# Stepwise Synthesis of Substituted Oligo(phenylenevinylene) via an Orthogonal Approach

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In this paper we report the synthesis of a series of all-trans-substituted oligo(phenylene vinylene) (OPV) compounds. The motivation of this work stems from our desire to synthesize a well-defined conjugated block for use as a rigid element in a diblock copolymer. Organic molecules which possess long conjugated systems are of interest for their electro-optic properties.[1] In particular, poly(phenylenevinylene) (PPV) has attracted much attention as an emissive material for use in electroluminiscent devices.[2] Incorporation of a conjugated block into a diblock system will provide us with new forms of materials. These diblock systems are expected to undergo microphase separation, leading to new forms of self-assembled nanoscale materials containing a conducting domain which will be interesting for the study of the quantum confinement effect. OPV molecules possessing well-defined conjugation lengths and structures may also serve as model systems for understanding the relationships between bulk material properties and molecular structures in conducting polymers.

Scheme 1 shows our strategy in synthesizing these OPVs. The open-ended OPV chain always has a handle for further growth or other modification. The key to the overall strategy is the synthesis of building block molecules, monomers **1** and **2**, both of which possess mutually complementary functional groups at their ends. Monomer 1 possesses an aldehyde at one end and a vinyl group at the other end. Monomer **2** possesses an iodo substituent at one end and a phosphonate ester group at the other end. The iodo terminus of monomer **2** can couple with the vinyl terminus of monomer **1** under the Heck reaction conditions. Similarly, the aldehyde terminus of monomer **1** can couple with the phosphonate terminus of monomer **2** via Horner−Wadsworth−Emmons chemistry. The strategic placement of the functional groups on monomers **1** and **2** allows for sequential and alternating addition of these monomers to an OPV chain as shown in Scheme 1. In order to control the growth of the OPV chain, it is necessary to effectively block one terminus of the growing OPV chain which was successfully accomplished with compound **3**. Growth of the OPV chain commences with compound **3**, and thereafter monomers **1** and **2** are added in a repetitive stepwise fashion (Scheme 1). An alternative approach to the rapid stepwise synthesis of OPV molecules is to react 2 equiv of monomer **1** with 1 equiv of 1,4-dibromobenzene. The product would have a conjugation length including five aryl rings and four double bonds, and in addition it would possess two aldehyde termini capable of reacting with 2 equiv of monomer **2**. The process could be repeated to quickly build up longer OPV molecules possessing functionalized termini. Both monomers and compound **3** are conveniently prepared from 4-iodo-2,5-dioctoxybenzaldehyde which is itself derived from 1,4-dihydroxybenzene in three simple steps.

The Horner−Wadsworth−Emmons reaction did give a detectable amount of the cis product (approximately 5%) as

**Scheme 1.** Synthesis of OPV Molecules



Reaction Conditions: i. Pd(OAc)$_2$, P(o-tolyl)$_3$, NBu$_3$, DMF. ii. NaH/DME. R = C$_8$H$_{17}$.
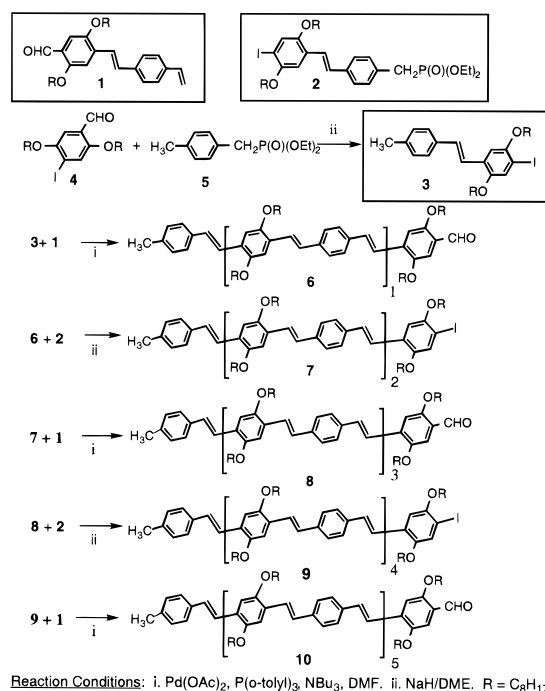
determined from $^1$H NMR (chemical shifts in parts per million). The Heck reaction also generates a small amount of regioisomers.[5] The minor double bond isomer from the Horner−Wadsworth−Emmons reaction and the Heck reaction could be separated from the product by flash column chromatography using a mixture of hexane and ethyl acetate as the mobile phase.[5] Interestingly, in the next Horner−Wadsworth−Emmons reaction to produce compound **9**, no cis product was detected. Reduced solubility of the longer oligomers poses a problem in the purification of these compounds, but analytically pure samples could be obtained through careful flash column chromatography using mixtures of chloroform and hexane as the mobile phase. Yields for each of the steps are good to moderate with decreased solubility of the longer oligomers limiting the yields somewhat.[6] Presently, we have succeeded in the synthesis and purification of compound **10** which has 12 aryl rings, 11 double bonds in its conjugation pathway, and a molecular weight of 2781. Synthesis of longer oligomers is still in progress. All of the spectroscopic studies and elemental analysis results are consistent with the proposed molecular structures.[7]

The absorption and emission spectra for the series of OPVs that possess an aldehyde end group are shown in Figure 1. All of the oligomers show strong and broad absorption in the visible region. Tripling the conjugation length from oligomer **4** to oligomer **8** results in a red shift of 32 nm. However, little or no red shift is noticed after the conjugation length reaches eight aryl rings and seven double bonds. The saturation in $\lambda_{max}$ has been observed previously and arises because of the limitations to electron delocalization in the longer oligomers.[8] Thus, the effective conjugation length in this series of oligomers is reached at compound **6**. The absorption wavelength maximum in the oligomers converges to that of PPV over relatively short

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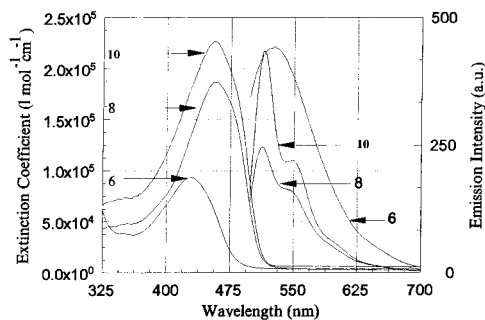(4) Boutagy, J.; Thomas, R. *Chem. Rev.* **1974**, *74*, 87.

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(6) The yields for each coupling step: **6**, 77%; **8**, 84%; **10**, 59%; **7**, 84%; **9**, 73%.
(7) (**10**) Anal. Calcd for C$_{192}$H$_{266}$O$_{13}$: C, 82.89; H, 9.58. Found: C, 82.63; H, 9.58. (**9**) Anal. Calcd for C$_{159}$H$_{224}$O$_{10}$I$_1$: C, 78.93; H, 9.20; I, 5.25. Found: C, 79.06; H, 9.20; I, 5.42.

**Figure 1.** Absorption and emission spectra for compounds **6**, **8**, and **10** taken in dilute solutions of chloroform.

**Table 1.** Thermal Transition Temperatures and Florescent Quantum Yield of OPVs

|                          | **6** | **7** | **8** | **9** | **10** |
|--------------------------|-------|-------|-------|-------|--------|
| $T_m$ (°C)               | 97    | 67    | 90    | 113   | 105    |
| $T_c$ (°C)[a]            |       | 87    | 158   | 176   | 185    |
| $\Phi_{fl}$ (%)[b]       | 75    | 87    | 81    | 89    | 82     |
| $\lambda_{max}$ (nm)     | 431   | 441   | 457   | 460   | 463    |

[a] Clearing temperature from the liquid crystalline phase to the isotropic phase. [b] Excited at $\lambda_{max}$.

conjugation lengths which suggests the validity of using OPV to better understand the electronic properties of electroactive PPV materials.

Solutions of these oligomers give a brilliant green fluorescence (Figure 1). With the exception of oligomer **6**, each of the oligomers exhibits three main features in their fluorescence spectrum in accord with theory.[9] There is a major band with a shoulder to the red of moderate intensity which is itself overlapped with a barely discernible weak band to the red. The emission spectrum of compound **6** is very broad and shows none of the fine structure present in the other spectra. The two main bands, discernible in other compounds, merged together in the fluorescence spectrum of compound **6** into a broad band with relatively higher intensity than the bands in each of the other oligomers. At present, it is not clear why this should be the case, but it does appear to follow the general trend that in oligomers possessing aldehyde end groups the intensity of the second band grows as the conjugation length decreases. The fluorescence quantum yields of each of the oligomers are shown in Table 1. No clear trend exists in the quantum yields, but it is interesting to note that the yields are substantially higher than the yields normally reported in PPV, suggesting that defect sites and impurities act to reduce fluorescence quantum yields in conjugated polymers. No change in any of the emission spectra was observed when fluorescence measurements were made over a wide range of concentrations, suggesting that excimer formation does not occur.

This series of *all-trans*-OPVs are rigid rod molecules, and thus it is not too surprising that each of the oligomers, except compound **6**, manifests a reversible thermotropic liquid crystalline phase.[10] The melting temperature ($T_m$) and clearing temperature ($T_c$) for each oligomer are shown in Table 1. These observations were made using polarized light microscopy to detect the mesoscopic state. The melting temperature and clearing temperature show a rough correlation with molecular weight. The temperature range over which the liquid crystalline phase persists becomes broader with increasing conjugation length and the melting temperature becomes higher as the length increases in a series with the same end group. Figure 2 shows a micrograph of the liquid crystalline texture of compound **6**.



**Figure 2.** Photograph of liquid crystal texture of compound **8** taken between crossed polarizers (magnification 200× (reproduced at 70% of original size), temperature 138 °C).

The phase texture shows strong patterns characteristic of a nematic phase with a disclineation of 1.

It should be pointed out that various syntheses of different OPVs have been reported in the past.[11–13] Schenk *et al.* have investigated the charging capacity of OPV molecules and the charge distribution within the OPV chain.[11] Katz *et al.* have studied the fluorescence dynamics of OPVs both in solution and the solid state and observed little difference between them.[12] The work presented in this paper is distinct from others in that our approach is open ended and very versatile, and it enables us to synthesize longer oligomers that more closely resemble organic polymeric conducting materials. Due to the fact that the Heck and Horner–Wadsworth–Emmons reactions tolerate a wide variety of functional groups, it should be possible to synthesize many different OPV molecules of various lengths and structures. This is useful for fine-tuning the band gap in emissive organic materials. Also noteworthy is the use of two reaction types to construct the same functionality; this eliminates the need of protecting groups. The use of a stilbene analog as the building blocks allows for efficient and fast construction of the OPV chain. After each step a functional group (either an aldehyde or iodo group) is left for further chemical manipulation which may include either continued elongation or reaction with an end-functionalized polymer to form novel diblock copolymers. Controlled bidirectional growth is also possible, enabling a very rapid construction of OPV compounds possessing functional groups at both ends.

In summary, a general strategy for the stepwise synthesis of long conjugated molecules has been demonstrated. The strategy employs the use of two reaction types to grow the conjugated chain stepwise, eliminating the need for protecting group chemistry. A similar strategy has recently been reported for the synthesis of dendritic molecules.[14] The molecules reported here showed high fluorescence quantum yields and a liquid crystalline phase. We intend to use these molecules in the production of novel diblock copolymers.

**Supporting Information Available:** Experimental details and NMR spectra (12 pages). See any current masthead page for ordering and Internet access instructions.

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