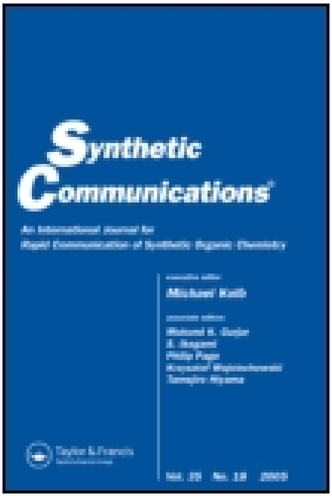

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Synthesis of Monodisperse Oligo[(1,4-Phenyleneethynylene)-A

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To cite this article: Guorong Li , Xianhong Wang , Ji Li , Xiaojiang Zhao & Fosong Wang (2005) Synthesis of Monodisperse Oligo[(1,4-Phenyleneethynylene)-Alt-(2,5-Thiopheneethynylene)]s, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 35:1, 115-119, DOI: 10.1081/SCC-200046517

To link to this article: http://dx.doi.org/10.1081/SCC-200046517

Synthetic Communications®, 35: 115–119, 2005

ISSN 0039-7911 print/1532-2432 online
DOI: 10.1081/SCC-200046517

Synthesis of Monodisperse Oligo[(1,4-Phenyleneethynylene)-Alt-(2,5-Thiopheneethynylene)]s

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Abstract: The synthesis of monodisperse oligo[(1,4-phenyleneethynylene)-alt-(2,5-thioph-eneethynylene)]s using an iterative divergent/convergent doubling strategy based on Sonogashira coupling reaction was presented.

Keywords: Oligo[(1,4-phenyleneethynylene)-alt-(2,5-thiopheneethynylene)]s, iterative divergent/convergent, sonogashira coupling reaction

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.[1–3] 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.[4–17] Different synthetic strategies and routes have been developed for

Received in Japan August 19, 2004

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preparing above oligomers by several groups. Tour et al. have demonstrated an iterative divergent/convergent strategy to rapid synthesis of oligo(1,4-phenyleneethynylene)s, oligo(2,5-thiopheneethynylene)s, and their block cooligomers.[4,6,7,10–12] Later, they developed an in situ desilylation/Pd-catalyzed coupling bidirectional synthesis strategy for the preparation of oligo(1,4-phenyleneethynylene)s.[13] Godt et al. reported an alternative route based on bromine-iodine selectivity of the Pd/Cu-catalyzed alkyne-aryl-coupling to synthesis of oligo(1,4-phenyleneethynylene)s.[9] Recently, Chen et al. described a new stepwise synthetic route for the preparation of oligo(1,4-phenyleneethynylen-e)s with high purity.[18] To our knowledge, there has not been any report on the preparation of oligo[(1,4-phenylene-ethynylene)-alt-(2,5-thiopheneethynylene)]s up to now. We report here the synthesis of soluble monodisperse oligo[(1,4-phenylene-ethynylene)-alt-(2,5-thiopheneethynylene)]s by means of an iterative divergent/convergent doubling strategy.

RESULTS AND DISCUSSION

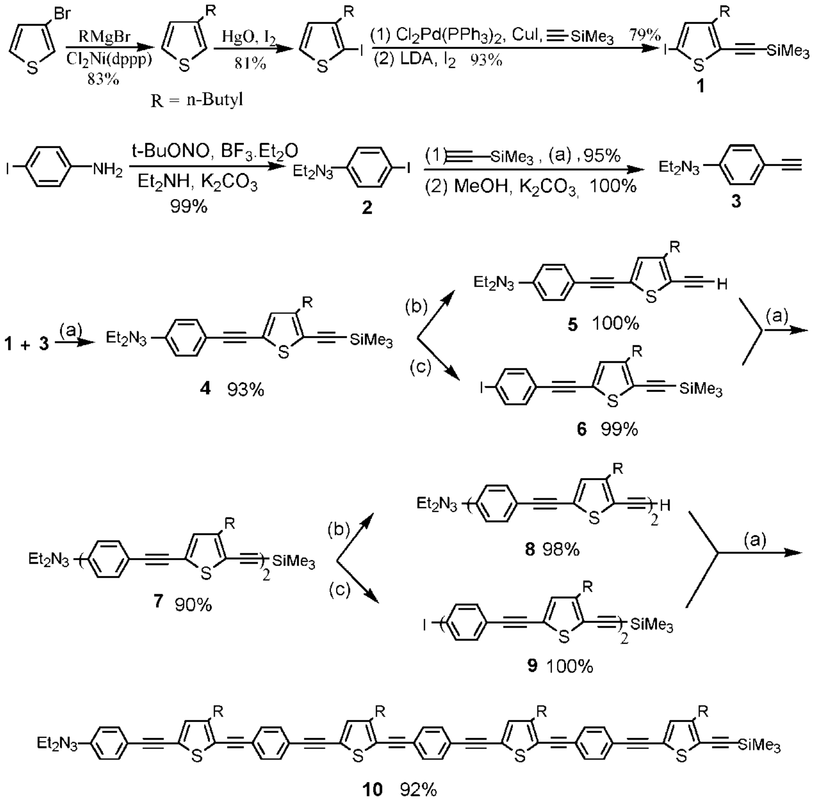
The synthetic route is outlined in Scheme 1. Compound **1** was conveniently synthesized according to previously reported procedure.[7] 4-iodoaniline was converted to the diethyltriazene **2**,[4,6] followed by coupling to trimethylsilylacetylene and then desilylation to afford **3** which was then coupled with **1** to give **4**, the desired “starting monomer” for the iterative divergent/convergent doubling strategy. **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, **5** was coupled with **6** yielding compound **7**. Iteration of above reaction sequence doubled the molecular length of compound **7** to afford **10**, which was 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 quantitive yields, and the coupling reactions were in high yields ($>$ 90%). Note that any product bearing triazene in our present system was easily decomposed on the silica gel! Fortunately, chromatographic purification on neutral alumina has proven to be efficient.

In summary, first synthesis of monodisperse oligo[(1,4-phenylene-ethynylene)-alt-(2,5-thiopheneethynylene)]s was reported in this communication.

EXPERIMENTAL

General Procedure for Iodide Formation from Triazenes

To a thick-walled flame-dried screw cap tube was added the corresponding triazene and iodomethane (10 equiv). The tube was flushed with argon,



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

Scheme 1.

sealed, and heated to 120°C overnight. The reaction was cooled to room temperature, and the solvent was removed *in vacuo*. The crude product was then filtered through a plug of silica gel with ethyl acetate.

General Procedure for Desilylation of Alkynes

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 subjected to an aqueous workup and the aqueous layer was extracted with dichloromethane. After drying the combined organic layers over magnesium sulfate, the solvent was removed *in vacuo*. The product was used without further purification.

General Procedure for Sonogashira Coupling Reaction

To a flame-dried vessel were added the alkyne, the iodo compound (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 days. The reaction mixture was then subjected to an aqueous workup and the aqueous layer was extracted three times with dichloromethane. After drying the combined organic layers over magnesium sulfate, the solvent was removed *in vacuo* to afford a crude product, which was then purified by column chromatography (neutral alumina, 200–300 mesh).

Spectral data for oligomers:

Oligomer **4.** ^{1}H NMR ($CDCl_3$, 600 MHz): δ7.45 (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 (p, 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): δ151.27, 148.64, 132.34, 132.18, 123.44, 120.44, 120.25, 118.69, 101.82, 97.05, 94.33, 82.39, 32.16, 32.05, 29.05, 22.18, 13.91, 13.81; LDI-MS: 436 (M^+), 407 (M - C_2H_5), 363 (M - TMS), 336 (M – Et_2N_3).

Oligomer **7.** ^{1}H NMR ($CDCl_3$, 600 MHz): δ7.48 (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): δ151.24, 148.63, 148.00, 132.91, 132.48, 132.12, 131.28, 131.11, 124.02, 123.07, 122.56, 122.41, 120.41, 120.18, 119.10, 118.59, 102.25, 96.80, 95.71, 94.89, 93.30, 84.70, 84.44, 82.38, 32.19, 32.07, 31.99, 29.16, 29.04, 28.98, 22.20, 22.13, 14.10, 13.87, 13.78; LDI-MS: 698 (M^+), 669 (M–C_2H_5), 598 (M–Et_2N_3).

Oligomer **10.** ^{1}H NMR ($CDCl_3$, 600 MHz): δ7.49–7.47 (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): δ151.32, 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; LDI-MS: MALDI-MS: 1223 (M^+), 1123 (M–Et_2N_3).

ACKNOWLEDGMENT

This work was supported by National Science Fund for Distinguished Young Scholars (No. 20225414).

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