

# Synthesis of novel phenylenevinylene linkers with electron-donating substituents by the Heck reaction



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## ABSTRACT

Three new carboxylic-acid substituted oligo-phenylenevinylenes (OPVs) with electron-donating substituents in the central ring were synthesized in high yield by the Mizoroki–Heck reaction. The linkers were optically characterized by UV–vis absorption spectrophotometry, fluorescence spectroscopy in solution and the solid state, and measurement of the emission quantum yield. A comparison of substituted and unsubstituted OPVs shows that the electron-donating groups significantly affect the luminescent properties of the linkers. As the electron-donating strength of the substituent increases, the absorption bands strengthen, the emission wavelength shifts bathochromically, and the emission quantum yield increases. Moreover, fluorescence analysis of the OPVs in the solid state shows that the nature of the substituent significantly affects the inter-chromophore interactions. These results suggest that the new linkers have potential for electro-optic applications in which high emission efficiency is required, such as chemical sensing.

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## 1. Introduction

Since the discovery of electroluminescence and photoluminescence in organic macromolecules, oligo-phenylenevinylenes (OPVs) have become among the most studied electronic conjugated systems [1–3]. This is in part due to their high fluorescence quantum yields, environmental stability, and the ease with which they can be structurally modified [4–6]. Currently, OPVs are used as the active layer in organic light emitting diodes (OLEDs) [2], photovoltaic cells [7], lasers [8], sensors [9], and more recently as linkers in the synthesis of luminescent metal organic frameworks (MOFs) [10]. OPVs exhibit stronger electronic conjugation than other linkers commonly used for creating MOFs. By using OPVs as linkers, luminescent MOFs can be created and their physical and chemical properties can be readily tuned through structural modification of the OPV-linker. Targeted structural modifications can also be used to make their optoelectronic properties sensitive to the presence of

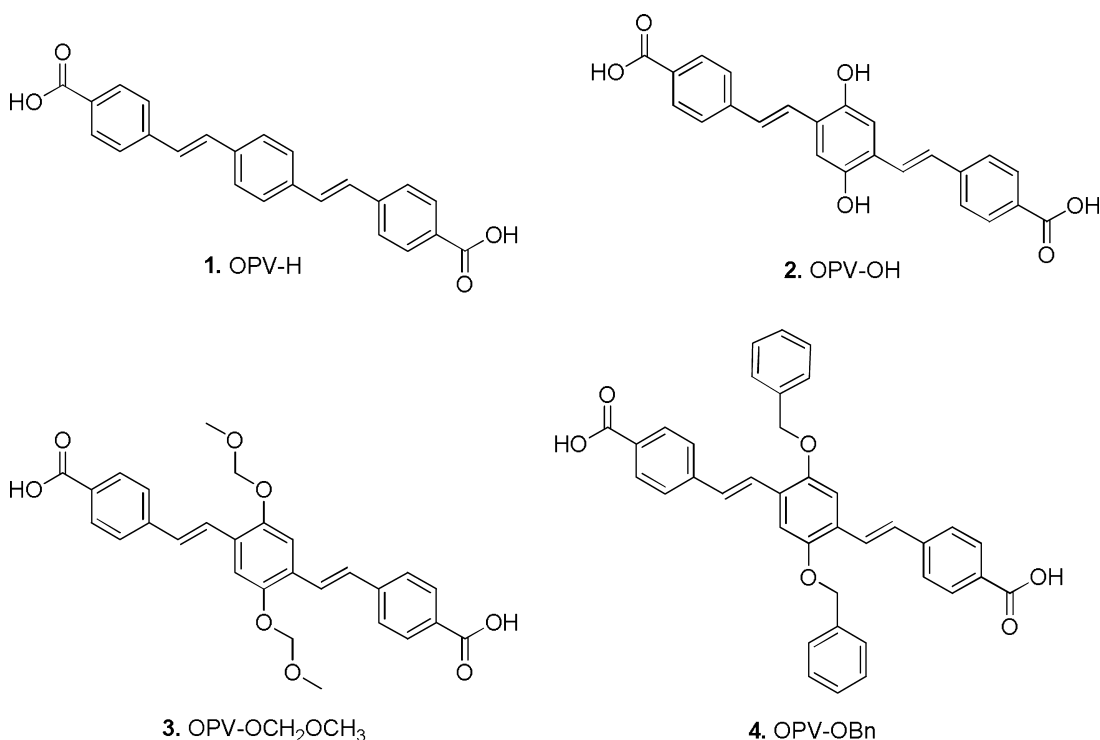
specific molecules. This opens a route to novel sensors based on OPV-linked MOFs [5,11].

To obtain a uniform MOF morphology, the OPV linkers must have a totally *trans* configuration. If a mixture of *EE*, *EZ*, and *ZZ* OPV isomers was used, then uniform MOF networks would not form, and the optoelectronic properties would be adversely affected [12]. Many advances have been reported for improving stereoselectivity in the synthesis of OPVs using common methodologies, such as the Wittig reaction [13–15]. The present work introduces an alternative route to OPVs based on the Heck reaction. Heck coupling is shown to be a suitable approach for creating all-*trans* OPV-linkers [16] with improved yields and lower reagent costs relative to conventional methods.

Four luminescent OPVs with carboxylic acids substituents (acid-OPVs) on both ends of the molecule were synthesized (Fig. 1). Including linkers on the ends of the OPV framework enable these molecules to be used as organic building blocks for luminescent MOFs and as repeating units for the preparation of supramolecular polymers. These OPVs were prepared with electron-donating groups at the 2,5-positions of the central aromatic ring to explore the effect of the substituents on the optoelectronic properties of both the isolated molecules and MOFs based upon them.

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**Fig. 1.** Molecular structures of OPVs reported in this work. The OPVs are carboxylic-acid terminated *bis*(styryl)benzenes that differ by the substituents in the 2- and 5-positions on the central aromatic ring.

## 2. Experimental

### 2.1. General considerations

Commercially available precursors were used as received without further purification and solvents were dried according to standard procedures [14]. Melting points were determined on a *Bibby Stuart Scientific SMP10* apparatus and are reported without correction.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded using a *Bruker Avance 400* spectrometer with  $\text{CDCl}_3$  and  $d_6$ -DMSO as solvents and tetramethylsilane (TMS) as an internal standard for chemical shifts. Fourier-transform infrared spectra were obtained using a *Shimadzu IR prestige-21* FT-IR spectrophotometer. High-resolution mass analysis was performed using a *Q-TOF 6540 UHD* (Agilent Technologies). MALDI-TOF spectra were obtained using a *Bruker UltrafleXtreme* system, equipped with a reflectron time of flight analyzer and a Nd:YAG laser (355 nm).

UV–vis spectra were measured using a *Thermo Scientific Evolution 300* UV–vis spectrophotometer. Samples were prepared from standard solutions that were  $5 \times 10^{-5}\text{ M}$  of the OPV to be analyzed in *N,N*-dimethylformamide (DMF). Once the solution was completely homogeneous, a scan from 260 nm to 600 nm was recorded and the data obtained were processed using Vision Pro Software. Emission spectra were recorded with a PTI QuantaMaster™ 300 spectrofluorimeter using the same solution as that used for the UV–vis absorption measurements. A PTI integrating sphere was fitted to the fluorimeter to obtain fluorescence measurements of the OPV in the solid-state.

Commercially available precursors (Sigma–Aldrich) that were used include ethyl 4-(bromomethyl) benzoate, 1,4-diiodobenzene, 1,4-dimethoxybenzene, 1,4-dibromobenzene, chloromethyl methyl ether and 2,5-dibromohydroquinone. Reagents that could be affected by air or moisture, such as palladium(II) acetate, were stored under nitrogen in a desiccator.

## 3. Results and discussion

### 3.1. Synthesis of the oligo-phenylenevinylenes

The Mizoroki–Heck reaction was used as a coupling method for the synthesis of the OPVs. *Scheme 1* outlines the general synthetic route used to obtain OPVs **1–4**. The initial synthetic plan was to perform the coupling reaction using 4-vinylbenzoic acid instead of 4-vinyl-ethylbenzoate (**5**). However, numerous attempts to obtain product directly from carboxylic acid precursors gave only low yields. As the reaction is intended to run in basic media, it was hypothesized that the acidic groups hindered formation of the active Pd(0) catalyst. Also, the acidic groups could hinder the catalytic cycle by forming a bond with the Pd-metal center, because the equilibrium constant for formation of carboxylic–palladium is larger than that for the triphenylphosphite–palladium complex [17]. Therefore, protection–deprotection steps were added during the Mizoroki–Heck reaction (*Scheme 1*).

Contrary to expectation, protecting the carboxylic acids did not reduce the overall yield. Instead, the purification process became easier and the overall yield increased because the product of the Heck reaction could be precipitated by addition of water, obviating the need to separate and purify by column chromatography. The stereospecificity of the Heck reaction was confirmed by the presence of an infrared absorption at  $963\text{--}964\text{ cm}^{-1}$  in each OPV, due to the *trans* out-of plane =CH bend. Additionally, the NMR spectra for all OPVs show a *trans*-ethenyl coupling of 16 Hz at 7.30–7.44 ppm (see Supporting information). Overall yields for **1** and **10** were higher than the yields reported previously for the same molecules [18,19]. Moreover, esters **11–13**, as well as acids **2–4**, are novel molecules that gave yields as high as 90% and 94% under the reaction conditions reported here.

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