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Rapid solution and solid phase synthesis of monodisperse oligo[(1,4-phenyleneethynylene)-alt-(2,5-thiopheneethynylene)]s

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Abstract—Monodisperse oligo[(1,4-phenyleneethynylene)-alt-(2,5-thiopheneethynylene)]s, new candidates for molecular wires, were rapidly synthesized via an iterative divergent/convergent doubling strategy in solution as well as on Merrifield's resin.

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1. Introduction

Conjugated oligomers of precise length and constitution have received considerable attention both as models for analogous bulk polymers and as candidates for molecular wires and molecular scale electronic devices.[1] Monodisperse, well-defined oligo(1,4-phenyleneethynylene)s and oligo(2,5-thiopheneethynylene)s are of particular interest due to their linear conjugated molecular structures as well as their interesting electronic characteristics.[2–8] Recently, we reported the first synthesis of monodisperse alternating cooligomers of oligo(1,4-phenyleneethynylene)s and oligo(2,5-thiopheneethynylene)s, new candidates for molecular wires, which may possess interesting characteristics different from previously reported oligo(1,4-phenyleneethynylene)s, oligo(2,5-thiopheneethynylene)s and their block cooligomers.[9] We describe here the synthetic details for the synthesis of monodisperse oligo[(1,4-phenyleneethynylene)-alt-(2,5-thiopheneethynylene)]s by means of an iterative divergent/convergent doubling strategy in solution as well as on Merrifield's resin.

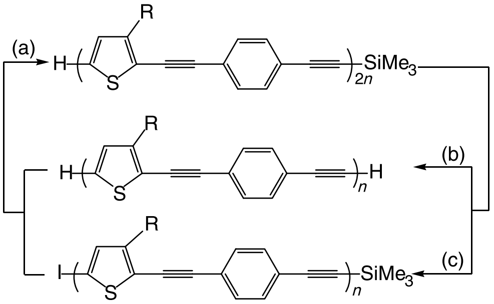
2. Results and discussion

2.1. Failed synthetic route

We initially designed a synthetic route outlined in Scheme 1 to the synthesis of monodisperse oligo[(1,4-phenyleneethynylene)-alt-(2,5-thiopheneethynylene)]s. However, the strategy failed because the products of the iodination reaction were too complicated to purify. Then, we designed another successful synthetic route described below to achieve our goal.

2.2. Oligomer synthesis in solution

The successful solution phase iterative divergent/convergent synthetic route was outlined in Scheme 2. Compound **1** was conveniently synthesized analogous to previously reported procedure.[5] 4-Iodoaniline was converted to the diethyltriazene **2**,[4] followed by coupling to trimethylsilylacetylene and then desilylation to afford **3**, which was then coupled with **1** to give **4**, the desired 'starting monomer' for the iterative divergent/convergent doubling strategy. Compound **4** was divided into two parts. One part was treated with base to give the desilylation terminal alkyne **5**, and the other was converted to the aryl iodide **6** with methyl iodide. Then, compound **5** was coupled with **6** yielding compound **7**. Iteration of above reaction sequence doubled the molecular length of compound **7** to afford **10**. The dimer



Scheme 1. (a) Pd(dba)$_2$, CuI, PPh$_3$, THF/Et$_3$N; (b) K_2CO_3, MeOH; (c) LDA, Et_2O, −78 to 0 °C then I_2, −78 °C.

Keywords: Molecular wires; Monodisperse oligomers; Resin; Synthesis.

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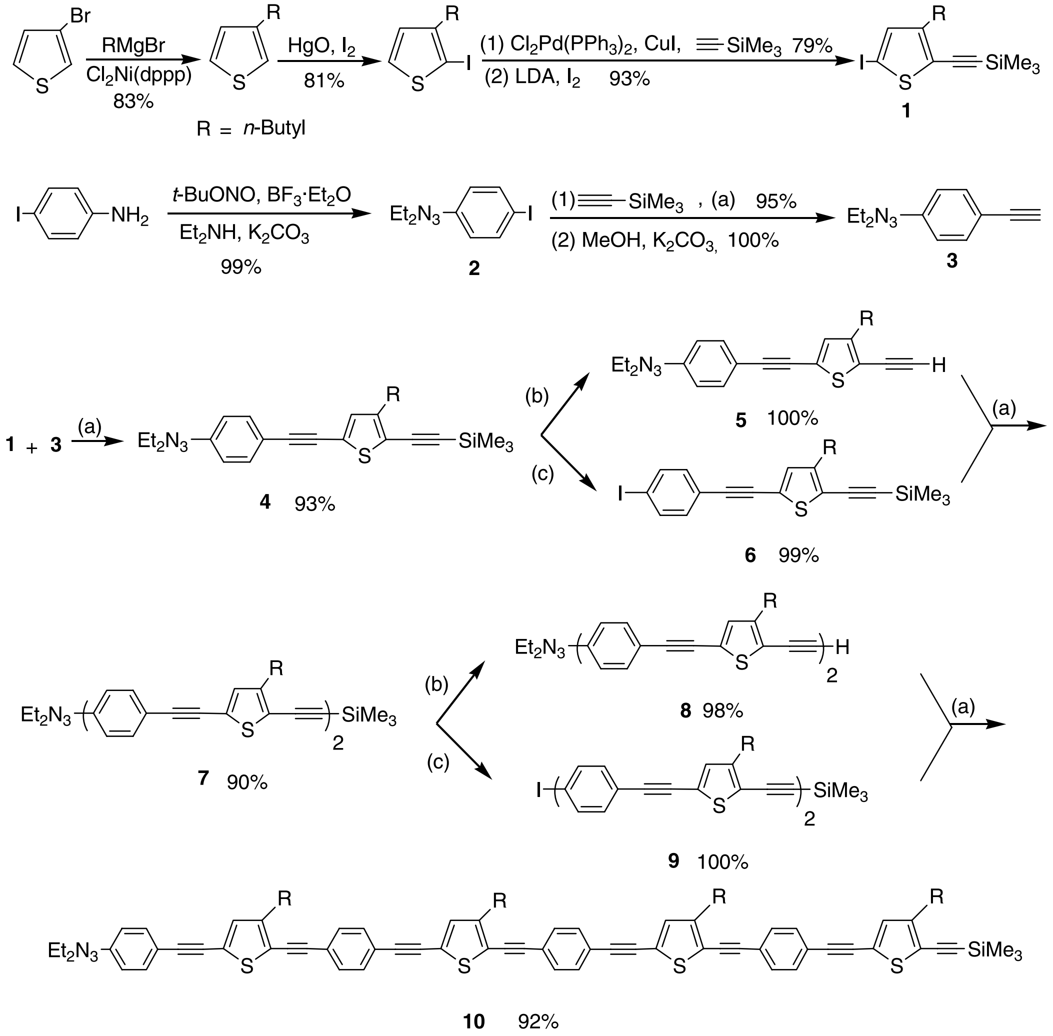


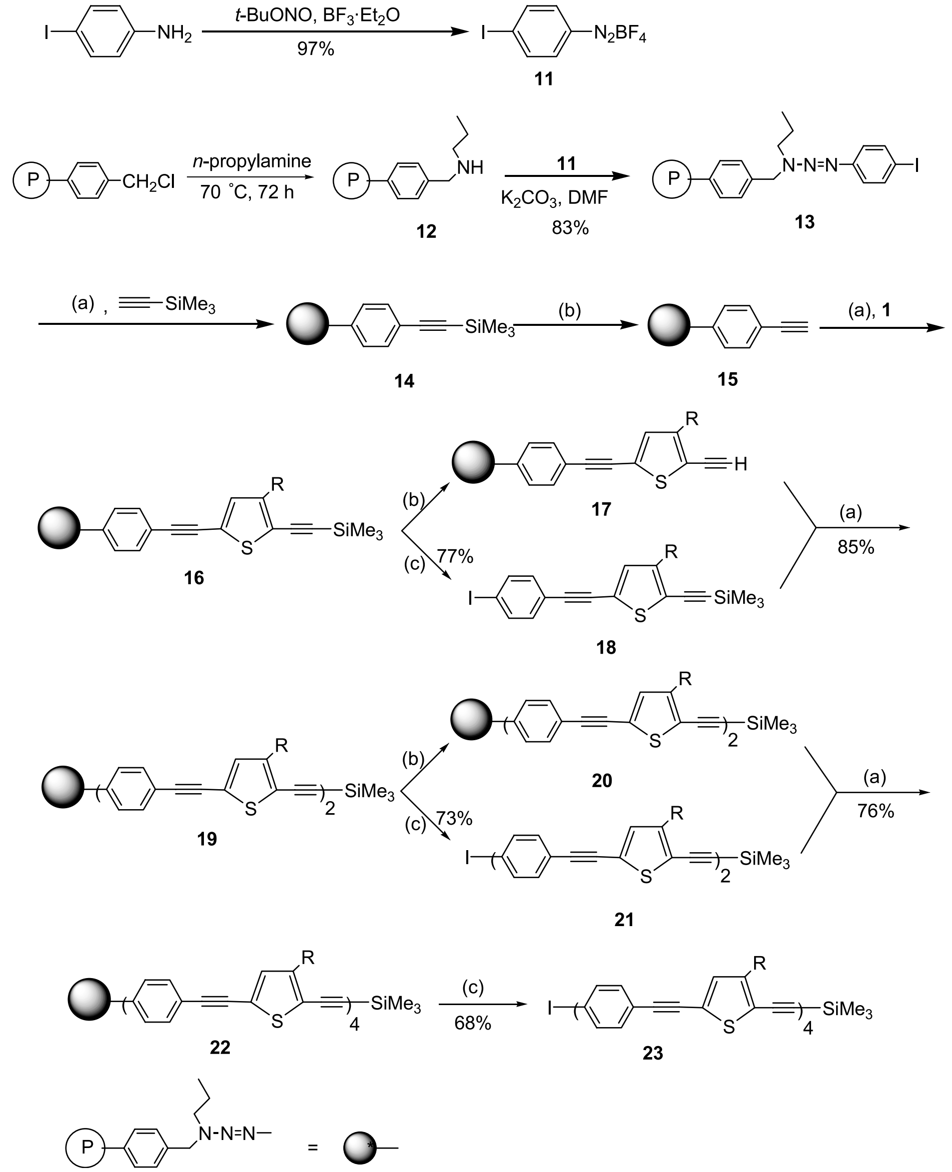
Scheme 2. (a) Pd(dba)$_2$, CuI, PPh$_3$, THF, Et$_3$N; (b) K$_2$CO$_3$, MeOH; (c) MeI.

4, tetramer **7** and octamer **10** were quite soluble in common organic solvents such as THF, CHCl$_3$ and so on. Both triazene–iodide conversion and trimethylsilyl deprotection reactions were almost in quantitative yields, and the coupling reactions were also in high yields (>90%). Note that any product bearing triazene in this report was easily decomposed when silica gel was used for chromatographic purification! Fortunately, chromatographic purification on neutral alumina has proven to be efficient.

2.3. Oligomer synthesis on Merrifield's resin

Since solid phase synthetic method has many remarkable advantages especially including simplified purification, we also synthesized monodisperse oligo[(1,4-phenyleneethynylene)-alt-(2,5-thiopheneethynylene)]s on Merrifield's resin. The synthetic route was outlined in Scheme 3. 4-Iodoaniline was converted to the diazonium tetrafluoroborate salt **11** in high yield.[10] Merrifield's resin was converted to resin **12** by reaction with degassed dry *n*-propylamine in a sealed vessel under argon at 70 °C for 3 days.[11] Compound **11** was attached to resin **12** in the presence of potassium carbonate at 0 °C, followed by coupling to trimethylsilylacetylene and then desilylation by treatment with tetrabutylammonium fluoride (TBAF) in THF at room temperature to give the resin-supported terminal acetylene **15**. Resin **16**, the desired 'starting monomer' for the iterative divergent/convergent doubling strategy, was prepared by coupling resin **15** with compound **1** using the above Pd/Cu catalyst system. One-third of **16** underwent desilylation with TBAF to afford the resin **17**. The remaining two-thirds of **16** were treated with MeI at 115 °C for 24 h to afford liberated compound **18**. Resin **17** was then coupled with all of the liberated iodide **18** under Pd/Cu cross coupling conditions to afford the resin **19**. The sequence was repeated to generate the resin **22**. Compound **23** was liberated from resin **22** by treatment with MeI at 115 °C for 12 h. The dimer **18**, tetramer **21** and octamer **23** were quite soluble in common organic solvents such as THF, CHCl$_3$ and so on.

During the synthesis, reagents attached to the resin were used in large excess amounts (usually 2–3 equiv) to drive the conversion completely and could be easily removed and recovered by filtration. Completion of each resin-supported reaction was monitored by FTIR analysis of the resin-supported substrate according to previously reported method.[4] Because the yield calculations for solid phase



Scheme 3. (a) Pd(dba)$_2$, CuI, PPh$_3$, Et$_3$N; (b) THF, TBAF; (c) MeI.

synthesis were quite difficult, the yields marked in Scheme 3 were therefore only rough estimations based on the weight changes of the resin after each reaction.

3. Conclusions

Monodisperse oligo[(1,4-phenyleneethynylene)-alt-(2,5-thiopheneethynylene)]s, new candidates for molecular wires, were rapidly synthesized via an iterative divergent/convergent doubling strategy in solution as well as on Merrifield's resin.

4. Experimental

4.1. General

All reagents were purchased from Aldrich, Sigma or Acros, and used as received unless otherwise noted. All operations, if not otherwise mentioned, were carried out under a dry, oxygen-free argon atmosphere. Tetrahydrofuran (THF) and ether were distilled under argon from sodium benzophenone ketyl. Triethylamine, iodomethane and diisopropylamine were distilled over calcium hydride. Diethylamine was distilled prior to use. Merrifield's resin was purchased from Sigma (chloromethylated polystyrene, 1% crosslinked with divinyl-benzene, 200–400 mesh, 0.83 mequiv Cl/g). 3-*n*-Butyl-2-[(trimethylsilyl)ethynyl]thiophene was synthesized according to literature procedure.[5] ^{1}H NMR (400 or 600 MHz) and ^{13}C NMR spectra (100 or 150 MHz) were measured on a Bruker AV600 or Varian Unity 400. Infrared spectroscopy was carried out on a Bio-Rad FTS - 135 FTIR or Bruker Tensor27 FTIR spectrometer. Matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) were recorded on LDI 1700, Linear Scientific Inc. USA, using a dithranol matrix in positive ion mode. Thin-layer chromatography (TLC) was performed on silica gel coated aluminum foils (Merck alumina foils 60F254). The terminal alkynes larger than the dimer stage were oxidatively unstable, and used immediately after preparation. Unless otherwise noted, all compounds were $>95\%$ pure as judged by NMR.

General procedure for the coupling of a terminal alkyne with an aryl iodide (procedure A). Analogous to literature procedure[4] with some modifications. All of the reagents were thoroughly dried and flushed with argon before use. To a flame-dried vessel were added the alkyne, the iodide (1.0 equiv based on per alkyne), bis(dibenzylideneacetone)-palladium(0) (5 mol% per alkyne), triphenylphosphine (25 mol% per alkyne), copper(I) iodide (10 mol% per alkyne) and THF–Et_3N (2/1) at room temperature under argon. The vessel was sealed and allowed to stir at room temperature for 2–3 days. The reaction mixture was then poured into water, and the aqueous layer was extracted three times with ethyl acetate. After drying the combined organic layers over magnesium sulfate, the solvent was removed in vacuum to afford a crude product, which was then purified by column chromatography (neutral alumina, 200–300 mesh). Eluents and other slight modifications were described below for each reaction.

General procedures for the desilylation of alkynes (procedure B). Analogous to literature procedure[4] with slight modifications. The silylated alkyne was dissolved in methanol and dichloromethane. Potassium carbonate (2 equiv) was then added, and the reaction was stirred overnight. The reaction mixture was poured into water and the aqueous layer was extracted with ethyl acetate. After drying the combined organic layers over magnesium sulfate, the solvent was removed in vacuum. The product was used without further purification.

General procedure for iodide formation from triazenes (procedure C). Analogous to literature procedure[4] with slight modification. To a thick-walled flame-dried tube were added the corresponding triazene and iodomethane (10 equiv). The tube was flushed with argon, sealed, and heated to 120 °C overnight. The reaction was cooled to room temperature, and the solvent was removed in vacuum. The crude product was then passed through a plug of silica gel with ethyl acetate.

General procedure for the coupling of a resin-supported terminal alkyne with an aryl iodide (procedure D). Analogous to literature procedure[4] but with great modification. All of the reagents were thoroughly dried and flushed with argon before use. To a thick-walled flame-dried sealed tube were added the resin-supported terminal alkyne, the aryl iodide (2.0–3.0 equiv based on per alkyne), bis(dibenzylideneacetone)palladium(0) (8 mol% per alkyne), triphenylphosphine (40 mol% per alkyne) and copper(I) iodide (16 mol% per alkyne) at room temperature. The tube was flushed with argon, and then injected with THF–Et_3N (2/1–4/1) (ca. 10 mL/g of resin) that were thoroughly degassed with argon before use. The tube was sealed and kept at 65 °C for 48–72 h, and it was shaken periodically. The resin was then poured onto a glass filter, and dichloromethane was used to transfer the remaining resin sticking to the sides of the tube. The resin was then washed sequentially (ca. 30 mL/g of resin) with the following: CH_2Cl_2, DMF, 0.05 M solution of sodium diethyl dithiocarbamate in 99:1 DMF/diisopropylethylamine, DMF, CH_2Cl_2, MeOH, and dried to constant mass in vacuum at 60 °C. Completion of each resin-supported coupling reaction was monitored by the disappearance of the 3310 cm^{-1} band (characteristic of the terminal alkynyl carbon–hydrogen stretch) and the appearance of the 2156 cm^{-1} band (characteristic of the carbon–carbon stretch of the trimethylsilylated terminal alkyne) measured by FTIR analysis of the resin.

General procedure for the desilylation of resin-supported silylated alkynes (procedure E). Analogous to literature procedure[4] with slight modification. To a round-bottomed flask were added the resin-supported (trimethylsilyl)alkyne (1.0 equiv), THF (10 mL/g of resin) and TBAF (2.0 equiv). The suspension was stirred slowly for 15–45 min at room temperature. The resin was then poured onto a glass filter, and washed sequentially (ca. 30 mL/g resin) with THF, MeOH, and dried to constant mass in vacuum at 60 °C. Completion of each resin-supported desilylation reaction was monitored by the appearance of the 3310 cm^{-1} band (characteristic of the terminal alkynyl carbon–hydrogen stretch) and the disappearance of the 2156 cm^{-1} band (characteristic of the carbon–carbon stretch of the trimethylsilylated terminal alkyne) measured by FTIR analysis of the resin.

General procedure for the liberation of resin-supported oligomers (procedure F). Analogous to literature procedure[4] with slight modification. To a thick-walled flame-dried tube were added the resin-supported oligomer and iodomethane (7–10 mL/g of resin). The tube was flushed with argon, sealed, and heated to 120 °C for 12–24 h without stirring. The reaction mixture was cooled to room temperature and then filtered through a glass filter. The resin was washed with hot CH_2Cl_2 (ca. 20 mL/g of resin) to extract any residual product trapped in the resin. The combined filtrate was evaporated under vacuum. The crude product was then passed through a plug of silica gel with ethyl acetate.

4.1.1. 5-Iodo-3-*n*-butyl-2-[(trimethylsilyl)ethynyl]thiophene (1). To a solution of diisopropylamine (3.42 g, 33.81 mmol) in ether (25 mL) at −78 °C was added dropwise *n*-butyllithium (19.35 mL, 30.96 mmol, 1.60 M in hexane), and then stirred at −78 °C for 15 min. The mixture was warmed to 0 °C for 30 min and then recooled to −78 °C. 3-*n*-Butyl-2-[(trimethylsilyl)ethynyl]thiophene (3.66 g, 15.48 mmol) in ether (15 mL) at room temperature was then added dropwise, and the solution was warmed from −78 to 0 °C for 15 min. After recooling to −78 °C, iodine (8.58 g, 33.81 mmol) in ether (40 mL) was added via cannula, and the solution was then warmed to room temperature and stirred overnight. The mixture was quenched with water, and the aqueous layer was extracted with ether. The organic layer was washed with brine and aqueous sodium thiosulfate, and then dried over magnesium sulfate. The solvent was removed under vacuum, and the crude product was purified by flash chromatography (silica gel, hexane) to afford 5.22 g (93%) of **1** as a yellow liquid. ^1H NMR (600 MHz, $CDCl_3$) δ 6.83 (s, 1H), 2.68 (t, $J=7.6$ Hz, 2H), 1.59 (quint, $J=7.6$ Hz, 2H), 1.35 (sext, $J=7.2$ Hz, 2H), 0.86 (t, $J=7.2$ Hz, 3H), 0.26 (s, 9H).

4.1.2. 4-(Diethyltriazenyl)-1-iodobenzene (2). To an oven-dried vessel containing boron trifluoride etherate (3.81 mL, 30 mmol) at −15 °C was added 4-iodoaniline (3.29 g, 15 mmol) in dichloromethane (40 mL) followed by *tert*-butyl nitrite (3.60 mL, 30 mmol) in dichloromethane (5 mL). The mixture was stirred at −15 °C for 30 min, and then warmed to 0 °C for 30 min. Diethylamine (12.35 mL, 120 mmol) and potassium carbonate (13.82 g, 100 mmol) were sequentially added. The reaction was stirred at 0 °C for 2 h. The reaction mixture was then poured into water and the aqueous layer was extracted three times with ethyl acetate. After drying the combined organic layers over magnesium sulfate, the solvent was removed in vacuum to afford a crude product, which was then purified by flash chromatography on neutral alumina (9:1; hexane/dichloromethane) to afford 4.72 g (99%) of **1** as a light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, $J=8.8$ Hz, 2H), 7.17 (d, $J=8.8$ Hz, 2H), 3.75 (q, $J=7.2$ Hz, 4H), 1.26 (t, $J=7.2$ Hz, 6H).

4.1.3. 4-Ethynyl-1-diethyltriazenylbenzene (3). First, 4-[(trimethylsilyl)ethynyl]-1-diethyltriazenylbenzene was synthesized according to procedure A. Used were **2** (1.65 g, 5.4 mmol), triethylamine (8.0 mL), (trimethylsilyl)-acetylene (0.92 mL, 6.50 mmol), bis(dibenzylideneacetone)palladium(0) (0.155 g, 0.27 mmol), triphenylphosphine (0.354 g, 1.35 mmol) and copper iodide (0.103 g, 0.54 mmol) for 1 day. The crude product was purified by flash chromatography on neutral alumina by first using 20:1 hexane/dichloromethane and then slowly increasing to 8:1 hexane/dichloromethane to afford 1.40 g (95%) of 4-[(trimethylsilyl)ethynyl]-1-diethyltriazenylbenzene as a yellow–orange waxy solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, $J=8.8$ Hz, 2H), 7.34 (d, $J=8.8$ Hz, 2H), 3.76 (q, $J=7.2$ Hz, 4H), 1.26 (t, $J=7.2$ Hz, 6H), 0.25 (s, 9H).

Then, **3** was synthesized according to procedure B. 4-[(Trimethylsilyl)ethynyl]-1-diethyltriazenylbenzene (0.42 g, 1.50 mmol), methanol (25 mL), and potassium carbonate (0.69 g, 5 mmol) afforded 0.30 g (100%) of **3** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, $J=8.8$ Hz, 2H), 7.36 (d, $J=8.8$ Hz, 2H), 3.77 (q, $J=7.2$ Hz, 4H), 2.95 (s, 1H), 1.27 (t, $J=7.2$ Hz, 6H).

4.1.4. Dimer (4). See procedure A. Compound **1** (2.54 g, 7.0 mmol), **3** (1.31 g, 6.5 mmol), bis(dibenzylideneacetone)-palladium(0) (0.20 g, 0.35 mmol), triphenylphosphine (0.46 g, 1.75 mmol), copper(I) iodide (0.13 g, 0.70 mmol) and triethylamine (30 mL) for 36 h afforded 2.69 g (95%) of **4** as a yellow sticky liquid after flash chromatography on neutral alumina (hexane). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, $J=8.4$ Hz, 2H), 7.39 (d, $J=8.4$ Hz, 2H), 6.98 (s, 1H), 3.77 (q, $J=7.2$ Hz, 4H), 2.65 (t, $J=7.8$ Hz, 2H), 1.60 (quint, $J=7.2$ Hz, 2H), 1.35 (sext, $J=7.2$ Hz, 2H), 1.27 (br s, 6H), 0.94 (t, $J=7.2$ Hz, 3H), 0.26 (s, 9H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 151.27, 148.64, 132.34, 132.18, 123.44, 120.44, 119.42, 118.69, 101.82, 97.05, 94.33, 82.39, 32.16, 32.05, 29.05, 22.18, 13.91, 13.81. LDI-MS (*m/z*): 436 (M^+), 407 ($M-C_2H_5$), 363 (M−TMS), 336 ($M-Et_2N_3$). Anal. Calcd for $C_{25}H_{33}N_3SSi$: H, 7.64; C, 68.93; N, 9.65. Found: H, 7.58; C, 69.02; N, 9.43.

4.1.5. Terminal alkynyl dimer (5). See procedure B. Compound **4** (0.54 g, 1.24 mmol), methanol (10 mL), dichloromethane (5 mL) and potassium carbonate (0.82 g, 5.0 mmol) afforded 0.45 g (100%) of **5** as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, $J=8.4$ Hz, 2H), 7.39 (t, $J=8.4$ Hz, 2H), 6.99 (s, 1H), 3.79 (q, $J=7.2$ Hz, 4H), 3.46 (s, 1H), 2.67 (t, $J=7.6$ Hz, 2H), 1.59 (quint, $J=7.6$ Hz, 2H), 1.35 (d, $J=8.4$ Hz, 2H), 1.28 (br s, 6H), 0.94 (t, $J=7.2$ Hz, 3H).

4.1.6. Iodide dimer (6). See procedure C. Compound **4** (0.48 g, 1.10 mmol) and iodomethane (5 mL) for 24 h afforded 0.51 g (99%) of **6** as a yellow liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, $J=8.4$ Hz, 2H), 7.21 (d, $J=8.4$ Hz, 2H), 7.01 (s, 1H), 2.65 (t, $J=7.6$ Hz, 2H), 1.59 (quint, $J=7.6$ Hz, 2H), 1.36 (sext, $J=7.4$ Hz, 2H), 0.95 (t, $J=7.2$ Hz, 3H), 0.26 (s, 9H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 148.65, 137.57, 137.43, 132.99, 132.84, 130.23, 122.47, 122.21, 120.28, 102.33, 96.79, 94.52, 92.58, 84.12, 32.05, 29.11, 22.19, 13.93. LDI-MS (*m/z*): 462 (M^+), 336 (M−I). Anal. Calcd for $C_{21}H_{23}ISSi$: H, 5.02; C, 54.54. Found: H, 5.06; C, 54.49.

4.1.7. Tetramer (7). See procedure A. Compound **5** (0.35 g, 0.97 mmol), **6** (0.43 g, 0.97 mmol), bis(dibenzylideneacetone)palladium(0) (0.0288 g, 0.05 mmol), triphenylphosphine (0.0629 g, 0.24 mmol), copper(I) iodide (0.0184 g, 0.09 mmol), THF (6 mL) and triethylamine (1 mL) for 2 days afforded 0.62 g (90%) of **7** as a yellow waxy solid after flash chromatography on neutral alumina by first using hexane and then slowly increasing to 9:1 hexane/dichloromethane. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, $J=8.4$ Hz, 2H), 7.46 (s, 4H), 7.40 (d, $J=8.4$ Hz, 2H), 7.03 (s, 1H), 7.01 (s, 1H), 3.77 (q, $J=7.2$ Hz, 4H), 2.72 (t, $J=7.2$ Hz, 2H), 2.65 (t, $J=7.2$ Hz, 2H), 1.65–1.59 (m, 4H), 1.41–1.34 (m, 4H), 1.26 (br s, 6H), 0.97–0.93 (m, 6H), 0.26 (s, 9H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 151.24, 148.63, 148.00, 132.91, 132.48, 132.12, 131.97, 131.28, 131.11, 124.02, 123.07, 122.56, 122.41, 120.41, 120.24, 120.18, 119.10, 118.59, 102.25, 96.80, 95.71, 94.89, 93.30, 84.70, 84.44, 82.38, 32.19, 31.99, 29.16, 28.98, 22.20, 22.13, 13.87, 13.78. LDI-MS (*m/z*): 698 (M^+), 669 ($M-C_2H_5$), 598 ($M-Et_2N_3$). Anal. Calcd for $C_{43}H_{47}N_3S_2Si$: H, 6.79; C, 74.00; N, 6.02. Found: H, 6.88; C, 73.87; N, 5.76.

4.1.8. Terminal alkynyl tetramer (8). See procedure B. Compound **7** (0.30 g, 0.43 mmol), methanol (10 mL), dichloromethane (5 mL) and potassium carbonate (0.24 g, 1.73 mmol) afforded 0.266 g (98%) of **8** as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (br s, 6H), 7.40 (d, $J=8.4$ Hz, 2H), 7.04 (s, 2H), 3.27 (q, $J=7.2$ Hz, 4H), 3.47 (s, 1H), 2.73–2.68 (m, 4H), 1.65–1.61 (m, 4H), 1.41–1.37 (m, 4H), 1.28 (m, 12H), 0.97–0.92 (m, 6H).

4.1.9. Iodide tetramer (9). See procedure C. Compound **7** (0.30 g, 0.43 mmol) and iodomethane (10 mL) for 24 h afforded 0.31 g (100%) of **9** as a yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, $J=8.4$ Hz, 2H), 7.47 (s, 4H), 7.22 (d, $J=8.4$ Hz, 2H), 7.07 (s, 1H), 7.02 (s, 1H), 2.73 (t, $J=7.2$ Hz, 2H), 2.65 (t, $J=7.2$ Hz, 2H), 1.65–1.59 (m, 4H), 1.40–1.35 (m, 4H), 0.97–0.93 (m, 6H), 0.26 (s, 9H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 148.69, 148.07, 137.59, 133.21, 133.00, 132.83, 131.37, 131.22, 123.05, 122.95, 122.66, 122.54, 122.18, 120.31, 120.02, 102.36, 96.80, 96.05, 94.55, 93.23, 93.07, 84.82, 84.16, 84.08, 32.22, 32.04, 29.19, 29.04, 22.24, 22.18, 13.89, 13.80. LDI-MS (*m/z*): 725 (M^+), 697 ($M-C_2H_5$), 598 (M−I). Anal. Calcd for $C_{39}H_{37}IS_2Si$: H, 5.15; C, 64.63. Found: H, 5.23; C, 64.46.

4.1.10. Octamer (10). See procedure A. Compound **8** (0.26 g, 0.42 mmol), **9** (0.30 g, 0.42 mmol), bis(dibenzylideneacetone)palladium(0) (0.0121 g, 0.021 mmol), triphenylphosphine (0.0275 g, 0.105 mmol), copper(I) iodide (0.0080 g, 0.042 mmol), THF (10 mL) and triethylamine (2 mL) for 3 days afforded 0.47 g (92%) of **10** as a yellow solid after flash chromatography on neutral alumina by first using hexane and then slowly increasing to 9:1 hexane/dichloromethane. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49–7.47 (m, 14H), 7.40 (d, $J=8.4$ Hz, 2H), 7.09 (s, 2H), 7.05 (s, 1H), 7.02 (s, 1H), 3.78 (q, $J=7.2$ Hz, 4H), 2.75–2.72 (m, 6H), 2.66 (t, $J=7.2$ Hz, 2H), 1.69–1.57 (m, 8H), 1.41–1.32 (m, 8H), 1.27–1.20 (m, 6H), 0.98–0.94 (m, 12H), 0.26 (s, 9H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 151.32, 148.70, 148.12, 133.23, 133.01, 132.56, 132.19, 131.37, 131.23, 124.09, 123.20, 123.17, 123.04, 122.98, 122.65, 122.61, 122.56, 122.46, 120.45, 120.30, 120.05, 120.01, 119.16, 118.67, 102.35, 96.80, 96.10, 95.73, 94.90, 93.84, 93.78, 93.24, 84.81, 84.71, 84.51, 84.28, 84.21, 82.39, 32.24, 32.04, 29.21, 29.04, 22.25, 22.18, 13.90, 13.80. MALDI-MS (*m/z*): 1223 (M^+), 1123 ($M-Et_2N_3$). Anal. Calcd for $C_{79}H_{75}N_3S_4Si$: H, 6.19; C, 77.61; N, 3.44. Found: H, 6.35; C, 77.36; N, 3.18.

4.1.11. 4-Iodobenzenediazonium tetrafluoroborate (11). To an oven-dried three-neck round-bottomed flask containing boron trifluoride etherate (25.36 mL, 200 mmol) precooled below −20 °C was added dropwise over 15 min a solution of 4-iodoaniline (13.14 g, 60 mmol) in dry THF (50 mL). A solution of *tert*-butyl nitrite (21.03 mL, 175.4 mmol) in dry THF (100 mL) was then added dropwise over 50 min to the chilled reaction mixture at −20 °C. The reaction was stirred an additional 30 min at −20 °C, and then slowly warmed to 5 °C. After reaction at 5 °C for 20 min, *n*-pentane (250 mL) was added to the reaction mixture and a white solid immediately precipitated. The suspension was cooled to 0 °C, stirred for 10 min, and then poured onto a glass filter. The solid was thoroughly washed with ethanol (30 mL) pre-cooled to 0–5 °C, and then dried in vacuum to give 18.50 g (97%) of **11** as a white powder. ^{1}H NMR (CD_3CN, 300 MHz) δ 8.37 (d, $J=9.1$ Hz, 2H), 8.18 (d, $J=9.1$ Hz, 2H).

4.1.12. Propylaminomethylated polystyrene (12). Compound **12** was prepared according to literature procedure.[11] Chloromethyl polystyrene (30 g, 0.83 mmol Cl/g resin) and *n*-propylamine (100 mL, 1.22 mol) afforded 30.48 g (0.67 mmol N/g resin) of **12** as white beads.

4.1.13. Resin-supported iodide (13). Analogous to literature procedure[11] with some modifications. To a chilled (0 °C) suspension of **12** (15.00 g, ca. 10 mmol N) and DMF (200 mL) was added sequentially potassium carbonate (5.53 g, 40 mmol) followed by **11** (6.36 g, 20 mmol) in portions over 30 min. The suspension was slowly stirred at 0 °C for 2 h, and then warmed to room temperature for 1 h. The suspension was transferred onto a glass filter using DMF and washed sequentially with 150 mL of the following solvents: CH_3CN, MeOH, H_2O, MeOH, THF, MeOH, and dried in vacuum to a constant mass to give 16.79 g (0.67 mmol I/g resin, 83%) of **13** as light yellow beads.

4.1.14. Resin-supported silylated alkynes (14). See procedure D. Compound **12** (8.16 g, ca. 4 mmol I), (trimethylsilyl)acetylene (1.14 mL, 8 mmol), bis(dibenzylideneacetone)-palladium(0) (0.1833 g, 0.32 mmol), copper(I) iodide (0.1238 g, 0.64 mmol), triphenylphosphine (0.4196 g, 1.60 mmol), triethylamine (15 mL) and THF (45 mL) for 2 days afforded 8.06 g (0.67 mmol Si/g resin) of **14** as mustard-colored beads. IR (CCl_4, neat) 2156 cm^{-1}.

4.1.15. Resin-supported terminal alkynyl (15). See procedure E. Compound **14** (8.05 g, 4 mmol Si), THF (80 mL) and TBAF (2.52 g, 8 mmol) afforded 7.78 g (0.51 mmol terminal alkynyl/g resin) of **15** as brown beads. IR (CCl_4, neat) 3317, 2107 cm^{-1}.

4.1.16. Resin-supported dimer (16). See procedure D. Compound **15** (16.00 g, 8.22 mmol terminal alkynyl), **1** (5.96 g, 16.44 mmol), bis(dibenzylideneacetone)palladium(0) (0.38 g, 0.66 mmol), copper(I) iodide (0.25 g, 1.32 mmol), triphenylphosphine (0.86 g, 3.29 mmol) and triethylamine (150 mL) for 2 days afforded 17.66 g (0.46 mmol Si/g resin, 86%) of **16** as brown beads. IR (CCl_4, neat) 2156 cm^{-1}.

4.1.17. Resin-supported terminal alkynyl dimer (17). See procedure E. Compound **16** (4.38 g, 2.04 mmol Si), THF (50 mL) and TBAF (1.29 g, 4.08 mmol) afforded 4.24 g (0.48 mmol terminal alkynyl/g resin) of **17** as brown beads. IR (CCl_4, neat) 3313, 2105 cm^{-1}.

4.1.18. Iodide dimer liberated from resin 16 (18). See procedure F. Compound **16** (13.14 g, 6.11 mmol Si) and iodomethane (120 mL) for 20 h afforded 2.17 g (77%) of **18** as a yellow liquid, which was analytically identical to **6**.

4.1.19. Resin-supported tetramer (19). See procedure D. Compound **17** (4.20 g, 2.02 mmol terminal alkynyl), **18** (2.00 g, 4.32 mmol), bis(dibenzylideneacetone)palladium(0) (0.099 g, 0.16 mmol), copper(I) iodide (0.061 g, 0.32 mmol), triphenylphosphine (0.212 g, 0.81 mmol) and triethylamine (50 mL) for 2 days afforded 4.77 g (0.36 mmol Si/g resin, 85%) of **19** as brown beads. IR (CCl_4, neat) 2155 cm^{-1}.

4.1.20. Resin-supported terminal alkynyl tetramer (20). See procedure E. Compound **19** (0.92 g, 0.33 mmol Si), THF (10 mL) and TBAF (0.21 g, 0.66 mmol) afforded 0.90 g (0.37 mmol terminal alkynyl/g resin) of **20** as brown beads. IR (CCl_4, neat) 3311, 2103 cm^{-1}.

4.1.21. Iodide tetramer liberated from resin 19 (21). See procedure F. Compound **19** (3.68 g, 1.32 mmol Si) and iodomethane (40 mL) for 16 h afforded 0.70 g (73%) of **21** as a yellow solid, which was analytically identical to **9**.

4.1.22. Resin-supported octamer (22). See procedure D. Compound **20** (0.86 g, 0.32 mmol terminal alkynyl), **21**

(0.66 g, 0.91 mmol), bis(dibenzylideneacetone)palladium(0) (0.0145 g, 0.025 mmol), copper(I) iodide (0.0096 g, 0.051 mmol), triphenylphosphine (0.0332 g, 0.126 mmol), THF (8 mL) and triethylamine (2 mL) for 3 days afforded 1.00 g (0.24 mmol Si/g resin, 76%) of **22** as brown beads. IR (CCl_4, neat) 2155 cm^{-1}.

4.1.23. Iodide octamer liberated from resin 22 (23). See procedure F. Compound **22** (0.96 g, 0.23 mmol Si) and iodomethane (10 mL) for 12 h afforded 0.19 g (68%) of **23** as a yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, $J=$ 8.4 Hz, 2H), 7.48 (s, 12H), 7.21 (d, $J=8.4$ Hz, 2H), 7.07 (ss, 2H), 7.03 (ss, 2H), 2.74 (br s, 6H), 2.66 (t, $J=7.2$ Hz, 2H), 1.67–1.60 (m, 8H), 1.42–1.35 (m, 8H), 0.97–0.93 (m, 12H), 0.26 (s, 9H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 148.69, 148.11, 137.58, 133.22, 133.00, 132.82, 132.56, 132.19, 132.03, 131.65, 131.36, 131.23, 123.15, 122.99, 122.96, 122.61, 122.55, 122.44, 122.16, 120.43, 120.29, 120.05, 119.15, 118.69, 102.34, 96.80, 96.10, 95.73, 94.88, 94.55, 93.77, 93.24, 93.08, 84.81, 84.71, 84.51, 84.21, 84.08, 82.41, 32.22, 32.11, 32.03, 29.69, 29.35, 29.20, 29.03, 22.25, 22.17, 13.89, 13.80. MALDI-MS (*m/z*): 1250 (M^+), 1220 ($M-C_2H_3$), 1122 ($M-I$). Anal. Calcd for $C_{75}H_{65}IS_4Si$: H, 5.25; C, 72.10. Found: H, 5.39; C, 71.75.

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