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Tetrahedron Letters 46 (2005) 8971–8973
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Tetrahedron Letters

A novel in situ deprotection/coupling and iterative divergent/convergent strategy for the synthesis of oligo(1,4-phenyleneethynylene)s

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Received 29 September 2005; revised 19 October 2005; accepted 24 October 2005
Available online 8 November 2005

Abstract—A novel in situ deprotection/coupling and iterative divergent/convergent strategy for the synthesis of oligo(1,4-phenyleneethynylene)s is described.

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] Shape persistent oligo(1,4-phenyleneethynylene)s appear especially attractive for their excellent main-chain rigidity and interesting electronic characteristics.[2] Several synthetic methods including solution and solid phase synthesis have been reported for preparing oligo(1,4-phenyleneethynylene)s.[3–6] However, in most of the previously reported methods, isolation of air unstable terminal alkyne or bis(terminal alkyne)s was necessary. Tour et al. therefore developed an in situ desilylation/coupling bi-directional synthesis strategy to avoid the problem of isolating air-sensitive intermediates, and they have successfully prepared oligo(1,4-phenyleneethynylene)s up to heptamer.[6] Some insoluble by-products, however, were obtained because of the undesired oligomerization via alkyne/bromide coupling, and the amount of the insoluble materials increased with the increase of chain length of the oligomers. Moreover, although the oligomers grow bi-directionally, this strategy is a stepwise approach in essence, which is therefore only suitable for the preparation of short-length oligo(1,4-phenyleneethynylene)s.

On the other hand, it is well known that the iterative divergent/convergent strategy has become the most efficient method for preparing long-chain oligomers, since the product can be readily separated from by-products and starting materials as a result of large differences in molecular length. Thus, it would be particularly important and attractive to develop a new strategy combining the advantages of the iterative divergent/convergent strategy and of the in situ desilylation/coupling strategy for the synthesis of oligo(1,4-phenyleneethynylene)s. In this letter, the feasibility and efficiency of such a novel strategy is demonstrated.

The synthetic route is outlined in Scheme 1. 1,4-Dibromo-2,5-didodecyloxybenzene (compound **1)** was easily synthesized analogous to previously reported procedures.[7] 4-Iodoaniline was converted to the diethyltriazene **2**,[4] followed by coupling to trimethylsilylacetylene and then desilylation to afford air stable compound **3**, which was then coupled with **1** to give **4,** the desired 'starting monomer' for the in situ desilylation/coupling iterative divergent/convergent doubling strategy. Compound **4** was divided into two parts. One part was coupled with trimethylsilylacetylene in the presence of Pd/Cu catalyst to afford compound **5** and the other was converted to compound **6** with methyl iodide. Then, **5** was coupled with **6** at room temperature in the presence of both Pd/Cu catalyst and MeOH/K_2CO_3 yielding the tetramer **7**. Iteration of the above reaction sequence doubled the molecular length of the tetramer **7** to afford the octamer **10**,

Keywords: Synthesis; Oligo(1,4-phenyleneethynylene)s; Molecular wires.

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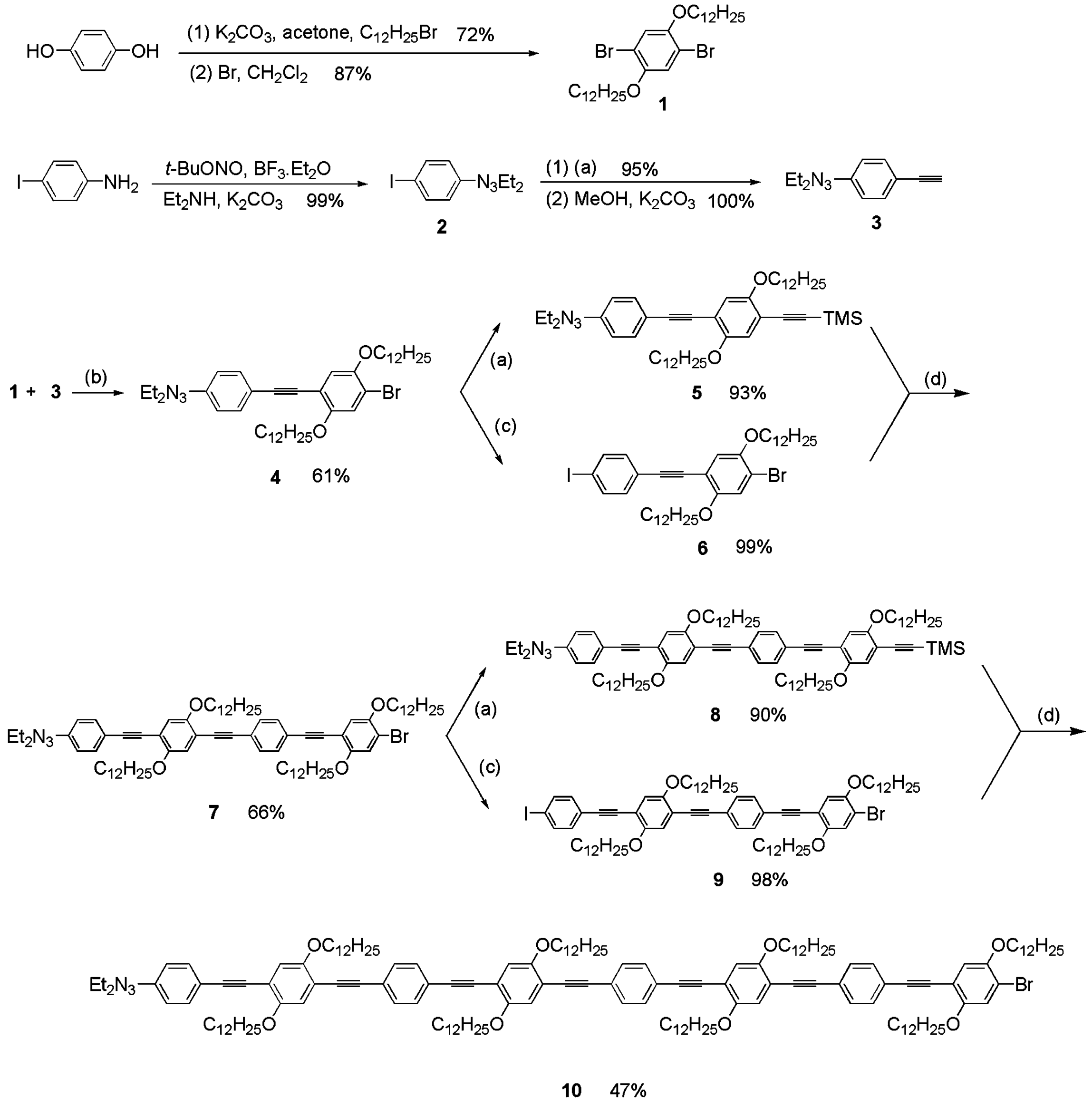
doi:10.1016/j.tetlet.2005.10.113



Scheme 1. Reagents: (a) trimethylsilylacetylene, Pd(dba)$_2$, CuI, PPh$_3$, THF, Et$_3$N; (b) Pd(dba)$_2$, CuI, PPh$_3$, THF, Et$_3$N; (c) MeI; (d) Pd(dba)$_2$, CuI, PPh$_3$, THF, Et$_3$N, MeOH, K$_2$CO$_3$.

which was quite soluble in common organic solvents, such as THF, CHCl$_3$ and so on. We found that compounds bearing the diethyl triazine group easily decomposed on silica gel, fortunately they were stable to column chromatographic purification on neutral alumina. Oligomers **4**, **7**, and **10** were fully characterized by ^{1}H NMR, ^{13}C NMR, and CHN analyses and matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS).

Compared with Tour's in situ deprotection/coupling bidirectional synthesis strategy,[6] this novel in situ deprotection/coupling and iterative divergent/convergent strategy has two main advantages: (1) easier chromatographic purification of the final product because of larger differences between the final product and byproducts and starting materials in molecular length, (2) higher yield of in situ deprotection/coupling reaction as a result of enhanced iodo-selectivity due to strong steric hindrance of the long-chain dodecyloxy substituent which hinders the coupling reaction of terminal alkyne with terminal aryl bromine.

In summary, the feasibility and efficiency of a novel in situ deprotection/coupling and iterative divergent/convergent strategy is demonstrated in this report. Since isolation of air unstable terminal alkyne or bis(terminal alkyne)s was avoided, and higher yields as well as easier chromatographic purification of the final products were also available, this strategy provides a facile and rapid method to prepare long-chain monodisperse oligo(1,4-phenyleneethynylene)s.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 29992535) and

National Science Fund for Distinguished Young Scholars of China (No. 20225414).

Supplementary data

General experimental procedure for the in situ deprotection/coupling reaction and characterization data including ^{1}H NMR, ^{13}C NMR, CHN and MALDI-MS data for oligomers **4**, **7**, and **10** are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2005.10.113.

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