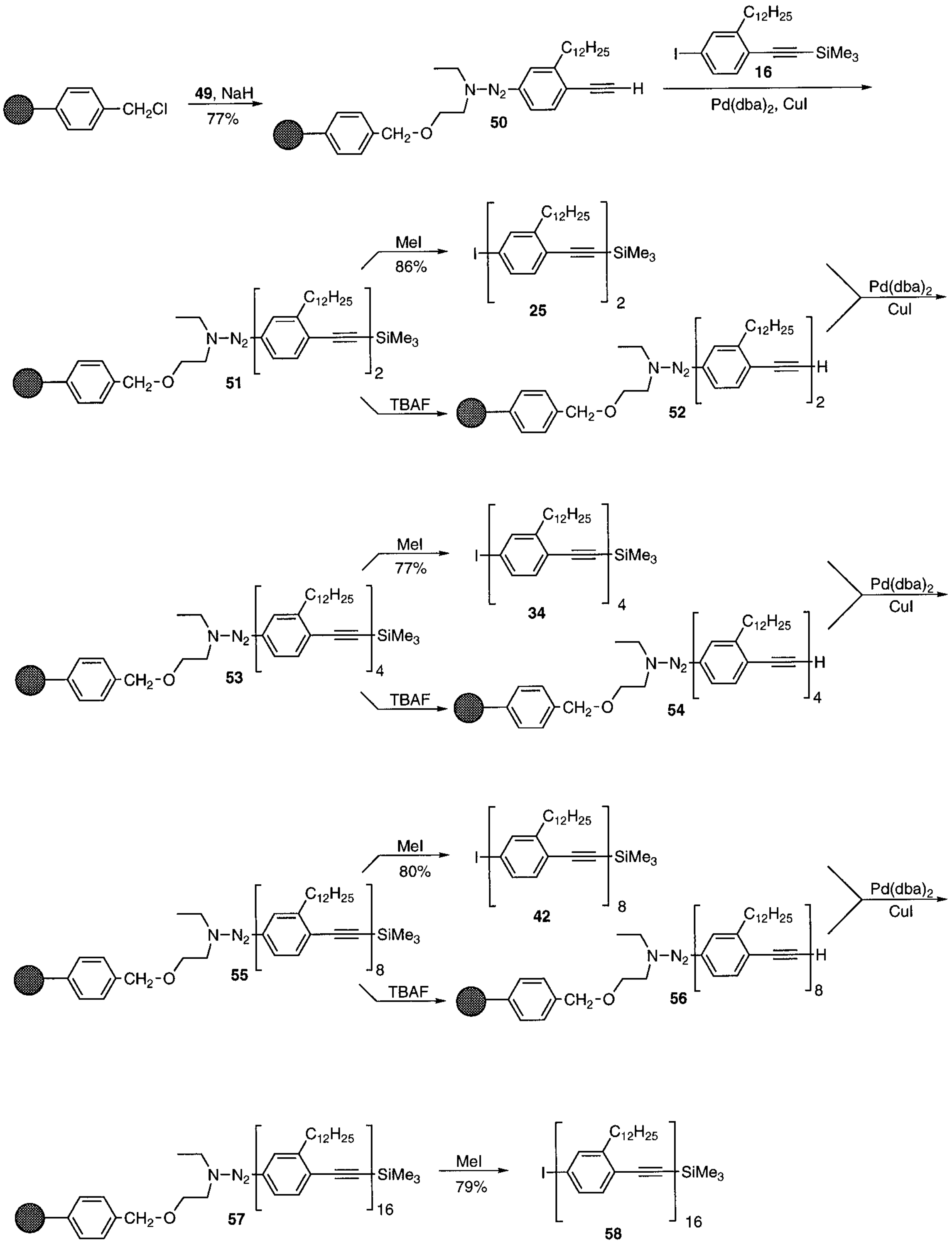
(11) Crowley, J. I.; Rapoport, H. *Acc. Chem. Res.* **1976**, *9*, 135. (b) Leznoff, C. C. *Chem. Soc. Rev.* **1974**, *3*, 65. (c) Leznoff, C. C. *Acc. Chem. Res.* **1978**, *11*, 327. (d) Dewitt, S. H.; Czarnik, A. W.; Ellman, J. A. *Acc. Chem. Res.* **1996**, *29*, 114. (e) Giralt, E.; Rizo, J.; Pedroso, E. *Tetrahedron* **1984**, *40*, 4141.

(12) Yan, B; Kumaravel, G; Anjaria, H; Wu, A; Petter, R. C.; Jewell, C. F., Jr.; Wareing, J. R. *J. Org. Chem.* **1995**, *60*, 5736.

(13) Grindley, T. B.; Johnson, D. F.; Katritzky, A. R.; Keogh, H. J.; Thirkettle, C.; Topsom, R. D. *J. Chem. Soc., Perkin Trans. 2* **1974**, *3*, 282.

(14) An analogous equation utilizing resin weight differences has been derived by Moore. See reference 5d.

Scheme 4



unreliable. Small mechanical mass losses naturally occurred during resin manipulations. Small mass increases due to residual solvent or impurities trapped in the polymer matrix were also observed. These small mass changes had an enormous effect on the calculated product yields since the weight changes due to the coupling or deprotection reactions were small relative to the weight of the initial resin. These errors were exacerbated when the weight change due to the reaction was small (for example, in a protodesilylation step), or when performing the reactions on a small scale. As a result, weight changes were only used as a rough guide to the success of a reaction.

The molar concentrations of the products in the final resins were also monitored for compounds **50**–**58**. The molar concentration decreases as the resin's mass increases due to modification of the reactive moiety. The actual concentration (mol/g) of the product in the final resin (N_{pf}) is given by

$$N_{pf} = YN_{si}/W_f = N_{si}Y/(1 + \Delta W) = YN_{si}/(1 + YN_{si}\,\Delta M) \quad (5)$$

where W_f is the weight of the final resin.

The theoretical concentration (mol/g) of product in the final resin is

Table 1. Data for Polymeric Support Reactions Derived Using Gravimetric Analysis

compound	theor wt change, ΔW_{theor} (g)	actual wt increase, ΔW (g)	% yield by wt diff, Y	theor product concn, N_{pf} (theor) (mmol/g)	exptl product concn, N_{pf} (mmol/g)
50	17.41	17.95	103	0.61	0.61
51	12.25	9.98	81	0.51	0.42
52	−0.84	−0.78	103	0.52	0.45
53	5.47	4.43	93	0.40	0.33
54	−0.20	−0.08	48	0.41	0.34[b]
55	2.56	1.71	168	0.28	0.21[b]
56	−0.04	0.03	–	0.29	0.21[b]
57	0.98	0.23	37[a]	0.17	0.07[b]

[a] Yield was calculated over two steps. [b] Based on quantitative yield for the deprotection step and the average two-step yield for the coupled product.

$$N_{\text{pf}}\,(\text{theor}) = N_{\text{si}}/1 + N_{\text{si}}\Delta M \qquad (6)$$

The theoretical and experimentally determined values for N_{pf} are listed in Table 1. In both cases the concentration of **50** in the final resin was determined via elemental analysis using a method that will be described later. This initial value of 0.61 mmol/g was then used as the basis for the remainder of the calculations. The errors of the weight measurement caused significant discrepancies in the calculated concentrations. As a result, the moles of reagent needed in the polymer-supported reactions were determined assuming quantitative yields for all previous steps other than the formation of **50**.

The yield of these reactions was also derived from the elemental analysis data. The calculations assumed that no side reactions were taking place and that unreacted functionality did not participate in any subsequent reactions. The element used for the calculations was unique either to the moiety being added to the resin or to the starting functionalized resin. Three distinct situations were encountered which required different methods of yield determination: (1) The tag element was added to the resin over the course of the reaction. (2) The tag element was removed from the resin. (3) The tag element was unique to the resin and present before and after the reaction. The derivation of the equations used for each case are outlined here.

Case 1: When the tag element is added to the resin during the course of the reaction the yield (Y) is given by

$$Y = (N_{\text{pi}}/N_{\text{si}}) \qquad (7)$$

where N_{pi} is the moles of product relative to 1 g of the initial resin, and N_{si} is again the moles of starting functionality in 1 g of the initial resin. Elemental analysis yields the weight fraction of the tag element (E). E is the weight in grams of an element (W_{e}) relative to the weight in grams of the final resin (W_{f}). Since the element is unique to the product, this can then be related to the moles of product in 1 g of the final resin (N_{pf}) by

$$E = W_{\text{e}}/W_{\text{f}} = N_{\text{pf}}M_{\text{e}}(N_{\text{e}}/N_{\text{p}}) \qquad (8)$$

where M_{e} is the molecular weight of the tag element in g/mol, N_{e} is the moles of the tag element, and N_{p} is the moles of product. N_{pf} is related to N_{pi} by

$$N_{\text{pf}} = N_{\text{p}}/W_{\text{p}} = N_{\text{p}}/(W_{\text{i}} + \Delta W) = N_{\text{pi}}/(1 + \Delta W/W_{\text{i}}) \qquad (9)$$

where W_{f} is the weight in grams of the final resin, W_{p} is the weight in grams of the product, and W_{i} is the weight in grams of the initial resin. With this relationship in hand, E can be expressed in terms of N_{pi}.

$$E = N_{\text{pi}}M_{\text{e}}(N_{\text{e}}/N_{\text{p}})/(1 + \Delta W/W_{\text{i}}) \qquad (10)$$

Rearrangement of this expression and substitution into eq 4 gives

$$Y = (N_{\text{p}}/N_{\text{e}})(E/M_{\text{e}}N_{\text{si}})\,(1+ \Delta W/W_{\text{i}}) \qquad (11)$$

Substituting the expression for ΔW (eq 4) into eq 8 gives the derivation of the yield from the elemental analysis.

$$Y = (N_{\text{p}}/N_{\text{e}})(E/M_{\text{e}}N_{\text{si}})(1 + YN_{\text{si}}\Delta M/W_{\text{i}}) = 1/[(N_{\text{e}}/N_{\text{p}})(M_{\text{e}}N_{\text{si}}/E) - N_{\text{si}}\Delta M] \qquad (12)$$

The yield for the formation of **50** based on the elemental analysis for N was

$$Y = 1/[3(14.0\text{ g/mol})(0.001\text{ mol/g})/0.0256] - (0.001\text{ mol/g})(349\text{ g/mol}) = 0.77 = 77\%$$

The moles per gram of Merrifield's resin has a reported error of ±0.05 mmoles. The error in the nitrogen determination is estimated to be ±0.2%. Therefore, an approximate expression for the error (e) in Y based on elemental analysis for nitrogen is

$$e = (5 \times 10^{-5}\text{ mol}/1.00 \times 10^{-3}\text{ mol}) + (0.002/\text{wt fraction } N) = \pm 0.13$$

This relatively high error is largely due to the low weight percent of nitrogen present in the final resin. Nevertheless, this method proved to be the most accurate for calculating the molar concentration of **50** on the polymer support. Calculation of the chloride concentration of Merrifield's resin by elemental analysis has a higher error than the titration method used by the manufacturer.

Case 2: When the tag element is removed during the course of the reaction the yield is given by

$$Y = 1 - (N^*_{\text{si}}/N_{\text{si}}) \qquad (13)$$

where N^*_{si} is the moles of unreacted starting functionality in the final resin relative to 1 g of starting resin. Because the tag element is unique to the unreacted resin, the weight fraction is now

$$E = W_{\text{e}}/W_{\text{f}} = N_{\text{sf}}M_{\text{e}}(N_{\text{e}}/N_{\text{p}}) \qquad (14)$$

where N_{sf} is the moles of starting functionality present in 1 g of final resin. N^*_{si} is related to N_{sf} by

$$N_{\text{sf}} = N^*_{\text{si}}/(1 + \Delta W/W_{\text{i}}) \qquad (15)$$

E can then be expressed in terms of N^*_{si}.

$$E = N^*_{\mathrm{si}} M_{\mathrm{e}} (N_{\mathrm{e}}/N_{\mathrm{s}})/(1 + \Delta W/W_{\mathrm{i}}) \tag{16}$$

where N_s is the moles of starting functionality. Rearrangement of this expression and substitution into eq 13 gives

$$Y = 1 - [(N_{\mathrm{s}}/N_{\mathrm{e}})(E/M_{\mathrm{e}}N_{\mathrm{si}})(1+ \Delta W/W_{\mathrm{i}})] \tag{17}$$

Substituting the expression for ΔW (eq 4) into eq 14 gives the calculation of the yield from element loss based on elemental analysis. Taking advantage of the ratio of tag element to product, $(N_p/N_e) = (N_s/N_e) = 1$ (for monosubstituted tag element on resin), the expression for calculating the yield becomes

$$Y = 1 - (N_{\mathrm{p}}/N_{\mathrm{e}})(E/M_{\mathrm{e}}N_{\mathrm{si}})(1+ YN_{\mathrm{si}}\Delta M/W_{\mathrm{i}}) = \frac{1 - [(N_{\mathrm{p}}/N_{\mathrm{e}})(E/M_{\mathrm{e}}N_{\mathrm{si}})]}{[\Delta M(N_{\mathrm{p}}/N_{\mathrm{e}})E/M_{\mathrm{e}}N_{\mathrm{e}}] + 1} \tag{18}$$

The yield for the formation of **50** based on loss of Cl is

$$Y = \frac{1 - [1(0.0061)/(35.45\ \mathrm{g/mol})(0.001\ \mathrm{mol/g})]}{1(349\ \mathrm{g/mol})(0.0061)/(35.45\ \mathrm{g/mol}) + 1} = 0.78 = 78\%$$

This yield is in good agreement with that based on analysis for nitrogen. The error for this measurement is estimated at ±0.29.

Case 3: If the tag element is unique to the resin but is not lost on reaction, the moles of the element are no longer directly related to the amount of product formed. The change in the elements' weight fraction is entirely due to the weight change of the resin. The weight change of the resin can be related to the change in the weight fraction of the tag element by

$$\Delta E = E_{\mathrm{f}} - E_{\mathrm{i}} = (W_{\mathrm{ef}}/W_{\mathrm{f}}) - (W_{\mathrm{ei}}/W_{\mathrm{i}}) = W_{\mathrm{ef}}/(W_{\mathrm{i}} + \Delta W) - W_{\mathrm{ei}}/W_{\mathrm{i}} \tag{19}$$

Recognizing that $W_{ei} = W_{ef}$, and expressing in terms of 1 g of initial resin, therefore $E_i = W_{ei}$, and eq 19 simplifies to

$$\Delta E = \left[\left(\frac{1}{1 + \Delta W}\right) - 1\right] W_{\mathrm{ei}} \tag{20}$$

Substituting eq 4 for ΔW and rearrangement gives the yield expressed in terms of weight fraction of the tag element before and after the reaction.

$$Y = \frac{\left(\frac{1}{1 + (\Delta E/E_{\mathrm{i}})}\right) - 1}{N_{\mathrm{si}}\Delta M} \tag{21}$$

The yield of the formation of **51** is then

$$Y = \frac{\{1/[1 + (-0.0025/0.0256)]\} - 1}{(0.00061\ \mathrm{mol/g})\ (341\ \mathrm{g/mol})} = 0.52 = 52\%$$

The estimated error for this measurement is ±0.92. The error was higher than the calculated value for all the compounds prepared. Clearly, the accuracy of this method is unacceptable for yield determination at the low nitrogen levels present in these systems.

Due to the inherent inaccuracies of yield determination based on elemental and gravimetric analysis, yields were also calculated based on the amount of cleaved product (by MeI treatment) recovered from the resin after each coupling step. The formula used for these determinations was

$$Y = \mathrm{N}_{\mathrm{p}}/N_{\mathrm{s}} = N_{\mathrm{p}}W_{\mathrm{i}}/N_{\mathrm{si}} \tag{22}$$

The value of 0.61 mmol/g, determined from elemental analysis, was used for the concentration of **50** in the polymer matrix. From that point onward, the yields were calculated over three steps. The moles of products were determined directly from purified compounds after cleavage from the resin. Subsequent to **50**, N_{si} for the initial polymer-supported compound of the three-step sequence was determined using eq 6. Using this method the yields of the cleaved dimer **25**, tetramer **34**, octamer **42**, and 16-mer **58** were 86%, 77%, 80%, and 79%, respectively. This corresponds to an average yield of 92−93% over the deprotection, coupling, and cleavage steps. The amount of material that remained uncleaved by the MeI treatment is not known, but the error in the nitrogen analysis excludes the possibility of this aiding in the determination.

In summary, the determination of the coupling efficiency on the polymer support has severe difficulties due to the fact that the resin comprises the vast majority of the materials' mass. Though the absolute error remains constant, the percent error increases at each iteration along the sequence. Therefore, yield determinations based on elemental composition changes along a series of steps eventually have such significant errors that the assessment becomes completely unreliable. However, if the initial linker's coupling efficiency is reasonably established, the yield determinations over the three-step sequence can be sufficiently utilized.

Characterization of the Oligomers. As mentioned above, while the ethyl-containing octamer **38** was nearly insoluble, the longer alkyl-bearing octamers **39** and **40**, as well as the corresponding 16-mers **45** and **46**, were quite soluble, and they could be adequately spectroscopically characterized. While many of the lower molecular weight oligomers could be characterized by direct exposure via electron impact MS, in order to obtain MS data on the soluble octamer **39** and 16-mer **45**, it was necessary to use matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) using a sinapinic acid matrix, positive ion mode. The dodecyl-containing octamer **40** and 16-mer **46** were simpler to characterize spectroscopically than the 3-ethylheptyl-containing oligomers since the former are not mixtures of diastereomers. However, **40** and **46**, being more lipophilic than **39** and **45**, were too insoluble in the polar MALDI-MS matrices, thus no MS data could be obtained. FAB-MS did not work on these samples, presumably due to charging difficulties. The 16-mers are 128 Å long as determined by a conformational minimization using MM2 with extended π-Hückel and multiconformational parameters.[15] This length is long enough to span the gaps between proximal patterned electronic probes.[1]

Absorption (Figure 1) and emission studies (Figure 2) were conducted on the oligomers. As expected, we

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[15] Oligomer lengths were simulated using standard molecular modeling procedures. All calculations were performed on a Power Macintosh 8100/80 AV using Personal CAChe version 3.7 for both structure drawing and minimization. The CAChe mechanics application implements a standard MM2 force field. All energy calculations were minimized over a large number of iterations to convergence at local minima nearest in energy to the starting compounds' energies.

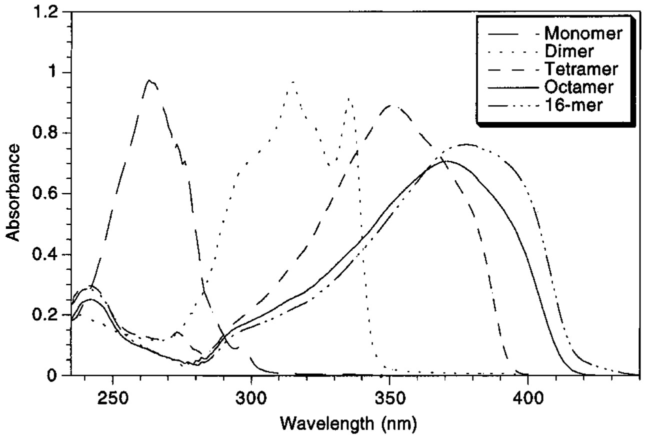


Figure 1. The UV-vis absorbance spectra (THF) of the monomer through 16-mer iodides, **16**, **25**, **34**, **42**, and **58**, respectively.

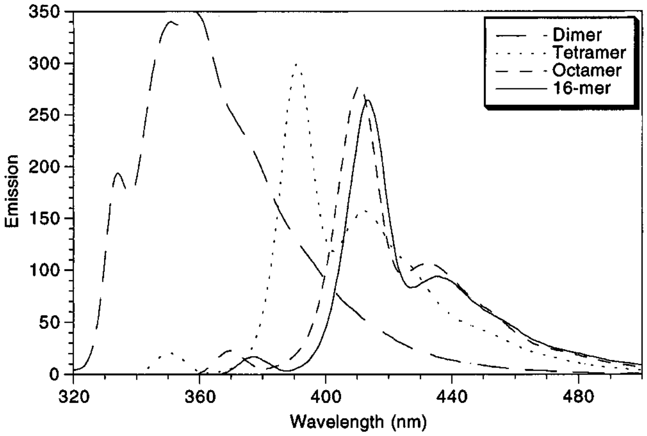


Figure 2. The fluorescence emission spectra (THF) of the dimer through 16-mer iodides, **25**, **34**, **42**, and **58**, respectively.

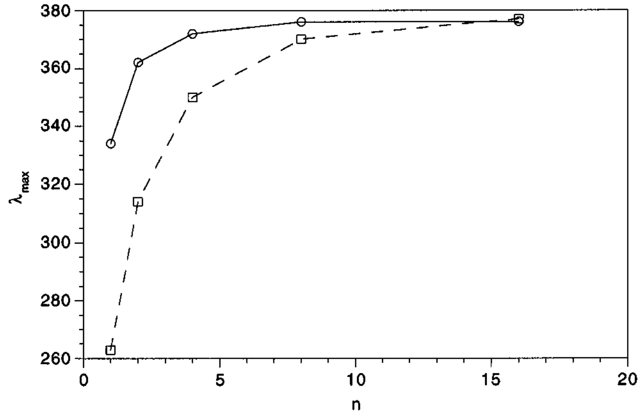


Figure 3. The optical absorbance maxima (λ_{max}) versus the number of repeat units (n) in the triazene-terminated oligomers **9**, **21**, **30**, **39**, and **45** (circles) and the iodide-terminated oligomers **16**, **25**, **34**, **42**, and **58** (squares).

observed an increase in the absorption maxima from shorter wavelength (263 nm) for the monomer **16** to longer wavelength (377 nm) for the 16-mer **58**. Likewise, an increase in the emission intensity from shorter wavelength (359 nm) for the dimer **25** to longer wavelength (414 nm) for the 16-mer **58** was observed (Figure 2). The monomer **16** did not fluoresce. Note that a near saturation of the systems appears to have occurred by the octamer stage so that doubling the conjugation length from the octamer to the 16-mer caused only a small bathochromic shift in absorption and emission maxima.

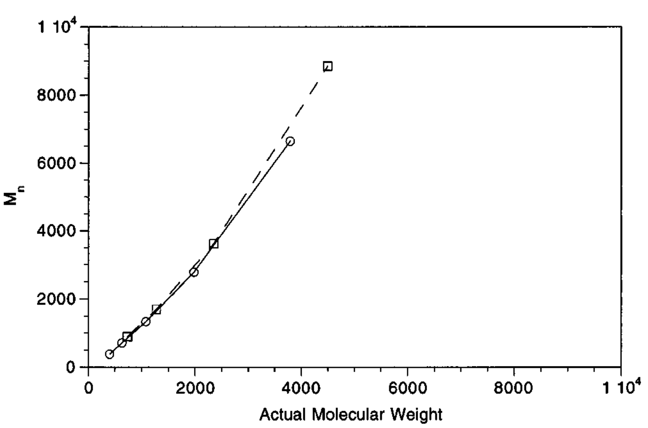
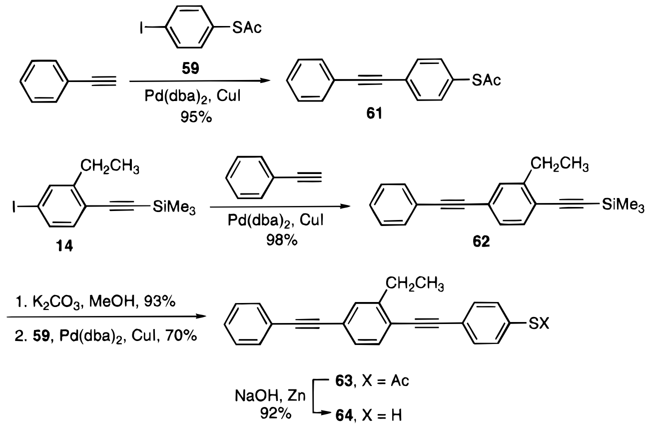


Figure 4. The values of M_n determined by SEC (relative to polystyrene standards in THF) versus the actual molecular weights for the triazene-terminated oligomers **9**, **21**, **30**, **39**, and **45** (circles) and the iodide-terminated oligomers **25**, **34**, **42**, and **58** (squares).

Scheme 5

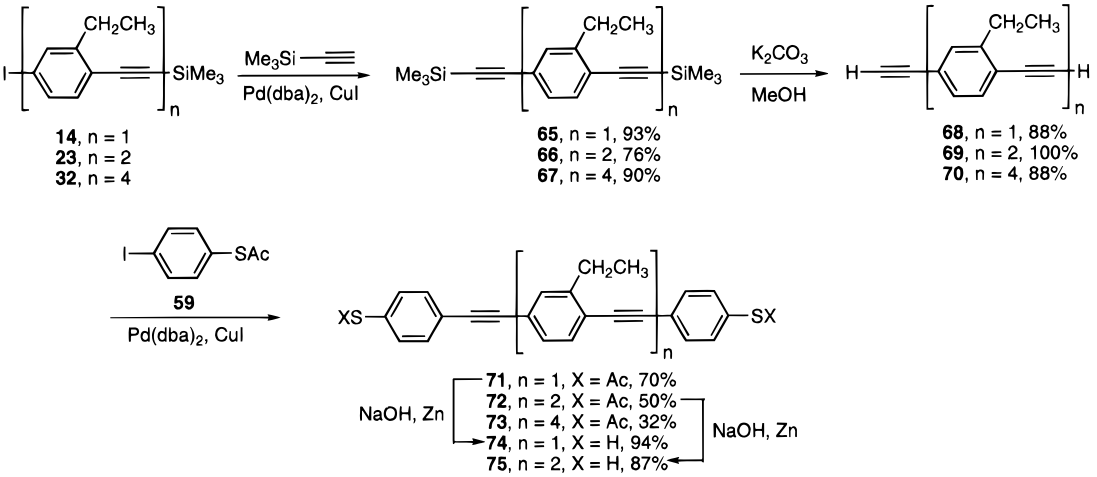


As illustrated in Figure 3, we also noticed that the π-extended triazene substituents shifted the absorption maxima bathochromically, relative to the corresponding iodides, for the monomers through octamers. However, the saturation effects are apparent at the 16-mer stage since the two absorptions are nearly identical (Figure 3).

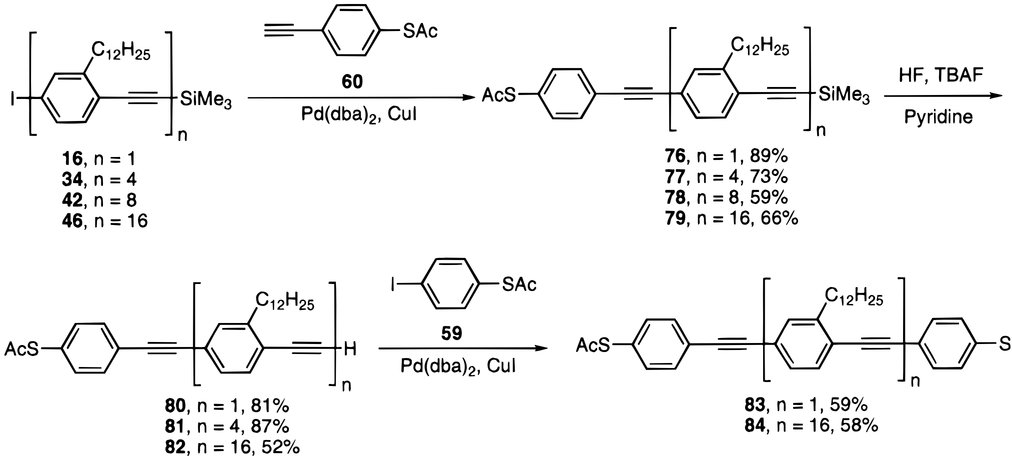
The results of the size exclusion chromatography (SEC), which is commonly used in the separation and identification of oligomers, are shown in Figure 4. SEC is not a direct measure of MW, but a measure of the hydrodynamic volume. Thus, the number average molecular weight (M_n) values of the rigid rod oligomers should be significantly inflated relative to the randomly coiled polystyrene standards. As expected, the M_n values of the monomer **9** (M_n = 390, actual MW = 400), dimer **21** (M_n = 715, actual MW = 626), dimer **25** (M_n = 900, actual MW= 736), tetramer **30** (M_n = 1335, actual MW = 1079), and tetramer **34** (M_n = 1705, actual MW= 1274) were reasonably close to the actual MWs (initial slope $\cong$ 1.0 in Figure 4), prior to significant polystyrene coiling. However, the M_n values of the octamer **39** (M_n = 2,790, actual MW= 1981), octamer **42** (M_n = 3625, actual MW= 2348), 16-mer **45** (M_n = 6650, actual MW= 3789), and 16-mer **58** (M_n = 8856, actual MW= 4495) were much greater than the actual MWs. As expected, these curves in Figure 4 are quite similar in their appearance to the curves generated from related thiopheneethynylene oligomers of similar molecular weights.[1]

Attachment of Thiol End Groups. With the requisite precisely defined oligo(phenylene ethynylene)s in

Scheme 6

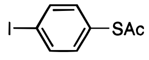


Scheme 7

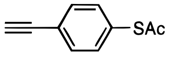


hand, we then addressed methods to affix protected thiols to the ends of the oligomers. The thiols serve as molecular alligator clips for adhesion to gold probe surfaces.[1,4] We recently used these thiol-terminated oligo(phenylene ethynylene)s to record electronic conduction through single undoped conjugated molecules that were end-bound onto a metal probe surface.[4c] These nearly linear molecules worked quite well for single molecule insertions into self-assembled monolayers of dodecane thiolate on gold, thereby providing a means of molecular isolation.[4c] Monothiol-terminated systems were prepared for adhesion of these oligomers to single gold surfaces, and in other cases, α,ω-difunctionalized systems were prepared for adhesion between proximal gold surfaces. Though the aromatic thiols could be synthesized under reductive base conditions, due to their oxidative instabilities, they proved difficult to use in actual surface deposition experiments. However, the acetyl-protected thiols were resilient enough for manipulations in air, yet they could be readily hydrolyzed with NH_4OH in the presence of the gold probe surfaces.[1,4]

Using a convergent method of molecular alligator clip formation and attachment, the two thioesters **59** and **60** were synthesized.[1] The aryl iodide **59** can be coupled to the alkynyl end (head) of the oligomers while the alkynyl arene **60** can be coupled to the aryl iodide end (tail) of the oligomers. Of course, our oligomers would permit orthogonal end group functionalization, for example, one end containing a thiol moiety for adhesion to gold and the other end a carboxy moiety for adhesion to an oxide. However, for all of our initial studies on difunctionalized systems, proximal gold connects were considered, thus identical end groups sufficed.



59



60

Scheme 5 shows the efficient attachment of **59** to the heads of both phenylacetylene and the dimeric system **62**. Scheme 6 shows an approach to a concomitant head and tail functionalization of the ethyl-containing monomer, dimer, and tetramer. Deprotection of the thiols was accomplished with NaOH under reductive conditions to minimize disulfide formation. Though this deprotection method proved effective for laboratory isolation and characterization of the thiols, it could not be used for molecular scale electronics study since exogenous metals such as zinc or Na^+ would interfere with electronic measurements.[4] Thus we developed the complementary *in situ* technique using NH_4OH.[4]

Both ends of the oligomers could be functionalized as shown in Scheme 6. However, the α,ω-bis-terminal alkynes **68**−**70** showed increasingly low yields in the couplings with **59**. Therefore, we used a stepwise procedure (Scheme 7) of tail functionalization, followed by protodesilylation, to afford **80**−**82**. The use of TBAF alone for the desilylation reactions also caused deacylation of sulfur; however, the buffered TBAF/HF conditions worked well. Finally, coupling with **59** permitted formation of the α,ω-dithioesters **83** and **84**.

Summary

We outlined the rapid syntheses of oligo(2-alkyl-1,4-phenylene ethynylene)s via an iterative divergent/convergent approach that needed only three sets of reaction conditions for the entire iterative synthetic sequence: an iodination, a protodesilylation, and a Pd/Cu-catalyzed cross coupling. The syntheses were conducted in solution and on a polymer support. At each stage in the iteration, the length of the framework doubled. Equations were derived for assessing the efficiency of the polymer-supported reactions based on resin weight differences, molar concentration differences, and elemental analysis data. Each of these methods had severe limitations. Attachment of the complementary thiol end groups, protected as thioester moieties, was achieved. These serve as binding units for adhesion to gold surfaces, and these rigid rod conjugated oligomers have been shown to exhibit single molecule conductivity.[4] This represents a step in the development of organic architectures for molecular scale electronic instruments.[1]

Experimental Procedures

General. The general instrumental methods and procedures used have been described previously.[1] Merrifield's resin was purchased from Aldrich. The *tert*-butyl nitrite diazonium formations,[7] methyl ketone to (trimethylsilyl)alkyne conversions,[6] Pd/Cu-catalyzed aryl halide−terminal alkyne couplings,[9] triazene formation and iodinations,[3a,b,7,10] and the protodesilylation reactions[16] were conducted according to reported procedures. Terminal alkynes beyond the dimer stage were often oxidatively unstable, and they were used immediately after preparation; thus spectroscopic characterization was minimized. The 3-ethylheptyl-containing oligomers could not be characterized by ^{13}C NMR due to the existence of multiple diastereomers. FTIR characterization of the polymer-supported reactions were carried out by placing ca. 10 mg of the polymer-supported material on a NaCl plate. After the beads were swollen with 2−3 drops of CCl_4, a second NaCl plate was pressed onto the beads, and an FTIR spectrum was recorded.[5] Gel-phase ^{13}C NMR spectra on the polymer-supported material were recorded at 125 MHz on a Brüker AM-500 spectrometer. The NMR gel samples were prepared as follows:[17] polymers were dried under vacuum at 60 °C until constant weight was obtained. 300 mg were weighed into a 10 mm NMR tube and $CDCl_3$ was added. Complete swelling of the polymers was normally achieved by allowing them to equilibrate with the solvent for 15−30 min. Sometimes, ultrasonic agitation (Bransonic 5200) was necessary to obtain well-dispersed samples. The syntheses of **59** and **60** have been described previously.[1] Unless otherwise noted, all compounds were >95% pure as judged by NMR, GC, or combustion analyses. The oligomers' puritites can be assessed by their polydispersity indexes M_w/M_n.

Calculation of Elemental Percentages for Merrifield's Resin. Merrifield's resin is a copolymer of styrene (x), 4-vinylbenzyl chloride (y), and divinylbenzene (z). The commercial resin was listed to contain 1% w/w divinylbenzene and 1.00 ± 0.05 mequiv/g of 4-vinylbenzyl chloride. Thus, the weight fraction of each unit can be determined as follows:

$$\text{wt fraction styrene (x)} + \text{wt fraction 4-vinylbenzyl chloride (y)} + \text{wt fraction divinylbenzene (z)} = 1.00$$

$$\text{wt fraction z} = 0.0100$$

$$\text{wt fraction y} = (0.001\ \text{mol y} \times 152.63\ \text{g/mol})/1\ \text{g resin} = 0.1526$$

$$\text{wt fraction x} = 1.000 - (0.1526 + 0.0100) = 0.8374$$

The percentages of the elements present in each unit were the following: x: C: 92.24%, H: 7.76%; y: C: 70.82%, H: 5.96%, Cl: 23.23%; z: C: 90.83%, 9.17%.

The percentage of a given element in the resin was then the sum of the weight fractions of each unit multiplied by the percentage of the element in each unit. Therefore, the percentage of each element in Merrifield's resin was:

$$\%\text{C} = (\%\text{C in x})(\text{wt fraction x}) + (\%\text{C in y})(\text{wt fraction y}) + (\%\text{C in z})(\text{wt fraction z}) = (92.24\%)(0.8374) + (70.82\%)(0.1526) + (90.83\%)(0.0100) = 88.96\%$$

$$\%\text{H} = (\%\text{H in x})(\text{wt fraction x}) + (\%\text{H in y})(\text{wt fraction y}) + (\%\text{H in z})(\text{wt fraction z}) = (7.76\%)(0.8374) + (5.96\%)(0.1526) + (9.17\%)(0.0100) = 7.50\%$$

$$\%\ \text{Cl} = (\%\ \text{Cl in y})(\text{wt fraction y}) = (23.23\%)(0.1526) = 3.54\%$$

Calculation of Elemental Percentages for the Functionalized Resins. The percentage of each element in the functionalized resins was determined in a manner analogous to that used for Merrifield's resin. Calculations were performed based on a 77% yield for the formation of **50** on the polymer support. For compounds **50**−**57**, the resin was treated as a mixture of x, y, z and the functionalized unit (y′). The relative percentages of y and y′ were assigned as 23% and 77% respectively, based on the yield derived from analysis for nitrogen. The formation of **51**−**57** was assumed to be quantitative. Sequential modification of the initial y unit caused a change in the relative percentages of the monomer units comprising the resin. The weight increase for 1 g of Merrifield's resin caused by the modification was:

$$\text{wt increase for 1 g of Merrifield's resin} = [(\text{molecular wt of y}') - (\text{molecular wt of y})](\text{mol y in 1 g of Merrifield's resin})$$

Using **50** as an example:

$$= [(501.8\ \text{g/mol}) - (152.6\ \text{g/mol})](0.001\ \text{mol} \times 0.77) = 0.269\ \text{g}$$

The weight fraction of each unit was then:

$$\text{wt fraction styrene (x)} + \text{wt fraction 4-vinylbenzyl chloride (y)} + \text{wt fraction functionalized 4-vinylbenzyl chloride (y}') + \text{wt fraction divinylbenzene (z)} = 1.00$$

Again using **50** as an example:

$$\text{wt fraction z} = 0.0100\ \text{g z}/1.269\ \text{g resin} = 0.0079$$

$$\text{wt fraction y} = (0.001\ \text{mol y} \times 0.23 \times 152.6\ \text{g/mol}) = 0.0351$$

$$\text{wt fraction y}' = (0.001\ \text{mol y}' \times 0.77 \times 501.8\ \text{g/mol})/1.269\ \text{g resin} = 0.3045$$

$$\text{wt fraction x} = 0.8374\ \text{g x}/1.269\ \text{g resin} = 0.6599$$

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(16) (a) Bengton, G.; Keyaniyan, S.; Demeijere, A. *Chem. Ber.* **1986**, *119*, 3607. (b) Hurst, D. T.; McInnes, A. G. *Can. J. Chem.* **1965**, *43*, 2004. (c) Gaffney, B. L.; Jones, R. A. *Tetrahedron Lett.* **1982**, *23*, 2257.

(17) Giralt, E.; Rizo, J.; Pedroso, E. *Tetrahedron* **1984**, *40*, 4141.

The percentage of each element could then be determined as before.

$$\%C = (\%C \text{ in } x)(\text{wt fraction } x) + (\%C \text{ in } y)(\text{wt fraction } y) + (\%C \text{ in } y')(\text{wt fraction } y') + (\%C \text{ in } z)(\text{wt fraction } z) = (92.24\%)(0.6599) + (70.82\%)(0.0351) + (78.98\%)(0.3045) + (90.83\%)(0.0079) = 88.12\%$$

$$\%H = (\%H \text{ in } x)(\text{wt fraction } x) + (\%H \text{ in } y)(\text{wt fraction } y) + (\%H \text{ in } y')(\text{wt fraction } y') + (\%H \text{ in } z)(\text{wt fraction } z) = (7.76\%)(0.6599) + (5.96\%)(0.0351) + (6.64\%)(0.3045) + (9.17\%)(0.0079) = 7.42\%$$

$$\%N = (\%N \text{ in } y')(\text{wt fraction } y') = (8.37\%)(0.3045) = 2.55\%$$

$$\%\,Cl = (\%\,Cl \text{ in } y)(\text{wt fraction } y) = (23.23\%)(0.0351) = 0.82\%$$

3-Ethylaniline.[2] Anhydrous ethanol (100 mL), 3-nitroacetophenone (16.52 g, 100 mmol), concentrated hydrochloric acid (20.0 mL), and 10% palladium on carbon (2 g) were placed in a Parr flask. The flask was purged with hydrogen before pressurizing to 60 psi and heating to 70 °C. The pressure was maintained overnight. The palladium on carbon was then filtered and the reaction mixture poured into 3 M sodium hydroxide (200 mL). The solution was extracted with ether (3×) and the combined organic layers were washed with brine and dried over magnesium sulfate. The magnesium sulfate was filtered and the solvent removed *in vacuo* to afford 12.29 g of the title compound as a brown oil which was taken on to the next step with no further purification. $R_f = 0.14$ (9:1; hexane:ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (t, $J = 7.7$ Hz, 1 H), 6.62 (d, $J = 7.1$ Hz, 1 H), 6.54 (s, 1 H), 6.53−6.51 (m, 1 H), 3.55 (br s, 2 H), 2.56 (q, $J = 7.6$ Hz, 2 H), 1.21 (t, $J = 7.6$ Hz, 3 H). HRMS calcd for $C_8H_{11}N$: 121.0891. Found: 121.0888.

3-Ethyl-*N*-(*tert*-butoxycarbonyl)aniline (1). To a solution of crude 3-ethylaniline (**7**) (100 mmol) and di-*tert*-butyl dicarbonate (34.50 g, 150 mmol) in THF (300 mL) was added 1 M sodium hydroxide (300 mL) in three portions. The reaction was heated to reflux for 2 h and cooled to room temperature. The reaction was poured into water and the organic layer extracted with ether (3×). The organic layer was dried over magnesium sulfate, filtered, and concentrated *in vacuo*. The crude mixture was purified by flash chromatography on silica gel (9:1; hexane:ether) to afford 21.12 g (96%) of the title compound as a yellow oil. $R_f = 0.39$ (9:1; hexane:ether). IR (neat) 3332, 2971, 2932, 2875, 1704, 1610, 1534, 1492, 1441, 1368, 1309, 1247, 1162, 1054, 986, 871, 774, 738, 721, 697 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, $J = 7.8$ Hz, 1 H), 7.15 (s, 1 H), 7.10 (d, $J = 8.1$ Hz), 6.86 (d, $J = 7.4$ 1 H), 6.42 (br s, 1 H), 2.62 (q, $J = 7.6$ Hz, 2 H), 1.50 (s, 9 H), 1.21 (t, $J = 7.6$ Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.0, 145.3, 138.4, 128.9, 122.6, 118.1, 116.0, 80.3, 29.0, 28.4, 15.6. HRMS calcd for $C_{13}H_{19}NO_2$: 221.1416. Found: 221.1420.

4-Amino-2-ethylacetophenone (2).[2] To a 250 mL three-neck round-bottomed flask equipped with a reflux condenser and drying tube containing aluminum chloride (4.93 g, 37 mmol) and carbon disulfide (50 mL) at 0 °C were added **1** (2.32 g, 10.5 mmol) in carbon disulfide (50 mL) and acetyl chloride (1.49 mL, 21 mmol). The reaction mixture was heated to reflux at 70 °C overnight. After cooling to 60 °C the reflux condenser was removed to allow the carbon disulfide layer to boil off before pouring it into ice−water (10 mL). The solution was then poured into 3 M potassium hydroxide (100 mL) and extracted with ether (5×). The combined organic extracts were washed with brine and dried over magnesium sulfate. The solution was filtered, and the solvent was removed *in vacuo* to give a brown oil that was purified by flash chromatography on silica gel (2:1; hexane:ether) to afford 0.82 g (48%) of the title compound as a dark brown liquid which solidified upon standing. $R_f = 0.27$ (2:1; hexane:ether). Mp 53−55 °C. IR (KBr) 3456.5, 3347.7, 3218.7, 2966.0, 1635.2, 1601.8, 1553.6, 1455.7, 1358.4, 1336.8, 1293.8, 1256.0, 1186.6, 1145.7, 1059.7, 1017.8, 954.0, 874.6, 857.6, 821.8, 585.7, 583.8, 547.8 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, $J = 7.9$ Hz, 1 H), 6.46 (s, 1 H), 6.44−6.42 (m, 1 H), 4.15 (s, 2 H), 2.89 (q, $J = 7.4$ Hz, 2 H), 2.47 (s, 3 H), 1.15 (t, $J = 7.4$ Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.0, 150.3, 148.5, 133.4, 126.5, 116.1, 111.0, 29.0, 28.0, 15.6. HRMS calcd for $C_{10}H_{13}NO$: 163.0997. Found: 163.0992.

4-(Diethyltriazenyl)-2-ethylacetophenone (3).[2] To **2** (12.60 g, 77.3 mmol) in water (316 mL) and hydrochloric acid (53 mL) was added sodium nitrite (5.48 g, 79.42 mmol) in water (10 mL) at 0 °C. The reaction was stirred at 0 °C for 30 min and then poured into water (530 mL), potassium carbonate (84 g), and diethylamine (63 mL) at 0 °C. The reaction was stirred for 30 min at 0 °C and then poured into water. The aqueous layer was extracted with diethyl ether (3 × 25 mL), the organic layer was dried over magnesium sulfate, and the product was concentrated *in vacuo* to afford 17.90 g (94%) of the title compound as a dark brown liquid. IR (neat) 2975, 2935, 2873, 1680, 1597, 1556, 1243, 1109, 952 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, $J = 8.2$ Hz, 1 H), 7.29−7.25 (m, 2 H), 3.77 (q, $J = 7.2$ Hz, 4 H), 2.93 (q, $J = 7.4$ Hz, 2 H), 1.27 (br t, 6 H), 1.22 (t, $J = 7.5$ Hz, 3 H). ^{13}C NMR δ 201.1, 154.1, 146.9, 133.8, 131.6, 123.1, 117.4, 30.0, 28.1, 16.2. HRMS calcd for $C_{14}H_{21}N_3O$: 247.1685. Found: 247.1687.

1-(Diethyltriazenyl)-3-ethyl-4-[(trimethylsilyl)ethynyl]benzene (4).[2] To a stirred solution of diisopropylamine (9.4 mL, 67 mmol) in THF (70 mL) was added at 0 °C under nitrogen *n*-butyllithium (40.6 mL, 65 mmol, 1.6 M in hexanes). The reaction mixture was stirred at 0 °C for 5 min and then cooled to −78 °C. To the LDA solution was added **3** (15.5 g, 62.8 mmol) in THF (40 mL). The reaction mixture was stirred at −78 °C for 1 h before adding, at the same temperature, diethyl chlorophosphate (9.1 mL, 63 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 3 h. The reaction solution was then transferred via cannula into 2.25 equiv of LDA [made as above with diisopropylamine (19.6 mL, 140 mmol) and *n*-butyllithium (88.3 mL, 141.3 mmol) in THF (150 mL)] at −78 °C. The ensuing reaction mixture was stirred at −78 °C for 30 min and then allowed to warm to room temperature overnight at which time the reaction was cooled to 0 °C and chlorotrimethylsilane (8.2 mL, 65 mmol) was added. The solution was poured into water (100 mL) and extracted with ether. The combined ether extracts were washed with brine and dried over magnesium sulfate. Filtration and removal of the solvent *in vacuo* left a brown oil which, upon purification by flash chromatography on silica gel (5:1; hexane:ethyl acetate), afforded 10.81 g (57%) of the title compound as a clear, colorless oil. IR (neat) 3290, 2105, 1585, 1482, 1390, 1090, 1065, 1005, 820, 620 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, $J = 8.2$ Hz, 1 H), 7.23 (d, $J = 1.7$ Hz, 1 H), 7.16 (dd, $J = 8.2, 2.1$ Hz, 1 H), 3.74 (q, $J = 7.2$ Hz, 4 H), 2.78 (q, $J = 7.5$ Hz, 2 H), 1.24 (t, $J = 7.2$ Hz, 9 H), 0.23 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.4, 147.6, 133.1, 120.3, 118.6, 117.5, 104.7, 97.2, 28.0, 14.7, 0.18. HRMS calcd for $C_{17}H_{27}N_3Si$: 301.1974. Found: 301.1983.

2-Ethyl-1-iodohexane.[2] To dichloromethane (150 mL) in a 500 mL oven-dried vessel equipped with a condenser was added sequentially triphenylphosphine (15.7 g, 60 mmol), imidazole (4.1 g, 60 mmol), and iodine (15.2 g, 60 mmol). The mixture was stirred until the iodine had dissolved and a reddish-yellow solid appeared. To the mixture was added dropwise 2-ethyl-1-hexanol (7.8 mL, 50 mmol), keeping the temperature of the reaction just below reflux. After addition of the alcohol was complete, the reaction was stirred for 2 h and monitored by gas chromatography. The completed reaction was concentrated in vacuo, and silica gel (10 g) was added to the resulting crude mixture in hexane (100 mL). The mixture was stirred for 15 min and filtered through a plug of silica gel. The resulting clear solution was concentrated *in vacuo* to afford the title compound in nearly quantitative yield. IR (neat) 2960, 2928, 2858, 1458, 1187 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.25 (2 sets of overlapping dd, $J = 14.1, 9.0$ Hz, 2 H), 1.4−1.1.0 (m, 9 H), 0.88 (t, $J = 6.5$ Hz, 3 H), 0.84 (t, $J = 7.4$ Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.7, 34.1, 29.2, 27.4, 23.2, 16.5, 14.5, 11.3.

3-Nitrobenzoyl Chloride (5).[2] To an oven-dried vessel were added 3-nitrobenzoic acid (83.56 g, 500 mmol) and benzene (1 L). The vessel was fitted with a reflux condenser and drying tube. To the reaction was added oxalyl chloride (65.4 mL, 750 mmol) at room temperature. After seeing no reaction after a period of 10 min, 1 drop of *N*,*N*-dimethylformamide was added. Stirring was continued until evolution of hydrogen chloride and carbon monoxide was complete. The reaction was concentrated in vacuo, and calcium hydride (2 g) and benzene (200 mL) were added. Stirring was continued for 1 h at which time the reaction was filtered through Celite and concentrated in vacuo to afford 92.3 g (99%) of the title compound as a brown solid. ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.94, (t, J = 2.0 Hz, 1 H), 8.53 (ddd, J = 8.2, 2.3, 1.0 Hz, 1 H), 8.42 (ddd, J = 7.9, 1.8, 1.2 Hz, 1 H), 7.75 (t, J = 8.0 Hz, 1 H).

1-(3′-Nitrophenyl)-3-ethylheptane-1-one (6).[2] To *tert*-butyllithium (37.4 mL, 80 mmol, 2.14 M in hexane) in ether (20 mL) was added 2-ethyl-1-iodohexane (9.6 g, 40 mmol) at −78 °C. The reaction mixture was stirred for 30 min and then added to flame-dried zinc chloride (7.6 g, 56 mmol) in THF (30 mL) at room temperature. The resulting cloudy solution was stirred for 30 min. In a separate vessel was combined tetrakis(triphenylphosphine)palladium(0) (0.7 g, 0.6 mmol) and 3-nitrobenzoyl chloride (5.57 g, 30 mmol) in THF (10 mL), and the vessel was flushed with nitrogen. To the resulting Pd(0) solution was then added the zinc reagent at room temperature. The reaction was stirred at room temperature overnight and then poured into water. The aqueous layer was extracted with ethyl acetate and dried over magnesium sulfate. The organic layer was filtered and concentrated in vacuo. The crude product was filtered and purified by flash chromatography on silica gel (5:1; hexane:ethyl acetate) to afford 1.8 g (39%) of the title compound as a clear yellow oil. IR (neat) 3086, 2929, 2873, 1694, 1614, 1538, 1351 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.75 (t, J = 0.8 Hz, 1 H), 8.40 (dt, J = 7.7, 0.8 Hz, 1 H), 8.26 (dt, J = 7.7, 0.8 Hz, 1 H), 7.66 (t, J = 7.7 Hz, 1 H), 2.90 (d, J = 6.6 Hz, 2 H), 2.03 (m, 1 H), 1.41−1.23 (m, 8 H), 0.88 (t, J = 7.2 Hz, 3 H), 0.85 (t, J = 7.4 Hz, 3 H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 198.3, 138.7, 133.6, 129.9, 127.1, 124.5, 123.0, 43.2, 35.6, 33.2, 28.9, 26.5, 22.9, 14.0, 10.9.

1-(3′-Nitrophenyl)-3-ethylheptan-1-ol.[2] To a suspension of sodium borohydride (1.89 g, 50 mmol) in ethanol (100 mL) at 0 °C was added **6** (26.3 g, 100 mmol) in ethanol (25 mL), and the reaction was stirred at 0 °C for 1 h. The reaction was quenched by the slow addition of 3 N hydrochloric acid at 0 °C, and the organic layer was extracted with ethyl acetate. The crude product was purified by flash chromatography on silica gel (7:1; hexane:ethyl acetate) to afford 17.88 g (67%) of the title compound as a brown oil. IR (neat) 3418, 2923, 1538, 1348, 1065, 807, 739, 691 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.21 (t, J = 2.0 Hz, 1 H), 8.10 (dd, J = 7.9, 2.1 Hz, 1 H), 7.67 (dd, J = 8.4, 0.9 Hz, 1 H), 7.50 (t, J = 7.9 Hz, 1 H), 4.87 (td, J = 8.4, 4.2 Hz, 1 H), 1.90 (d, J = 3.6 Hz, 1 H), 1.78−1.69 (m, 1 H), 1.61−1.22 (m, 9 H), 0.90−0.81 (m, 6 H).

1-(3′-Nitrophenyl)-1-acetoxy-3-ethylheptane.[2] To a solution of 4-(*N*,*N*-dimethylamino)pyridine (0.16 g, 1.3 mmol) and 1-(3′-nitrophenyl)-3-ethylheptan-1-ol (36.02 g, 135.9 mmol) in pyridine (150 mL) at 0 °C was added acetic anhydride (18.9 mL, 200 mmol) dropwise over 10 min. The reaction was stirred for 30 min and monitored by TLC. The reaction was poured into cold 3 N hydrochloric acid, and the organic layer extracted with ethyl acetate. The organic layer was dried over magnesium sulfate, filtered, and concentrated in vacuo to afford 40.49 g (97%) of the title compound as a brown oil. No purification was necessary. IR (neat) 2926, 1746, 1538, 1463, 1351, 1232, 1023 cm $^{-1}$. ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.19 (s, 1 H), 8.13 (d, J = 7.1 Hz, 1 H). 7.62 (d, J = 7.7 Hz, 1 H), 7.50 (t, J = 8.0 Hz, 1 H), 5.83 (2 overlapping d, J = 8.9, 8.9 Hz, 1 H), 2.07 (s, 3 H), 1.97−1.82 (m, 1 H), 1.65−1.57 (m, 2 H), 1.44−1.16 (m, 8 H), 0.89−0.79 (m, 6 H).

1-(3′-Aminophenyl)-3-ethylheptane.[2] To a 1 L oven-dried round-bottomed flask equipped with a dry ice condenser was condensed liquid ammonia (400 mL), and then lithium metal (13.9 g, 2 mequiv) was added in small portions over 30 min. The resulting blue solution was stirred at −33 °C for 30 min and 1-(3′-nitrophenyl)-1-acetoxy-3-ethylheptane (61.4 g, 200 mmol) was added dropwise in THF (400 mL) at −78 °C over 30 min. The reaction was stirred at −33 °C for 1 h and quenched by the slow addition of ethanol. The crude mixture was subjected to aqueous workup and the organic layer extracted with ethyl acetate (4 × 50 mL). The organic layer was dried over magnesium sulfate and purified by flash chromatography on silica gel (5:1, hexane:ethyl acetate) to afford 26.1 g (60 % yield) of the title compound as a light brown oil. IR (neat) 3450, 3370, 2926, 1621, 1462, 1392, 1166 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.05 (t, J = 8.0 Hz, 1 H), 6.57 (d, J = 8.0 Hz, 1 H), 6.51 (s, 1 H), 6.49 (d, J = 7.7 Hz, 1 H), 3.58 (br s, 2 H), 2.47 (2 sets of overlapping ddd, J = 16.6, 5.7, 5.5 Hz, 2 H), 1.57−1.43 (m, 2 H), 1.33−1.22 (m, 9 H), 0.9−0.82 (m, 6 H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 146.4, 144.7, 129.2, 118.8, 115.3, 112.5, 38.7, 35.1, 33.2, 32.7, 28.9, 25.8, 23.2, 14.2, 10.8.

1-(3′-Amino-*N*-[(*tert*-butoxycarbonyl)phenyl]-3-ethylheptane (7).[2] To a solution of 1-(3′-aminophenyl)-3-ethylheptane (1.1 g, 5 mmol) and di-*tert*-butyl dicarbonate (1.5 mL, 6.5 mmol) in THF (15 mL) was added 1 N sodium hydroxide (15 mL) in three portions. The reaction was heated to reflux for 2 h and cooled to room temperature. The reaction was poured into water and the organic layer extracted with ethyl acetate. The organic layer was dried over magnesium sulfate, filtered, and concentrated *in vacuo*. The crude mixture was purified by flash chromatography on silica gel (6:1; hexane: ethyl acetate) to afford 1.39 g (87%) of the title compound as a brown oil. IR (neat) 3336, 2928, 1704, 1594, 1531, 1442, 1367, 1237, 1164, 1055 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.19 (s, 1 H), 7.15 (d, J = 7.3 Hz, 1 H), 7.12 (2 line m, 1 H), 6.84 (d, J = 7.2 Hz, 1 H), 6.40 (br s, 1 H), 2.53 (2 sets of overlapping ddd, J = 17.1, 6.0, 5.1 Hz, 2 H), 1.53−1.49 (m, 1 H), 1.50 (s, 9 H), 1.32−1.22 (m, 10 H), 0.88 (t, J = 6.3 Hz, 3 H), 0.84 (t, J = 7.7 Hz, 3 H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 152.8, 144.4, 138.3, 128.8, 123.1, 118.5, 115.8, 80.3, 39.3, 38.7, 35.2, 33.3, 32.7, 28.9, 28.4, 25.7, 23.2, 14.2, 10.8.

4-Amino-2-(3′-ethylheptyl)acetophenone.[2] To a 25 mL three-neck round-bottomed flask equipped with a reflux condenser and drying tube containing aluminum chloride (0.93 g, 7.0 mmol) and carbon disulfide (10 mL) at 0 °C were added **7** (0.64 g, 2.0 mmol) in carbon disulfide (10 mL) and acetyl chloride (0.28 mL, 4.0 mmol). The reaction mixture was heated to reflux at 70 °C for 3 h. After cooling to 60 °C, the reflux condenser was removed to allow the carbon disulfide layer to boil off before pouring it into ice−water (20 mL). The solution was then poured into 3 N sodium hydroxide (20 mL) and extracted with ether. The combined organic extracts were washed with brine and dried over magnesium sulfate. The solution was filtered and the solvent removed *in vacuo* to give a brown oil that was purified by flash chromatography on silica gel (3:1; hexane:ethyl acetate) to afford 0.36 g (70%) of the title compound as a dark liquid. IR (neat) 3500, 3362, 2926, 1601, 1455, 1252, 1141, 1054 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.59 (d, J = 9.1 Hz, 1 H), 6.47 (s, 1 H), 6.45 (d, J = 9.9 Hz, 1 H), 3.96 (br s, 2 H), 2.86−2.80 (4 line m, 2 H), 2.49 (s, 3 H), 1.47−1.43 (m, 2 H), 1.39−1.22 (m, 9 H), 0.88 (t, J = 7.5 Hz, 3 H), 0.86 (t, J = 7.5 Hz, 3 H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 199.23, 150.05, 148.11, 133.55, 127.58, 117.25, 111.39, 39.75, 35.69, 33.15, 32.76, 29.41, 29.39, 26.15, 23.53, 14.58, 11.24.

4-(Diethyltriazenyl)-2-(3′-ethylheptyl)acetophenone (8).[2] To an oven-dried vessel containing boron trifluoride etherate (0.37 mL, 3.0 mmol) at 0 °C was added 4-amino-2-(3′-ethylheptyl)acetophenone (0.52 g, 2.0 mmol) in dichloromethane (2 mL) followed by *tert*-butyl nitrite (0.3 mL, 2.5 mmol). The reaction was stirred for 30 min at 0 °C, and potassium carbonate (1 g) and diethylamine (1 mL) were added sequentially. The reaction was stirred for 1 h and poured into water. The organic layer was extracted with ethyl acetate and dried over magnesium sulfate. The sample was concentrated in vacuo to afford 0.65 g (95%) of the title compound as a dark liquid. IR (neat) 2929, 1677, 1352, 1240, 1107 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.66 (d, J = 8.8 Hz, 1 H), 7.25 (2 line m, 2 H), 3.77 (q, J = 7.1 Hz, 4 H), 3.02−3.00 (4 line m, 1 H), 2.88−2.82 (4 line m, 1 H), 2.55 (s, 3 H), 1.55 (br s, 1 H), 1.46−1.15 (m, 16 H), 0.95−0.82 (m, 6 H).

1-(Diethyltriazenyl)-3-(3′-ethylheptyl)-4-[(trimethylsilyl)ethynyl]benzene (9).[2] To a stirred solution of diisopropylamine (1.8 mL, 13 mmol) in THF (15 mL) was added at 0 °C, under nitrogen, *n*-butyllithium (8.1 mL, 12 mmol, 1.49 M in hexanes). The reaction mixture was stirred at 0 °C for 5 min and then cooled to −78 °C. To the LDA solution was added **8** (3.71 g, 10.8 mmol) in THF (2 mL). The reaction mixture was stirred at −78 °C for 1 h before adding, at the same temperature, diethyl chlorophosphonate (1.7 mL, 12 mmol). The reaction mixture was allowed to warm to room temperature and then stirred for 3 h. The reaction solution was then transferred via cannula into 2.25 equiv of LDA [made as above with diisopropylamine (3.1 mL, 22 mmol) and *n*-butyllithium (16.3 mL, 24.3 mmol)] in THF (25 mL) at −78 °C. The ensuing reaction mixture was stirred at −78 °C for 30 min and then allowed to warm to room temperature for 1 h, at which time the reaction was cooled to 0 °C and chlorotrimethylsilane (1.4 mL, 11 mmol) was added. The reaction was stirred for 2 h at room temperature, and the solution was poured into water (20 mL) and extracted with ether. The combined ether extracts were washed with brine and dried over magnesium sulfate. Filtration and removal of the solvent *in vacuo* left a brown oil which upon purification by flash chromatography on silica gel (9:1; hexane:ethyl acetate) afforded 1.9 g (43%) of the title compound as a yellow oil. IR (neat) 2959, 2148, 1598, 1402, 1248, 1103, 843, 759 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, J = 8.2 Hz, 1 H), 7.21 (s, 1 H), 7.16 (d, J = 8.2 Hz, 1 H), 3.74 (q, J = 7.1 Hz, 4 H), 2.78 (m, 2 H), 1.63 (m, 1 H), 1.30−1.17 (m, 16 H), 0.95−0.81 (m, 6 H), 0.23 (s, 9 H). LRMS calcd for $C_{23}H_{41}N_3Si$: 399. Found: 399. λ_{max} (CH_2Cl_2) = 334 nm. UV 10% edge value = 388 nm. M_n = 390, M_w = 417, M_w/M_n = 1.07.

General Procedure for the Coupling of a Terminal Alkyne with an Aryl Halide. Before beginning the reaction, all of the starting materials were thoroughly flushed with argon and/or nitrogen. To a stirring solution of the aryl halide, bis(dibenzylideneacetone)palladium(0) (2 mol %), triphenylphosphine (2.5 equiv based on Pd(0)), and copper(I) iodide (2 mol %) in THF was added the terminal alkyne followed by the amine (4 equiv based on aryl halide) at room temperature (unless otherwise stated) under argon and/or nitrogen in a screw cap tube. The vessel was flushed with argon and/or nitrogen, sealed, and allowed to stir overnight. The reaction mixture was then subjected to an aqueous workup and the aqueous layer extracted with ether, dichloromethane, or ethyl acetate (3×). After drying the combined organic layers over magnesium sulfate, the solvent was removed *in vacuo* to afford a crude product which was purified by column chromatography (silica gel). Eluents and other slight modifications are described below for each reaction.

3-(1′-Dodecynyl)nitrobenzene. 1-Iodo-3-nitrobenzene (12.45 g, 50 mmol), 1-dodecyne (11.76 mL, 55 mmol), bis(dibenzylideneacetone)palladium(0) (0.57 g, 1.0 mmol), triphenylphosphine (0.66 g, 2.50 mmol), copper(I) iodide (0.19 g, 1.0 mmol), *N*,*N*-diisopropylethylamine (35 mL, 200 mmol), and THF (50 mL) afforded 14.21 g (99%) of the title compound as a light brown oil after gravity liquid chromatography (9:1; hexane:ether). R_f = 0.76 (9:1; hexane:ether). IR (neat) 3084, 2921, 2855, 2229, 1959, 1902, 1825, 1795, 1728, 1572, 1534, 1467, 1351, 1301, 1165, 1096, 900, 805, 736, 675 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1 H), 8.10 (ddd, J = 8.3, 2.2, 1.0 Hz, 1 H), 7.65 (d, J = 7.7 Hz, 1 H), 7.43 (t, J = 8.1 Hz, 1 H), 7.24 (s, 1 H), 2.40 (t, J = 7.1 Hz, 2 H), 1.60 (p, J = 7.0 Hz, 2 H), 1.43 (p, J = 7.0 Hz, 2 H), 1.28−1.25 (m, 12 H), 0.86 (t, J = 7.1 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.01, 137.22, 129.04, 126.26, 125.94, 122.10, 93.58, 78.46, 31.90, 29.59, 29.52, 29.32, 29.14, 28.93, 28.47, 22.68, 19.33, 14.06. HRMS calcd for $C_{18}H_{25}NO_2$: 287.1885. Found: 287.1891.

3-Dodecylaniline (10). Anhydrous ethanol (50 mL), 3-(1′-dodecynyl)nitrobenzene (14.21 g, 49.51 mmol) and 10% palladium on carbon (2.50 g) were placed in a Parr flask. The flask was purged with hydrogen before pressurizing to 65 psi and heating to 65 °C. The pressure was maintained at 65 psi for 5 h. The palladium on carbon was then filtered and the solvent removed *in vacuo* to afford 12.54 g (97%) of the title compound as a brown liquid which solidified upon standing into a tan solid. R_f = 0.63 (4:1; hexane:ethyl acetate). IR (neat) 3464, 3379, 3036, 2925, 2854, 1620, 1590, 1494, 1461, 1265, 1167, 909, 738 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (dt, J = 7.4, 0.90 Hz, 1 H), 6.57 (d, J = 7.7 Hz, 1 H), 6.49 (d, J = 7.5 Hz, 1 H), 6.48 (d, J = 7.3 Hz, 1 H), 3.57 (s, 2 H), 2.49 (t, J = 7.9 Hz, 2 H), 1.56 (p, J = 7.3 Hz, 2 H) 1.28−1.24 (m, 18 H), 0.87 (t, J = 7.0 Hz, 3 H).). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.51, 144.22, 129.18, 118.86, 115.40, 112.67, 36.19, 32.14, 31.60, 29.91, 29.87, 29.84, 29.78, 29.62, 29.59, 22.89, 14.28. HRMS calcd for $C_{18}H_{31}N$: 261.2456. Found: 261.2448.

1-[*N*-(*tert*-Butoxycarbonyl)amino]-3-dodecylbenzene. To a solution of 3-dodecylaniline (**10**) (119.84 g, 459 mmol) and di-*tert*-butyl dicarbonate (116 mL, 505 mmol) in THF (500 mL) was added 1 M sodium hydroxide (500 mL) in three portions. The reaction mixture was heated to reflux overnight and then cooled to room temperature. The reaction mixture was poured into water and the organic layer extracted with ether (3×). The organic layer was dried over magnesium sulfate, filtered, and concentrated *in vacuo.* The crude mixture was purified by flash liquid chromatography on silica gel (24:1; hexane:ether) to afford 163.86 g (99%) of the title compound as a light brown oil which solidified upon standing. R_f = 0.41 (24:1; hexane:ether). IR (neat) 3320, 3145, 2920, 2853, 2356, 1693, 1597, 1539, 1440, 1366, 1251, 1162, 1054, 873 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (br s, 1 H), 7.16 (t, J = 7.9 Hz, 1 H), 7.10 (d, J = 8.1 Hz, 1 H), 6.83 (d, J = 7.5 Hz, 1 H), 6.41 (br s, 1 H), 3.55 (t, J = 7.6 Hz, 2 H), 1.58 (p, J = 7.3 Hz, 2 H), 1.50 (s, 9 H), 1.28−1.23 (m, 18 H), 0.89 (t, J = 6.9 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.20, 144.42, 138.64, 129.13, 123.57, 118.90, 116.21, 80.73, 36.44, 32.31, 31.84, 30.06, 30.05, 30.02, 29.98, 29.90, 29.77, 29.74, 28.75, 23.07, 14.49. HRMS calcd for $C_{23}H_{39}NO_2$: 361.2981. Found: 361.2993.

4-Amino-2-dodecylacetophenone (11). To a two-neck round-bottomed flask equipped with a reflux condenser containing aluminum chloride (23.48 g, 176.10 mmol) and chlorobenzene (50 mL) at 0 °C was added 1-[*N*-(*tert*-butoxycarbonyl)amino]-3-dodecylbenzene (18.15 g, 50.30 mmol) in chlorobenzene (50 mL) and acetyl chloride (3.93 mL, 55.3 mmol). The reaction mixture was heated to reflux overnight and then allowed to cool to room temperature. The solution was then slowly poured into 3 M potassium hydroxide (100 mL) and extracted with ether (3×). The combined organic extracts were washed with brine and dried over magnesium sulfate. The solution was filtered and the solvent removed *in vacuo* to give a brown oil that was purified by gravity liquid chromatography on silica gel (1:1; hexane:ether) to afford 12.90 g (85%) of the title compound as a brown liquid which solidified upon standing. R_f = 0.37 (1:1; hexane:ether). IR (neat) 3484, 3369, 3228, 3051, 2957, 2926, 2855, 1660, 1622, 1602, 1563, 1460, 1356, 1252, 1143, 909, 814, 738 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 9.1 Hz, 1 H), 6.48−6.44 (m, 2 H), 3.96 (br s, 2 H), 2.85 (t, J = 7.7 Hz, 2 H), 2.49 (s, 3 H), 1.50 (p, J = 7.7 Hz, 2 H), 1.40−1.23 (m, 18 H), 0.86 (t, J = 7.0 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.78, 150.46, 147.23, 133.44, 126.30, 116.76, 110.96, 35.17, 31.98, 31.62, 31.61, 30.03, 29.79 (2 C), 29.73, 29.70, 29.43, 28.87, 22.74, 22.68, 14.15. HRMS calcd for $C_{20}H_{33}NO$: 303.2562. Found: 303.2568.

4-(Diethyltriazenyl)-2-dodecyl-1-acetophenone (12). To an oven-dried vessel containing boron trifluoride etherate (0.21 mL, 1.68 mmol) at 0 °C was added **11** (0.26 g, 0.86 mmol) in dichloromethane (2 mL) followed by *tert*-butyl nitrite (0.17 mL, 1.4 mmol). The mixture was stirred for 30 min at 0 °C, and potassium carbonate (0.56 g) and diethylamine (0.56 mL) were sequentially added. The reaction was stirred for 2 h and poured into water. The organic layer was extracted with ethyl acetate and dried over magnesium sulfate. The sample was concentrated *in vacuo*, and the crude oil that was purified by flash liquid chromatography (9:1; hexane:ether) to afford 0.33 g (99%) of the title compound as a light brown oil. R_f = 0.36 (9:1; hexane:ether). IR (neat) 2927, 2855, 1677, 1597, 1559, 1449, 1431, 1395, 1348, 1239, 1105, 952, 893, 824 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.3 Hz, 1 H), 7.26 (d, J = 1.9 Hz, 1 H), 7.23 (dd, J = 8.3, 2.0 Hz, 1 H), 3.72 (q, J = 7.2 Hz, 4 H), 2.88 (t, J = 7.8 Hz, 2 H), 2.50 (s, 3 H), 1.59 (p, J = 8.3 Hz, 2 H), 1.40−1.22 (m, 24 H), 0.86 (t, J = 7.0 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.76, 153.83, 145.51, 133.98, 131.47, 123.85, 117.38, 35.05, 32.31, 32.17, 30.29, 30.09, 30.07, 30.06, 30.04, 29.95, 29.88, 29.74, 23.07, 14.49. HRMS calcd for $C_{24}H_{41}N_3O$: 387.3250. Found: 387.3254.

1-(Diethyltriazenyl)-3-dodecyl-4-[(trimethylsilyl)ethynyl]benzene (13). To a stirred solution of diisopropylamine (0.79 mL, 6.05 mmol) in THF (5 mL) was added at −78 °C, under nitrogen, *n*-butyllithium (3.59 mL, 5.50 mmol, 1.53 M in hexanes). The reaction mixture was allowed to warm to 0 °C for 10 min and then cooled to −78 °C. To the LDA solution was added **12** (1.94 g, 5.00 mmol) in THF (5 mL). The reaction mixture was stirred at −78 °C for 1 h before adding, at the same temperature, diethyl chlorophosphonate (0.73 mL, 5.05 mmol). The reaction mixture was allowed to warm to room temperature over 30 min before being recooled to −78 °C. The reaction solution was then transferred via cannula into 2.25 equiv of LDA [made as above with diisopropylamine (1.62 mL, 12.38 mmol) and *n*-butyllithium (7.35 mL, 11.25 mmol, 1.53 M in hexane)] in THF (15 mL) at −78 °C. The ensuing reaction mixture was allowed to warm to 0 °C over 30 min and then recooled to −78 °C before chlorotrimethylsilane (1.59 mL, 12.5 mmol) was added. The solution was allowed to stir overnight at room temperature before being poured into water and extracted with ether (3×). The combined ether extracts were washed with brine and dried over magnesium sulfate. Filtration and removal of the solvent *in vacuo* left a brown oil which, upon purification by gravity liquid chromatography on silica gel (100:1; hexane:ether), afforded 1.17 g (53%) of the title compound as a light brown oil. $R_f = 0.64$ (9:1; hexane: ether). IR (neat) 2957, 2925, 2854, 2149, 1598, 1453, 1434, 1402, 1341, 1238, 1203, 1104, 867, 843, 759, 654 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.2 Hz, 1 H), 7.21 (d, J = 1.9 Hz, 1 H), 7.16 (dd, J = 8.3, 2.0 Hz, 1 H), 3.74 (q, J = 7.2 Hz, 4 H), 2.74 (t, J = 7.8 Hz, 2 H), 1.68 (p, J = 7.7 Hz, 2 H), 1.40−1.24 (m, 24 H), 0.86 (t, J = 7.0 Hz, 3 H), 0.24 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.12, 146.48, 133.01, 120.92, 118.76, 117.33, 104.79, 96.96, 34.99, 31.92, 30.75, 29.74, 29.69, 29.65, 29.57, 29.36, 22.69, 14.12, 0.10. HRMS calcd for $C_{27}H_{47}N_3Si$: 441.3539. Found: 441.3549.

General Procedure for Iodide Formation from Triazenes.[5] To a thick-walled oven-dried screw cap tube was added the corresponding triazene and iodomethane (8 equiv) as the solvent. The tube was flushed with nitrogen or argon, sealed, and heated to 120 °C overnight. The reaction was cooled to room temperature and diluted with hexane. The smaller oligomers were then filtered through a plug of silica gel with hexane, and the larger oligomers were filtered through a plug of silica gel with ethyl acetate.

General Procedures for the Desilylation of Alkynes. (a) The silylated alkyne was dissolved in methanol, or in some cases, methanol and dichloromethane to aid in the solubility of the substrate. Potassium carbonate (2 equiv) was added, and the reaction was stirred overnight. The reaction mixture was then subjected to an aqueous workup and the aqueous layer extracted with ether, dichloromethane or ethyl acetate (3×). After drying the combined organic layers over magnesium sulfate, the solvent was removed *in vacuo*. The crude product was then filtered through a plug of silica gel, yielding the free alkyne which was used without further purification. Eluents and other slight modifications are described below for each material. (b) The silylated alkynes was dissolved in THF and cooled to 0 °C. TBAF (1.5 equiv, 1.0 M in THF) was added, and the reaction was stirred overnight. The reaction mixture was then subjected to an aqueous workup and the aqueous layer extracted with ether, dichloromethane, or ethyl acetate (3×). After drying the combined organic layers over magnesium sulfate, the solvent was removed *in vacuo*. The crude product was then filtered through a plug of silica gel, yielding the free alkyne which was used without further purification. Eluents and other slight modifications are described below for each material. (c) The silylated alkynes was dissolved in pyridine (0.5 M) in a plastic vessel. A preformed solution of concentrated hydrofluoric acid (1.1 equiv) in TBAF (2.2 equiv, 1.0 M in THF) was added at room temperature and allowed to stir for 15 to 30 min before being quenched with silica gel. The reaction mixture was then filtered and subjected to an aqueous workup, and the aqueous layer was extracted with ether, dichloromethane, or ethyl acetate (3×). After drying the combined organic layers over magnesium sulfate, the solvent was removed *in vacuo*. The crude product was then purified by column chromatography (silica gel), yielding the free alkyne which was immediately taken onto the next step. Eluents and other slight modifications are described below for each material.

1-Iodo-3-ethyl-4-[(trimethylsilyl)ethynyl]benzene (14).[2] **4** (3.05 g, 10.0 mmol) and iodomethane (5 mL) afforded 3.25 g (99%) of the title compound as a dark brown liquid. $R_f = 0.55$ (hexane). IR (neat) 2964, 2156, 1579, 1472, 1393, 1250, 1183, 1125, 1081, 841, 760, 699, 657 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, J = 1.5 Hz, 1 H), 7.44 (dd, J = 8.1, 1.8 Hz, 1 H), 7.11 (d, J = 8.1 Hz, 1 H), 2.71 (q, J = 7.6 Hz, 2 H), 1.20 (t, J = 7.5 Hz, 3 H), 0.23 (s, 9 H). HRMS calcd for $C_{13}H_{17}ISi$: 328.0144. Found: 328.0135. λ_{max} (CH_2Cl_2) = 266 nm. UV 10% edge value = 300 nm.

1-(Diethyltriazenyl)-3-ethyl-4-ethynylbenzene (17).[2] **4** (2.98 g, 9.9 mmol), methanol (50 mL), and potassium carbonate (4.1 g, 30 mmol) afforded 2.22 g (98%) of the title compound as a clear yellow oil. IR (neat) 3294, 2970, 2099, 1600, 1402, 1236, 1105, 891, 829 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, J = 8.2 Hz, 1 H), 7.25 (d, J = 1.9 Hz, 1 H), 7.18 (dd, J = 8.2, 2.1 Hz, 1 H), 3.75 (q, J = 7.2 Hz, 4 H), 3.22 (s, 1 H), 2.80 (q, J = 7.6 Hz, 2 H), 1.25 (t, J = 7.5 Hz, 9 H). HRMS calcd for $C_{14}H_{19}N_3$: 229.1579. Found: 229.1574.

Ethyl-Containing Dimer 20.[2] **14** (2.95 g, 9 mmol), **17** (2.24 g, 9.78 mmol), THF (20 mL), bis(dibenzylideneacetone)-palladium(0) (0.26 g, 0.45 mmol), triphenylphosphine (0.59 g, 2.25 mmol), copper(I) iodide (0.01 g, 0.90 mmol), and *N*,*N*-diisopropylethylamine (6.23 mL, 36 mmol) for 1 d afforded 3.48 g (90%) of the title compound as a yellow oil after gravity liquid chromatography (24:1; hexane:ether). $R_f = 0.56$ (24:1; hexane: ether). IR (neat) 2971, 2200, 2153, 1595, 840 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, J = 8.2 Hz, 1 H), 7.37 (d, J = 7.9 Hz, 1 H), 7.33 (d, J = 1.2 Hz, 1 H), 7.29 (d, J = 1.7 Hz, 1 H), 7.25 (dd, J = 7.9, 1.6 Hz, 1 H), 7.22 (dd, J = 8.3, 2.0 Hz, 1 H), 3.76 (q, J = 7.2 Hz, 4 H), 2.87 (q, J = 7.6 Hz, 2 H), 2.78 (q, J = 7.6 Hz, 2 H), 1.30 (t, J = 7.5 Hz, 6 H), 1.25 (t, J = 7.4 Hz, 6 H), 0.25 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.4, 147.1, 146.7, 133.0, 132.4, 130.8, 128.6, 124.2, 121.8, 120.4, 118.5, 117.7, 103.7, 99.5, 92.7, 90.5, 28.0, 27.7, 14.9, 14.5, 0.04. HRMS calcd for $C_{27}H_{35}N_3Si$: 429.2600. Found: 429.2592.

Ethyl-Containing Iodide Dimer 23.[2] **20** (1.93 g, 4.50 mmol) and iodomethane (2.26 mL) afforded 1.98 g (96%) of the title compound as a brown oil. IR (neat) 2964, 2152, 1579, 1490, 1393, 1250, 1183, 1125, 1081, 841, 760, 699, 657 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J = 1.6 Hz, 1 H), 7.49 (dd, J = 8.1, 1.8 Hz, 1 H), 7.39 (d, J = 7.9 Hz, 1 H), 7.34 (d, J = 1.1 Hz, 1 H), 7.27 (dd, J = 7.9, 1.6 Hz, 1 H), 7.18 (d, J = 8.1 Hz, 1 H), 2.81 (q, J = 7.5 Hz, 2 H), 2.80 (q, J = 7.5 Hz, 2 H), 1.28 (t, J = 7.6 Hz, 3 H), 1.26 (t, J = 7.5 Hz, 3 H), 0.26 (s, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.5, 147.2, 137.5, 135.3, 133.9, 132.8, 131.2, 129.0, 123.7, 122.9, 122.3, 103.8, 100.3, 95.1, 94.6, 89.1, 28.0, 27.9, 15.7, 15.0, 14.8, 0.4. HRMS calcd for $C_{23}H_{25}ISi$: 456.0770. Found: 456.0769. λ_{max} (CH_2Cl_2) = 316 nm. UV 10% edge value = 350 nm.

Ethyl-Containing Terminal Alkynyl Dimer 26.[2] **20** (1.07 g, 2.50 mmol), methanol (10 mL) and potassium carbonate (1.04 g, 7.50 mmol) afforded 0.89 g (100%) of the title compound as a brown oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, J = 8.0, 0.3 Hz, 1 H), 7.41 (d, J = 7.9 Hz, 1 H), 7.35 (d, J = 1.3 Hz, 1 H), 7.28 (d, J = 1.8 Hz, 1 H), 7.27 (ddd, J = 8.1, 1.8, 0.3 Hz, 1 H), 7.22 (dd, J = 8.2, 1.9 Hz, 1 H), 3.76 (q, J = 7.2 Hz, 4 H), 3.31 (s, 1 H), 2.86 (q, J = 7.5 Hz, 3 H), 2.80 (q, J = 7.6 Hz, 3 H), 1.30 (t, J = 7.6 Hz, 3 H), 1.25 (t, J = 7.5 Hz, 6 H), 1.19 (t, J = 7.0 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.9, 147.5, 147.3, 133.4, 133.2, 131.2, 129.0, 124.9, 121.2, 120.8, 118.9, 118.1, 92.9, 91.0, 82.6, 82.5, 28.4, 27.9, 15.3, 15.1. HRMS calcd for $C_{24}H_{27}N_3$: 357.2205. Found: 357.2202.

Ethyl-Containing Tetramer 29. **23** (0.91 g, 2.0 mmol), **26** (0.73 g, 2.06 mmol), THF (4 mL), bis(dibenzylideneacetone)-palladium(0) (57.40 mg, 0.10 mmol), triphenylphosphine (105 mg, 0.40 mmol), copper(I) iodide (38.1 mg, 0.20 mmol), and *N*,*N*-diisopropylethylamine (1.38 mL, 8 mmol) for 5 d afforded 1.17 g (93%) of the title compound as a yellow solid after gravity liquid chromatography (24:1; hexane:ether). $R_f = 0.26$ (24:1; hexane:ether). IR (KBr) 2965, 2872, 2151, 1590, 1503, 1401, 1246, 841 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.46 (d, $J = 7.9$ Hz, 1 H), 7.45 (d, $J = 8.0$ Hz, 1 H), 7.45 (d, $J = 8.2$ Hz, 1 H), 7.40 (d, $J = 7.8$ Hz, 1 H), 7.39 (br m, 2 H), 7.35 (d, $J = 1.3$ Hz, 1 H), 7.32 (dd, $J = 7.9$, 1.7 Hz, 1 H), 7.32 (dd, $J = 7.9$, 1.7 Hz, 1 H), 7.29 (d, $J = 1.9$, 1 H), 7.27 (dd, $J = 8.2$, 1.6 Hz, 1 H), 7.23 (dd, $J = 8.2$, 2.1 Hz, 1 H), 3.76 (q, $J = 7.2$ Hz, 4 H), 2.885 (q, $J = 7.5$ Hz, 2 H), 2.884 (q, $J = 8.2$ Hz, 2 H), 2.87 (q, $J = 7.5$ Hz, 2 H), 2.79 (q, J = 7.6 Hz, 2 H), 1.32 (t, J = 7.6 Hz, 6 H), 1.31 (t, J = 7.6 Hz, 3 H), 1.26 (t, $J = 7.6$ Hz, 3 H), 0.25 (s, 9 H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 151.75, 147.50, 147.22, 146.69, 146.62, 133.29, 132.75, 132.54, 132.50, 131.33, 131.26, 131.21, 129.18, 129.06, 129.03, 124.45, 123.85, 123.79, 122.78, 122.68, 122.16, 120.72, 118.88, 117.96, 103.82, 100.29, 94.99, 94.80, 93.08, 90.93, 89.98, 89.73, 28.33, 28.05, 28.03, 27.99, 15.21, 15.05, 15.01, 14.80, 0.33. HRMS calcd for $C_{47}H_{51}N_3Si$: 685.3852. Found: 685.3843.

Ethyl-Containing Iodide Tetramer 32. **29** (136.70 mg, 0.20 mmol) and iodomethane (4 mL) afforded 142.40 mg (98%) of the title compound as a light yellow solid. IR (KBr) 2965, 2930, 2151, 1500, 1459, 1249, 888, 841 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.60 (d, $J = 1.6$ Hz, 1 H), 7.51 (dd, $J = 8.1$, 1.7 Hz, 1 H), 7.47 (d, $J = 7.7$ Hz, 2 H), 7.41−7.38 (4 line m, 3 H), 7.37−7.28 (m, 4 H), 7.20 (d, $J = 8.1$ Hz, 1 H), 2.89 (q, $J = 7.5$ Hz, 2 H), 2.88 (q, $J = 7.5$ Hz, 2 H), 2.83 (q, $J = 7.6$ Hz, 2 H), 2.81 (q, $J = 7.6$ Hz, 2 H), 1.33 (t, $J = 7.6$ Hz, 3 H), 1.29 (t, $J = 7.6$ Hz, 6 H), 1.27 (t, $J = 7.6$ Hz, 3 H), 0.27 (s, 9 H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 148.57, 147.23, 146.73, 146.72, 137.47, 135.26, 133.88, 132.77, 132.72, 132.57, 131.35, 131.33, 131.27, 129.22, 129.19, 129.05, 128.38, 126.07, 123.77, 123.72, 123.63, 122.87, 122.83, 122.31, 103.83, 100.34, 95.16, 95.11, 94.66, 89.76, 89.70, 89.16, 28.06, 28.01, 27.93, 15.03, 14.96, 14.82, 0.35. HRMS calcd for $C_{43}H_{41}ISi$: 712.2022. Found: 712.2028. λ_{max} (CH$_2$Cl$_2$) = 352 nm. UV 10% edge value = 385 nm.

Ethyl-Containing Terminal Alkynyl Tetramer 35. **29** (0.29 g, 0.42 mmol), THF (5 mL), and TBAF (0.6 mL, 0.6 mmol, 1.0 M in THF) afforded 0.14 g (55%) of the title compound as a light yellow solid. A ^{1}H NMR was run to examine the loss of the trimethylsilyl peak, and the material was used directly in the next reaction.

Ethyl-Containing Octamer 38. Bis(dibenzylideneacetone)-palladium(0) (3.4 mg, 0.006 mmol), triphenylphosphine (7.9 mg, 0.03 mmol), copper(I) iodide (2.3 mg, 0.012 mmol), **32** (41.9 mg g, 0.06 mmol), **35** (42.9 mg, 0.07 mmol), THF (2 mL), and diisopropylamine (0.5 mL, 3.5 mmol) at 60 °C overnight afforded a solid that was filtered and rinsed with water and dichloromethane. Due to its insolubility, the solid was only characterized by direct exposure mass spectrometry and UV spectroscopy. Direct exposure MS statistical isotopic range calcd for $C_{87}H_{83}N_3Si$: 1198 (95%), 1199 (100%), 1200 (55%). Found: 1098.6 (signifying loss of the triazene moiety at 100 amu). λ_{max} (CH$_2$Cl$_2$) = 364 nm. UV 10% edge value = 500 nm.

3-Ethylheptyl-Containing Iodide Monomer 15. **9** (0.79 g, 2.0 mmol) and iodomethane (2 mL) afforded 0.78 g (92%) of the title compound as a yellow liquid. IR (neat) 2957, 2156, 1579, 1472, 1249, 1184, 844, 760 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.52 (s, 1 H), 7.43 (d, $J = 8.1$ Hz, 1 H), 7.11 (d, $J = 8.1$ Hz, 1 H), 2.72−2.62 (m, 2 H), 1.60 (br s, 1 H), 1.32−1.21 (m, 8 H), 0.95−0.84 (m, 6 H), 0.23 (s, 9 H).

3-Ethylheptyl-Containing Terminal Alkynyl Monomer 18. **9** (0.93 g, 2.3 mmol), THF (6 mL), and TBAF (2.6 mL, 2.6 mmol, 1.0 M in THF) afforded 0.72 g (96%) of the title compound as a yellow liquid. IR (neat) 3311, 2931, 2099, 1599, 1402, 1239, 891 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.39 (d, $J = 8.2$ Hz, 1 H), 7.22 (s, 1 H), 7.18 (d, $J = 8.2$ Hz, 1 H), 3.74 (q, $J = 7.2$ Hz, 4 H), 3.21 (s, 1 H), 2.79−2.74 (4 line m, 2 H), 1.64−1.55 (m, 1 H), 1.50−1.19 (m, 16 H), 0.99−0.83 (m, 6 H).

3-Ethylheptyl-Containing Dimer 21. Bis(dibenzylideneacetone)palladium(0) (57.4 mg, 0.1 mmol), triphenylphosphine (130 mg, 0.5 mmol), copper(I) iodide (38.1 mg, 0.2 mmol), **15** (0.78 g, 1.8 mmol), **18** (0.61 g, 1.8 mmol), THF (5 mL), diisopropylamine (1.0 mL) and purification by flash chromatography on silica gel (19:1; hexane:ethyl acetate) afforded 0.88 g (78 %) of the title compound as a yellow oil. IR (neat) 2957, 2151, 1464, 1402, 1236, 1103, 843 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.45−7.27 (m, 6 H), 3.76 (q, $J = 7.2$ Hz, 4 H), 2.83−2.62 (m, 4 H), 1.80−1.60 (m, 2 H), 1.40−1.11 (m, 26 H), 0.99−0.80 (m, 12 H), 0.25 (s, 9 H). LRMS calcd for $C_{41}H_{63}N_3Si$: 625. Found: 625. λ_{max} (CH$_2$Cl$_2$) = 362 nm. UV 10% edge value = 410 nm. $M_n = 715$, $M_w = 744$, $M_w/M_n = 1.04$.

3-Ethylheptyl-Containing Iodide Dimer 24. **21** (0.22 g, 0.35 mmol) and iodomethane (2 mL) afforded 0.23 g (100%) of the title compound as a yellow liquid. IR (neat) 2956, 2152, 1464, 1249, 843, 760 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.57 (s, 1 H), 7.48 (d, $J = 8.1$ Hz, 1 H), 7.38 (d, $J = 8.0$ Hz, 1 H), 7.31 (s, 1 H), 7.23 (d, $J = 7.7$ Hz, 1 H), 7.17 (d, $J = 8.1$ Hz, 1 H), 2.74 (m, 4 H), 1.64−1.58 (m, 2 H), 1.43−1.20 (m, 20 H), 0.96−0.82 (m, 12 H), 0.25 (s, 9 H).

3-Ethylheptyl-Containing Terminal Alkynyl Dimer 27. **21** (0.23 g, 0.37 mmol), THF (2 mL), and TBAF (0.5 mL, 0.5 mmol, 1.0 M in THF) afforded 0.2 g (98%) of the title compound as a yellow oil. IR (neat) 3300, 2956, 2200, 2102, 1597, 1464, 1237, 1104 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.44−7.40 (m, 2 H), 7.33 (s, 1 H), 7.26−7.21 (m, 3 H), 3.75 (q, $J = 7.1$ Hz, 4 H), 3.30 (s, 1 H), 2.85−2.63 (m, 4 H), 1.63−1.57 (m, 2 H), 1.44−1.22 (m, 26 H), 0.98−0.81 (m, 12 H).

3-Ethylheptyl-Containing Tetramer 30. Bis(dibenzylideneacetone)palladium(0) (13.8 mg, 0.024 mmol), triphenylphosphine (31.5 mg, 0.12 mmol), copper(I) iodide (9.1 mg, 0.048 mmol), **24** (0.29 g, 0.48 mmol), **27** (0.27 mg, 0.48 mmol), THF (5 mL), diisopropylamine (0.5 mL), and purification by flash chromatography on silica gel (3:1; hexane:dichloromethane) afforded 0.23 g (44%) of the title compound as a yellow oil. IR (neat) 2956, 2151, 1595, 1464, 1402, 1236, 1103 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.48−7.27 (m, 12 H), 3.76 (q, $J = 7.1$ Hz, 4 H), 2.98−2.70 (m, 8 H), 1.82−1.63 (m, 4 H), 1.59−1.05 (m, 46 H), 1.05−0.78 (m, 24 H), 0.27 (s, 9 H). LRMS calcd for $C_{75}H_{107}N_3Si$: 1077.8. Found: 1077.9. λ_{max} (CH$_2$Cl$_2$) = 372 nm. UV 10% edge value = 421 nm. $M_n = 1335$, $M_w = 1388$, $M_w/M_n = 1.06$.

3-Ethylheptyl-Containing Iodide Tetramer 33. **30** (0.13 g, 0.12 mmol) and iodomethane (3 mL) afforded 0.12 g (100%) of the title compound as a yellow oil. IR (neat) 2955, 2151, 1464, 1378, 1249, 859 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.59 (s, 1 H), 7.50−7.24 (m, 10 H), 7.19 (d, J = 8.5 Hz, 1 H), 2.96−2.65 (br m, 8 H), 1.80−1.59 (m, 4 H), 1.59−1.10 (m, 40 H), 1.10−0.89 (m, 24 H), 0.28 (s, 9 H). LRMS calcd for $C_{73}H_{97}ISi$: 1104.6. Found: 1104.7.

3-Ethylheptyl-Containing Terminal Alkynyl Tetramer 36. **30** (0.11 g, 0.1 mmol), THF (2 mL), and TBAF (0.15 mL, 0.15 mmol, 1.0 M in THF) afforded 0.1 g (100%) of the title compound as a yellow oil. IR (neat) 2928, 2360, 2344, 1464, 1401, 1236, 1103, 827 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.42−7.21 (m, 12 H), 3.76 (q, $J = 7.2$ Hz, 4 H), 3.36 (s, 1 H), 2.95−2.76 (m, 8 H), 1.80−1.60 (m, 4 H), 1.60−1.10 (m, 46 H), 1.10−0.75 (m, 24 H).

Octomer 39. Bis(dibenzylideneacetone)palladium(0) (6.9 mg, 0.012 mmol), triphenylphosphine (15.7 mg, 0.06 mmol), copper(I) iodide (2.3 mg, 0.012 mmol), **33** (0.13 g, 0.12 mmol) **36** (0.1 mg, 0.1 mmol), THF (2 mL), and diisopropylamine (0.5 mL) at 60 °C for 12 h, and flash chromatography on silica gel (3:1; hexane:dichloromethane) afforded 0.17 g (70%) of the title compound as a yellow solid. IR (neat) 2952, 2198, 2147, 1464, 827 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.48−7.27 (m, 24 H), 3.77 (q, $J = 7.1$ Hz, 4 H), 2.98−2.63 (m, 16 H), 1.84−1.58 (m, 8 H), 1.58−1.10 (m, 86 H), 1.10−0.78 (m, 48 H), 0.27 (9 H). λ_{max} (CH$_2$Cl$_2$) = 376. UV 10% edge value = 422 nm. $M_n = 2800$, $M_w = 2960$, $M_w/M_n = 1.05$. MALDI MS (sinapinic acid matrix, positive ion mode) average molecular weight calculated for $C_{143}H_{195}N_3Si$: 1984. Found peak maximum (M + 1): 1791 ± 9 (large error due to broad signal), (loss of SiMe$_3$ at 73 amu, N$_3$Et$_2$ at 100 amu, C≡C at 24 amu which is a common phenyl−alkynyl cleavage route).[18]

3-Ethylheptyl-Containing Iodide Octamer 41. **39** (83.7 mg, 0.04 mmol) and iodomethane (3 mL) afforded 80 mg (100%) of the title compound as a yellow solid. IR (neat) 2955, 2926, 2858, 2160, 1592, 1502, 1461, 826 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.58−7.18 (m, 24 H), 2.98−2.62 (m, 16 H), 1.82−1.55 (m, 8 H), 1.55−1.10 (m, 80), 1.10−0.70 (m, 48 H), 0.26 (s, 9 H).

3-Ethylheptyl-Containing Terminal Alkynyl Octamer 43. **39** (28.6 g, 0.01 mmol), THF (2 mL), and TBAF (0.1 mL, 0.1 mmol, 1.0 M in THF) afforded 19.1 mg (100%) of the title compound as a yellow solid. IR (neat) 2927, 2361, 2343, 1458 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.47−7.23 (m, 24 H), 3.74 (q, J = 7.9 Hz, 4 H), 3.22 (s, 1 H), 2.98−2.65 (m, 16 H), 1.80−1.60 (m, 8 H), 1.60−1.05 (m, 86 H), 1.05−0.70 (m, 48 H).

3-Ethylheptyl-Containing 16-mer 45. Bis(dibenzylideneacetone)palladium(0) (1.6 mg, 0.0028 mmol), triphenylphosphine (3.7 mg, 0.014 mmol), copper(I) iodide (0.5 mg, 0.0028 mmol), **41** (37.0 g, 0.018 mmol), **43** (0.26.3 mg, 0.014 mmol), THF (2 mL), and diisopropylamine (0.25 mL) at 60 °C for 12 h, and flash chromatography on silica gel (3:1; hexane: dichloromethane), afforded 30.8 mg of a 1:1 mixture of the title compound and unreacted iodide **41** (approximately 15.4 mg (26%) of the title compound). The two compounds could not be separated by flash chromatography, but they could be detected by SEC using UV detection ($\lambda_{\max}$ = 376). One of the two peaks indeed corresponded to the iodooctamer **41**, and the second peak had an M_n value more than double that of the **41**. An analytically pure sample of the 16-mer **45** was obtained by adding diethyl ether and centrifuging the mixture. The liquid was decanted away from the remaining solid, and the procedure was repeated. After four such washing cycles, the remaining solid was examined by SEC to reveal a single product which was used for the analytical analysis. IR (neat) 2956, 2927, 2360, 2340, 1506, 1458 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.47−7.24 (m, 48 H), 3.77 (q, J = 7.1 Hz, 4 H), 2.95−2.65 (m, 32 H), 1.82−1.58 (m, 16 H), 1.58−1.10 (m, 166 H), 1.10−0.70 (m, 96 H), 0.26 (s, 9 H). $\lambda_{\max}$ (CH$_2$Cl$_2$) = 376 nm. UV 10% edge value = 422 nm. M_n = 6649, M_w = 7114, M_w/M_n = 1.07. MALDI-MS (sinapinic acid matrix, positive ion mode) average molecular weight calculated for **23** with C$_{279}$H$_{371}$N$_3$Si: 3795. Found (M + 1): 3486 ± 14 (large error due to broad signal) (signifying loss in the MS of the SiMe$_3$ at 73 amu, N$_3$Et$_2$ at 100 amu, C≡C at 24 amu which a common phenyl−alkynyl cleavage route, and a C$_8$H$_{17}$ fragment at 113 amu which represents a typical benzylic methylene−ethylene cleavage site.)[18]

1-Iodo-3-dodecyl-4-[(trimethylsilyl)ethynyl]benzene (16) Prepared from 13. **13** (4.70 g, 10.64 mmol) and iodomethane (5.30 mL) afforded 4.70 g (94%) of the title compound as a light brown oil. R_f = 0.88 (hexane). IR (neat) 2956, 2924, 2854, 2156, 1579, 1543, 1472, 1392, 1250, 1183, 1128, 844, 816, 760, 658 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.51 (d, J = 1.7 Hz, 1 H), 7.43 (dd, J = 8.1, 1.8 Hz, 1 H), 7.11 (d, J = 8.1 Hz, 1 H), 2.66 (t, J = 7.7 Hz, 2 H), 1.58 (p, J = 7.2 Hz, 2 H), 1.30−124 (m, 18 H), 0.86 (t, J = 7.1 Hz, 3 H), 0.23 (s, 9 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 147.59, 137.65, 134.61, 133.63, 122.10, 103.04, 99.24, 94.69, 34.53, 31.95, 30.53, 29.70, 29.68 (2 C), 29.65, 29.61, 29.49, 29.39, 22.72, 14.16, −0.050. Anal. Calcd for C$_{23}$H$_{37}$ISi: C, 58.96; H, 7.96; I, 27.09. Found: C, 58.70; H, 7.91; I, 27.27. HRMS calcd for C$_{23}$H$_{37}$ISi: 468.1709. Found: 468.1700. λ (THF) = *263* (ϵ 2.50 × 10^4 M^{-1} cm^{-1}), 273, 275, 296 nm.

1-(Diethyltriazyl)-3-dodecyl-4-ethynylbenzene (19). **13** (4.70 g, 10.64 mmol), methanol (10 mL), dichloromethane (10 mL), and potassium carbonate (4.41 g, 31.92 mmol) afforded 3.79 g (97%) of the title compound as a yellow oil. R_f = 0.20 (hexane). IR (neat) 3310, 2926, 2855, 2099, 1677, 1600, 1458, 1400, 1340, 1237, 1101, 829 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.45 (d, J = 8.2 Hz, 1 H), 7.30 (d, J = 2.0 Hz, 1 H), 7.25 (dd, J = 8.2, 2.0 Hz, 1 H), 3.76 (q, J = 7.1 Hz, 4 H), 3.24 (s, 1 H), 2.33 (t, J = 7.7 Hz, 2 H), 1.71 (p, J = 7.3 Hz, 2 H), 1.43−1.24 (m, 24 H), 0.92 (t, J = 7.1 Hz, 3 H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 151.81, 146.76, 133.89, 121.46, 118.25, 117.86, 83.54, 80.40, 35.11, 32.40, 31.12, 30.18 (2 C), 30.13, 30.09, 30.01, 29.98, 29.84, 23.16, 14.57. HRMS calcd for C$_{24}$H$_{39}$N$_3$: 369.3144. Found: 369.3144.

Dodecyl-Containing Dimer 22. **16** (0.38 g, 0.82 mmol), **19** (0.42 g, 1.15 mmol), THF (4 mL), bis(dibenzylideneacetone)palladium(0) (0.024 g, 0.041 mmol), triphenylphosphine (0.055 g, 0.21 mmol), copper(I) iodide (0.016 g, 0.082 mmol), and N,N-diisopropylethylamine (0.57 mL, 3.28 mmol) for 3 d afforded 0.50 g (85%) of the title compound as a yellow oil after gravity liquid chromatography (24:1; hexane:ether). R_f = 0.44 (24:1; hexane:ether). IR (neat) 2922, 2853, 2202, 2151, 1596, 1495, 1465, 1404, 1378, 1332, 1249, 1210, 1103, 862, 760, 633 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.42 (d, J = 8.2 Hz, 1 H), 7.37 (d, J = 7.9 Hz, 1 H), 7.30 (s, 1 H), 7.26−7.25 (m, 1 H), 7.22 (d, J = 8.2 Hz, 1 H), 7.21 (d, J = 8.3 Hz, 1 H), 3.76 (q, J = 7.2 Hz, 4 H), 2.82 (t, J = 7.7 Hz, 2 H), 2.73 (t, J = 7.7 Hz, 2 H), 1.69 (p, J = 7.2 Hz, 2 H), 1.63 (p, J = 7.2 Hz, 2 H), 1.32−1.22 (m, 42 H), 0.86 (t, J = 7.0 Hz, 6 H), 0.24 (s, 9 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 151.19, 145.97, 145.59, 132.84, 132.30, 131.49, 128.42, 124.03, 121.99, 121.15, 118.78, 117.59, 103.85, 99.24, 92.58, 90.71, 35.03, 34.73, 31.99, 31.65, 30.91, 30.64, 29.78, 29.76, 29.73, 29.64, 29.61, 29.43, 22.75, 22.71, 14.17, 0.01 HRMS calcd for C$_{47}$H$_{75}$N$_3$Si: 709.5730. Found: 709.5697.

Dodecyl-Containing Iodide Dimer 25 from 22. **22** (0.25 g, 0.35 mmol) and iodomethane (3 mL) afforded 0.24 g (95%) of the title compound as a yellow oil. R_f = 0.63 (hexane). IR (neat) 2923, 2854, 2152, 1945, 1892, 1775, 1600, 1579, 1541, 1490, 1465, 1406, 1393, 1378, 1351, 1302, 1249, 1225, 1194, 1144, 1117, 1092, 1015, 947, 843, 760, 722, 700, 687, 633 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.56 (d, J = 1.5 Hz, 1 H), 7.48 (dd, J = 8.1, 1.7 Hz, 1 H), 7.37 (d, J = 7.9 Hz, 1 H), 7.30 (d, J = 1.0 Hz, 1 H), 7.23 (dd, J = 8.0, 1.4 Hz, 1 H), 7.17 (d, J = 8.1 Hz, 1 H), 2.76−2.71 (m, 4 H), 1.64−1.62 (m, 4 H), 1.32−1.22 (m, 36 H), 0.86 (t, J = 7.0 Hz, 6 H), 0.24 (s, 9 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 147.10, 145.70, 137.76, 134.80, 133.43, 132.34, 131.58, 128.52, 123.14, 122.64, 122.01, 103.57, 99.70, 94.55, 94.08, 88.88, 34.68, 34.50, 31.95, 30.60, 30.64, 29.70, 29.68, 29.65, 29.56, 29.50, 29.39, 22.71, 14.15, 14.14, −0.031. Anal. Calcd for C$_{43}$H$_{65}$ISi: C, 70.08; H, 8.89; I, 17.22. Found: C, 69.84; H, 8.77; I, 17.42. HRMS calcd for C$_{43}$H$_{65}$ISi: 736.3900. Found: 736.3904. M_n = 900, M_w = 929, M_w/M_n = 1.03. λ (THF) = *314* (ϵ 5.94 × 10^4 M^{-1} cm^{-1}), 335 nm. Emiss (THF) = 334, 351, *386* nm.

Dodecyl-Containing Terminal Alkynyl Dimer 28. **22** (2.84 g, 4 mmol), methanol (4 mL), dichloromethane (4 mL), and potassium carbonate (1.66 g, 12 mmol) afforded 2.55 g (100%) of the title compound as a dark yellow oil. IR (neat) 3302, 2925, 2853, 2201, 2102, 1596, 1496, 1465, 1401, 1332, 1237, 1210, 1103, 891, 828, 721, 644 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.48 (d, J = 8.2 Hz, 1 H), 7.45 (d, J = 8.0 Hz, 1 H), 7.38 (d, J = 1.2 Hz, 1 H), 7.33 (dd, J = 4.3, 1.8 Hz, 1 H), 7.29 (d, J = 8.2 Hz, 1 H), 7.28 (d, J = 7.9 Hz, 1 H), 3.77 (q, J = 7.2 Hz, 4 H), 3.33 (s, 1 H), 2.89 (t, J = 7.5 Hz, 2 H), 2.81 (t, J = 7.5 Hz, 2 H), 1.77 (p, J = 7.3 Hz, 2 H) 1.69 (p, J = 7.3 Hz, 2 H), 1.43−1.20 (m, 42 H), 0.91 (t, J = 6.9 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 151.24, 145.98, 145.61, 132.86, 132.81, 131.48, 128.47, 127.54, 124.39, 121.18, 121.03, 118.73, 117.62, 92.43, 90.78, 82.31, 81.86, 35.06, 34.39, 32.01, 30.93, 30.54, 29.81, 29.78, 29.75, 29.69, 29.67, 29.56, 29.54, 29.47, 29.46, 22.77, 14.19. HRMS calcd for C$_{44}$H$_{67}$N$_3$: 637.5335. Found: 637.5325.

Dodecyl-Containing Tetramer 31. **25** (2.69 g, 3.65 mmol), **28** (2.55 g, 4.01 mmol), THF (8 mL), bis(dibenzylideneacetone)palladium(0) (0.10 g, 0.18 mmol), triphenylphosphine (0.24 g, 0.91 mmol), copper(I) iodide (0.070 g, 0.37 mmol), and N,N-diisopropylethylamine (2.54 mL, 14.60 mmol) for 2 d afforded 3.97 g (87%) of the title compound as a yellow oil which solidified upon standing after gravity liquid chromatography (24:1; hexane:ether). R_f = 0.54 (24:1; hexane:ether). IR (neat) 2921, 2851, 2898, 2151, 1592, 1502, 1467, 1406, 1378, 1352, 1247, 1235, 1212, 1095, 884, 862, 843, 828, 759, 721, 634 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.50 (d, J = 8.2 Hz, 1 H), 7.49 (d, J = 7.9 Hz, 2 H), 7.44 (d, J = 8.0 Hz, 1 H), 7.42 (s, 1 H), 7.38−7.34 (m, 4 H), 7.32 −7.29 (m, 2 H), 3.78 (q, J = 7.1 Hz, 4 H), 2.90 (m, 6 H), 2.82 (t, J = 7.9 Hz, 2 H), 1.90−1.70 (m, 8 H), 1.40−1.28 (m, 78 H), 0.94−0.89 (m, 12 H), 0.31 (s, 9 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 151.21, 145.98, 145.71, 145.19, 145.11, 132.88, 132.38, 132.16, 132.12, 131.73, 131.64, 131.61, 128.76, 128.63, 128.61, 124.02, 123.42, 123.38, 122.62, 122.53, 122.03, 121.20, 118.84, 117.63, 103.69, 99.65, 94.58, 94.40, 92.70, 90.86, 89.90, 89.65, 35.08, 34.76, 32.03, 30.94,

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(18) McLafferty, F. W.; Turecek, F. *Interpretation of Mass Spectra*, 4th ed.; University Science: Mill Valley, California, 1993.

30.74, 30.65, 29.83, 29.82, 29.78, 29.69, 29.67, 29.65, 29.63, 29.49, 29.46, 22.78, 22.73, 14.20, 0.01. LRMS calcd for $C_{87}H_{131}N_3Si$: 1246 (96%), 1247 (100%), 1248 (54%). Found: 1246 (100%), 1247 (91%), 1248 (55%).

Dodecyl-Containing Iodide Tetramer 34 from 31. 31 (1.99 g, 1.60 mmol) and iodomethane (2 mL) afforded 1.88 g (92%) of the title compound as a yellow oil which solidified upon standing. IR (KBr) 2924, 2853, 2203, 2151, 1697, 1657, 1598, 1543, 1500, 1463, 1384, 1252, 1183, 1005, 656, 761, 723, 634 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.57 (d, J =1.7 Hz, 1 H), 7.49 (dd, J = 8.0, 1.7 Hz, 1 H), 7.45 (d, J = 7.9 Hz, 2 H), 7.44 (d, J = 7.8 Hz, 1 H), 7.39 (d, J = 1.0 Hz, 1 H), 7.35 (d, J = 1.3 Hz, 1 H), 7.31−7.26 (m, 4 H), 7.18 (d, J = 8.2 Hz, 1 H), 2.85−2.75 (m, 8 H), 1.67 (m, 8 H), 1.40−1.20 (m, 72 H), 0.86−0.84 (m, 12 H), 0.25 (s, 9 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 147.11, 145.70, 145.21, 137.78, 134.82, 133.44, 132.87, 132.36, 132.15, 131.70, 131.62, 128.72, 128.57, 123.28, 123.21, 123.11, 122.68, 122.62, 122.12, 103.63, 99.70, 94.68, 94.61, 94.57, 94.17, 89.60, 89.55, 89.00, 34.69, 34.53, 34.36, 31.97, 30.67, 30.62, 30.49, 29.75, 29.71, 29.66, 29.59, 29.53, 29.42, 28.00, 27.15, 22.73, 19.70, 14.15, 11.42, −0.018. Anal. Calcd for $C_{83}H_{121}ISi$: C, 78.26; H, 9.57. Found: C, 77.30; H, 9.24. LRMS calcd for $C_{83}H_{121}ISi$: 1273 (99%), 1274 (100%), 1275 (53%). Found: 1273 (100%), 1274 (98%), 1275 (50%). M_n = 1706, M_w = 1777, M_w/M_n = 1.04. λ (THF) = 241, 273, *350* (ϵ 1.10 × 10^5 M^{-1} cm^{-1}) nm. Emiss (THF) = *391*, 412 nm.

Dodecyl-Containing Terminal Alkynyl Tetramer 37. 31 (0.14 g, 0.11 mmol), methanol (2 mL), dichloromethane (4 mL), and potassium carbonate (0.14 g, 1.0 mmol) afforded 0.13 g (100%) of the title compound as a yellow oil which solidified upon standing. IR (neat) 3314, 3029, 2921, 2851, 2198, 2100, 1594, 1503, 1465, 1403, 1350, 1234, 1095, 885, 828, 722, 648 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.49−7.44 (m, 4 H), 7.40−7.31 (m, 7 H), 7.29−7.25 (m, 1 H), 3.77 (q, J = 7.1 Hz, 4 H), 3.33 (s, 1 H), 2.90 (m, 6 H), 2.80 (t, J = 7.1 Hz, 2 H), 1.75−1.67 (m, 8 H), 1.43−1.26 (m, 78 H), 0.90−0.87 (m, 12 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 151.20, 146.00, 145.74, 145.21, 145.11, 132.86, 132.15, 132.10, 131.73, 131.62, 128.74, 128.61, 123.99, 123.70, 123.44, 122.43, 121.98, 121.60, 121.15, 118.79, 117.60, 94.34, 92.66, 90.83, 89.89, 89.66, 82.15, 35.04, 34.72, 34.37, 32.00, 30.91, 30.71, 30.51, 29.80, 29.78, 29.76, 29.74, 29.69, 29.66, 29.64, 29.52, 29.45, 29.43, 22.75, 14.17. LRMS calcd for $C_{84}H_{123}N_3$: 1174 (100%), 1175 (98%), 1176 (47%). Found: 1174 (100%), 1175 (50%), 1176 (33%).

Dodecyl-Containing Octamer 40. 34 (1.88 g, 1.47 mmol), **37** (1.73 g, 1.47 mmol), THF (8 mL), bis(dibenzylideneacetone)palladium(0) (0.042 g, 0.074 mmol), triphenylphosphine (0.097 g, 0.37 mmol), copper(I) iodide (0.029 g, 0.15 mmol), and *N*,*N*-diisopropylethylamine (1.02 mL, 5.88 mmol) for 3 d afforded 1.62 g (48%) of the title compound as a yellow solid after flash liquid chromatography (8:1; hexane:dichloromethane). R_f = 0.12 (8:1; hexane:dichloromethane). IR (KBr) 2922, 2851, 2199, 2149, 1594, 1503, 1460, 1402, 1348, 1235, 1096, 835, 722, 643 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.49−7.42 (m, 8 H), 7.40−7.38 (m, 4 H), 7.36−7.25 (m, 12 H), 3.77 (q, J = 7.1 Hz, 4 H), 2.87−2.75 (m, 16 H), 1.73−1.64 (m, 16 H), 1.54−1.25 (m, 150 H), 0.89−0.85 (m, 24 H), 0.27 (s, 9 H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 151.60, 146.39, 146.14, 146.11, 145.61, 145.51, 145.31, 133.25, 132.76, 132.54, 132.49, 132.12, 132.02, 132.00, 131.91, 131.77, 129.15, 129.00, 128.96, 124.37, 124.09, 123.83, 123.79, 123.68, 123.64, 123.04, 123.02, 122.92, 122.83, 122.69, 122.38, 121.98, 121.53, 119.18, 117.98, 104.02, 100.10, 95.07, 95.00, 94.71, 93.03, 91.20, 90.27, 90.04, 89.94, 82.55, 82.48, 35.41, 35.10, 34.75, 32.36, 31.26, 31.08, 30.99, 30.88, 30.15, 30.14, 30.13, 30.11, 30.08, 30.06, 30.02, 30.00, 29.96, 29.89, 29.81, 29.78, 23.12, 14.53, 0.37.

Dodecyl-Containing Iodide Octamer 42 from 40. 40 (0.81 g, 0.35 mmol) and iodomethane (5 mL) afforded 0.82 g (100%) of the title compound as a yellow solid. R_f = 0.29 (9:1; hexane:dichloromethane). IR (KBr) 3028, 2924, 2853, 2201, 2151, 1923, 1849, 1775, 1744, 1708, 1656, 1588, 1502, 1461, 1382, 1307, 1255, 1084, 886, 839, 723 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.59 (d, J = 1.0 Hz, 1 H), 7.51 (d, J = 1.3 Hz, 1 H), 7.49−7.46 (m, 5 H), 7.42−7.25 (m, 16 H), 7.19 (d, J = 8.1 Hz, 1 H), 2.90−2.70 (m, 16 H), 1.74−1.66 (m, 16 H), 1.45−1.25 (m, 144 H), 0.89−0.86 (m, 24 H), 0.28 (s, 9 H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 147.52, 147.47, 146.11, 145.62, 145.55, 145.31, 143.57, 138.18, 138.14, 135.23, 135.18, 133.85, 133.60, 132.77, 132.56, 132.14, 132.03, 131.91, 131.86, 129.16, 129.12, 128.98, 128.80, 124.09, 123.81, 123.70, 123.64, 123.52, 123.50, 123.38, 123.20, 123.09, 123.06, 122.65, 122.54, 104.04, 100.10, 95.20, 95.10, 95.02, 94.97, 94.78, 94.67, 94.58, 91.43, 90.06, 89.96, 89.88, 88.74, 88.53, 87.90, 39.82, 39.50, 39.44, 39.28, 37.53, 37.06, 36.91, 35.50, 35.11, 34.94, 34.81, 34.77, 34.71, 33.21, 32.83, 32.70, 32.51, 32.38, 32.34, 31.77, 31.41, 31.34, 31.08, 31.02, 31.00, 30.82, 30.60, 30.42, 30.17, 30.13, 30.08, 30.01, 29.93, 29.91, 29.83, 29.80, 29.67, 29.41, 28.91, 28.61, 28.40, 28.31, 27,85, 27.74, 27.55, 27.43, 27.14, 23.49, 23.26, 23.13, 23.09, 22.99, 20.57, 20.11, 19.65, 14.82, 14.68, 14.55, 14.40, 11.83, 4.96, 0.38. Anal. Calcd for $C_{163}H_{233}ISi$: C, 83.39; H, 10.00. Found: C, 81.43; H, 9.32. M_n = 3625, M_w = 4350, M_w/M_n = 1.20. λ (THF) = 242, *370* (ϵ 1.72 × 10^5 M^{-1} cm^{-1}) nm. Emiss (THF) = *411*, 433 nm.

Dodecyl-Containing Terminal Alkynyl Octamer 44. 40 (0.18 g, 0.11 mmol), methanol (5 mL), dichloromethane (15 mL), and potassium carbonate (0.15 g, 1.05 mmol) at 65 °C afforded 0.13 g (100%) of the title compound as a yellow oil which solidified upon standing. IR (KBr) 3310, 2924, 2854, 2198, 1593, 1502, 1460, 1403, 1343, 1234, 1096, 889, 837, 723, 612 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.50−7.43 (m, 9 H), 7.38−7.26 (m, 15 H), 3.76 (q, J = 7.0 Hz, 4 H), 3.32 (s, 1 H), 2.83 (m, 16 H), 1.71 (m, 16 H), 1.34 −1.23 (m, 152 H), 0.85−0.83 (m, 24 H).

Dodecyl-Containing 16-mer 46. 42 (0.82 g, 0.35 mmol), **44** (0.68 g, 0.30 mmol), THF (10 mL), bis(dibenzylideneacetone)palladium(0) (0.020 g, 0.035 mmol), triphenylphosphine (0.046 g, 0.18 mmol), copper(I) iodide (0.0070 g, 0.035 mmol), and *N*,*N*-diisopropylethylamine (0.49 mL, 2.80 mmol) for 4 d at 65 °C afforded 1.20 g (90%) of the title compound as a yellow solid after flash liquid chromatography (3:1; hexane:dichloromethane). R_f = 0.64 (3:1; hexane:dichloromethane). IR (KBr) 2924, 2854, 2199, 2150, 1593, 1502, 1460, 1402, 1345, 1235, 1096, 888, 838, 723, 658, 612 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.50−7.46 (m, 16 H), 7.38 (m, 16 H), 7.31−7.27 (m, 16 H), 3.77 (q, J = 7.1 Hz, 4 H), 2.84 (m, 32 H), 1.71 (m, 32 H), 1.23 (m, 288 H), 0.85−0.83 (m, 48 H), 0.25 (s, 9 H). ^{13}C NMR (125 MHz, CD$_2$Cl$_2$) δ 151.77, 146.44, 146.23, 145.75, 145.44, 136.24, 135.28, 134.84, 134.72, 133.80, 133.15, 132.54, 132.15, 131.23, 130.74, 130.45, 130.14, 129.87, 129.17, 128.97, 128.74, 128.63, 127.61, 127.48, 127.14, 126.58, 126.09, 125.85, 124.96, 124.40, 124.24, 123.72, 123.11, 122.68, 122.48, 121.50, 119.05, 118.02, 95.14, 93.07, 90.05, 41.17, 39.88, 39.71, 39.48, 39.31, 38.51, 38.12, 37.84, 37.55, 37.24, 37.09, 36.96, 36.40, 36.16, 35.41, 35.11, 34.90, 34.75, 34.14, 33.85, 33.51, 33.25, 32.86, 32.43, 31.82, 31.38, 31.15, 30.87, 30.19, 30.07, 29.88, 29.41, 29.02, 28.67, 28.45, 28.35, 27.89, 26.78, 27.60, 27.23, 26.81, 26.35, 25.19, 25.70, 24.24, 24.13, 23.17, 22.91, 20.60, 20.31, 19.95, 19.48, 18.47, 14.66, 14.39, 11.67, 11.23, 0.10.

***N*-Ethyl-*N*-(hydroxyethyl)-4-triazenyl-2-dodecylacetophenone.** To a 3000 mL round-bottom flask equipped with a mechanical stirrer, nitrogen inlet, and 0 °C condenser, containing boron trifluoride etherate (102.35 mL, 832.20 mmol) at 0 °C, was added **11** (129.31 g, 426.77 mmol) in dichloromethane (1.5 L) followed by *tert*-butyl nitrite (83.75 mL, 704.17 mmol). The reaction was stirred for 30 min at 0 °C before potassium carbonate (277.22 g, 2.06 mol) and 2-(ethylamino)ethanol (262.22 mL, 2.69 mol) were added sequentially. The reaction was then warmed to room temperature over 2 d before water (450 mL) was added in three portions. The potassium carbonate was then filtered and the solvent removed *in vacuo* before the organic layer was extracted with dichloromethane and dried over magnesium sulfate. The sample was concentrated in vacuo yielding a crude oil that was purified by flash liquid chromatography (4:1; hexane:ethyl acetate) to afford 146.43 g (85%) of the title compound as a brown oil. R_f = 0.22 (3:1; hexane:ethyl acetate). IR (neat) 3439, 2927, 2853, 1678, 1600, 1557, 1454, 1430, 1395, 1349, 1243, 1130, 1074, 951, 896, 825, 721, 624 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.65 (d, J = 8.9 Hz, 1 H), 7.26−7.25 (m, 2 H), 3.88−3.86 (m, 5 H), 2.87 (t, J = 8.0 Hz, 2 H), 2.55 (s, 3 H), 1.55 (m, 2 H), 1.40−1.20 (m, 23 H), 0.86 (t, J = 7.0 Hz, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 200.66, 153.10, 145.14, 133.74, 131.10, 123.35, 117.00, 60.80, 51.13, 34.59, 31.87, 31.73, 29.85, 29.64, 29.51, 29.39, 29.31, 22.63, 14.07. HRMS calcd for $C_{24}H_{41}N_3O_2$: 403.3199. Found: 403.3206.

***N*-Ethyl-*N*-[(trimethylsiloxy)ethyl]-4-triazyl-2-dodecylacetophenone (47).** To a solution of *N*-ethyl-*N*-(hydroxyethyl)-4-triazenyl-2-dodecynylacetophenone (1.99 g, 4.94 mmol) in THF (20 mL) was added dropwise triethylamine (4.13 mL, 29.64 mmol) at room temperature. The mixture was allowed to stir for 10 min before chlorotrimethylsilane (1.88 mL, 14.82 mmol) was added slowly. The resulting reaction mixture was allowed to stir for 1 d before being poured into water. The organic layer was extracted with ether and dried over magnesium sulfate. The sample was concentrated *in vacuo* to afford 2.23 g (95%) of the title compound as a brown oil which was taken on to the next step without purification. $R_f = 0.61$ (9:1; hexane:ether). IR (neat) 2927, 2857, 1679, 1598, 1559, 1454, 1532, 1388, 1348, 1246, 1200, 1101, 944, 843, 752, 720, 620 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, $J = 9.0$ Hz, 1 H), 7.25−7.23 (m, 2 H), 3.84−3.82 (m, 5 H), 2.87 (t, $J = 7.9$ Hz, 2 H), 2.55 (s, 3 H), 1.56 (p, $J = 7.0$ Hz, 2 H), 1.26−1.23 (m, 22 H), 0.86 (t, $J = 7.0$ Hz, 3 H), 0.095 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.32, 153.14, 145.10, 133.72, 131.04, 123.45, 117.09, 60.21, 58.33, 45.80, 34.63, 31.91, 31.75, 29.87, 29.68, 29.66, 29.64, 29.55, 29.49, 29.35, 22.67, 14.09, −0.60. HRMS calcd for $C_{27}H_{49}N_3O_2Si$: 475.3594. Found: 475.3589.

***N*-Ethyl-*N*-[(trimethylsiloxy)ethyl]-1-triazyl-3-dodecyl-4-[(trimethylsilyl)ethynyl]benzene (48).** To a stirred solution of diisopropylamine (0.88 mL, 6.70 mmol) in THF (5 mL) was added at −78 °C, under nitrogen, *n*-butyllithium (3.90 mL, 6.08 mmol, 1.56 M in hexanes). The reaction mixture was allowed to warm to 0 °C for 10 min and then cooled to −78 °C. To the LDA solution was added triazene **47** (2.31 g, 4.86 mmol) in THF (5 mL). The reaction mixture was stirred at −78 °C for 1 h before adding, at the same temperature, diethyl chlorophosphonate (0.88 mL, 6.08 mmol). The reaction mixture was allowed to warm to room temperature over 30 min before being recooled to −78 °C. The reaction solution was then transferred via cannula into 2.25 equiv of LDA [made as above with diisopropylamine (1.58 mL, 12.04 mmol) and *n*-butyllithium (7.01 mL, 10.94 mmol, 1.56 M in hexanes)] in THF (15 mL) at −78 °C. The ensuing reaction mixture was allowed to warm to 0 °C over 1 h and then recooled to −78 °C before chlorotrimethylsilane (1.54 mL, 12.15 mmol) was added. The solution was allowed to warm to room temperature overnight before being poured into water and extracted with ether (3×). The combined ether extracts were washed with brine and dried over magnesium sulfate. Filtration and removal of the solvent *in vacuo* afforded 2.83 g of the title compound as a brown oil which was used directly for the next step. IR (neat) 2926, 2855, 2150, 1602, 1454, 1401, 1378, 1348, 1289, 1251, 1198, 1159, 1094, 978, 940, 842, 758, 721, 697, 654 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, $J = 8.2$ Hz, 1 H), 7.19 (s, 1 H), 7.16 (d, $J = 8.2$ Hz, 1 H), 3.80−3.78 (m, 4 H), 2.74 (t, $J = 8.0$ Hz, 2 H), 1.63 (m, 2 H), 1.24−1.14 (m, 23 H), 0.86 (t, $J = 6.9$ Hz, 3 H), 0.23 (s, 9 H), 0.090 (s, 9 H). HRMS calcd for $C_{30}H_{55}N_3OSi_2$: 529.3884. Found: 529.3892.

***N*-Ethyl-*N*-[(hydroxyethyl)ethyl]-1-triazyl-3-dodecyl-4-ethynylbenzene (49).** **48** (2.83 g, 4.86 mmol), methanol (10 mL), dichloromethane (10 mL), potassium carbonate (4.15 g, 30 mmol), and gravity liquid chromatography (3:1; hexane: ethyl acetate) afforded 0.94 g (50% over two steps) of the title compound as a brown oil. $R_f = 0.34$ (3:1; hexane:ethyl acetate). IR (neat) 3415, 3313, 2925, 2855, 2100, 1740, 1600, 1560, 1452, 1434, 1400, 1378, 1345, 1239, 1181, 1152, 1101, 1078, 1048, 892, 829, 791, 721, 643 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, $J = 8.2$ Hz, 1 H), 7.21 (d, $J = 1.9$ Hz, 1 H), 7.18 (dd, $J = 8.2, 1.2$ Hz, 1 H), 3.87−3.81 (m, 5 H), 3.22 (s, 1 H), 2.76 (t, $J = 8.0$ Hz, 2 H), 1.63 (p, $J = 7.0$ Hz, 2 H), 1.32−1.23 (m, 23 H), 0.86 (t, $J = 7.0$ Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.22, 146.53, 133.55, 120.98, 118.56, 117.43, 82.82, 80.44, 61.28, 51.59, 34.64, 31.96, 30.68, 29.73 (2 C), 29.69, 29.65, 29.56, 29.52, 29.40, 22.72, 14.15. HRMS calcd for $C_{24}H_{39}N_3O$: 385.3093. Found: 385.3087.

1-Iodo-3-dodecyl-4-[(trimethylsilyl)ethynyl]benzene (16) Prepared from 48. **48** (6.62 g, 12.5 mmol) and iodomethane (10 mL) afforded 2.83 g (60% over two steps) of the title compound as a brown oil which was analytically identical to the titled material prepared from **13**.

Polymer-Supported Monomer 50. A three-neck 2 L round-bottomed flask equipped with a mechanical stirrer and a water condenser was charged with chloromethyl polystyrene (50.00 g, 50.00 mmol, 1.00 ± 0.05 mequiv g^{-1}, 1% cross-linked with divinylbenzene, 200−400 mesh). The vessel was flushed thoroughly with nitrogen before a solution of anchor **49** (57.75 g, 150 mmol) in dry THF (250 mL) was added via a cannula followed by additional dry THF (350 mL) to facilitate free stirring. The reaction mixture was cooled to −78 °C, and sodium hydride (5.62 g, 140.50 mmol, 60% dispersion in oil) was added carefully in portions under a nitrogen blanket. After the addition was complete, the reaction mixture was warmed to room temperature over 30 min and then heated at 75 °C for 48 h with gentle stirring. The mixture was then cooled to 0 °C, quenched with methanol (60 mL) and water (60 mL), and filtered. The polymer was then transferred to a preweighed fritted filter using dichloromethane, and washed sequentially (ca. 3 × 30 mL/g polymer) with the following: THF, H_2O, MeOH, EtOAc, *n*-hexane, CH_2Cl_2, and MeOH, and dried to constant mass in a vacuum oven at 40 °C to afford 67.95 g ($\Delta W_{theor} = 17.41$ g, $\Delta W = 17.95$ g) of the title polymer as yellow beads. IR (CCl_4) 3305, 3025, 2937, 2869, 2504, 2403, 2289, 2211, 2098, 1944, 1873, 1803, 1745, 1593, 1558, 1446, 1366, 1237, 1197, 1081, 1023, 893, 775 cm^{-1}. Gel-phase ^{13}C NMR showed some remaining benzylic chloride peak at δ 46.77. Anal. Calcd for the functionalized resin: C, 87.61; H, 8.21; Cl, 0.64; N, 2.55; O, 0.97. Found: C, 87.12; H, 8.30; Cl, 0.61; N, 2.56. This signifies that 77% of the chloride was substituted. All subsequent calculated elemental composition data reflect this initial substitution.

General Procedure for the Coupling of a Polymer-Supported Terminal Alkyne with an Aryl Halide.[5] A thick-walled oven-dried screw cap tube was charged with the polymer-supported terminal alkyne (1.0 equiv) and the monomeric or oligomeric aryl iodide (2.0 equiv). To the reaction flask was added, via cannula, the supernatant of a premade solution (6 mL/g of polymer) of bis(dibenzylideneacetone)-palladium(0) (4 mol %), triphenylphosphine (20 mol %), and copper(I) iodide (4 mol %) in dry triethylamine which had been degassed and stirred at 70 °C for 2 h. The tube was flushed with nitrogen, capped, and kept at 65 °C for 12−48 h without stirring, and the vessel was shaken periodically. The polymer was then poured onto a preweighed fritted filter using dichloromethane to wash the beads that were sticking to the sides of the flask. The beads were then washed sequentially (ca. 30 mL/g of polymer) with the following: CH_2Cl_2, DMF, 0.05 M solution of sodium diethyl dithiocarbamate in 99/1 DMF/diisopropylethylamine,[19] DMF, CH_2Cl_2, MeOH, and dried to constant mass in a vacuum oven at 60 °C. The degree of substitution of each reaction was estimated by infrared analysis of the polymer bound substrate. Absorptions at 3311 cm^{-1} (strong) and 2109 cm^{-1} (weak) were characteristic of the terminal alkynyl carbon−hydrogen and carbon−carbon stretches, respectively, and an absorption at 2156 cm^{-1} (strong) was characteristic of the carbon−carbon stretch of the trimethylsilyl-protected terminal alkyne.[13] The excess aryl halide was recovered from the washings and repurified before further use. The amount of aryl iodide recovered after purification was generally ca. 30% less than expected.

Polymer-Supported Silyl Dimer 51. **16** (33.72 g, 72.05 mmol), **50** (59.07 g, 36.03 mmol, 0.61 mmol g^{-1}), bis(dibenzylideneacetone)palladium(0) (1.65 g, 2.88 mmol), triphenylphosphine (3.78 g, 14.41 mmol), copper(I) iodide (0.55 g, 2.88 mmol), and triethylamine (500 mL) for 2 d afforded 69.05 g ($\Delta W_{theor} = 12.25$ g, $\Delta W = 9.98$ g) of the title polymer as yellow beads. IR (CCl_4) 3062, 3027, 2952, 2914, 2853, 2291, 2201, 2150, 2009, 1943, 1873, 1803, 1746, 1663, 1595, 1549, 1491, 1447, 1345, 1244, 1196, 1156, 1093, 1008, 981, 790, 707, 627 cm^{-1}. Gel-phase ^{13}C NMR showed the gain of a trimethylsilyl peak at δ 0.47. Anal. Calcd for the functionalized resin: C, 86.51; H, 8.63; Cl, 0.53; N, 2.11; O, 0.80; Si, 1.41. Found: C, 86.12; H, 8.66; N, 2.31.

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[19] Briscoe, G. B.; Humphries, S. *Talanta* **1969**, *16*, 1403.

General Procedure for the Liberation of Polymer-Supported Oligomers.[5] A thick-walled oven-dried screw cap tube was charged with a suspension of the polymer-supported oligomer and iodomethane (7 mL/g of polymer). The tube was flushed with nitrogen, capped, and heated to 120 °C for 12−24 h without stirring. The reaction mixture was cooled and passed through a fritted filter before the resin was introduced to hot CH$_2$Cl$_2$ (3×) to extract any residual product trapped in the polymer matrix. The combined filtrate was then passed through a plug of silica gel with CH$_2$Cl$_2$.

Dodecyl-Containing Iodide Dimer 25 from 51. 51 (45.72 g, 23.31 mmol, 0.51 mmol g^{-1}) and iodomethane (320 mL) afforded 14.66 g (86%) of the title compound as a light brown oil which was analytically identical to the titled material prepared from **22**.

General Procedure for the Desilylation of Polymer-Supported Silylated Alkynes.[5] To a suspension of polymer-supported aryl (trimethylsilyl)alkyne (1.0 equiv) and THF (9 mL/g of polymer) in an Erlenmeyer flask was added a solution of TBAF (2.0 equiv, 1.0 M in THF). The suspension was swirled periodically for 15 min. The polymer was then transferred to a preweighed fritted filter using THF, washed sequentially (ca. 30 mL/g polymer) with THF followed by MeOH, and dried to constant mass in a vacuum oven at 60 °C. The efficiency of each reaction was estimated by infrared analysis of the polymer bound substrate. An absorption at 3311 cm^{-1} (strong) and 2109 cm^{-1} (weak) are characteristic of the terminal alkynyl carbon−hydrogen and carbon−carbon stretches, respectively, and an absorption at 2156 cm^{-1} (strong) is characteristic of the carbon−carbon stretch of the trimethylsilyl-protected alkyne.[19]

Polymer-Supported Terminal Alkynyl Dimer 52. 51 (22.87 g, 11.66 mmol, 0.51 mmol g^{-1}), THF (206 mL), and TBAF (6.96 mL, 24.00 mmol, 1.00 M in THF) afforded 22.09 g ($\Delta W_{\text{theor}} = -0.84$ g, $\Delta W = -0.78$ g) of the title polymer as goldish yellow beads. IR (CCl$_4$) 3307, 3083, 3061, 3027, 2935, 2851, 2201, 2102, 1941, 1869, 1802, 1746, 1663, 1600, 1548, 1493, 1452, 1401, 1377, 1345, 1238, 1194, 1154, 1094, 1027, 1005, 979, 892, 804, 699, 648, 609 cm^{-1}. Gel-phase ^{13}C NMR showed the loss of a trimethylsilyl peak at δ 0.47. Anal. Calcd for the functionalized resin: C, 87.89; H, 8.53; Cl, 0.55; N, 2.19; O, 0.83. Found: C, 87.94; H, 8.49; N, 2.31.

Polymer-Supported Silyl Tetramer 53. 25 (13.73 g, 18.65 mmol), **52** (17.28 g, 8.99 mmol, 0.52 mmol g^{-1}), bis(dibenzylideneacetone)palladium(0) (0.43 g, 0.75 mmol), triphenylphosphine (0.98 g, 3.75 mmol), copper(I) iodide (0.14 g, 0.75 mmol), and triethylamine (200 mL) for 1 d afforded 21.71 g ($\Delta W_{\text{theor}} = 5.47$ g, $\Delta W = 4.43$ g) of the title polymer as mustard-colored beads. IR (CCl$_4$) 3061, 3026, 2919, 2853, 2198, 2151, 1940, 1867, 1800, 1746, 1660, 1600, 1548, 1493, 1453, 1402, 1378, 1344, 1250, 1194, 1154, 1093, 1028, 1005, 979, 891, 792, 700 cm^{-1}. Gel-phase ^{13}C NMR showed the gain of a trimethylsilyl peak at δ 0.40. Anal. Calcd for the functionalized resin: C, 87.14; H, 9.03; Cl, 0.42; N, 1.66; O, 0.63; Si, 1.11. Found: C, 86.89; H, 8.97; N, 1.82.

Dodecyl-Containing Iodide Tetramer 34 from 53. 53 (14.47 g, 5.79 mmol, 0.40 mmol g^{-1}) and iodomethane (100 mL) afforded 6.02 g (77%) of the title compound as a light brown oil which solidified upon standing and was analytically identical to the titled material prepared from **31**.

Polymer-Supported Terminal Alkynyl Tetramer 54. 53 (6.88 g, 2.75 mmol, 0.40 mmol g^{-1}), THF (62 mL), and TBAF (1.60 mL, 5.50 mmol, 1.00 M in THF) afforded 6.80 g ($\Delta W_{\text{theor}} = -0.20$ g, $\Delta W = -0.08$ g) of the title polymer as orange beads. IR (CCl$_4$) 3308, 3061, 3027, 2920, 2853, 2198, 2102, 1941, 1870, 1802, 1745, 1662, 1596, 1550, 1495, 1450, 1401, 1375, 1345, 1239, 1195, 1155, 1092, 1007, 980, 892, 795, 702 cm^{-1}. Gel-phase ^{13}C NMR showed the loss of a trimethylsilyl peak at δ 0.40. Anal. Calcd for the functionalized resin: C, 88.24; H, 8.97; Cl, 0.43; N, 1.71; O, 0.65. Found: C, 86.13; H, 8.44; N, 1.88.

Polymer-Supported Silyl Octamer 55. 34 (5.70 g, 4.48 mmol), **54** (5.46 g, 2.24 mmol, 0.41 mmol g^{-1}), bis(dibenzylideneacetone)palladium(0) (0.10 g, 0.18 mmol), triphenylphosphine (0.23 g, 0.90 mmol), copper(I) iodide (0.034 g, 0.18 mmol), and triethylamine (60 mL) afforded 7.17 g ($\Delta W_{\text{theor}} = 2.56$ g, $\Delta W = 1.71$ g) of the title polymer as rusty orange beads. IR (CCl$_4$) 3061, 3027, 2917, 2198, 2151, 1941, 1871, 1802, 1745, 1660, 1596, 1548, 1498, 1451, 1402, 1345, 1247, 1195, 1154, 1094, 1006, 980, 892, 794, 703 cm^{-1}. Gel-phase ^{13}C NMR showed the gain of a trimethylsilyl peak at δ 0.36. Anal. Calcd for the functionalized resin: C, 87.84; H, 9.47; Cl, 0.29; N, 1.17; O, 0.44; Si, 0.78. Found: C, 87.56; H, 9.00; N, 1.44.

Dodecyl-Containing Iodide Octamer 42 from 55. 55 (4.78 g, 1.34 mmol, 0.28 mmol g^{-1}) and iodomethane (35 mL) afforded 2.51 g (80%) of the title compound as a waxy yellow solid which was analytically identical to the titled material prepared from **40**.

Polymer-Supported Terminal Alkynyl Octamer 56. 55 (1.90 g, 0.53 mmol, 0.28 mmol g^{-1}), THF (20 mL), and TBAF (0.31 mL, 1.06 mmol, 1.00 M in THF) afforded 1.93 g ($\Delta W_{\text{theor}} = -0.04$ g, $\Delta W = 0.03$ g) of the title polymer as rusty orange beads. IR (CCl$_4$) 3308, 3061, 3027, 2923, 2855, 2198, 2103, 1943, 1870, 1799, 1772, 1740, 1696, 1652, 1594, 1547, 1498, 1455, 1399, 1343, 1242, 1197, 1154, 1090, 1007, 891, 793, 706 cm^{-1}. Gel-phase ^{13}C NMR showed the loss of a trimethylsilyl peak at δ 0.36. Anal. Calcd for the functionalized resin: C, 88.62; H, 9.44; Cl, 0.30; N, 1.22; O, 0.45. Found: C, 87.93; H, 8.92; N, 1.49.

Polymer-Supported Dodecyl-Containing 16-mer 57. 42 (2.18 g, 0.93 mmol), **56** (1.53 g, 0.44 mmol, 0.29 mmol g^{-1}), bis(dibenzylideneacetone)palladium(0) (0.021 g, 0.037 mmol), triphenylphosphine (0.050 g, 0.19 mmol), copper(I) iodide (0.0070 g, 0.037 mmol), and triethylamine (40 mL) afforded 1.76 g ($\Delta W_{\text{theor}} = 0.98$ g, $\Delta W = 0.23$ g) of the title polymer as rusty orange beads. IR (CCl$_4$) 3061, 3027, 2923, 2855, 2198, 2151, 1942, 1869, 1798, 1772, 1740, 1696, 1675, 1652, 1594, 1545, 1499, 1455, 1401, 1343, 1244, 1195, 1152, 1088, 1007, 889, 793, 706 cm^{-1}. Gel-phase ^{13}C NMR showed the gain of a trimethylsilyl peak at δ 0.36. Anal. Calcd for the functionalized resin: C, 88.46; H, 9.86; Cl, 0.18; N, 0.73; O, 0.28; Si, 0.49. Found: C, 86.95; H, 9.08; N, 1.30.

Dodecyl-Containing Iodide 16-mer 58. 57 (1.37 g, 0.23 mmol, 0.17 mmol g^{-1}) and iodomethane (25 mL) afforded 0.84 g (79%) of the title compound as a waxy yellow solid. R_f = 0.27 (9:1; hexane:dichloromethane). IR (KBr) 2924, 2855, 2146, 1590, 1502, 1461, 1384, 1262, 1088, 888, 837, 724, 618 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.58 (br s, 2 H), 7.50−7.47 (m, 12 H), 7.40−7.30 (m, 32 H), 7.19 (d, J = 8.0 Hz, 2 H), 2.90−2.70 (m, 32 H), 1.80−1.60 (m, 32 H), 1.40−1.20 (m, 288 H), 0.88−0.86 (m, 48 H), 0.27 (s, 9 H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 152.57, 147.51, 145.61, 145.41, 138.19, 135.60, 135.23, 133.84, 136.76, 132.56, 132.14, 131.90, 129.16, 128.78, 125.95, 125.46, 123.65, 123.54, 123.06, 122.54, 107.71, 95.19, 95.09, 95.08, 95.05, 95.02, 94.97, 94.60, 94.59, 94.58, 94.57, 94.55, 90.15, 90.05, 90.02, 89.95, 89.93, 89.39, 89.37, 46.73, 46.41, 44.43, 42.73, 41.80, 41.09, 40.62, 40.52, 39.92, 39.86, 39.81, 39.50, 39.45, 39.29, 38.85, 38.17, 37.93, 37.88, 37.84, 37.82, 37.80, 37.73, 37.53, 37.42, 37.38, 37.09, 36.92, 36.71, 36.57, 36.07, 36.02, 35.77, 35.51, 35.12, 34.94, 34.83, 34.14, 33.90, 33.84, 33.65, 33.53, 33.33, 33.20, 33.18, 32.91, 32.83, 32.79, 32.70, 32.64, 32.38, 32.37, 32.08, 31.42, 31.09, 30.59, 30.47, 30.18, 30.14, 30.10, 30.02, 29.93, 29.90, 29.83, 29.80, 29.41, 29.26, 29.00, 28.48, 28.40, 27.96, 27.86, 27.74, 27.52, 27.22, 27.18, 27.14, 26.90, 26.83, 26.57, 267.34, 25.88, 25.62, 25.23, 24.90, 24.29, 24.11, 23.92, 23.85, 23.60, 23.48, 23.13, 23.08, 23.04, 22.04, 20.71, 20.57, 20.22, 20.16, 20.11, 19.68, 19.64, 19.13, 18.11, 14.97, 14.83, 14.54, 12.86, 11.82, 11.30, 8.11, 7.94, 7.89, 0.37. Anal. Calcd for C$_{323}$H$_{457}$ISi: C, 86.31; H, 10.25. Found: C, 85.92; H, 10.76. M_{n} = 8860, M_{w} = 10,940, $M_{\text{w}}/M_{\text{n}}$ = 1.23. λ (THF) = 240, *377* (ϵ 3.59 × 10^5 M^{-1} cm^{-1}) nm. Emiss (THF) = *414*, 436 nm.

1-(Phenylethynyl)-4-(thioacetyl)benzene (61). 59 (0.36 g, 1.30 mmol), phenylacetylene (0.16 mL, 1.43 mmol), bis(dibenzylideneacetone palladium(0) (37.31 mg, 0.070 mmol), triphenylphosphine (85.20 mg, 0.33 mmol), copper(I) iodide (24.80 mg, 0.13 mmol), *N*,*N*-diisopropylethylamine (0.90 mL, 5.20 mmol), and THF (3 mL) for 2 d afforded 0.31 g (95%) of the title compound as a yellow solid after gravity liquid chromatography (24:1; hexane:ether). R_f = 0.26 (24:1; hexane:ether). IR (KBr) 1699, 1587, 1493, 1442, 1396, 1352, 1314, 1211, 1175, 1112, 1012, 944, 877, 826, 756, 690, 622 cm^{-1}. ^{1}H

NMR (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.5 Hz, 2 H), 7.53 (dd, *J* = 5.5, 2.4 Hz, 2 H), 7.38 (d, *J* = 8.5 Hz, 2 H), 7.36−7.33 (m, 3 H), 2.42 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.31, 134.16, 132.12, 131.65, 128.50, 128.35, 128.03, 124.52, 122.89, 91.04, 88.60, 30.21. HRMS calcd for $C_{16}H_{12}OS$: 252.0609. Found: 252.0607. λ (CH_2Cl_2) = 228, *293*, 309 nm.

2-Ethyl-4-(phenylethynyl)-1-(trimethylsilyethynyl)benzene (62). **14** (0.98 g, 3 mmol), phenylacetylene (0.36 mL, 3.30 mmol), bis(dibenzylideneacetone)palladium(0) (86.10 mg, 0.15 mmol), triphenylphosphine (196.70 mg, 3.30 mmol), copper(I) iodide (57.10 mg, 0.30 mmol), *N*,*N*-diisopropylethylamine (2.10 mL, 12 mmol), and THF (6 mL) for 6 d afforded 0.89 g (98%) of the title compound as a yellow oil after gravity liquid chromatography (hexane). R_f = 0.39 (hexane). IR (neat) 3061, 2967, 2874, 2246, 2152, 1602, 1496, 1458, 1444, 1407, 1380, 1250, 1222, 1115, 1068, 1026, 909, 860, 756, 734, 690, 626 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.53−7.50 (m, 2 H), 7.38 (d, *J* = 7.9 Hz, 1 H), 7.36 (s, 1 H), 7.35−7.32 (m, 3 H), 7.27 (dd, *J* = 7.9, 1.7 Hz, 1 H), 2.78 (q, 7.6 Hz, 2 H), 1.25 (t, *J* = 7.6 Hz, 3 H), 0.25 (s, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.19, 132.91, 132.17, 131.57, 129.37, 128.91, 128.90, 124.07, 123.75, 122.84, 104.19, 100.24, 91.54, 90.06, 28.18, 14.99, 0.54.

3-Ethyl-1-(phenylethynyl)-4-ethynylbenzene. **62** (0.89 g, 2.95 mmol), methanol (15 mL) and potassium carbonate (1.24 g, 9 mmol) afforded 0.63 g (93%) of the title compound as a yellow oil. IR (neat) 3293, 3059, 2969, 2933, 2874, 2100, 1603, 1495, 1458, 1443, 1241, 1066, 1026, 912, 894, 831, 756, 689, 600 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.53−7.50 (m, 2 H), 7.42 (d, *J* = 7.9 Hz, 1 H), 7.38 (s, 1 H), 7.36−7.32 (m, 3 H), 7.29 (dd, *J* = 7.9, 1.6 Hz, 1 H), 3.32 (s, 1 H), 2.81 (q, *J* = 7.6 Hz, 2 H), 1.25 (t, *J* = 7.6 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.32, 133.34, 133.02, 132.16, 131.57, 129.33, 128.91, 124.31, 123.62, 121.82, 91.53, 89.87, 82.82, 82.55, 27.95, 15.12. HRMS calcd for $C_{18}H_{14}$: 230.1096. Found: 230.1089.

Trimer Thioacetate 63. **59** (0.70 g, 2.50 mmol), 3-ethyl-1-(phenylethynyl)-4-ethynylbenzene (0.61 g, 2.67 mmol), THF (5 mL), bis(dibenzylideneacetone)palladium(0) (71.80 mg, 0.13 mmol), triphenylphosphine (164 mg, 0.63 mmol), copper(I) iodide (47.60 mg, 0.25 mmol), *N*,*N*-diisopropylethylamine (1.73 mL, 10 mmol) for 5 d afforded 0.67 g (70%) of the title compound as a yellow solid after gravity liquid chromatography (9:1; hexane:ethyl acetate). R_f = 0.49 (9:1; hexane:ethyl acetate). IR (KBr) 2962, 2930, 2874, 2201, 1691, 1589, 1501, 1459, 1442, 1396, 1356, 1304, 1266, 1118, 1014, 953, 887, 827, 753, 684, 668, 628 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.4 Hz, 2 H), 7.52 (dd, *J* = 7.5, 2.2 Hz, 1 H), 7.46 (d, *J* = 7.9 Hz, 1 H), 7.42 (d, *J* = 2 Hz, 1 H), 7.38 (d, *J* = 8.4 Hz, 2 H), 7.36−7.33 (m, 5 H), 2.85 (q, *J* = 7.6 Hz, 2 H), 2.43 (s, 3 H), 1.30 (t, *J* = 7.5 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.33, 146.40, 134.33, 132.23, 132.10, 131.70, 131.20, 129.00, 128.48, 128.46, 128.25, 124.61, 123.60, 123.17, 122.07, 93.87, 91.10, 89.70, 89.52, 30.30, 27.71, 14.70. HRMS calcd for $C_{26}H_{20}O_2$: 380.1235. Found: 380.1224. λ (CH_2Cl_2) = 230, 234, *328* nm.

General Procedures for the Hydrolysis of Thioesters to Thiols.[20] (a) A mixture of the thioester, sodium hydroxide (2 equiv), zinc dust (5 mg), and water (5 mL/mmol of thioester) were deoxygenated with argon gas for 1 h before THF (5 mL/mmol of thioester) was added. The reaction was allowed to stir overnight at room temperature while being purged with argon gas. 3 M hydrochloric acid was to permit neutralization. The resulting precipitate was dissolved in degassed chloroform (5 mL/mmol of thioester) and the organic layer was withdrawn via syringe and transferred to a Schlenk flask without exposure to air. Chloroform was added to the aqueous layer and withdrawn another 3× to permit complete extraction before the combined organic solvent was removed *in vacuo* to afford a solid which was immediately taken into the dry box. Eluents and other slight modifications are described below for each material. (b) A mixture of the thioester, 30% ammonium hydroxide (10 equiv) and THF (2.50 mL/mmol of thioester) were allowed to stir for 15 min at room temperature while being purged with argon gas. The reaction mixture was then worked up in the same manner as above. Eluents and other slight modifications are described below for each material.

Trimer Thiol 64. **63** (0.19 g, 0.50 mmol), sodium hydroxide (40 mg, 1.0 mmol), zinc dust (5.0 mg, 0.076 mequiv), water (3 mL), THF (5 mL), and 3 M hydrochloric acid (0.33 mL) afforded 0.16 g (92%) of the title compound as a yellow solid with slight impurities. R_f = 0.44 (9:1; hexane:ethyl acetate). IR (neat) 2963, 2929, 2869, 2562, 2204, 1722, 1654, 1598, 1499, 1460, 1400, 1271, 1118, 1015, 893, 824, 756, 691, 619 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.8 Hz, 2 H), 7.51 (dd, *J* = 7.5, 2.1 Hz, 1 H), 7.43 (d, *J* = 7.9 Hz, 1 H), 7.40 (s, 1 H), 7.36 (d, *J* = 8.4 Hz, 2 H), 7.34 (dd, *J* = 8.1, 3.4 Hz, 1 H), 7.33 (d, *J* = 7.9 Hz, 2 H), 7.23 (d, *J* = 7.5 Hz, 2 H), 3.52 (s, 1 H), 2.85 (q, *J* = 7.6 Hz, 2 H), 1.29 (t, *J* = 7.5 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.18, 146.57, 132.92, 132.47, 132.45, 132.41, 132.07, 131.54, 131.32, 129.43, 129.34, 129.24, 129.12, 128.82, 94.55, 91.32, 89.94, 88.83, 28.06, 15.01. LRMS Calcd for $C_{24}H_{18}S$: 338. Found: 338. λ (CH_2Cl_2) = *228*, 234, 282, 339 nm.

2-Ethyl-1,4-bis[(trimethylsilyl)ethynyl]benzene (65). **14** (0.98 g, 3.0 mmol), (trimethylsilyl)acetylene (0.47 mL, 3.30 mmol), bis(dibenzylideneacetone)palladium(0) (86.10 mg, 0.15 mmol), triphenylphosphine (0.20 g, 0.75 mmol), copper(I) iodide (57.10 mg, 0.30 mmol), *N*,*N*-diisopropylethylamine (2.10 mL, 12 mmol), and THF (6 mL) for 1 d afforded 0.83 g (93%) of the title compound as a yellow oil after gravity liquid chromatography (hexane). R_f = 0.55 (hexane). IR (neat) 2963, 2935, 2899, 2875, 2157, 1602, 1484, 1458, 1406, 1250, 1213, 1120, 916, 859, 760, 700, 628 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.9 Hz, 1 H), 7.28 (d, *J* = 1.1 Hz, 1 H), 7.19 (dd, *J* = 7.9, 1.6 Hz, 1 H), 2.74 (q, *J* = 7.5 Hz, 2 H), 1.21 (t, *J* = 7.5 Hz, 3 H), 0.23 (s, 9 H), 0.22 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.57, 132.19, 131.37, 129.07, 123.17, 122.50, 104.97, 103.38, 99.75, 95.60, 27.52, 14.35, −0.056, −0.074. HRMS calcd for $C_{18}H_{26}Si_2$: 298.1573. Found: 298.1569.

2-Ethyl-1,4-diethynylbenzene (68). **65** (0.60 g, 2 mmol), methanol (10 mL), and potassium carbonate (1.66 g, 12 mmol) afforded 0.27 g (88%) of the title compound as a yellow oil. R_f = 0.27 (hexane). IR (neat) 3294, 2969, 2935, 2875, 2107, 1603, 1485, 1460, 1243, 896, 832, 735 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.9 Hz, 1 H), 7.33 (d, *J* = 1.1 Hz, 1 H), 7.25 (dd, *J* = 7.9, 1.6 Hz, 1 H), 3.31 (s, 1 H), 3.12 (s, 1 H), 2.78 (q, *J* = 7.6 Hz, 2 H), 1.23 (t, *J* = 7.6 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.83, 132.74, 131.60, 129.26, 122.53, 121.89, 83.39, 82.29, 81.74, 78.53, 27.33, 14.51.

Diphenylthioester Monomer 71. **59** (0.70 g, 2.50 mmol), **68** (0.15 g, 1.0 mmol), THF (3 mL), bis(dibenzylideneacetone)-palladium(0) (72 mg, 0.13 mmol), triphenylphosphine (164 mg, 0.63 mmol), copper(I) iodide (48 mg, 0.25 mmol), *N*,*N*-diisopropylethylamine (0.70 mL, 4 mmol) for 1 d afforded 0.32 g (70%) of the title compound as a yellow solid after gravity liquid chromatography (9:1; hexane:ether). R_f = 0.11 (9:1; hexane:ether). IR (KBr) 2964, 2928, 2874, 2206, 1912, 1695, 1590, 1500, 1396, 1354, 1118, 1095, 1014, 955, 825, 720, 694, 617 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.1 Hz, 4 H), 7.46 (d, *J* = 8.1 Hz, 1 H), 7.41 (d, *J* = 1.7 Hz, 1 H), 7.39 (d, *J* = 8.2 Hz, 2 H), 7.38 (d, *J* = 8.3 Hz, 2 H), 7.33 (dd, *J* = 8.1, 1.7 Hz, 1 H), 2.86 (q, *J* = 7.6 Hz, 2 H), 2.43 (s, 3 H), 2.42 (s, 3 H), 1.30 (t, *J* = 7.5 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.39, 146.41, 134.29, 134.22, 132.18, 132.07, 131.22, 128.98, 124.54, 124.36, 123.11, 122.34, 93.93, 91.05, 90.15, 89.52, 30.29, 27.64, 14.60. HRMS calcd for $C_{28}H_{22}O_2S_2$: 454.1061. Found: 454.1059. λ (CH_2Cl_2) = 205, 230, 234, *334* nm.

Diphenylthiol Monomer 74. **71** (0.19 g, 0.40 mmol), sodium hydroxide (64 mg, 1 mmol), zinc dust (5.0 mg, 0.076 mequiv), water (1 mL), THF (2 mL), and 3 M hydrochloric acid (0.53 mL) afforded 0.14 g (94%) of the title compound as a yellow solid with slight impurities. R_f = 0.12 (4:1; hexane:ether). IR (KBr) 2962, 2927, 2869, 2561, 2204, 1902, 1712, 1656, 1587, 1498, 1461, 1401, 1266, 1099, 1016, 892, 823 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 1 H), 7.37 (d, *J* = 8.2 Hz, 4 H), 7.36 (s, 1 H), 7.29 (dd, *J* = 8.0, 1.6 Hz, 1 H), 7.23 (d, *J* = 8.2 Hz, 2 H), 7.22 (d, *J* = 8.4 Hz, 2 H), 3.51 (s, 1 H), 3.50 (s, 1 H), 2.84 (q, *J* = 7.5 Hz, 2 H), 1.29 (t, *J* = 7.5 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.56, 132.56, 132.43,

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[20] Zervais, L.; Photaki, I.; Ghelis, N. *J. Am. Chem. Soc.* **1963**, *85*, 1337.

131.44, 129.39, 129.37, 129.25, 123.51, 122.76, 120.88, 120.70, 94.57, 90.78, 90.33, 88.78, 28.02, 14.97. LRMS calcd for $C_{24}H_{18}S_2$: 370. Found: 370. λ (CH_2Cl_2) = *229*, 234, 340 nm.

Bis(trimethylsilyl) Dimer 66. **23** (0.91 g, 2.0 mmol), (trimethylsilyl)acetylene (0.31 mL, 2.20 mmol), bis(dibenzylideneacetone)palladium(0) (57.40 mg, 0.10 mmol), triphenylphosphine (0.11 g, 0.40 mmol), copper(I) iodide (38.10 mg, 0.20 mmol), *N,N*-diisopropylethylamine (1.38 mL, 8 mmol), and THF (4 mL) for 5 d afforded 0.65 g (76%) of the title compound as a yellow oil after gravity liquid chromatography (hexane). R_f = 0.21 (hexane). IR (neat) 2964, 2899, 2875, 2154, 1598, 1495, 1458, 1407, 1250, 1222, 857, 760, 701, 636 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.9 Hz, 1 H), 7.38 (d, *J* = 7.9 Hz, 1 H), 7.33 (d, *J* = 1.2 Hz, 1 H), 7.32 (d, *J* = 1.1 Hz, 1 H), 7.25 (dd, 8.0, 1.3 Hz, 2 H), 2.82 (q, *J* = 7.6 Hz, 2 H), 2.78 (q, *J* = 7.6 Hz, 2 H), 1.27 (t, *J* = 7.5 Hz, 3 H), 1.25 (t, *J* = 7.5 Hz, 3 H), 0.25 (s, 9 H), 0.24 (s, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.20, 146.48, 132.77, 132.40, 131.86, 131.27, 129.65, 129.04, 123.80, 123.53, 122.91, 122.82, 105.44, 103.85, 100.27, 96.13, 94.99, 94.99, 89.65, 28.01, 27.97, 14.97, 14.82, 0.37, 0.35. HRMS calcd for $C_{28}H_{34}Si_2$: 426.2199. Found: 426.2202.

Diethynyl Dimer 69. **66** (0.64 g, 1.50 mmol), methanol (10 mL), dichloromethane (5 mL), and potassium carbonate (1.24 g, 9.0 mmol) afforded 0.42 g (100%) of the title compound as a yellow oil. IR (neat) 3297, 3091, 3071, 3036, 2968, 2933, 2874, 1960, 1815, 1727, 1603, 1527, 1479, 1394, 1036, 910, 832, 734, 676 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.9 Hz, 1 H), 7.42 (d, *J* = 7.9 Hz, 1 H), 7.360 (d, *J* = 1.3 Hz, 1 H), 7.355 (d, *J* = 1.1 Hz, 1 H), 7.28 (dd, *J* = 7.9, 1.4 Hz, 2 H), 3.33 (s, 1 H), 3.14 (s, 1 H), 2.87−2.79 (two quartets, 4 H), 1.28 (t, *J* = 7.6 Hz, 3 H), 1.27 (t, *J* = 7.6 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.34, 146.63, 133.28, 132.49, 132.05, 131.34, 131.29, 129.82, 129.22, 127.14, 124.12, 123.25, 94.90, 89.54, 84.01, 82.72, 82.37, 78.98, 27.98, 27.86, 15.03, 14.95. HRMS calcd for $C_{22}H_{18}$: 282.1408. Found: 282.1407.

Diphenylthioester Dimer 72. **59** (1.04 g, 3.75 mmol), **69** (42 g, 1.50 mmol), THF (10 mL), bis(dibenzylideneacetone)palladium(0) (0.11 g, 0.19 mmol), triphenylphosphine (0.25 g, 0.94 mmol), copper(I) iodide (72.40 mg, 0.38 mmol), *N,N*-diisopropylethylamine (2.60 mL, 15 mmol) for 5 d to afforded 0.44 g (50%) of the title compound as a yellow waxy solid after gravity liquid chromatography (9:1; hexane:ethyl acetate). R_f = 0.26 (9:1; hexane:ethyl acetate). IR (KBr) 2966, 2931, 2871, 2203, 1910, 1701, 1588, 1542, 1500, 1478, 1460, 1435, 1396, 1350, 1264, 1115, 1088, 1014, 947, 888, 826, 616 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 2 H), 7.47 (d, *J* = 7.9 Hz, 2 H), 7.41 (s, 1 H), 7.39 (d, *J* = 8.4 Hz, 2 H), 7.38 (d, *J* = 8.4 Hz, 2 H), 7.35−7.32 (m, 3 H), 7.21 (d, *J* = 7.8 Hz, 2 H), 2.89−2.86 (two quartets, 4 H), 2.43 (s, 3 H), 2.42 (s, 3 H), 1.32 (t, *J* = 7.6 Hz, 3 H), 1.31 (t, *J* = 7.6 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.43, 146.49, 146.32, 134.32, 134.26, 134.09, 132.24, 132.20, 132.09, 131.20, 131.04, 129.69, 129.01, 128.87, 128.40, 128.22, 124.58,124.41, 123.54, 122.60, 122.19, 94.77, 93.91, 91.13, 90.13, 89.60, 89.46, 30.33, 27.71, 27.65, 14.68, 14.63. HRMS calcd for $C_{38}H_{30}O_2S_2$: 582.1687. Found: 582.1684. λ (CH_2Cl_2) = *229*, 234, 272, 350 nm.

Diphenylthiol Dimer 75. **72** (0.17 g, 0.30 mmol), sodium hydroxide (0.10 g, 2.50 mmol), zinc dust (5.0 mg, 0.076 mequiv), water (5 mL), THF (5 mL), and 3 M hydrochloric acid (0.83 mL) afforded 0.13 g (87%) of the title compound as a yellow solid with slight impurities. R_f = 0.17 (9:1; hexane: ethyl acetate). IR (KBr) 2963, 2929, 2868, 2561, 2201, 1899, 1719, 1654, 1589, 1542, 1499, 1459, 1400, 1265, 1181, 1116, 1096, 1013, 954, 890, 823, 744, 700, 620 cm^{-1}. Impurities, presumably due from disulfide formation, prevented complete assignment of the aromatic region. ^1H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.0 Hz, 1 H), 7.45 (d, *J* = 8.0 Hz, 1 H), 7.37 (d, *J* = 8.3 Hz, 4 H), 7.32 (d, *J* = 7.9 Hz, 1 H), 7.31 (d, *J* = 7.9 Hz, 2 H), 7.30 (d, *J* = 7.9 Hz, 1 H), 7.25 (d, *J* = 8.4 Hz, 2 H), 7.24 (d, *J* = 8.5 Hz, 2 H), 3.52 (s, 1 H), 3.51 (s, 1 H), 2.90−2.80 (two quartets, 4 H), 1.31 (t, *J* = 7.5 Hz, 3 H), 1.30 (t, *J* = 7.5 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.64, 132.55, 132.54, 132.48, 132.43, 132.40, 131.44, 131.36, 131.27, 129.40, 129.37, 129.25, 129.22, 123.66, 123.62, 122.86, 122.73, 120.89, 120.72, 95.12, 94.61, 90.82, 90.32, 89.78, 88.78, 28.06, 28.02, 15.00, 14.99. LRMS calcd for $C_{34}H_{26}S_2$: 498. Found: 498. λ (CH_2Cl_2) = 207, 229, *352* nm.

Bis(trimethylsilyl) Tetramer 67. **32** (0.56 g, 0.78 mmol), (trimethylsilyl)acetylene (0.12 mL, 0.86 mmol), bis(dibenzylideneacetone)palladium(0) (22.40 mg, 0.04 mmol), triphenylphosphine (51.10 mg, 0.20 mmol), copper(I) iodide (15 mg, 0.08 mmol), *N,N*-diisopropylethylamine (0.54 mL, 3.12 mmol), and THF (5 mL) for 4 d afforded 0.48 g (90%) of the title compound as a yellow oil after flash liquid chromatography (9:1; hexane:dichloromethane). R_f = 0.74 (9:1; hexane:dichloromethane). IR (neat) 2963, 2930, 2868, 2152, 1919, 1592, 1501, 1459, 1409, 1248, 1117, 1062, 842, 759, 698, 666, 624 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.9, 1.9 Hz, 2 H), 7.42 −7.39 (m, 4 H), 7.35−7.31 (m, 4 H), 7.29−7.26 (m, 2 H), 2.91−2.78 (m, 8 H), 1.33−1.24 (m, 12 H), 0.25 (s, 9 H), 0.24 (s, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.24, 146.71, 146.51, 132.79, 132.58, 132.41, 131.89, 131.36, 131.29, 129.67, 129.23, 129.07, 123.81, 123.76, 123.54, 122.93, 122.83, 105.45, 103.86, 100.34, 96.18, 95.16, 95.11, 95.08, 89.82, 89.77, 89.74, 30.13, 28.08, 28.03, 28.00, 15.05, 14.99, 14.84, 0.38, 0.37. HRMS calcd for $C_{48}H_{50}Si_2$: 682.3451. Found: 682.3474.

Diethynyl Tetramer 70. **67** (0.48 g, 0.70 mmol), methanol (25 mL), dichloromethane (50 mL), and potassium carbonate (0.58 g, 4.20 mmol) afforded 0.33 g (88%) of the title compound as a yellow solid. IR (KBr) 3300, 2964, 2929, 2867, 1593, 1500, 1459, 1409, 1373, 1116, 1062, 888, 838, 745, 642, 616 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.49−7.46 (m, 3 H), 7.43 (s, 1 H), 7.40−7.37 (m, 4 H), 7.35−7.28 (m, 4 H), 3.33 (s, 1 H), 3.14 (s, 1 H), 2.90−2.81 (m, 8 H), 1.35−1.24 (m, 12 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.35, 146.75, 146.73, 146.61, 133.25, 132.58, 132.56, 132.54, 132.45, 132.04, 131.37, 131.32, 129.78, 129.23, 129.10, 123.32, 122.49, 95.12, 94.87, 89.79, 89.76, 89.52, 84.00, 82.62, 82.36, 78.85, 30.10, 28.05, 27.95, 27.83, 15.02, 14.93.

Diphenylthioester Tetramer 73. **59** (55.60 mg, 0.20 mmol), **70** (35.97 mg, 0.07 mmol), bis(dibenzylideneacetone)palladium(0) (5.74 mg, 0.01 mmol), triphenylphosphine (13.11 mg, 0.05 mmol), copper(I) iodide (3.80 mg, 0.02 mmol), *N,N*-diisopropylethylamine (0.14 mL, 0.80 mmol), and THF (3 mL) for 5 d to afforded 17.30 mg (32%) of the title compound as a yellow waxy solid with slight impurities after flash liquid chromatography (9:1; hexane:ethyl acetate). R_f = 0.20 (9:1; hexane:ethyl acetate). Impurities, presumably from disulfide formation, prevented complete assignment of the aromatic region. ^1H NMR (400 MHz, $CDCl_3$) δ 7.56−7.32 (m, 20 H), 3.00−2.80 (four quartets, 8 H), 2.43 (s, 3 H), 2.42 (s, 3 H), 1.40−1.30 (four triplets, 12 H). LRMS Calcd for $C_{58}H_{46}O_2S_2$: 838 (100%), 839 (68%), 840 (32%). Found: 838 (100%), 839 (60%), 840 (40%). λ (CH_2Cl_2) = 197, 209, 218, 228, *359* nm.

Thioester Silane 76. **16** (0.35 g, 0.74 mmol), **60** (0.14 mL, 0.81 mmol), bis(triphenylphosphino)palladium(II) chloride (0.0052 g, 0.0074 mmol), triphenylphosphine (0.0039 g, 0.015 mmol), copper(I) iodide (0.0029 g, 0.015 mmol), and triethylamine (1 mL) for 2 d afforded 0.34 g (89%) of the title compound as a brown oil after gravity liquid chromatography (9:1; hexane:ether). R_f = 0.62 (9:1; hexane:ether). IR (neat) 3054, 2926, 2853, 2209, 2152, 1904, 1715, 1601, 1541, 1497, 1466, 1435, 1397, 1352, 1249, 1224, 1118, 1090, 1016, 949, 842, 760, 744, 721, 697, 638, 617 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.6 Hz, 2 H), 7.38 (d, *J* = 7.9 Hz, 1 H), 7.37 (d, *J* = 8.5 Hz, 2 H), 7.33 (d, *J* = 1.3 Hz, 1 H), 7.26 (dd, *J* = 8.0, 1.6 Hz, 1 H), 2.74 (t, *J* = 7.8 Hz, 2 H), 2.42 (s, 3 H), 1.62 (p, *J* = 7.2 Hz, 2 H), 1.32−1.24 (m, 18 H), 0.86 (t, *J* = 7.0 Hz, 3 H), 0.24 (s, 9 H). HRMS calcd for $C_{33}H_{44}OSSi$: 516.2882. Found: 516.2878.

Thioester Alkyne 80. **76** (0.32 g, 0.62 mmol), 49% concentrated hydrofluoric acid (0.021 mL, 1.36 mmol), TBAF (0.20 mL, 0.68 mmol, 1.0 M in THF) and pyridine (1.24 mL) at room temperature for 20 min afforded 0.22 g (81%) of the title compound as a brown oil after gravity liquid chromatography (9:1; hexane:ether). R_f = 0.55 (9:1; hexane:ether) IR (neat) 3298, 2924, 2853, 2101, 1712, 1601, 1494, 1461, 1120, 1016, 949, 828 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.5 Hz, 2 H), 7.42 (d, *J* = 7.9 Hz, 1 H), 7.37 (d, *J* = 8.6 Hz, 2 H), 7.35 (d, *J* = 1.3 Hz, 1 H), 6.38 (dd, *J* = 7.9, 1.6 Hz, 1 H), 3.31 (s, 1 H), 2.75 (t, J = 7.8 Hz, 2 H), 2.42 (s, 3 H), 1.63 (p, J = 7.2 Hz, 2 H), 1.32−1.24 (m, 18 H), 0.86 (t, J = 7.1 Hz, 3 H).

Bisthioester 83. 59 (0.26 g, 0.92 mmol), **80** (0.21 g, 0.46 mmol), triethylamine (1 mL), bis(triphenylphosphino)palladium(II) chloride (0.0065 g, 0.0092 mmol), triphenylphosphine (0.0047 g, 0.018 mmol), and copper(I) iodide (0.0034 g, 0.018 mmol) for 1 d afforded 0.16 g (59%) of the title compound as a yellow solid after gravity liquid chromatography (9:1; hexane: ether). $R_f = 0.20$ (9:1; hexane:ether). IR (KBr) 3032, 2924, 2855, 2677, 2254, 2211, 1907, 1705, 1594, 1541, 1498, 1461, 1400, 1354, 1305, 1267, 1116, 1012, 950, 908, 829, 731, 615 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.3 Hz, 2 H), 7.53 (d, J = 8.2 Hz, 2 H), 7.46 (d, J = 7.9 Hz, 1 H), 7.41−7.38 (m, 5 H), 7.33 (dd, J = 8.0, 2.5 Hz, 1 H), 2.83 (t, J = 7.6 Hz, 2 H), 2.42 (s, 3 H), 2.41 (s, 3 H), 1.69 (p, J = 7.5 Hz, 2 H), 1.38−1..25 (m, 18 H), 0.89 (t, J = 7.0 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.27 (2C), 145.28, 134.29, 134.23, 132.24, 132.19, 132.05, 131.98, 129.00, 128.29, 128.24, 124.56, 124.36, 122.98, 122.56, 93.85, 91.13, 90.21, 89.79, 34.64, 31.98, 30.64, 30.29, 29.75, 29.75, 29.72, 29.69, 29.63, 29.61, 29.43, 22.76, 14.21. HRMS calcd for $C_{38}H_{42}O_2S_2$: 594.2626. Found: 594.2618.

Thioester Silane 77. 34 (0.38 g, 0.29 mmol), **60** (0.13 mL, 0.75 mmol), bis(dibenzylideneacetone)palladium(0) (0.0086 g, 0.015 mmol), triphenylphosphine (0.020 g, 0.073 mmol), copper(I) iodide (0.0055 g, 0.029 mmol), *N,N*-diisopropylethylamine (0.40 mL, 2.32 mmol), and THF (4 mL) for 3 d afforded 0.28 g (73%) of the title compound as a waxy yellow solid after gravity liquid chromatography (9:1; hexane:ether). $R_f = 0.61$ (9:1; hexane:ether). IR (KBr) 2924, 2853, 2206, 2150, 1710, 1594, 1500, 1460, 1403, 1250, 1118, 950, 835, 758, 617 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.4 Hz, 2 H), 7.46 (d, J = 7.9 Hz, 2 H), 7.45 (d, J = 7.9 Hz, 2 H), 7.39 (d, J = 8.2 Hz, 2 H), 7.38 (d, J = 8.3 Hz, 2 H), 7.37−7.26 (m, 6 H), 2.83 (t, J = 7.4 Hz, 6 H), 2.75 (t, J = 6.3 Hz, 2 H), 2.42 (s, 3 H), 1.70−1.20 (m, 8 H), 1.41−1.22 (m, 72 H), 0.86−0.83 (m, 12 H), 0.25 (s, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.37, 146.11, 145.60, 134.73, 134.70, 134.44, 132.92, 132.88, 132.65, 132.57, 132.48, 132.43, 132.27, 132.22, 132.00, 131.90, 129.60, 129.38, 129.22, 129.07, 128.86, 128.70, 128.65, 124.85, 123.80, 123.73, 123.71, 123.30, 123.25, 123.08, 104.14, 100.08, 95.25, 95.21, 95.12, 91.65, 91.40, 90.57, 90.12, 90.08, 35.51, 35.18, 34.83, 34.63, 34.45, 31.27, 31.15, 31.06, 30.96, 30.87, 30.70, 30.63, 30.58, 30.25, 30.21, 30.08, 29.92, 29.34, 28.54, 28.38, 23.33, 23.21, 23.10, 14.74, 14.66, 14.60, 14.52. LRMS calcd for $C_{93}H_{128}OSSi$: 1321 (88%), 1322 (100%), 1323 (63%). Found: 1321 (95%), 1322 (100%), 1323 (70%).

Thioester Alkyne 81. 77 (0.15 g, 0.11 mmol), 49% concentrated hydrofluoric acid (0.0074 mL, 0.48 mmol), TBAF (0.070 mL, 0.24 mmol, 1.0 M in THF), and pyridine (1.24 mL) at room temperature for 30 min afforded 0.12 g (87%) of the title compound as a waxy yellow solid after flash liquid chromatography (9:1; hexane:ether). $R_f = 0.57$ (9:1; hexane: ether) IR (KBr) 3302, 2926, 2856, 2206, 2101, 1906, 1713, 1597, 1498, 1459, 1116, 827, 616 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.4 Hz, 2 H), 7.46 (d, J = 7.8 Hz, 2 H), 7.43 (d, J = 7.9 Hz, 2 H), 7.38 (d, J = 8.5 Hz, 2 H), 7.37−7.27 (m, 8 H), 3.32 (s, 1 H), 2.83 (t, J = 7.4 Hz, 6 H), 2.77 (t, J = 7.3 Hz, 2 H), 2.43 (s, 3 H), 1.70−1.60 (m, 8 H), 1.34−1.22 (m, 72 H), 0.86−0.83 (m, 12 H). LRMS calcd for $C_{90}H_{120}OS$: 1249 (98%), 1250 (100%), 1251 (55%). Found: 1249 (96%), 1250 (100%), 1251 (63%).

Thioester Silane 78. 42 (0.13 g, 0.055 mmol), **60** (0.020 g, 0.75 mmol), bis(dibenzylideneacetone)palladium(0) (0.0016 g, 0.0028 mmol), triphenylphosphine (0.0037 g, 0.014 mmol), copper(I) iodide (0.00053 g, 0.0028 mmol), *N,N*-diisopropylethylamine (2 mL), and THF (3 mL) for 3 days afforded 0.077 g (59%) of the title compound as a waxy yellow solid after gravity liquid chromatography (2:1; hexane:chloroform). $R_f =$ 0.56 (2:1; hexane:chloroform). IR (KBr) 2928, 2858, 2198, 2154, 1716, 1510, 1468, 1398, 1262, 1126, 960, 840, 732 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.4 Hz, 2 H), 7.48−7.46 (m, 8 H), 7.40−7.32 (m, 18 H), 2.85−2.75 (m, 16 H), 2.42 (s, 3 H), 1.75−1.65 (m, 16 H), 1.40−1.20 (m, 144 H), 0.90−0.80 (m, 24 H), 0.25 (s, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.77, 146.11, 145.62, 145.32, 143.56, 134.62, 134.60, 133.37, 132.76, 132.57, 132.47, 132.36, 132.34, 132.32, 132.14, 132.02, 131.90, 131.84, 129.36, 129.16, 128.95, 128.85, 128.80, 128.70, 128.67, 128.60, 128.31, 124.83, 123.63, 123.37, 123.24, 123.16, 123.04, 104.01, 100.11, 95.07, 91.52, 90.46, 90.05, 39.80, 29.42, 39.26, 37.50, 37.04, 36.90, 36.18, 36.14, 35.48, 35.09, 34.75, 34.70, 33.20, 32.81, 32.50, 32.36, 32.22, 32.00, 31.72, 31.30, 31.07, 31.03, 30.98, 30.81, 30.67, 30.14, 30.13, 30.10, 30.05, 30.01, 30.00, 29.93, 29.90, 29.80, 29.78, 29.72, 29.68, 29.54, 29.47, 29.34, 28.88, 28.60, 28.39, 28.30, 27.82, 27.72, 27.51, 25.69, 23.24, 23.11, 23.07, 22.97, 21.11, 20.55, 20.10, 19.64, 14.81, 14.53, 14.39, 11.82, 4.96, 0.37.

Thioester Silane 79. 46 (0.49 g, 0.11 mmol), **60** (0.039 mL, 0.22 mmol), bis(dibenzylideneacetone)palladium(0) (0.0032 g, 0.0055 mmol), triphenylphosphine (0.0073 g, 0.028 mmol), copper(I) iodide (0.0010 g, 0.0055 mmol), *N,N*-diisopropylethylamine (2 mL), and THF (4 mL) for 3 days afforded 0.33 g (66%) of the title compound as a waxy yellow solid after gravity liquid chromatography (2:1; hexane:chloroform). $R_f = 0.53$ (2: 1; hexane:chloroform). IR (KBr) 2924, 2855, 2203, 2151, 1710, 1594, 1502, 1460, 1386, 1261, 1094, 1027, 806 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.0 Hz, 2 H), 7.50−7.46 (m, 14 H), 7.38−7.31 (m, 36 H), 2.90−2.80 (m, 32 H), 2.42 (s, 3 H), 1.80−1.70 (m, 32 H), 1.40−1.20 (m, 288 H), 0.90−0.80 (m, 48 H), 0.25 (s, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.68, 145.62, 145.56, 145,32, 143.57, 143.55, 140.46, 134.61, 133.42, 132.88, 132.58, 132.48, 132.37, 132,34, 132.32, 132.15, 132.06, 131.92, 131.86, 129.80, 129.60, 129.39, 129.35, 129.28, 129.19, 129.00, 128.986, 128.86, 128.81, 128.76, 128.71, 128.68, 128.63, 128.33, 125.13, 124.84, 124.11, 123.82, 123.64, 123.51, 123.40, 123.26, 123.20, 123.08, 122.68, 95.41, 95.14, 91.88, 91.57, 91.45, 90.50, 90.41, 90.08, 89.42, 89.36, 88.66, 88.55, 78.78, 39.83, 39.52, 39.44, 39.29, 37.53, 37.08, 36.93, 36.21, 36.17, 35.52, 35.13, 35.08, 34.83, 34.78, 34.72, 33.23, 33.04, 33.00, 32.84, 32.53, 32.40, 32.26, 31.78, 31.75, 31.44, 31.36, 31.10, 31.06, 30.84, 30.66, 30.19, 30.14, 30.10, 30.06, 30.03, 29.93, 29.85, 29.76, 29.72, 28.91, 28.77, 28.62, 28.41, 28.32, 27.87, 27.76, 27.56, 27.45, 27.15, 23.50, 23.27, 23.24, 23.15, 23.11, 23.01, 20.59, 20.13, 19.70, 19.66, 14.84, 14.70, 14.57, 14.43, 11.85, 4.97, 0.40. Anal. Calcd for $C_{333}H_{464}OSSi$: C, 88.03; H, 10.30. Found: C, 86.71; H, 10.80.[21]

Thioester Alkyne 82. 79 (0.27 g, 0.060 mmol), 49% HF (0.40 mL, 25.95 mmol), TBAF (3.84 mL, 13.26 mmol, 1.0 M in THF), pyridine (2 mL), and THF (15 mL) overnight afforded 0.14 g (52%) of the title compound as a waxy yellow solid after flash liquid chromatography (2:1; hexane:chloroform). $R_f =$ 0.50 (2:1; hexane:chloroform). IR (KBr) 3302, 2926, 2856, 2204, 2096, 1714, 1655, 1590, 1504, 1466, 1386, 1262, 1116, 1030, 960, 896, 836, 798, 724 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.0 Hz, 2 H), 7.49−7.46 (m, 14 H), 7.38−7.31 (m, 36 H), 3.36 (s, 1 H), 2.90−2.80 (m, 32 H), 2.42 (s, 3 H), 1.80−1.70 (m, 32 H), 1.40−1.20 (m, 288 H), 0.90−0.80 (m, 48 H).

Bisthioester 84. 59 (0.011g, 0.039 mmol), **82** (0,12 g, 0.026 mmol), bis(dibenzylideneacetone)palladium(0) (0.0012 g, 0.0020 mmol), triphenylphosphine (0.0026 g, 0.0098 mmol), copper(I) iodide (0.00038 g, 0.0020 mmol), *N,N*-diisopropylethylamine (2 mL, 11.48 mmol), and THF (3 mL) for 3 days afforded 0.070 g (58%) of the title compound as a waxy yellow solid after gravity liquid chromatography (3:1; hexane:chloroform). $R_f =$ 0.43 (3:1; hexane:chloroform). IR (KBr) 2923, 2853, 2204, 1716, 1662, 1556, 1502, 1464, 1388, 1314, 1260, 1120, 1018, 890, 826, 692 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.4 Hz, 2 H), 7.48−7.46 (m, 14 H), 7.40−7.32 (m, 40 H), 2.90−2.80 (m, 32 H), 2.43 (s, 3 H), 2.41 (s, 3 H), 1.75−1.65 (m, 32 H), 1.4−1.20 (m, 288 H), 0.90−0.80 (m, 48 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.80, 145.62, 138.76, 136.34, 135.42, 134.61, 132.80, 132.56, 132.54, 132.46, 132.36, 132.32, 132.14, 131.89, 131.16, 129.34, 129.14, 128.94, 128.84, 128.80, 128.69, 128.59, 124.82, 124.06, 123.61, 123.46, 123.23, 123.14, 123.04, 95.06, 91.51, 90.44, 90.02, 36.17, 35.07, 34.72, 32.33, 31.74, 31.05, 31.01, 30.79, 30.67, 30.59, 30.12, 30.11, 30.08, 30.03, 29.99,

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(21) Incomplete carbon combustion in high MW materials with high unsaturated carbon content is a commonly observed property. See reference 8 and (a) Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 7411. (b) Stephens, E. B.; Tour, J. M. *Macromolecules* **1993**, *26*, 2420.

29.97, 29.88, 29.78, 28.36, 28.11, 27.80, 27.70, 23.24, 23.09, 20.09, 14.51. Anal. Calcd for $C_{338}H_{462}O_2S_2$: C, 87.84; H, 10.08. Found: C, 83.52; H, 9.70.[21]

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Supporting Information Available: ^{1}H NMR spectra for compounds **1**−**34**, **36**, **37**, **39**−**49**, **58**, and **61**−**84** (101 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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