

Iterative Synthesis of Heterotelechelic Oligo(phenylene-vinylene)s by Olefin Cross-Metathesis

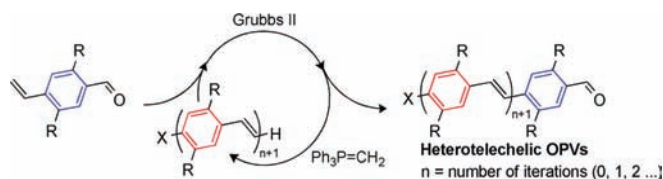
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ABSTRACT



A novel iterative synthesis of heterotelechelic oligo(phenylene-vinylene)s using olefin cross-metathesis is reported. The metathesis homologation proceeds in good yields and allows for further functionalization, including the facile formation of donor-acceptor complexes and repeating sequence copolymers.

In the ongoing search for more efficient organic electronics, conjugated materials with discrete repeating sequences may offer advantages over easier-to-prepare random copolymers.¹ However, examples of such sequenced copolymers are rare.² We are interested in developing new syntheses for and exploring the properties of repeating sequence copolymers (RSCs).³ Herein, we present a novel homologation strategy for producing heterotelechelic sequenced oligo(phenylene-vinylene)s (OPVs) and for assembling these oligomers into RSCs.

Our synthetic approach to heterotelechelic OPVs is based on olefin cross-metathesis (CM), which is attractive for the following reasons: (1) *simplicity*, the coupling of vinyl groups to give internal olefins avoids the need for complex functionality in the monomer, compared to Suzuki⁴ or Horner–Wadsworth–Emmons⁵ approaches; (2) *generality*, the Grubbs II catalyst is highly tolerant; and (3) *utility*, the resultant heterotelechelic oligomers exhibit orthogo-

nally reactive end groups that can be elaborated into more complex materials.⁶ This last advantage is particularly important since many approaches to OPVs generate symmetric⁷ or low-functionality^{4,5,8} oligomers. The use of orthogonally functionalized or protected monomers to produce OPVs is not a new strategy,⁸ but this is the first report to utilize this approach with olefin metathesis. Prior metathesis approaches to OPVs have not focused on the creation of well-defined molecules, but rather on the creation and separation of mixtures of oligomers.⁹

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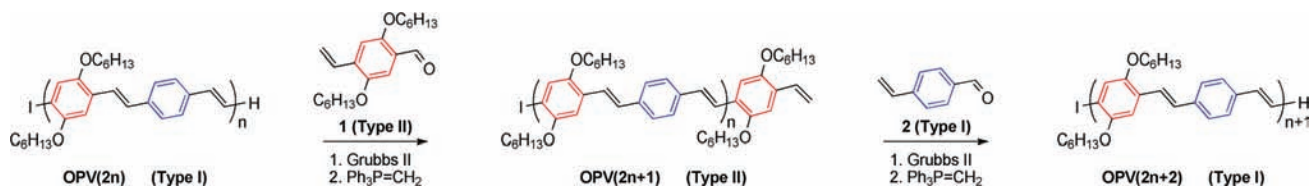
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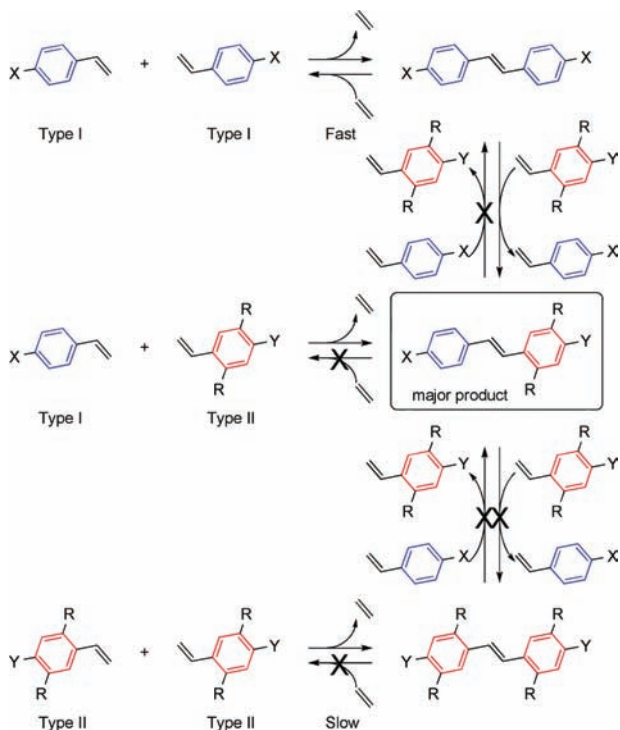
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Scheme 1. Homologation Strategy



Our strategy for the synthesis of heterotelechelic OPVs involves the sequential coupling of phenyl monomers (Scheme 1). End-to-end homologation allows for the creation of oligomers of any desired length. The key step is a CM reaction between olefin-terminated growing oligomers and a vinylbenzaldehyde. The aldehyde end group of the $n + 1$ oligomer product can then be converted into a metathesis-ready vinyl moiety or exploited for further functionalization.

Scheme 2. CM Selectivity with Styrenes



To promote CM over homometathesis, we exploit the known reactivity difference between ortho-substituted and ortho-unsubstituted styrenes.¹⁰ Styrenes lacking ortho substituents, Type I olefins, undergo rapid and reversible homodimerization (Scheme 2). Styrenes with ortho substituents, Type II olefins, are slow to homodimerize and the coupling reaction, which produces a Type IV olefin, is nearly irreversible. Thus, the reaction of a Type I with a Type II

alkene is driven toward the desired CM product, which, as a Type IV olefin, is unreactive toward further metathesis.

Alternation between Type I and Type II vinylbenzaldehydes allows for stepwise growth of the oligomer. An OPV terminated with a Type I olefin can undergo selective homologation with a Type II monomer, 2,5-bis(hexyloxy)-4-vinylbenzaldehyde, **1**. This new OPV will be terminated with a Type II olefin and can undergo homologation with a Type I monomer, 4-vinylbenzaldehyde, **2**, to give another OPV terminated with a Type I olefin, and so on. Since all of the CM products are internal olefins of Type IV, scrambling of extant vinylene groups is suppressed.

Type II monomer **1** was prepared from hydroquinone in 5 steps with an overall yield of 51%. Type I monomer **2** was prepared as previously reported.¹¹ The full synthetic scheme for monomer **1** (Scheme S1) can be found in the Supporting Information.

The first homologation involved CM between styrene **3** (Type II) and monomer **2** (Type I) to give aldehyde terminated **OPV1a** in a 75% yield (Scheme 3). This CM requires very low catalyst loading (7.5×10^{-3} equiv) and can be performed on multigram scales. The use of a 2-fold excess of monomer **2** improved the yield of the cross-coupled product. The homologation is *trans*-specific; the ¹H NMR spectrum bears no peaks between δ 6.5 and 7.0, the characteristic range for *cis*-phenylene-vinylenes.^{7b} The homologation, completed by a Wittig olefination with $\text{Ph}_3\text{P}=\text{CH}_2$, gave vinyl-terminated **OPV1b** in a 96% yield.

Subsequent homologations followed an alternating pattern. Each CM reaction used 3 equiv or less of the vinylbenzaldehyde and 0.01 equiv or less of Grubbs II catalyst, proceeded in moderate to good yields, and was *trans*-specific. The Wittig reactions all proceeded in good to excellent yields. The excess vinylbenzaldehyde, especially monomer **1**, complicated the isolation and purification of the oligomers, as evidenced by the lower yields of **OPV2a** and **OPV4a** compared to those of **OPV1a** and **OPV3a**.

The absorption and emission spectra of the OPVs were obtained in CHCl_3 (Table 1). Within each series (**OPVa** and **OPVb**), the absorption and emission maxima, and molar extinction coefficients, increase with increasing conjugation, while the HOMO–LUMO gap, ΔE_{gap} , decreases. The absorption and emission spectra of the **OPVa** series are red-

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Scheme 3. Synthesis of OPVs

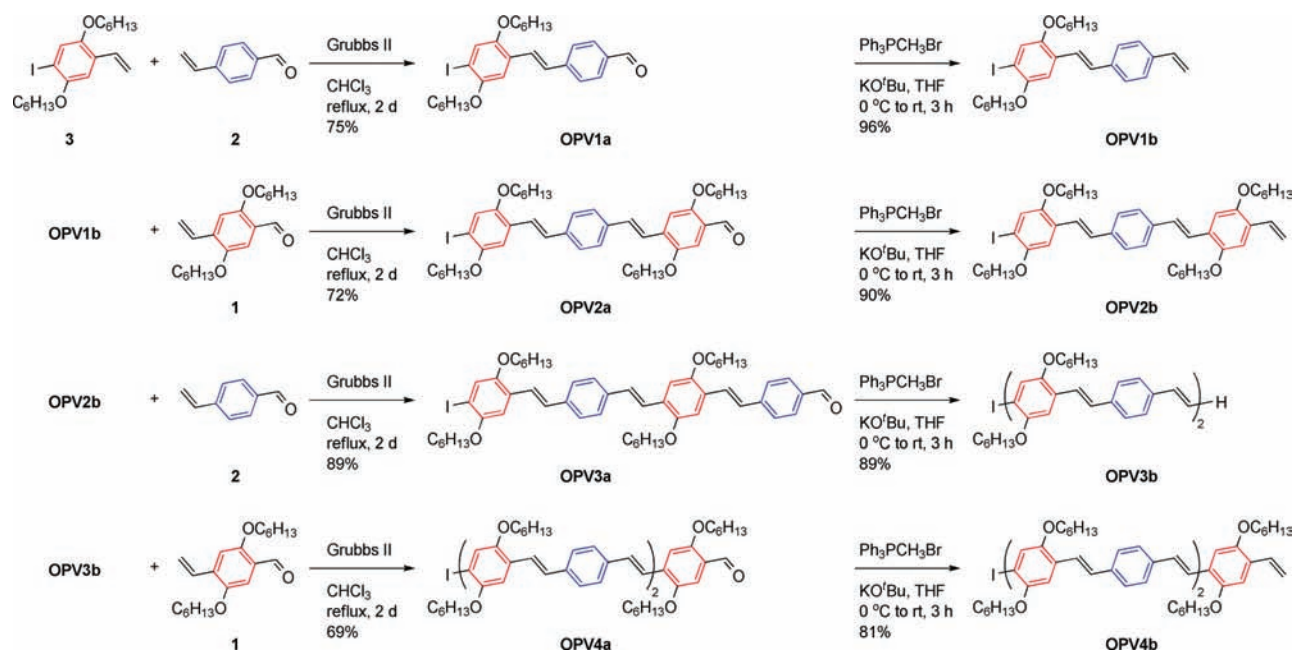


Table 1. Optical Properties of OPVs^a

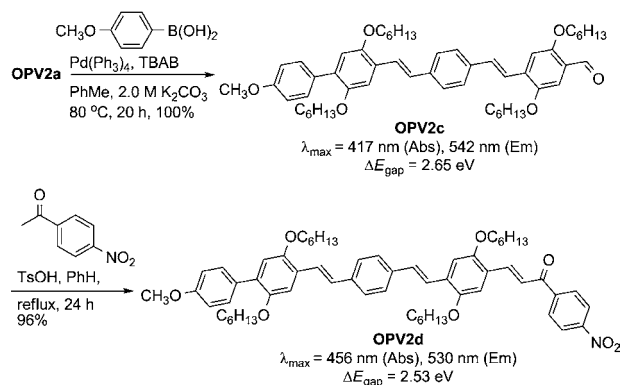
OPV	λ_{max} (abs)/nm	λ_{max} (em)/nm	$\epsilon^b/M^{-1} \text{ cm}^{-1}$	$\Delta E_{\text{gap}}^c/\text{eV}$
OPV1a	376	492	29, 100	2.89
OPV2a	411	503	35, 300	2.69
OPV3a	427	519	82, 800	2.51
OPV4a	443	548	77, 500	2.48
OPV1b	360	423	40, 500	3.06
OPV2b	399	473	70, 900	2.76
OPV3b	419	480	94, 400	2.58
OPV4b	437	496	118, 000	2.52

^a Obtained in CHCl_3 ($\sim 10^{-5}$ M). ^b Calculated at absorption maximum. ^c HOMO–LUMO gap estimated as the onset of absorption.

shifted relative to the **OPVb** series, and the HOMO–LUMO gaps of the **OPVa** series are smaller than those of the **OPVb** series. These effects are most pronounced in the **OPV1** oligomers and become progressively smaller with increasing conjugation. The extinction coefficients of the **OPVb** series are higher than those of the **OPVa** series, with the difference most pronounced in the **OPV2** and **OPV4** oligomers.

Further functionalization of OPVs permits the physical and electronic properties of the material to be adjusted to meet the needs of various applications.⁵ We highlight the ability of our heterotelechelic OPVs to serve as modular platforms for orthogonal functionalization by elaborating upon **OPV2a** using a Suzuki coupling to produce green-emitting donor–acceptor chromophore **OPV2c** followed by an aldol condensation to produce blue-green absorbing but weakly emitting chromophore **OPV2d** (Scheme 4). Both reactions are simple, robust, and proceed in excellent yields.

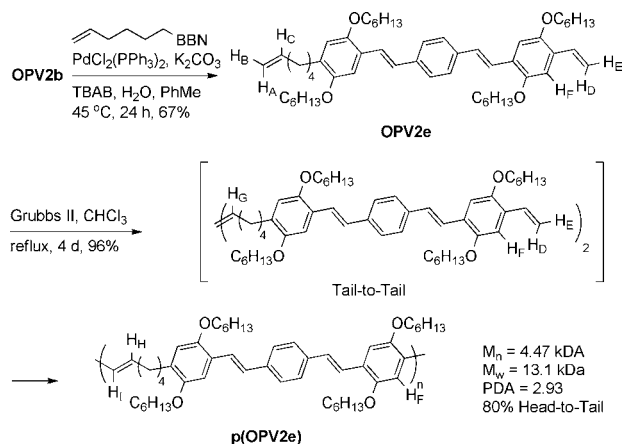
Scheme 4. Synthesis of Donor–Acceptor Chromophores



As an initial demonstration of the types of complex copolymers that could be prepared from heterotelechelic OPVs, we have converted **OPV2b** to **OPV2e** and onward to copolymer **p(OPV2e)** (Scheme 5), using a Suzuki–Miyaura coupling followed by acyclic diene metathesis (ADMET) polymerization, chemistry amenable to producing a family of such RSCs.^{3b} We believe **p(OPV2e)** should exhibit a high degree of head-to-tail regioregularity because **OPV2e** is an AB monomer containing a Type II styrenyl olefin (head) and a Type I aliphatic olefin (tail). Selective metathesis has previously been used to prepare AABB alternating copolymers,¹² but, to the best of our knowledge, there is only one other example of a head-to-tail polymer prepared in this fashion.^{12b} The incorporation of a flexible unit into the

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Scheme 5. Synthesis of Head-to-Tail Copolymers



backbone of a highly conjugated structure can lead to improved solubilities, interesting liquid crystal behavior, and/or modulated physical properties,^{3b} and the inherent dissymmetry of the AB copolymer could lead to enhanced optoelectronic properties.¹³

OPV2e was polymerized with Grubbs II catalyst in CHCl₃. The polymerization was monitored with ¹H NMR spectroscopy by observing the disappearance of the signals for the aliphatic alkenyl group (H_A, δ ~5.2; H_B, δ ~5.1; and H_C, δ ~5.9) and the styrenyl group (H_D, δ ~5.3; and H_E, δ ~5.8) and the appearance of the signals for the tail-to-tail (H_G, δ ~5.5) and head-to-tail (H_H, δ ~6.7; and H_I, δ ~6.3) connections. We estimated the percent head-to-tail based on conversion of styrenyl groups to head-to-tail groups (Figure 1). After 24 h, no OPV2e remains, having been converted first to the tail-to-tail intermediate followed by further metathesis to give head-to-tail connections. At longer reaction times there is some decrease in percent head-to-tail couplings which can be attributed to head-to-head couplings, which are improbable but accumulate slowly. It should be noted that the presence of either head-to-head or tail-to-tail couplings in the final polymer chain disrupts the sequence of the RSC and interferes with the desired polymer directionality. Future work will focus on optimization to minimize such mistakes and/or characterization of the effects of these errors on properties.

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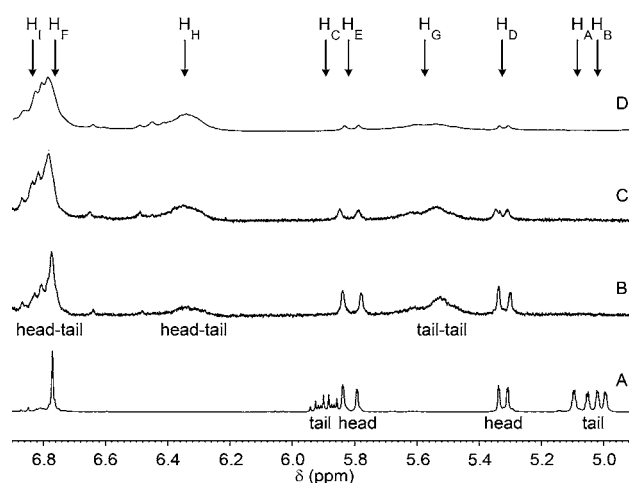


Figure 1. ¹H NMR spectra of the head-to-tail polymerization as a function of time: (A) at 0 h (OPV2e); (B) after 24 h, 50% consumption of head groups, 100% conversion to head-to-tail; (C) after 48 h, 80% consumption of head groups, 75% conversion to head-to-tail; (D) after 96 h, 90% consumption of head groups, 80% conversion to head-to-tail. Head-to-head protons (δ ~7.2) are not assignable due to overlap. Labels (H_{A–H}) refer to labeled protons in Scheme 5.

In summary, we have developed a new synthetic method for the preparation of a homologous series of heterotelechelic OPVs. The preparation, which relies on selective CM, produces oligomers that can be further elaborated to make donor-acceptor complexes or repeating sequence copolymers. A key advantage of this method is the generality; the functional group-friendly metathesis-based couplings should be applicable to phenylene monomers bearing substituents other than the alkoxy groups used in this study.

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Supporting Information Available: Synthetic scheme for compounds **1** and **3**, experimental procedures and characterization data for all new compounds, and NMR, absorption, and emission spectra for all OPVs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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