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Rapid Solid-Phase Syntheses of Conjugated Homooligomers and [AB] Alternating Block Cooligomers of Precise Length and Constitution

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A new iterative divergent/convergent solid-phase synthesis of precisely defined oligomers is described. The starting monomer is affixed to the solid support so that both ends are free for growth. The polymer-supported *n*-mer bearing α,ω-terminal iodides is divided into two portions. The smaller portion is converted to the polymer-supported ($n + 2$)-mer by coupling an α,ω-dialkyne to the two iodide ends. The larger portion is liberated from the polymer support and then coupled with the polymer-supported portion to form a polymer-supported ($3n + 2$)-mer with new α,ω-terminal iodide end groups. The process is then repeated. The solid-supported material thereby grows in two directions, unlike the common approach of unidirectional growth. This polymer-supported strategy serves as a pseudo high dilution system so that unwanted polymerization does not ensue. Therefore, after each iteration, the oligomer length is more than tripled, making this a rapid growth methodology for precise oligomer syntheses. The methodology is demonstrated by the synthesis of a 17-mer oligo(1,4-phenylene ethynylene) of approximately 120 Å length in seven steps with an overall 20% yield. This solid-supported divergent/convergent tripling protocol is also used for the synthesis of an [AB] alternating block 23-mer containing oligo(1,4-phenylene ethynylene)s and oligo(2,5-thiophene ethynylene)s in an overall 21% yield. The length of the 23-mer is approximately 160 Å.

Introduction

Large conjugated molecules of precise length and constitution have attracted much attention recently.[1] These compounds can serve as models for analogous bulk polymers, and they can also be used for the construction of nanoarchitectures such as molecular wires and molecular scale electronic devices.[1,2] Two main methods exist for the solution-phase synthesis of conjugated oligomers. The stepwise approach features successive addition of monofunctional monomer to the end of a growing chain, while the iterative divergent/convergent approach doubles the molecular length with each iteration.[1,3] These two methods both require chromatographic purification at every growth stage. Conversely, solid-supported chemistry has several advantages for the synthesis of conjugated oligomers.[3,4] (1) The reaction procedures are considerably simplified because time-consuming chromatographic separations are limited; only washing with appropriate solvents is needed in order to purify the polymer-supported substrates. (2) The reactions can be driven to completion using large amounts of reagents which can then be easily recovered by filtration. (3) While solution-phase oligomer syntheses require the functional end groups to be orthogonally (selectively) protected and deprotected before each length-growing reaction, solid-supported chemistry can suppress unwanted reactions by site isolation conditions, thereby minimizing protection/deprotection steps. (4) Solid phase synthesis is amenable to automation and combinatorial chemistry. To demonstrate the efficiency of solid-phase synthesis, we and others previously developed an iterative divergent/convergent method for preparing oligo(phenylene ethynylene)s in which the molecular length was doubled after each coupling reaction step.[3b,d] We report here the details of a new solid-supported method for the preparation of homooligomers and [AB] alternating block oligomers that more than triples the molecular length with each iteration and avoids the masking and unmasking steps normally required for aryl iodides.[3f]

The tripling strategy is outlined in Figure 1. The starting monomer is affixed to the solid support so that

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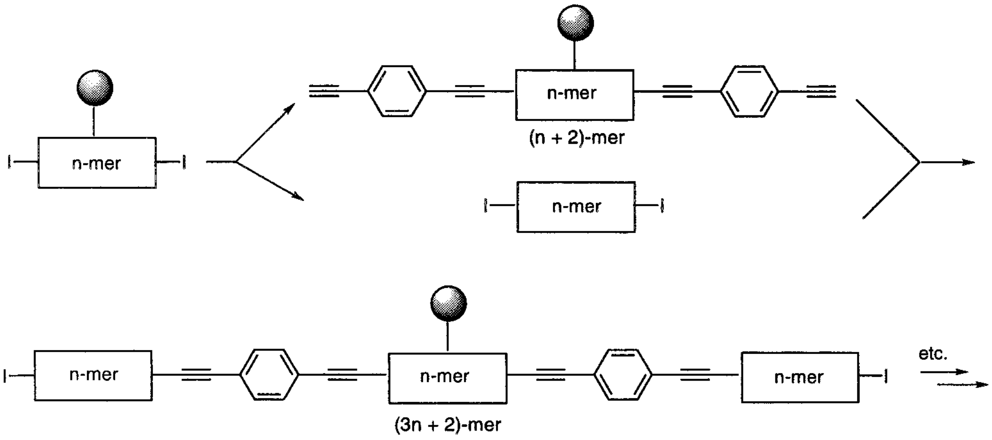


Figure 1. Schematic representation of the iterative divergent/convergent approach with (3n + 2) molecular growth.

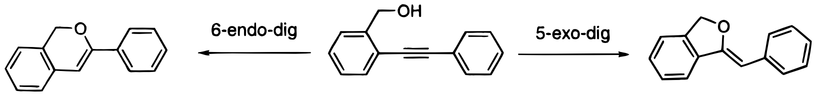
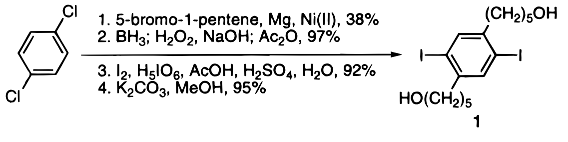


Figure 2. Intramolecular hydroxyl addition to an unactivated carbon−carbon triple bond via 6-endo- or 5-exo-digonal pathways.

both ends are free for growth. The polymer supported n-mer bearing α,ω-bis-terminal iodides is divided into two portions. The smaller portion is converted to polymer-supported (n + 2)-mer with 1,4-diethynylbenzene addition at the two iodide ends. The larger portion is liberated from the polymer support and then coupled with the polymer-supported portion to form a polymer-supported (3n + 2)-mer with new α,ω-bis-terminal iodide end groups. A functionalized insoluble polymer can provide an environment of "high dilution" thereby retarding polymerization that would be obtained by a solution-phase process. Since the end groups in this polymer-supported (3n + 2)-mer are the same as the polymer-supported n-mer, the procedure can be repeated. The solid supported material grows in two directions, unlike the common approach of unidirectional growth. Each iteration extends the chain by three times the original length plus the length of two linker molecules.

Results and Discussion

Monomer Synthesis. The syntheses of the three monomers were performed as shown in eqs 1−3. Nickel-catalyzed cross-coupling of 4-pentenylmagnesium bromide with 1,4-dichlorobenzene yielded 1,4-di(4′-pentenyl)-benzene.[5,6] Hydroboration and oxidation afforded the diol that was subsequently protected as the diacetate. Electrophilic iodination[7] and deprotection yielded the desired 1,4-diiodo-2,5-di(5′-hydroxypentyl)benzene (**1**) (eq 1). The long hydroxyalkyl moieties provide good solubility for the longer oligomers. Additionally, shorter alkyl spacers can result in intramolecular addition of the hydroxyl group to the alkyne unit that is subsequently attached at the iodide-bearing positions (Figure 2).[8] Monosilylation of 1,4-diethynylbenzene[9] afforded 1-ethynyl-4-(trimethylsilylethynyl)benzene (**2**) (eq 2). The separation of monosilylated product, **2**, from the disilylated side product was difficult; however, this impurity had no effect on the coupling reaction and was carried with **2** to the next step. Finally, 2,5-didodecyl-1,4-diiodobenzene (**3**) was generated by dilithiation of 1,4-diiodobenzene, a displacement reaction with dodecyl bromide, and finally iodination (eq 3).[7]



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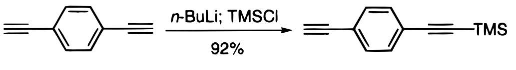

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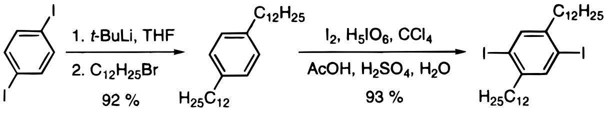

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(3)

Homooligomer Synthesis. The new solid-phase iterative divergent/convergent synthetic approach is outlined in Scheme 1. 2-(Hydroxymethyl)-3,4-dihydro-2H-pyran was converted to its sodium salt and then treated with Merrifield's resin (1.0 mequiv of Cl/g, 2% DVB cross-linked, 200−400 mesh, Aldrich) in dimethylacetamide at room temperature to afford the dihydropyran-modified resin **4**.[10] Compound **1** was then attached to **4** through the hydroxy group in the presence of acid to afford **5**.[10] The loading level of **1** in **5** was determined by cleaving the alcohol from the resin employing PPTS in 1:1 n-butanol/1,2-dichloroethane at 80 °C.[10] Compound **5** (0.48 mequiv of **1**/g) was subjected to a Pd/Cu-catalyzed cross-coupling[11] with monomer **2** to afford the polymer-supported trimer **6** that was deprotected with tetra-n-

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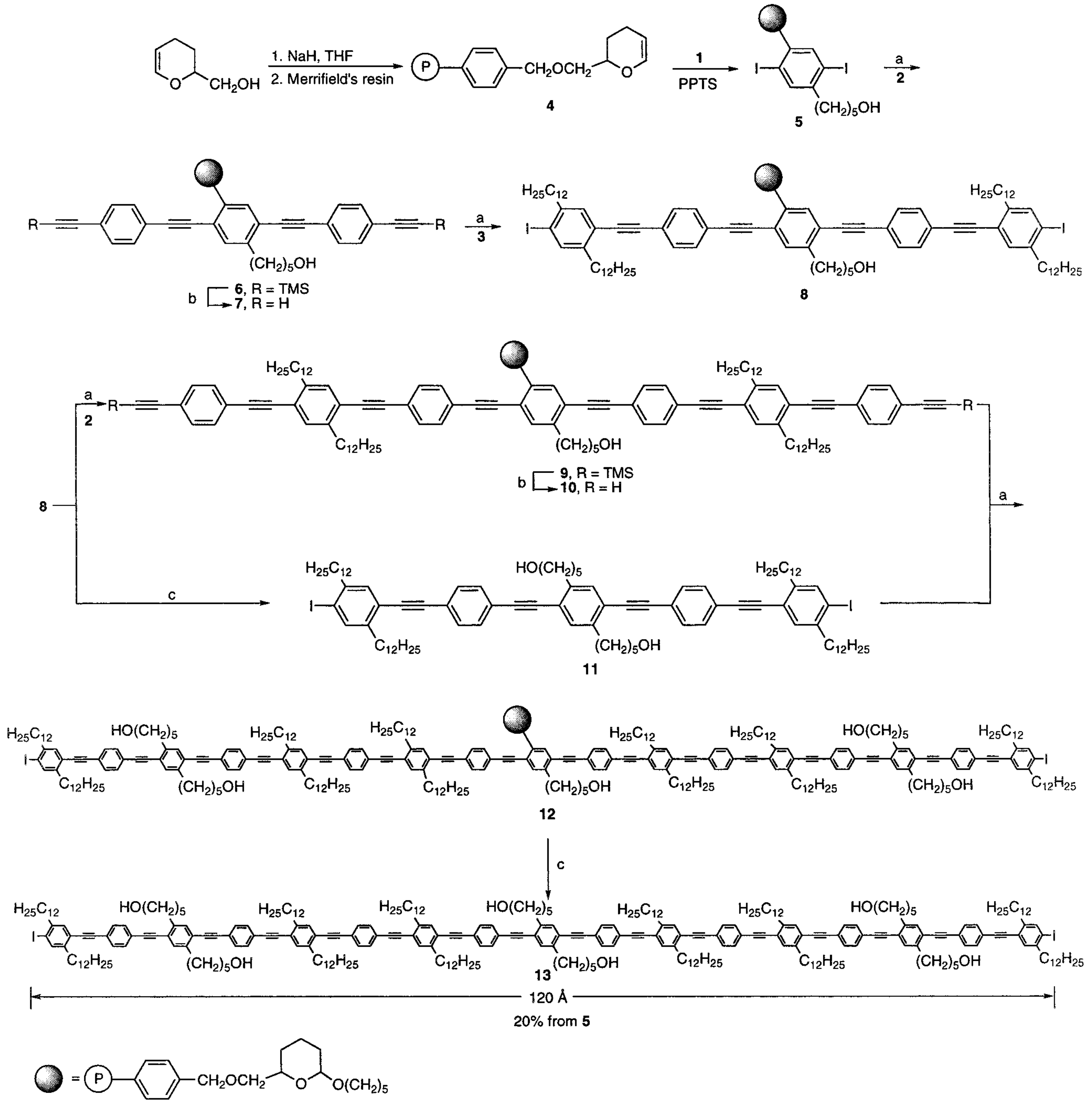
Scheme 1



Reagents: a. Pd(dba)$_2$, PPh$_3$, and CuI (5 mol %, 10 mol %, and 5 mol %, respectively, per iodide atom), Et$_2$NH/THF (1:4). b. TBAF, THF. c. PPTS, *n*-C$_4$H$_9$OH, ClCH$_2$CH$_2$Cl

butylammonium fluoride (TBAF) to produce polymer-supported trimer **7**. Attempts to generate **7** directly from **5** and 1,4-diethynylbenzene failed, possibly due to rapid trace-oxygen-catalyzed homocoupling of 1,4-diethynylbenzene. Compound **7** was then cross-coupled with **3** (5–6 mol of **3** per mol of **7**) to afford polymer-supported pentamer **8**. Excess **3** was easily recovered by filtration. One portion of **8** was coupled with **2** to produce the polymer-supported heptamer **9** that was desilylated to afford polymer-supported heptamer **10**. Another portion of polymer-supported pentamer **8** was treated with acid to liberate pentamer **11**. Treatment of **10** with the liberated pentamer **11** (6–8 mol of **11** per mol of **10**) under Pd/Cu cross-coupling conditions (23 °C for 24 h, and then 60–70 °C for 24 h) afforded the polymer-supported 17-mer **12**. Directly heating the mixture of **10** and **11** caused a much lower yield, possibly due to decomposition of the polymer-supported α,ω-diyne **10**. Recovery of excess **11** was achieved simply by filtration from the beads followed by passage through silica gel. Finally, treatment of **12** with acid liberated the 120 Å long 17-mer **13**.[10] The overall yield was 20% for the seven-step sequence from **5**.

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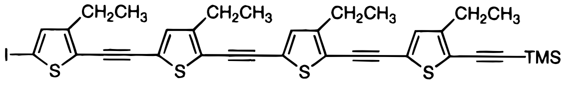
[AB] Alternating Block Cooligomer Synthesis. Block copolymers are fascinating materials exhibiting interesting phase behaviors. They can self-assemble into nanometer-scale multiphase domain structures as a consequence of the compatibility restraints on the blocks.[12−14] On the basis of our experience with conjugated oligomers,[1] we decided to use the aforementioned solid-support methodology to prepare conjugated block oligomers containing oligo(1,4-phenylene ethynylene)s and oligo(2,5-thiophene ethynylene)s. Oligo(2,5-thiophene ethynylene) **14** was synthesized as we described previously.[3g,h] The two-directional solid-phase synthesis of block oligomers is outlined in Scheme 2. Compound **8** was coupled with (trimethylsilyl)acetylene to generate the polymer-supported bis-terminal silyl pentamer **15**.[11] Desilylation of **15** and cross-coupling with the thiophene-containing tetramer **14** afforded the polymer-supported triblock 13-mer **17**. Desilylation of **17** and coupling with the pentamer **11** gave the polymer-supported alternating [AB] pentablock 23-mer **19**. Treatment of **19** with acid generated the desired block 23-mer **20**.[10] The yield was 21% over a total of nine reactions steps from **5** to afford the 160 Å long system.



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Spectroscopic Reaction Monitoring Techniques on the Resin. Completion of each polymer-supported reaction step was determined by FTIR analysis of the polymer bound substrate.[3b,d,15] Polymer-supported material was mixed with oven-dried KBr and ground to a powder, and an FTIR spectrum was acquired from the formed pellet. Absorptions at 3290 cm^{-1} (strong) and 2110 cm^{-1} (weak) are characteristic of the terminal alkynyl carbon−hydrogen and carbon−carbon stretches, respectively, and a strong absorption at 2150 cm^{-1} is characteristic of the carbon−carbon stretch of the trimethylsilyl-terminated alkyne. As expected, we observed that the coupling reaction of a polymer-supported aryl diiodide with **2** was accompanied by the appearance of the 2150 cm^{-1} absorption. The trimethylsilyl removal step was confirmed by the appearance of the 3290 cm^{-1} band and the diminution of the 2150 cm^{-1} band. The coupling reaction of polymer-supported α,ω-dialkynes with aryl diiodides was accompanied by the disappearance of the 3290 cm^{-1} band.[3b,d,15]

Characterization of the Oligomers. While the pentamer **11** afforded a molecular ion peak by direct exposure via electron impact mass spectrometry (MS), neither this method nor FAB or electrospray MS sufficed to obtain a molecular ion of the 17-mer **13** or the 23-mer **20**. For these latter compounds, it was necessary to use matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) using α-cyano-4-hydroxycinnamic acid matrix in positive ion mode. MALDI-MS of **13** afforded a peak that was 254 amu lower than the actual molecular weight of **13**, corresponding to the molecular ion minus the two iodides. MALDI-MS of **20** did afford the desired M + 1 peak.

Size exclusion chromatography (SEC) was conducted after benchtop chromatography on the obtained oligomers.[1,3] SEC is not a direct measure of molecular weight but a measure of the hydrodynamic volume. Thus, the number average molecular weight (M_n) values of rigid rod oligomers should be significantly inflated relative to the randomly coiled polystyrene standards. As expected, the M_n values of the pentamer **11** (M_n = 2200, PDI = 1.18, actual molecular weight = 1576), 17-mer **13** (M_n = 8000, PDI = 1.06, actual molecular weight = 4468) and 23-mer **20** (M_n = 12000, PDI = 1.03, actual molecular weight = 5342) were much greater than the actual molecular weights. Additionally, SEC on a crude reaction mixture was used to determine whether polymerization or oligomerization could ensue using this synthetic protocol. The heptamer on **9** was cleaved from the polymer support, and the crude material was analyzed. As expected, the site isolation inhibited polymerization. However, in addition to the expected heptamer derived from **9** (M_n = 2700, PDI = 1.01), there was an equal area broadened peak at slightly higher molecular weight which likely arose from undesired oligomer formation. This could have arisen from several intersite interactions along the synthetic sequence, for example, coupling of **7** with **8** followed by capping with **2**. Therefore, although this technique inhibits polymer formation, the conformational flexibility of Merrifield resin does not allow the functionalized sites to be exclusively isolated from each other. We may be able to overcome this problem in the future using a lower degree of loading and a more rigid matrix through higher DVB cross-link levels.[4e] Additionally, although the final yields of the 17-mer **13** and 23-mer **20** were relatively high for the size of the oligomers formed, using a more suitable polymer support would likely provide higher yields and higher purities of the final products by permitting definitive site isolation.

Optical absorption (Figure 3) and emission (Figure 4) spectra of the oligomers were recorded. As expected, we observed an increase in the absorption maxima from shorter wavelength (365 nm) for the pentamer **11** to longer wavelength (385 nm) for the 17-mer **13**. These absorptions corresponded very closely to our oligo(1,4-phenylene ethynylene)s prepared previously.[3d] The absorption maximum for the block 23-mer **20** was 390 nm with a shoulder at 445 nm and a longer tail extending to 500 nm. The shoulder at 445 nm is characteristic of the tetra(1,4-thiophene ethynylene) absorption tails.[3g,11d] Oligo(1,4-phenylene ethynylene)s **11** and **13** had an emission maximum at 425 and 415 nm, respectively, thereby indicating a larger Stokes shift for the pentamer. Oligo(2,5-thiophene ethynylene)s exhibit emission maximum at 495 nm. As expected, the emission spectrum of the block 23-mer **20** consisted of both oligo(phenylene ethynylene) and oligo(thiophene ethynylene) characteristics. All excitations were at the maxima for λ_{abs}.

Conclusion

A highly efficient synthetic approach to precisely sized conjugated homooligomers and block cooligomers has been developed. Since molecular growth is bidirectional,

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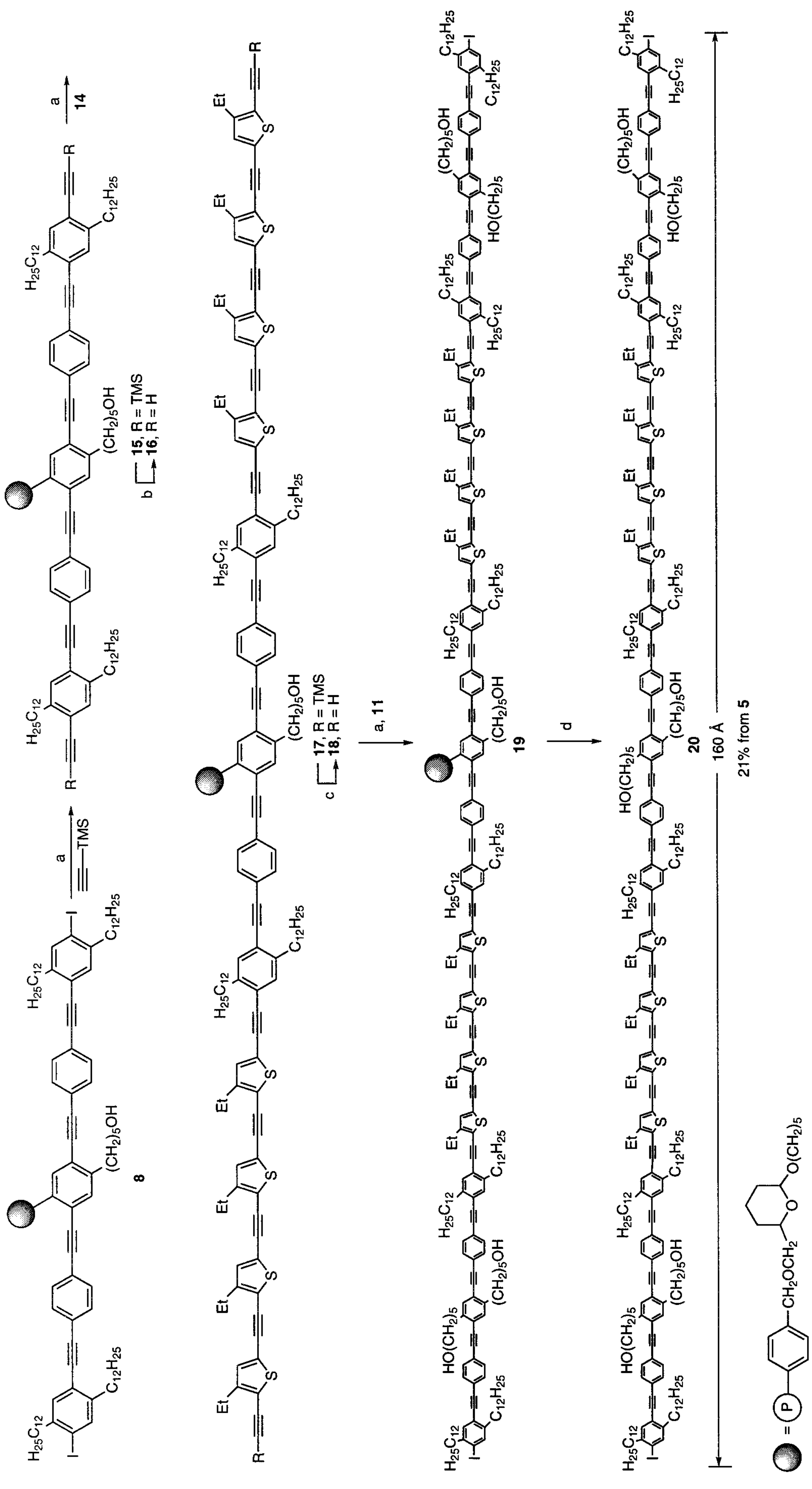
[15] (a)Yan, B.; Kumaravel, G.; Anjaria, H.; Wu, A.; Petter, R. C.; Jewell, C. F., Jr.; Wareing, J. R. *J. Org. Chem.* **1995**, *60*, 5736. (b) Grindley, T. B.; Johnson, D. F.; Katritzky, A. R.; Keogh, H. J.; Thirkettle, C.; Topsom, R. D. *J. Chem. Soc., Perkin Trans. 2* **1974**, *3*, 282.

Scheme 2



Reagents: a. Pd(dba)$_2$, PPh$_3$, and CuI (5 mol %, 10 mol %, and 5 mol %, respectively, per iodide atom), Et$_2$NH/THF (1:4). b. TBAF, THF. c. K$_2$CO$_3$, CH$_3$OH, CH$_2$Cl$_2$. d. PPTS, *n*-C$_4$H$_9$OH, ClCH$_2$CH$_2$Cl.

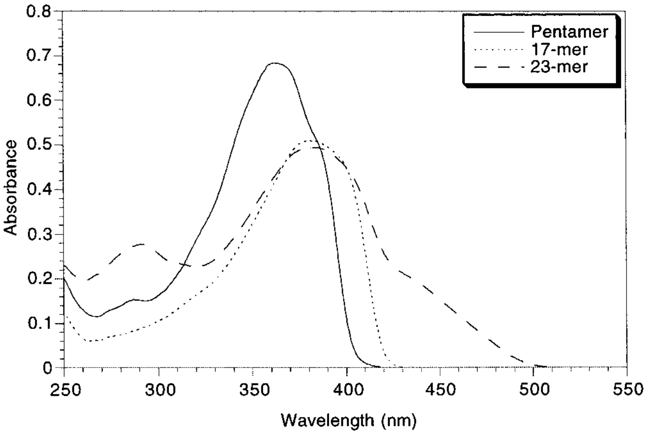


Figure 3. The UV/vis spectra (CH_2Cl_2) of pentamer **11**, 17-mer **13**, and 23-mer **20**.

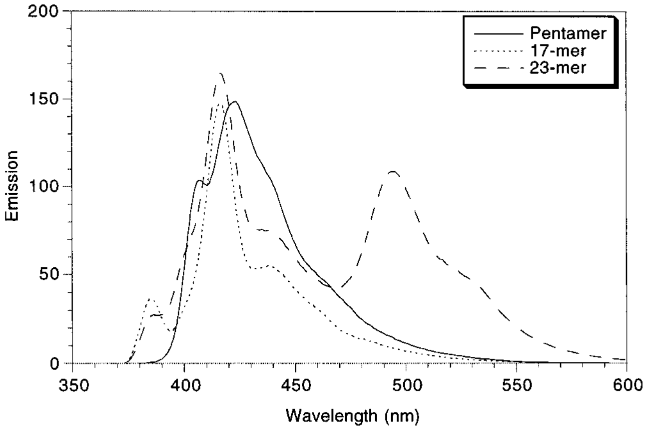


Figure 4. The emission spectra (CH_2Cl_2) of pentamer **11**, 17-mer **13**, and 23-mer **20**.

the molecular length triples at each iteration. A 17-membered homooligomer **13** and alternating block 23-membered cooligomer **20** were prepared whose molecular weights are in the range of many conjugated polymers.[16] Using this solid-phase methodology, undesired polymerizations are not encountered through the pseudo high dilution conditions. Additionally, with the approach described here, masking and unmasking of the aryl iodides were unnecessary. This solid-phase divergent/convergent tripling protocol should find widespread use in the synthesis of many precisely defined homo- and block-oligomers.

Experimental Section

General. All nonaqueous operations were carried out under a dry, oxygen-free, nitrogen atmosphere. Molecular weight analyses (SEC) were performed using two 30 × 75 cm GPC columns (10^5 Å 10 μm and 500 Å 5 μm) eluted with THF at 60 °C (flow rate 1.0 mL/min). SEC results were based on six polystyrene standards (M_w = 135 500, 96 000, 52 000, 22 000, 5050, and 510 with a correlation coefficient > 0.9998) purchased from Polymer Laboratories Ltd. Unless otherwise noted, all starting materials were obtained from commercial suppliers and used without further purification. Merrifield's resin was purchased from Aldrich Chemical Co. (1.0 mequiv of Cl/g, 2% DVB cross-linked, 200−400 mesh). Alkyllithium reagents were obtained from FMC. (Trimethylsilyl)acetylene was obtained from FAR Research Inc. Reagent grade diethyl ether and tetrahydrofuran (THF) were distilled under nitrogen from sodium benzophenone ketyl. Reagent grade dichloromethane, diethylamine, and diisopropylamine were distilled under nitrogen from CaH_2. Bulk grade hexane was distilled prior to use. Gravity column chromatography and flash chromatography were carried out on silica gel (230−400 mesh from EM Science). Pd/Cu-catalyzed Pd/Cu-catalyzed couplings of aryl halides with terminal alkynes were conducted according to reported procedures.[11] Oligomer purities were assessed by their polydispersity indexes (M_w/M_n). If a compound has previously been reported, a reference to that compound is shown directly after the compound number in the title of the synthetic procedure. The FTIR spectra of the polymer-supported compounds often showed significant overtone bands at ca. 1945, 1870, and 1800 cm^{-1}, and these have been recorded.

1,4-Di(4′-pentenyl)benzene.[6] A 500 mL three-necked flask was equipped with a mechanical stirrer and a reflux condenser. The flask was charged with magnesium turnings (24.31 g, 1.00 mol) and ether (200 mL). Approximately 5 mL of a solution of 5-bromo-1-pentene[5] (74.52 g, 500.00 mmol) in 100 mL of diethyl ether was added. The mixture was stirred at room temperature, and within a few minutes, an exothermic reaction occurred. The flask was immersed in an ice bath, and the remaining ether solution was added dropwise over 1 h. After addition was complete, the mixture was heated to reflux for 30 min and then cooled to room temperature. Another 500 mL three-necked flask was equipped with a mechanical stirrer and a reflux condenser. The second flask was charged with dichloro[1,3-bis(diphenylphosphino)propane]nickel(II) (2.71 g, 5.00 mmol), 1,4-dichlorobenzene (14.70 g, 100.00 mmol), and diethyl ether (150 mL), and the mixture was cooled in an ice bath. The Grignard reagent prepared above was transferred via cannula to the mixture. After addition, the mixture was warmed to room temperature and stirred for 2 h and then heated to reflux overnight. After cooling in an ice bath, the mixture was slowly hydrolyzed with 250 mL of 2 N aqueous hydrochloric acid. The organic layer was separated, and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried over $MgSO_4$. The solvent was removed in vacuo, and the residue was purified by flash chromatography (silica gel, hexane) to afford 8.13 g (38%) of the desired compound as a colorless liquid. FTIR (neat) 3077, 3006, 2977, 2930, 2856, 1897, 1826, 1641, 1514, 1492, 1441, 1416, 1348, 1208, 1093, 1016, 991, 911, 832, 760 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (s, 4 H), 5.81 (m, 2 H), 5.04 (dd, J = 17.5, 1.7 Hz, 2 H), 4.98 (dd, J = 17.5, 1.5 Hz, 2 H), 2.58 (t, J = 7.6 Hz, 4 H), 2.09 (q, J = 6.9 Hz, 4 H), 1.72 (p, J = 7.5 Hz, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.78, 138.72, 128.40, 114.70, 34.98, 33.40, 30.75. HRMS calcd for $C_{16}H_{22}$: 214.1721. Found: 214.1732.

1,4-Di(5′-hydroxypentyl)benzene. To a nitrogen-purged flask was added 1,4-di(4′-pentenyl)benzene (8.5 g, 39.7 mmol) and THF (100 mL). Borane−tetrahydrofuran complex solution in tetrahydrofuran (158.8 mL, 158.8 mmol, 1.0 M) was added dropwise. The mixture was heated to 50 °C for 3 h. After cooling to 0 °C, ethanol (22 mL, 477 mmol) was slowly added, and then 2 N aqueous NaOH (39.7 mL, 79.4 mmol) and 30% H_2O_2 (45 mL, 397 mmol) were added sequentially. The mixture was stirred at room-temperature overnight and then poured into water and extracted with ethyl acetate. The combined organic layers were dried over anhydrous $MgSO_4$. The solvent was removed in vacuo to afford 9.7 g (97%) of the desired product as a colorless liquid. FTIR (neat) 3332, 3008, 2925, 1898, 1790, 1660, 1644, 1514, 1462, 1372, 1116, 1048, 960, 808 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (s, 4 H), 3.57 (t, J = 6.5 Hz, 4 H), 2.81 (br s, 2 H), 2.58 (t, J = 7.6 Hz, 4 H), 1.60 (m, 8 H), 1.38 (m, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.86, 128.32, 62.61, 35.54, 32.60, 31.40, 25.52. HRMS calcd for $C_{16}H_{26}O_2$: 250.1933. Found: 250.1922.

1,4-Di(5′-acetoxypentyl)benzene. To a nitrogen-purged flask were added 1,4-di(5′-hydroxylpentyl)benzene (10.3 g, 41.2 mmol), pyridine (200 mL), and acetic anhydride (39 mL, 412 mmol). The mixture was stirred at room-temperature over-

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[16] (a) Heitz, W. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1991**, *32*(1), 327. (b) Solomin, V. A.; Heitz, W. *Macromol. Chem. Phys.* **1994**, *195*, 303.

night. The solvent was removed in vacuo to afford 13.8 g (100%) of the desired product as a colorless liquid. FTIR (neat) 3644, 3458, 3048, 3007, 2934, 2858, 1901, 1732, 1514, 1463, 1386, 1366, 1236, 1118, 1044, 958, 896, 823, 730, 634, 606 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.05 (s, 4 H), 4.02 (t, $J =$ 6.8 Hz, 4 H), 2.56 (t, $J = 7.5$ Hz, 4 H), 2.00 (s, 6 H), 1.60 (m, 8 H), 1.38 (m, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.16, 139.69, 128.29, 64.48, 35.35, 31.12, 28.47, 25.57, 20.97. HRMS calcd for $C_{20}H_{30}O_4$: 334.2144. Found: 334.2142.

2,5-Di(acetoxypentyl)-1,4-diiodobenzene.[7] To a nitrogen-purged flask were added acetic acid (50 mL), water (10 mL), sulfuric acid (1.5 mL), iodine (1.1 g, 4.4 mmol), periodic acid (0.5 g, 2.2 mmol), and 1,4-di(5′-acetoxypentyl)benzene (1.5 g, 4.4 mmol). The mixture was heated to 80 °C for 3 h. The solvent was then removed in vacuo. The residue was dissolved in ethyl acetate and washed with water, 1 N aqueous K_2CO_3, and 1 N aqueous $Na_2S_2O_3$. After drying with anhydrous $MgSO_4$, the solvent was removed in vacuo, and the residue was purified by flash chromatography (silica gel, CH_2Cl_2) to afford 2.4 g (92%) of the desired product as a white solid. Mp $=$ 84−86 °C. FTIR (KBr) 2937, 2856, 1744, 1461, 1385, 1240, 1042, 956, 881 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.55 (s, 2 H), 4.03 (t, $J = 6.7$ Hz, 4 H), 2.57 (t, $J = 7.4$ Hz, 4 H), 2.01 (s, 6 H), 1.64 (p, $J = 7.6$ Hz, 4 H), 1.54 (m, 4 H), 1.39 (m, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.16, 144.52, 139.36, 100.32, 64.39, 39.63, 29.79, 28.39, 25.61, 21.07. HRMS calcd for $C_{20}H_{28}O_4I_2$: 586.0077. Found: 586.0072.

2,5-Di(5′-hydroxypentyl)-1,4-diiodobenzene (1). 1,4-Diiodo-2,5-di(5′-acetoxypentyl)benzene (1.5 g, 2.6 mmol) was dissolved in dichloromethane (2 mL). Methanol (50 mL) and potassium carbonate (3.6 g, 26.0 mmol) were added to the solution. The mixture was stirred at room-temperature overnight. The solvent was then removed in vacuo. The solid was transferred into a fritted glass funnel and then washed with water to afford 1.28 g (95%) the desired product as a white solid. Mp $=$ 100−103 °C. FTIR (KBr) 3185, 2924, 2853, 1457, 1384, 1351, 1260, 1233, 1187, 1127, 1073, 1036, 990, 877, 787, 725, 686 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.23 (s, 2 H), 3.65 (t, $J = 6.3$ Hz, 4 H), 2.60 (t, $J = 7.6$ Hz, 4 H), 1.58 (m, 8 H), 1.45 (m, 4 H), 1.23 (br s, 2 H). ^{13}C NMR (75 MHz, CH_3OD) δ 145.15, 139.72, 100.00, 61.97, 39.80, 32.48, 30.37, 25.69. HRMS calcd for $C_{16}H_{24}O_2I_2$: 501.9866. Found: 501.9866.

1-Ethynyl-4-(trimethylsilylethynyl)benzene (2). To a flame-dried and nitrogen-purged flask were added THF (200 mL) and 1,4-diethynylbenzene[9] (2.0 g, 15.9 mmol). The mixture was cooled to −78 °C, and *n*-BuLi (10.2 mL, 1.56 M in hexane) was added via syringe pump over 1 h. After stirring at −78 °C for 2 h, trimethylsilyl chloride (3.0 mL, 23.9 mmol) was added. The mixture was warmed to room temperature and then stirred at room-temperature overnight. After concentration in vacuo, the residue was poured into water and extracted with ether. The combined organic layers were dried over anhydrous $MgSO_4$. The solvent was removed in vacuo. The residue was left on the vacuum pump (0.5 mmHg) for 12 h to remove the unreacted 1,4-diethynylbenzene. The desired product (3.14 g, 92%) was obtained which contained ∼5% of the disilylated side product which did not participate in or adversely affect the next reaction step. Mp $=$ 41−43 °C. FTIR (KBr) 3295, 2960, 2899, 2159, 1495, 1403, 1251, 1222, 1103, 1018, 839, 760, 732, 700, 628 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.40 (s, 4 H), 3.15 (s, 1 H), 0.24 (s, 9 H). ^{13}C NMR ($CDCl_3$) δ 131.76, 131.67, 123.46, 121.99, 104.28, 96.39, 83.17, 78.93, 0.08. HRMS calcd for $C_{13}H_{14}Si$: 198.0865. Found: 198.0863.

1,4-Didodecylbenzene. To a flame-dried and nitrogen-purged flask were added 1,4-diiodobenzene (10.0 g, 30.3 mmol) and THF (150 mL). The mixture was cooled to −78 °C, and *t*-BuLi (75.8 mL, 1.60 M in pentane) was added dropwise. After stirring at −78 °C for 1 h, 1-bromododecane (10.3 mL, 60.6 mmol) was added dropwise. The mixture was kept at −78 °C for 1 h and then warmed to room temperature and stirred at room temperature for 24 h. The mixture was poured into water and extracted with hexane (3×). The combined organic layers were dried over anhydrous $MgSO_4$. The solvent was removed in vacuo. The residue was recrystallized from ethanol to afford 11.5 g (92%) of the desired product as a white solid. Mp $=$ 37−39 °C. FTIR (KBr) 2918, 2850, 1897, 1656, 1516, 1467, 1384, 1121, 1020, 887, 823, 764, 721 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.07 (s, 4 H), 2.55 (t, $J = 7.1$ Hz, 4 H), 1.58 (br s, 4 H), 1.24 (br s, 36 H), 0.87 (t, $J = 5.8$ Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.09, 128.22, 35.59, 31.94, 31.61, 29.69, 29.66, 29.62, 29.55, 29.42, 29.37, 22.71, 14.13. HRMS calcd for $C_{30}H_{54}$: 414.4216. Found: 414.4226.

2,5-Didodecyl-1,4-diiodobenzene (3).[7] To a nitrogen-purged flask were added water (10 mL), acetic acid (100 mL), sulfuric acid (3 mL), carbon tetrachloride (20 mL), iodine (4.5 g, 17.6 mmol), periodic acid (2.0 g, 8.8 mmol), and 1,4-di(dodecyl)benzene (7.3 g, 17.6 mmol). The mixture was heated to reflux overnight and then poured into water and extracted with hexane. The combined organic layers were washed with 1 N aqueous Na_2CO_3 and 1 N aqueous $Na_2S_2O_3$ and then dried over $MgSO_4$. The solvent was removed in vacuo. The residue was washed with ethanol to afford 10.9 g (93%) of the desired product as a white solid that was used without purification. Mp $=$ 65−66 °C. FTIR (KBr) 2919, 2848, 1463, 1418, 1378, 1327, 1244, 1194, 1121, 1038, 939, 870, 777, 721 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.58 (s, 2 H), 2.58 (t, $J = 7.6$ Hz, 4 H), 1.53 (br s, 4 H), 1.26 (br s, 36 H), 0.88 (t, $J = 6.3$ Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.85, 139.31, 100.37, 39.87, 31.96, 30.22, 29.72, 29.69, 29.60, 29.44, 29.39, 29.35, 22.73, 14.17. HRMS calcd for $C_{30}H_{52}I_2$: 666.2151. Found: 666.2159.

Dihydropyran-Modified Resin 4.[10] To a nitrogen-purged flask were added THF (100 mL), 2-(hydroxymethyl)-3,4-dihydro-2*H*-pyran (6.84 g, 60.00 mmol), and 95% NaH (1.67 g, 66.10 mmol). The mixture was stirred at room temperature for 2 h and then concentrated. To the residue were added dimethylacetamide (300 mL) and Merrifield's resin (20 g). The mixture was stirred at room temperature for 16 h. The polymer was then poured onto a preweighed fritted funnel using dichloromethane to wash the beads that were adhering to the sides of the flask. The beads were then washed sequentially with CH_2Cl_2 (1×), 1:1 DMF/H_2O (4×), DMF (3×), and CH_2Cl_2 (3×) and dried in a vacuum oven at 60 °C 12 h to afford 22.0 g of the dihydropyran functionalized resin. FTIR (KBr) 3025, 2920, 1601, 1492, 1450, 1384, 1069, 1027, 905, 756, 690 cm^{-1}.

Polymer-Supported Aryl Diiodide 5.[10] Resin **4** (16.17 g, 15.00 mmol of the DHP moiety) was suspended in 1,2-dichloroethane (350 mL). The aryl diiodide **1** (22.59 g, 45.00 mmol) and PPTS (7.53 g, 30.00 mmol) were added. The mixture was stirred at 80 °C for 2 d. The polymer was then poured onto a preweighed fritted funnel using dichloromethane to wash the beads that were adhering to the sides of the flask. The beads were then washed sequentially with CH_2Cl_2 (1×), 1:1 DMF/H_2O (4×), DMF (3×), and CH_2Cl_2 (3×) and dried in a vacuum oven at 60 °C overnight to afford 21.35 g of the desired product. The loading level was 0.48 mequiv of **1** per gram of polymer as determined by PPTS-induced cleavage (vide infra) and recovery of **1**. FTIR (KBr) 3448, 3025, 2924, 2854, 1600, 1493, 1451, 1384, 1251, 1073, 837, 757, 699 cm^{-1}.

General Procedure for the Coupling of a Polymer-Supported Aryl Diiodide with an Alkyne (Procedure A).[11] A heavy-walled, oven-dried flask was charged with the polymer-supported aryl diiodide, the alkyne, bis(dibenzylideneacetone)palladium(0) (10 mol % based on the diiodide), copper(I) iodide (10 mol % based on the diiodide), triphenylphosphine (20 mol % based on the diiodide), and diethylamine/THF (1:4) (10 mL/g of polymer). The flask was flushed with nitrogen and kept at 70 °C for 24 h with stirring. The polymer was then poured onto a preweighed fritted funnel using dichloromethane to wash the beads that were adhering 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, DMF, CH_2Cl_2, MeOH, and dried to constant mass in a vacuum oven at 60 °C.

Polymer-Supported Bis(terminal silyl) Trimer 6. See procedure A. **5** (10.0 g), **2** (2.19 g, 11.04 mmol), bis(dibenzylideneacetone)palladium(0) (0.26 g, 0.46 mmol), copper(I) iodide (0.087 g, 0.46 mmol), triphenylphosphine (0.24 g, 0.92 mmol), diethylamine (20 mL), and THF (80 mL) afforded 10.5 g of the title polymer as yellow beads. FTIR (KBr) 3454, 3059, 3026, 2923, 2854, 2154, 1944, 1873, 1802, 1657, 1600, 1493, 1448, 1384, 1251, 1114, 1029, 840, 755, 696 cm^{-1}.

General Procedure for the Desilylation of a Polymer-Supported Silylated Alkyne (Procedure B). To a suspension of polymer-supported arylbis(trimethylsilyl)alkyne and THF (10 mL/g of polymer) in a heavy-walled, oven-dried flask was added a solution of TBAF (1.0 M in THF). The suspension was swirled periodically for 30 min. The polymer was then transferred to a preweighed fritted funnel using THF, washed sequentially (ca. 30 mL/g polymer) with THF, MeOH, CH_2Cl_2, and MeOH, and dried to constant mass in a vacuum oven at 60 °C.

Polymer-Supported Bis(terminal alkynyl) Trimer 7. See procedure B. **6** (10.5 g), THF (100 mL), and TBAF (18.4 mL, 18.4 mmol, 1.0 M in THF) afforded 10.3 g of the title polymer as yellow beads. FTIR (KBr) 3451, 3287, 3059, 3025, 2922, 2854, 1944, 1802, 1656, 1600, 1492, 1449, 1383, 1071, 1029, 901, 837, 756, 697 cm^{-1}.

General Procedure for the Coupling of a Polymer-Supported Bis(terminal alkyne) with an Aryl Diiodide (Procedure C).[11] A thick-walled, oven-dried flask was charged with the polymer-supported bis-terminal alkyne, the aryl diiodide, bis(dibenzylideneacetone)palladium(0) (10 mol % per diiodide), copper(I) iodide (10 mol % per diiodide), triphenylphosphine (20 mol % per diiodide), and diethylamine/THF (1:4) (10 mL/g of polymer). The flask was flushed with nitrogen and kept at room temperature for 24 h with stirring and then heated to 60 °C for 24 h. The polymer was then poured onto a preweighed fritted funnel 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, DMF, CH_2Cl_2, MeOH, and dried to constant mass in a vacuum oven at 60 °C.

Polymer-Supported Bis(terminal iodo) Pentamer 8. See procedure C. **7** (10.3 g), **3** (7.36 g, 11.04 mmol), bis(dibenzylideneacetone)palladium(0) (0.26 g, 0.46 mmol), copper(I) iodide (0.087 g, 0.46 mmol), triphenylphosphine (0.24 g, 0.92 mmol), diethylamine (20 mL), and THF (80 mL) afforded 13.9 g of the title polymer as yellow beads. FTIR (KBr) 3450, 3058, 3024, 2920, 2853, 2341, 2206, 1944, 1802, 1656, 1599, 1490, 1448, 1384, 1264, 1068, 1028, 899, 833, 754, 696 cm^{-1}.

Polymer-Supported Bis(terminal silyl) Heptamer 9. See procedure A. **8** (1.00 g), **2** (0.16 g, 0.79 mmol), bis(dibenzylideneacetone)palladium(0) (18.98 mg, 0.033 mmol), copper(I) iodide (6.27 mg, 0.033 mmol), triphenylphosphine (17.29 mg, 0.066 mmol), diethylamine (2 mL), and THF (8 mL) afforded 1.03 g of the title polymer as yellow beads. FTIR (KBr) 3425, 3058, 3025, 2922, 2853, 2154, 1655, 1600, 1543, 1515, 1492, 1450, 1384, 1250, 1106, 1031, 838, 757, 698 cm^{-1}.

Polymer-Supported Bis(terminal alkynyl) Heptamer 10. See procedure B. **9** (1.03 g), THF (10 mL), and TBAF (1.32 mL, 1.32 mmol, 1.0 M in THF) afforded 0.98 g of the title polymer as yellow beads. FTIR (KBr) 3468, 3289, 3025, 2918, 2206, 1943, 1800, 1656, 1599, 1491, 1446, 1382, 1265, 1068, 1026, 898, 833, 751, 693, 537, 440, 407 cm^{-1}.

General Procedure for the Liberation of Polymer-Supported Oligomers (Procedure D). A heavy-walled, oven-dried flask was charged with a suspension of the polymer-supported oligomer and 1:1 *n*-butanol/1,2-dichloroethane. PPTS was added. The flask was flushed with nitrogen and heated to 80 °C for 16 h. The reaction mixture was cooled and passed through a fritted funnel. The resin was washed with dichloromethane to remove any residual product trapped in the polymer matrix. The combined filtrate was washed with water and then concentrated in vacuo. The residue was purified by flash chromatography (silica gel). Eluents are described below for each reaction.

Bis(terminal iodo) Pentamer 11. See procedure D. **8** (6.0 g), PPTS (0.95 g, 3.78 mmol), 1,2-dichloroethane (20 mL), and *n*-butanol (20 mL) afforded 1.62 g of the title compound as a yellow solid after flash chromatography (CH_2Cl_2). FTIR (KBr) 3356, 2920, 2848, 1512, 1464, 1377, 1185, 1100, 1056, 957, 885, 830, 723 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.66 (s, 2 H), 7.48 (s, 8 H), 7.36 (s, 2 H), 7.29 (s, 2 H), 3.64 (t, $J = 6.6$ Hz, 4 H), 2.82 (t, $J = 7.7$, 4 H), 2.72 (t, $J = 7.6$, 4 H), 2.62 (t, $J = 7.7$, 4 H), 1.75 (p, $J = 7.3$ Hz, 4 H), 1.65−1.41 (m, 12 H), 1.24 (m, 76 H), 0.86 (t, $J = 7.0$ Hz, 6 H), 0.85 (t, $J = 7.0$ Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.12, 142.84, 142.05, 139.54, 132.46, 132.25, 131.44, 123.34, 123.19, 122.61, 122.47, 101.26, 93.97, 93.16, 90.26, 89.91, 62.89, 40.24, 34.06, 33.86, 32.67, 31.96, 30.66, 30.36, 30.24, 29.70, 29.52, 29.39, 25.63, 22.72, 14.15. SEC (THF): $M_n = 2200$, $M_w = 2600$, $M_w/M_n = 1.18$. λ_{abs} (CH_2Cl_2) 365 nm, ϵ (THF) $= 9.6 \times 10^4$. λ_{emis} (CH_2Cl_2, excitation at 365 nm) 425 nm. LRMS (EI) calcd for $C_{96}H_{136}I_2O_6$: 1576. Found: 1576.

Polymer-Supported Bis(terminal iodo) 17-mer 12. See procedure C. **10** (0.98 g), **11** (1.25 g, 0.79 mmol), bis(dibenzylideneacetone)palladium(0) (18.98 mg, 0.033 mmol), copper(I) iodide (6.27 mg, 0.033 mmol), triphenylphosphine (17.29 mg, 0.066 mmol), diethylamine (2 mL), and THF (8 mL) afforded 1.30 g of the title polymer as yellow beads. FTIR (KBr) 3449, 3059, 3024, 2921, 2854, 2201, 1802, 1736, 1655, 1598, 1491, 1448, 1384, 1237, 1069, 1026, 896, 833, 753, 696 cm^{-1}.

Bis(terminal iodo) 17-mer 13. See procedure D. **12** (1.30 g), PPTS (0.17 g, 0.66 mmol), 1,2-dichloroethane (5 mL), and *n*-butanol (5 mL) afforded 0.31 g (20% after seven steps)[17] of the title compound as a yellow solid after flash chromatography (CH_2Cl_2/THF 9:1). FTIR (KBr) 3418, 2924, 2854, 1727, 1601, 1514, 1463, 1378, 1273, 1177, 1121, 1071, 894, 833, 721, 694 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 2 H), 7.49 (br s, 34 H), 7.36 (br s, 14 H), 3.65 (br t, $J = 6.4$ Hz, 12 H), 2.81 (m, 36 H), 1.8−1.2 (m, 282 H), 0.85 (m, 36 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.19, 141.87, 139.38, 132.32, 132.25, 131.29, 123.00, 122.46, 94.22, 93.97, 93.81, 93.72, 90.48, 90.40, 90.28, 90.21, 64.20, 34.25, 34.15, 32.77, 32.04, 30.78, 30.45, 29.81, 29.78, 29.75, 29.67, 29.48, 25.73, 22.82, 14.27. SEC (THF) $M_n = 8000$, $M_w = 8500$, $M_w/M_n = 1.06$. (The initial polydispersity index was 1.2, and all spectra were recorded at that purity level. Preparative TLC on a portion was used to sharpen the index to 1.06.) λ_{abs} (CH_2Cl_2) 385 nm, ϵ (THF) $= 1.1 \times 10^5$. λ_{emis} (CH_2Cl_2, excitation at 385 nm) 415 nm. MALDI-MS (α-cyano-4-hydroxycinnamic acid matrix in positive ion mode) calcd for $C_{308}H_{416}I_2O_6$: 4468.5. Found: 4215 ± 10 (loss of two iodides).

Polymer-Supported Bis(terminal silyl) Pentamer 15. See procedure A. Polymer-supported bis-terminal iodo pentamer **8** (2.00 g), (trimethylsilyl)acetylene (0.27 mL, 1.89 mmol), bis(dibenzylideneacetone)palladium(0) (34.5 mg, 0.06 mmol), copper(I) iodide (11.4 mg, 0.06 mmol), triphenylphosphine (31.44 mg, 0.12 mmol), diethylamine (10 mL), and THF (20 mL) afforded 2.05 g of the title polymer as yellow beads. FTIR (KBr) 3450, 3059, 3026, 2921, 2852, 2148, 1944, 1872, 1802, 1678, 1600, 1491, 1448, 1381, 1250, 1115, 1070, 1027, 837, 754, 694, 600 cm^{-1}.

Polymer-Supported Bis(terminal alkynyl) Pentamer 16. See procedure B. Polymer-supported bis-terminal silyl pentamer **15** (2.05 g), THF (20 mL), and TBAF (2.52 mL, 2.52 mmol, 1.0 M in THF) afforded 1.98 g of the title polymer as

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(17) The overall yields of the final 17-mer **13** and the 23-mer **20** were determined by comparing the loading of the monomer **1** on the polymer support (compound **5**) and the yield of the final oligomer when liberated from the polymer support. The loading level of the starting material **1** on the polymer support, compound **5**, was determined by cleavage of **1** from **5** using the acidic conditions described. Each synthetic process then started with **5** (10.0 g, 4.8 mmol of loading of **1**). The sequence followed for the 17-mer **13** is as follows: **5** (10.0 g, 4.8 mmol of loading of **1**) → **6** (10.5 g) → **7** (10.3 g) → **8** (13.9 g) of which only a 7.2% mass portion (1.00 g) was taken on in the polymer supported form → **9** (1.03 g) → **10** (0.98 g) → **12** (1.30 g) → **13** (0.31 g, 0.069 mmol). Starting from 4.8 mmol of **1** in **5** and using only 7.2% mass of the material during the conversion of **8** → **9**, gives a theoretical yield of 0.35 mmol and an actual yield of 20% for **13**. The sequence followed for the 23-mer **20** is as follows: **8** (13.9 g, from above) of which only a 14.4% mass portion (2.00 g) was used for the next step → **15** (2.05 g) → **16** (1.98 g) → **17** (2.50 g) of which only a 15.9% mass portion (0.40 g) was used for the next step → **18** (0.39 g) → **19** (0.60 g) → **20** (0.124 g, 0.023 mmol). Starting from 4.8 mmol of **1** in **5** and using only 14.4% of the material in the conversion of **8** → **15**, and only a 15.9% portion in the conversion of **17** → **18**, gives a theoretical yield of 0.11 mmol and an actual yield of 21% for **20**.

yellow beads. FTIR (KBr) 3429, 3297, 3025, 2923, 2853, 1945, 1803, 1600, 1492, 1450, 1382, 1214, 1115, 1070, 1029, 899, 836, 755, 697 cm^{-1}.

Polymer-Supported Bis(terminal silyl) 13-mer 17. See procedure C. Polymer-supported bis-terminal alkynyl pentamer **16** (1.98 g), iodinated tetramer **14**[3g] (1.39 g, 1.89 mmol), bis(dibenzylideneacetone)palladium(0) (34.5 mg, 0.06 mmol), copper(I) iodide (11.4 mg, 0.06 mmol), triphenylphosphine (31.44 mg, 0.12 mmol), diethylamine (10 mL), and THF (20 mL) afforded 2.5 g of the title polymer as yellow beads. FTIR (KBr) 3449, 3059, 3025, 2924, 2852, 2139, 1457, 1385, 1249, 1120, 1029, 902, 865, 837, 755, 697, 600 cm^{-1}.

Polymer-Supported Bis(terminal alkynyl) 13-mer 18. To a suspension of polymer-supported bis-terminal silyl 13-mer **17** (0.40 g) and CH_2Cl_2 (10 mL) in a thick-walled oven-dried flask were added K_2CO_3 (0.14 g, 1.00 mmol) and MeOH (10 mL). The suspension was stirred at room temperature for 24 h. The polymer was then transferred to a preweighed fritted funnel using THF, washed sequentially with THF (3×), MeOH (3×), CH_2Cl_2 (3×), and MeOH (3×), and dried in a vacuum oven at 60 °C to afford 0.39 g of the title polymer as yellow beads. FTIR (KBr) 3450, 3299, 3025, 2920, 2854, 1944, 1802, 1656, 1597, 1493, 1448, 1383, 1262, 1070, 1025, 897, 836, 751, 692 cm^{-1}.

Polymer-Supported Bis(terminal iodo) 23-mer 19. See procedure C. Polymer-supported bis-terminal alkynyl 13-mer **18** (0.39 g), bis-terminal iodo pentamer **11** (0.47 g, 0.30 mmol), bis(dibenzylideneacetone)palladium(0) (5.7 mg, 0.01 mmol), copper(I) iodide (1.9 mg, 0.01 mmol), triphenylphosphine (2.6 mg, 0.01 mmol), diethylamine (10 mL) and THF (20 mL) afforded 0.60 g of the title polymer as yellow beads. FTIR (KBr) 3449, 3059, 3025, 2920, 2851, 1802, 1656, 1599, 1491, 1449, 1384, 1263, 1069, 1027, 896, 835, 753, 696 cm^{-1}.

Bis(terminal iodo) 23-mer 20. See procedure D. Polymer-supported bis-terminal iodo 23-mer **19** (0.6 g), PPTS (0.5 g, 0.2 mmol), 1,2-dichloroethane (20 mL), and *n*-butanol (20 mL) afforded 0.124 g (21% over nine steps)[17] of the title compound as a yellow solid after flash chromatography (CH_2Cl_2/THF 9:1). FTIR (KBr) 3378, 2924, 2853, 2200, 1728, 1601, 1512, 1461, 1405, 1377, 1271, 1186, 1122, 1070, 895, 835, 721 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 2 H), 7.51 (m, 24 H), 7.38 (m 16 H), 7.08 (m, 8 H), 3.67 (br t, $J = 8$ Hz, 12 H), 2.75 (m, 52 H), 1.65−1.25 (m, 306 H), 0.86 (br t, $J = 8$ Hz, 36 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.19, 142.88, 133 (br), 132.9 (br), 132.3 (br), 132.29, 124 (br), 123.44, 95 (br), 63.95, 35 (br), 33.77, 33.04, 31.8 (br), 31.5 (br), 30.81, 30.66, 30.49, 26.73, 24.12, 23.84, 15.82, 15.66, 15.29. SEC (THF) $M_n = 12000$, $M_w = 12350$, $M_w/M_n = 1.03$. (The initial polydispersity index was 1.2, and all spectra were recorded at that purity level. Preparative TLC on a portion was used to sharpen the index to 1.03.) λ_{abs} (CH_2Cl_2) 390, 445 (sh) nm, ϵ (THF) $= 1.8 \times 10^4$. λ_{emis} (CH_2Cl_2, excitation at 390 nm) 415, 495 nm. MALDI-MS (α-cyano-4-hydroxycinnamic acid matrix in positive ion mode) calcd for $C_{356}H_{456}I_2O_6S_8$: 5342. Found: 5349 ±10, 5221 ± 10 (loss of iodide).

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Supporting Information Available: Copies of spectral and MS data for the compounds reported here. This material is available free of charge via the Internet at http://pubs.acs.org.

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