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Synthesis of Alkoxy-Substituted *ortho*-Phenylene Ethynylene Oligomers

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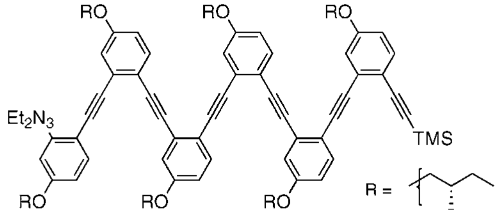
ABSTRACT



This Letter describes the first published synthesis and characterization of alkoxy-substituted *ortho*-phenylene ethynylene (*o*-PE) oligomers. Sonogashira coupling was used to assemble discrete chain lengths, using a key monomer with orthogonal groups. Deprotection or activation allowed stepwise coupling to produce the dimer, trimer, and tetramer, while convergent coupling of appropriately substituted trimers produced the hexamer. The placement of alkoxy side chains renders these oligomers soluble in common organic solvents permitting solution characterization. Absorption and emission spectra of the trimer, tetramer, and hexamer are provided.

The study of supramolecular chemistry and, in particular, foldamers, which mimic the folding behavior of biological molecules with abiotic molecules, has produced considerable interest.[1−7] The need for a wide variety of structurally sound scaffolds upon which to build diverse molecular architectures is vital. At the same time, the study of defined-length oligomers with interesting optical and electronic properties remains important.[8]

Phenylene ethynylene (PE) oligomers represent an important class of scaffolding backbones due to their ease of synthesis and compatibility with a variety of substituents. The scaffold can adopt either extended or helical conformations; para-substituted derivatives are considered rigid rods. A number of meta derivatives have been made, including those designed to adopt helices in solution or the solid state.[9−14] Recently, we patterned meta derivatives with polar, cationic, and nonpolar groups to generate facially amphiphilic extended structures.[15,16]

Both the *meta*- and *ortho*-PEs are capable of forming a helical structure with six and three rings per turn, respectively, but little is known of the ortho conformations. Of the two isomers, *meta*-PEs have been studied more thoroughly[10,12,17−19] than ortho isomers for their folding

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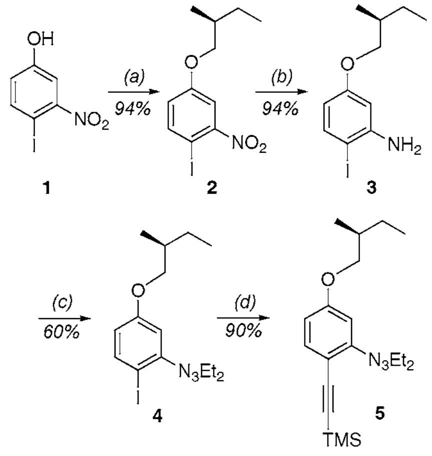
Scheme 1. Synthesis of Pivotal Monomer **5**[a]



[a] Legend: (a) (*S*)-2-methyl-1-butanol, DIAD, PPh_3, THF, 0−20 °C 30 min. (b) $FeCl_3$, $N_2H_4{\cdot}H_2O$, carbon black, CH_3OH, 70 °C, 2 h. (c) (1) HCl, CH_3CN, H_2O, 0 °C; (2) $NaNO_2$, H_2O, 0 °C, 30 min; (3) K_2CO_3, Et_2NH, H_2O, 0−20 °C, 15 min. (d) $PdCl_2(PPh_3)_2$, CuI, TMS−acetylene, TEA, 45 °C, 12 h.

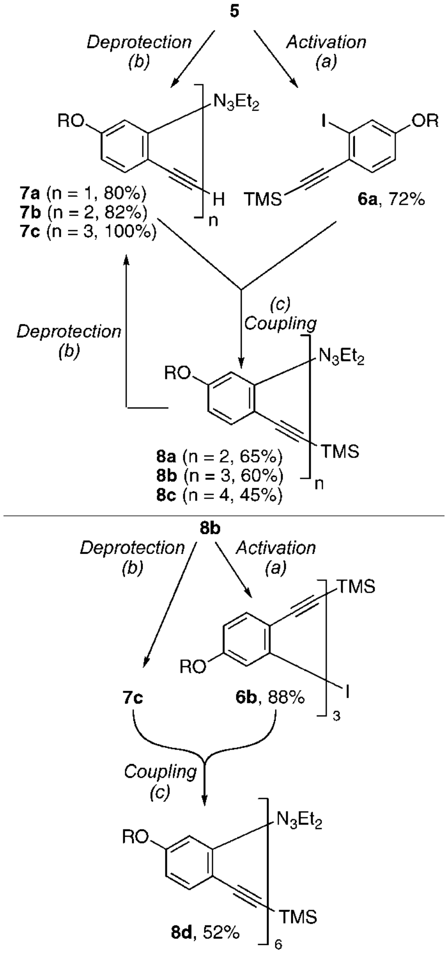
behavior. The few known syntheses of *o*-PEs have *not* reported the framework with side chain substituents and have discussed difficulties with Sonogashira methods.[20−23] This work is significant because it establishes the utility of known reactions for preparing new *o*-PE frameworks that are soluble. Computational studies suggest that these oligomers can adopt helical structures as minimum energy conformations.[24] These oligomers are decorated with the (*S*)-2-methylbutoxy side chain to facilitate the study of potential helical conformations and chiral aggregates.[25−27]

The synthesis of oligomers involves production of pivotal monomer **5** (Scheme 1). Scheme 2 shows the cycle of acetylene deprotection, triazene activation, and Sonogashira coupling used to produce dimer **8a**, trimer **8b**, and tetramer **8c**. Convergent coupling of appropriate trimer molecules (**6b** and **7c**) produces hexamer **8d**.

Beginning with the commercially available 3-nitro-4-iodophenol **1**, the synthesis of monomer **5** is notable for the reduction of the nitro group in the presence of the aryl iodide.[28] In our hands, a traditional method for reducing the nitro compound ($SnCl_2$) also reduced the aryl iodide, but alternate conditions gave excellent yield of **3**. Formation of the triazene from aniline **3** requires vigorous mixing to achieve good yield. The orthogonally protected **5** yields the two fundamental starting materials, **6a** and **7a**, for stepwise oligomer synthesis in separate steps shown in Scheme 2. Despite the ortho proximity of the triazene and acetylene, the overall synthesis of **5** proceeds in very good yield.[29−32]

Elaboration of the monomer to produce a series of oligomers was carried out in satisfactory yield. The ether side chain, *ortho*-diacetylene moieties, and the TMS protecting group are easily able to withstand the triazene depro-

Scheme 2. Synthesis of Oligomers[a]



[a] Legend: (a) CH_3I, 110 °C, 6 h. (b) K_2CO_3, CH_3OH, THF, rt, 0.25−3 h. (c) $PdCl_2(PPh_3)_2$, CuI, **6a** or **6b**, TEA, 45 °C, 12 h.

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tection conditions (methyl iodide, 110 °C, 12 h). Moreover, the key deprotection, activation, and coupling steps are not hindered by sterics related to ortho substitution. ^{1}H NMR data for compounds **8b**−**d** show excellent resolution even in the aryl region of the hexamer; nearly aryl all resonances are assignable at 300 MHz in chloroform. All oligomers, including the hexamer, are soluble in common organic solvents, including THF, ethyl acetate, chloroform, and hexanes.

The UV−vis spectra for compounds **8b**−**d** in chloroform display bands at 280, 290, and 300 nm, consistent with the three-peak pattern of a diphenylacetylene chromophore.[29] The band near 350 nm appears to be consistent with other *o*-PE oligomers reported, although these do not contain side chain substituents.[20] Further, the longer-wavelength band at 350 nm is not associated with the triazene, as the trimer **6b** still contains this band (not shown).

Emission from the oligomers is found near 400 nm with a red shift from the trimer to tetramer to hexamer. Until longer oligomers are prepared, it will remain unclear whether the red shift has saturated in these oligomers, although previous reports indicate that the $\lambda_{\max}$ saturates around the hexamer for unsubstituted oligomers.[20] In summary, we have synthesized oligomers **8b**−**d**, the first ether-substituted *o*-PEs through a series of deprotection, activation, and Sonogashira coupling steps. These oligomers are readily soluble so that solution studies can be performed. We are currently optimizing the synthesis to prepare and study longer oligomers, which will be reported in due course.

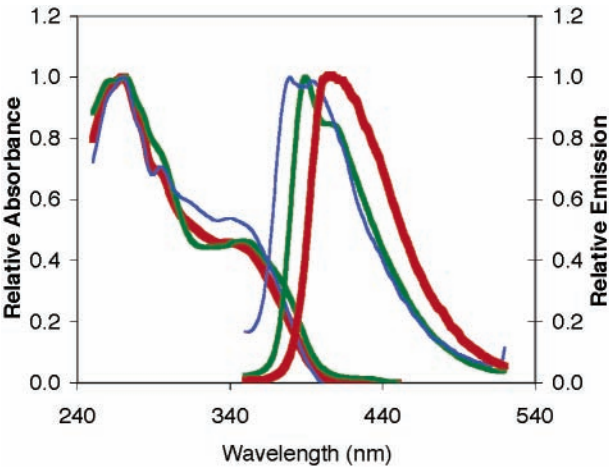

Figure 1. Normalized UV (left curves) and fluorescence (right curves) spectra of oligomers **8b** (blue), **8c** (green), and **8d** (red) in chloroform.

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Supporting Information Available: Synthetic procedures and NMR data are available for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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