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Rapid Bi-directional Synthesis of Oligo(1,4-phenylene ethynylene)s

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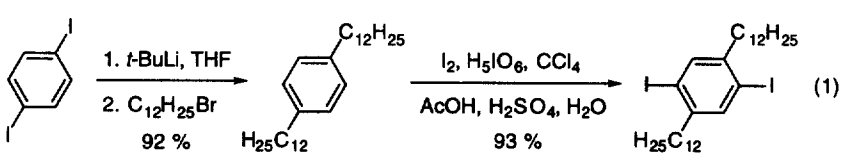
Abstract

A new method for the preparation of oligo(1,4-phenylene ethynylene)s is described. Only two sets of reaction conditions are needed for the entire iterative synthetic sequence: (1) Pd-catalyzed cross-coupling of trimethylsilylacetylene with an aryl halide and (2) in situ desilylation/Pd-catalyzed coupling with an aryl iodide. This method provides a fast synthetic route to short length oligo(1,4-phenylene ethynylene)s by oligomer growth at both ends.

Keywords: Oligomers; Alkynes

Conjugated oligomers of precise length and constitution have attracted much recent attention.[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 in molecular scale electronic devices.[1] We and others have previously reported iterative divergent/convergent routes to the synthesis of oligo(1,4-phenylene ethynylene)s.[2] In most of these iterative methods, the aryl iodide needs to be masked as a dialkyltriazene and then converted to the iodide before each coupling reaction. Godt et al. later demonstrated the efficacy of using 1-bromo-4-iodobenzenes since the iodides reacted selectively over the bromides.[2c] In all of the solution-based synthetic schemes, the chain length grew in one direction. Here we reported a simple method for the preparation of oligo(1,4-phenylene ethynylene)s using just two sets of reaction conditions. There is no need to mask the iodides and the oligomer grows bi-directionally. Since bis(terminal alkyne)s are oxidatively unstable during work-up, an *in situ* deprotection/Pd-catalyzed coupling is described so that isolation of the unstable intermediates is unnecessary. The method outlined here is useful for the shorter oligomers, generally up to the octamer. However, since many applications require only the shorter oligomeric systems,[1] this very simple method should prove to be efficacious.

The starting 1,4-diiodo-2,5-didodecylbenzene (**1**) was generated by dilithiation of 1,4-diiodobenzene, then displacement with dodecyl bromide, and finally iodination (eq 1).



(1)

1

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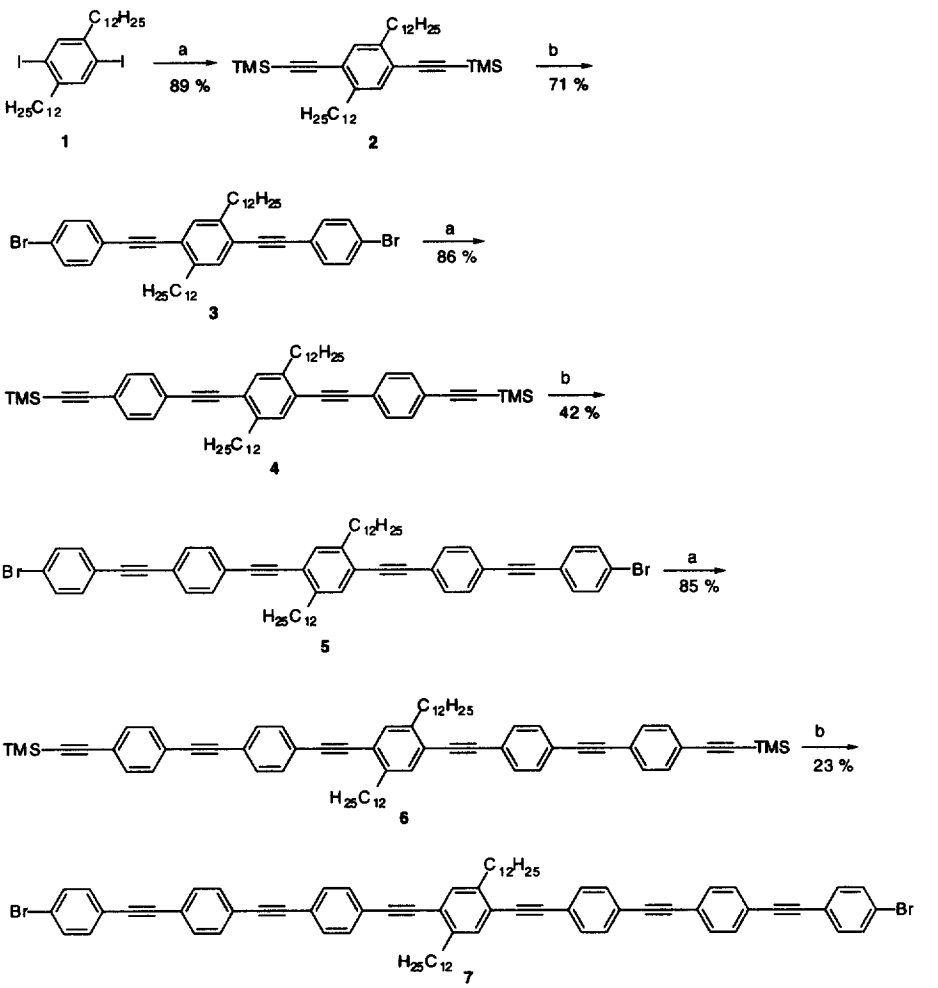
PII: S0040-4039(99)00463-3

Scheme 1



Conditions: a. Trimethylsilylacetylene, $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, Et_3N, THF. b. 1-Bromo-4-iodobenzene, $Pd(dba)_2$, CuI, PPh_3, K_2CO_3, MeOH, THF.

Compound **1** provided the solublizing moieties for the oligomers. The oligomeric growth using only two sets of reaction conditions is shown in Scheme 1. Sonogashira coupling[3] of **1** with trimethylsilylacetylene generated 1,4-bis(trimethylsilylethynyl)-2,5-didodecylbenzene (**2**). Without desilylation of **2** and isolation of the bis(terminal alkyne), we performed the *in situ* desilylation and coupling of **2** with 1-bromo-4-iodo-benzene to generate **3**. Pd-catalyzed coupling of **3** with trimethylsilylacetylene generated **4**. Since **4** had trimethylsilyl-protected alkynes at both ends, the *in situ* desilylation and coupling process could be repeated. Iteration of this reaction sequence added another two units on **4** to afford **5**. Coupling of **5** with trimethylsilylacetylene generated **6** which was subjected to *in situ* desilylation and

coupling with 1-bromo-4-iodobenzene to afford **7**. The cross coupling proceeded with predominantly iodo-selectivity;[2c] however, some insoluble by-products may have been the result of undesired oligomerization via alkyne/bromide coupling. Although the amount of the insoluble materials increased with the increased length of the oligomers, this *in situ* desilylation and coupling method is ideal for the synthesis of short length oligo(1,4-phenylene ethynylene)s.

Optical absorption studies were conducted on the oligomers (Figure 1).[4] As expected, we observed an increase in the absorption maxima from shorter wavelength (245 nm) for the monomer **1** to longer wavelength (370 nm) for the heptamer **7**.

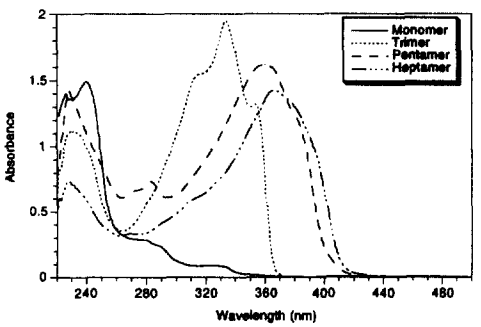


Figure 1. The UV-vis absorbance spectra (CH_2Cl_2) of monomer **1**, trimer **3**, pentamer **5**, and heptamer **7**, respectively. Values of ε (THF) are 2.0×10^4 (monomer **1**), 5.2×10^4 (trimer **3**), 5.7×10^4 (pentamer **5**), and 9.4×10^4 (heptamer **7**).

In summary, only two sets of reaction conditions are needed for the entire iterative synthetic sequence: Pd-catalyzed cross-coupling of trimethylsilylacetylene with an aryl halide and in situ desilylation/Pd-catalyzed coupling of an alkyne with an aryl halide. This method provides a fast synthetic route to short length oligo(1,4-phenylene ethynylene)s by oligomer growth at both ends.[4]

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References and Notes

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3. Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467.
4. **General procedure for the coupling of trimethylsilylacetylene with aryl halides**: To a stirring solution of the aryl halide, bis(triphenylphosphine)palladium(II) dichloride (5 mol % per halide atom), and copper(I) iodide (10 mol % per halide atom) in THF was added triethylamine (3 equiv based on per halide atom) followed by trimethylsilylacetylene (1.2 equiv based on per halide atom) at room temperature under nitrogen in a screw cap tube. The vessel was capped and heated to 70 °C overnight. The

reaction mixture was then subjected to an aqueous work-up and the aqueous layer was extracted with dichloromethane. After drying the combined organic layers over $MgSO_4$, the solvent was removed in vacuo to afford a crude product that was purified by column chromatography (silica gel). **General procedure for the in situ desilylation and coupling of silylated alkynes with aryl iodides:** To a thick-walled oven-dried screw cap tube was added the silylated alkyne, potassium carbonate (3 equiv based on per silylated alkyne), bis(dibenzylideneacetone)palladium(0) (5-10 mol % per silylated alkyne), triphenylphosphine (10-20 mol % per silylated alkyne), copper(I) iodide (5-10 mol % per silylated alkyne), 1-bromo-4-iodobenzene (1.2 equiv based on per silylated alkyne, Aldrich) and THF/MeOH (4:1). The tube was capped and the mixture was stirred overnight. The reaction mixture was filtered through a plug of silica gel with dichloromethane and then subjected to an aqueous work-up and the aqueous layer was extracted with dichloromethane. After drying the combined organic layers over $MgSO_4$, the solvent was removed *in vacuo* to afford a crude product that was purified by column chromatography (silica gel). The heptamer was further recrystallized from dichloromethane. **(2):** Mp = 37-39 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (s, 2 H), 2.65 (t, J = 7.8 Hz, 4 H), 1.52 (m, 4 H), 1.24 (m, 36 H), 0.86 (t, J = 6.5 Hz, 6 H), 0.23 (s, 18 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.66, 132.45, 122.56, 103.97, 98.87, 34.15, 31.95, 30.64, 29.70, 29.67, 29.55, 29.38, 22.71, 14.13, -0.014. HRMS calcd for $C_{40}H_{70}Si_2$: 605.5021. Found: 605.5016. **(3):** Mp = 63-65 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, J = 8.2 Hz, 4 H), 7.38 (m, 6 H), 2.78 (t, J = 7.6 Hz, 4 H), 1.69 (br p, J = 7 Hz, 4 H), 1.25 (m, 36 H), 0.89 (t, J = 6.0 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.35, 132.88, 132.36, 131.70, 122.54, 122.49, 122.45, 92.98, 89.61, 34.18, 32.00, 30.71, 29.77, 29.75, 29.70, 29.61, 29.45, 22.77, 14.20. HRMS calcd for $C_{46}H_{60}Br_2$: 770.3062. Found: 770.3059. **(4):** Mp = 92-93 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (br s, 8 H), 7.35 (s, 2 H), 2.79 (t, J = 7.5 Hz, 4 H), 1.69 (br p, J = 7 Hz, 4 H), 1.25 (m, 36 H), 0.89 (t, J = 6.7 Hz, 6 H), 0.27 (s, 18 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.34, 132.39, 131.95, 131.25, 123.55, 122.97, 122.54, 104.70, 96.31, 93.72, 90.43, 34.15, 31.97, 30.69, 29.73, 29.71, 29.66, 29.57, 29.41, 22.74, 14.17, -0.05. HRMS calcd for $C_{56}H_{78}Si_2$: 806.5642. Found: 806.5664. **(5):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (m, 12 H), 7.40 (d, J = 7.2 Hz, 4 H), 7.37 (s, 2 H), 2.82 (t, J = 7.7 Hz, 4 H), 1.70 (m, 4 H), 1.24 (m, 36 H), 0.87 (t, J = 6.6 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.39, 133.04, 132.41, 131.70, 131.58, 131.45, 123.57, 122.75, 122.54, 122.03, 93.74, 90.54, 90.26, 34.16, 31.96, 30.70, 29.73, 29.66, 29.58, 29.40, 22.73, 14.15. HRMS calcd for $C_{62}H_{68}Br_2$: 970.3688. Found: 970.3683. **(6):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (br s, 8 H), 7.46 (br s, 8 H), 7.37 (s, 2 H), 2.81 (t, J = 8.6 Hz, 4 H), 1.70 (m, 4 H), 1.25 (m, 36 H), 0.87 (t, J = 6.6 Hz, 6 H), 0.26 (s, 18 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.38, 132.40, 131.94, 131.60, 131.42, 123.52, 123.16, 123.10, 122.84, 122.54, 104.61, 96.47, 93.76, 91.04, 90.96, 90.53, 34.15, 31.95, 30.68, 29.72, 29.69, 29.65, 29.57, 29.39, 22.71, 14.14, -0.08. HRMS calcd for $C_{72}H_{86}Si_2$: 1006.6268. Found: 1006.6296. **(7):** FTIR (KBr) 2922, 2851, 1656, 1515, 1481, 1434, 1385, 1097, 1069, 1010, 894, 835, 742, 693 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (m, 20 H), 7.41 (d, J = 8.6, 4 H), 7.38 (s, 2 H), 2.81 (t, J = 7.7 Hz, 4 H), 1.71 (m, 4 H), 1.25 (m, 36 H), 0.89 (t, J = 6.2 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.37, 133.03, 132.40, 131 (br with peaks at 131.70, 131.60, 131.44), 123.16, 122.98, 122.82, 122.01, 90 (br), 34.33, 32.13, 30.87, 29.89, 29.74, 29.57, 22.90, 14.34. HRMS calcd for $C_{78}H_{76}Br_2$: 1170.4314. Found: 1170.4327.