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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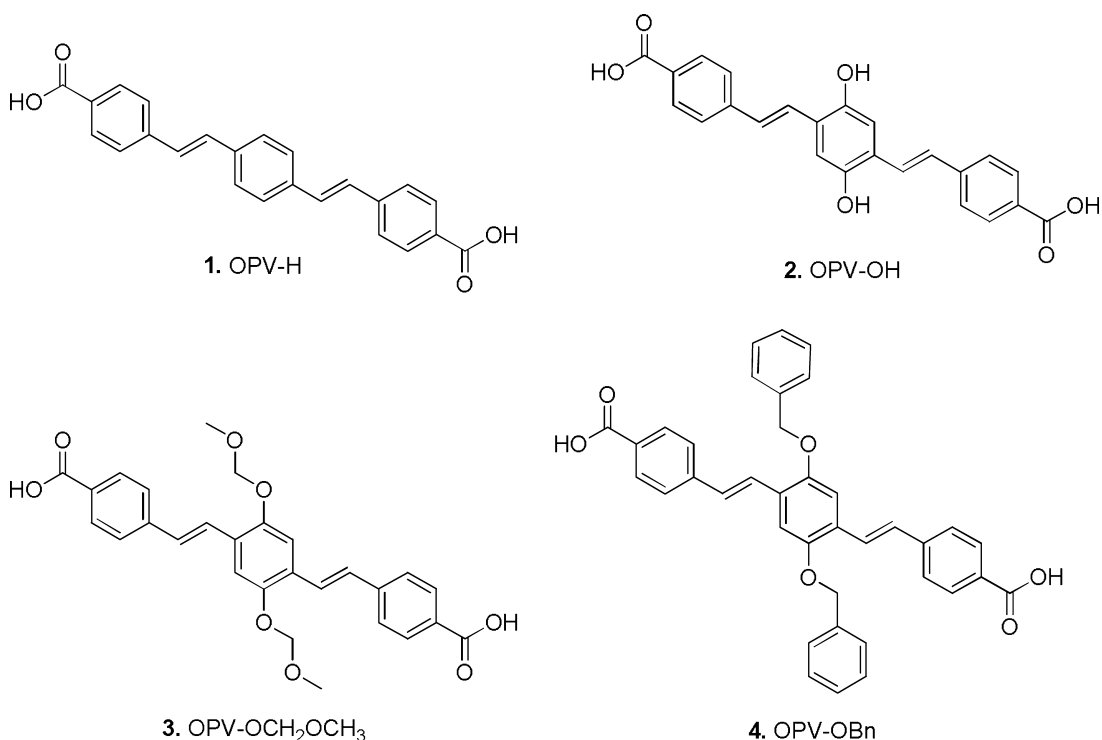E-mail address: casierraa@unal.edu.co (C.A. Sierra).

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}H and ^{13}C NMR spectra were recorded using a *Bruker Avance 400* spectrometer with 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 5×10^{-5} 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[TM] 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 963–964 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.
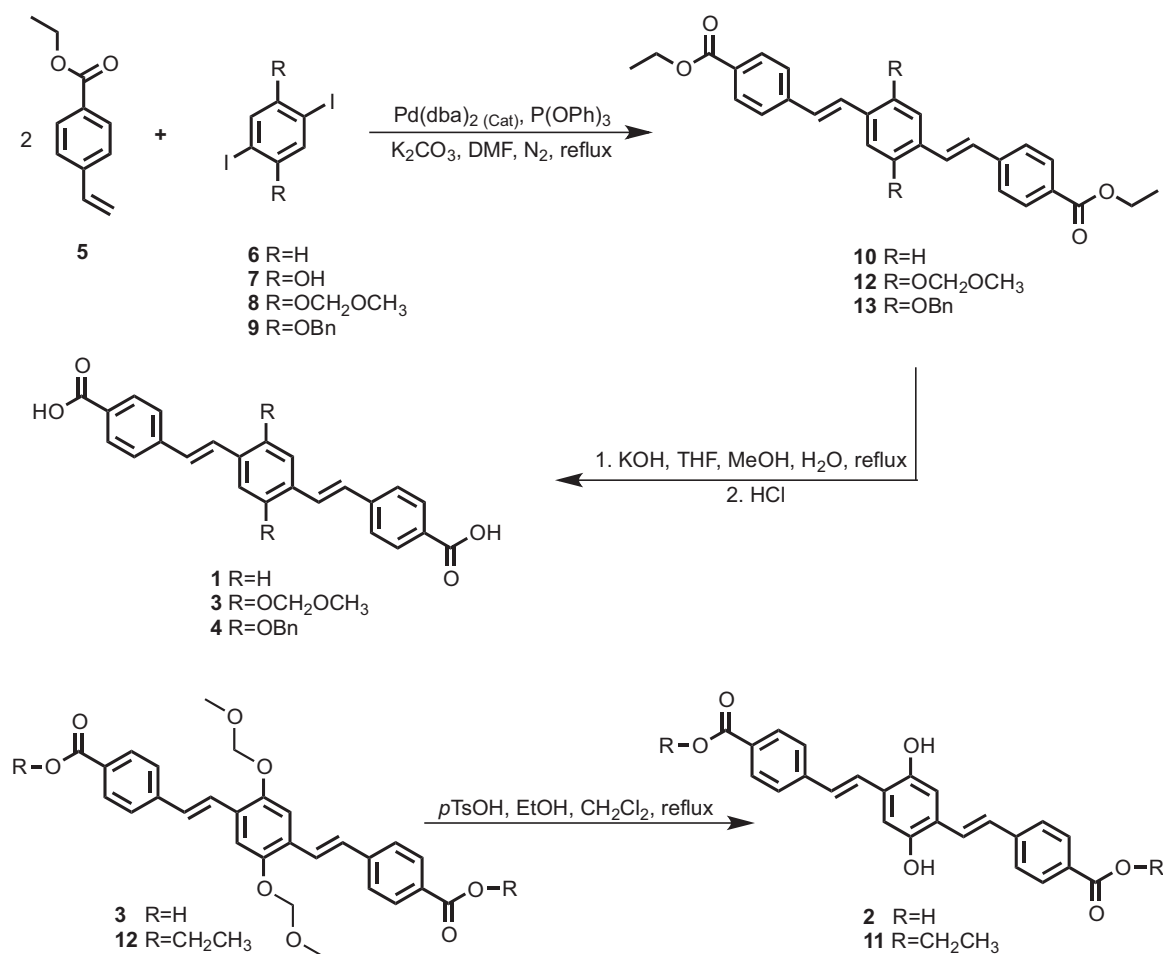
Scheme 1. General synthetic route to OPVs. "OBn" stands for "benzyloxy".

3.2. Optical properties of the oligo-phenylenevinylenes

All of the OPVs are highly colored solids that fluoresce intensely under UV light. The UV–vis absorption and fluorescence (FL) spectra of the OPVs were measured and analyzed to explore how their optoelectronic properties are affected by substituents on the central aromatic ring and to evaluate their viability as building-blocks for chemosensors. The OPVs all exhibit absorptions in the range of 250–460 nm (Fig. 2). According to literature reports [20,21], OPVs usually exhibit a single dominant absorption band in the UV region of 320–400 nm, with a small shoulder at shorter wavelengths, as seen for OPV—H (1). This differs from the spectra of the other OPVs, which exhibit two distinct bands. For example, in the absorption spectrum of OPV—OH (2) two intense absorption bands are observed at 347 nm and 425 nm. This phenomenon is exceptional because usually the first band is attributed to a $\pi \rightarrow \pi^*$ transition, and the second is attributed to a lower energy $n \rightarrow \pi^*$ transition, which is usually less intense because it is symmetry forbidden. However, this phenomenon has been previously observed in some OPV systems having substituents at the 2- and 5-positions of the central benzene ring [22]. The strong influence of the substituents on the central ring is apparent from the presence of these two bands. The appearance of two bands may also be in part due to the presence of COOH substituents on opposite ends of the molecule. The OPVs also exhibit a large Stokes shift (greater than 50 nm) between absorption to the first excited state and emission from the vibrationally relaxed excited state. Having a large Stokes shift

decreases self-absorption, which makes the OPVs more emissive and good candidates for further development into chemosensors.

The emission spectra of the OPVs dissolved in DMF are shown in Fig. 2. To study the influence of substituents on the luminescent properties of the OPVs, the emission quantum yield (ϕ) of each compound was measured. The calculation was made from data obtained by absorption and fluorescence spectrophotometry following the method of Williams et al. [23]. A summary of the absorption and emission properties is provided in Table 1. The absorption and emission spectra of the OPVs are similar in shape, but there are key differences to note. Consistent with the report of Ndayikengurukiye et al. [22], the electron-donating substituents cause a bathochromic shift in the energy of the emission band. The largest shift is observed for OPV—OH, which has the strongest electron donors on the central ring.

Fig. 3 shows the emission spectra of the OPVs as microcrystalline powders. Each compound fluoresces at higher energy in the solid state relative to their emission in solution. The influence of the substituents on the optoelectronic properties is also apparent from the solid-state emission spectra. As is observed from the solution spectra, OPV—OH exhibits the longest-wavelength emission.

Upon comparing the emission spectra of each OPV in solution and as solid powders, we observe a 31 nm red shift for OPV—H, the absence of shift in OPV—OCH$_2$—OCH$_3$ and OPV—OBn, and a 28 nm blue shift for OPV—OH. These results are in agreement with our previous reports and are attributed to the extent of the interchromophore interactions [24], where the value of the shift indicates the magnitude of the solid-state interaction. The
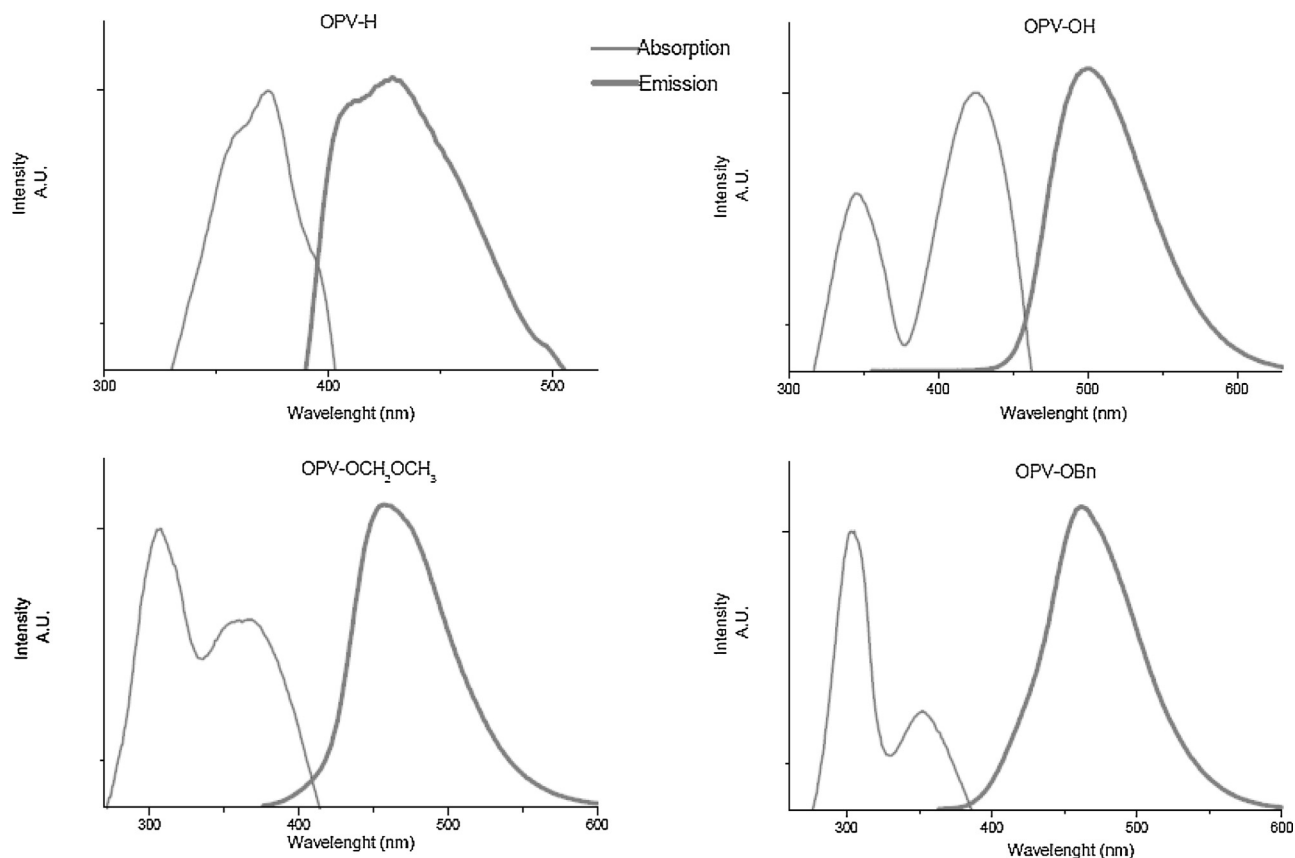
Fig. 2. Absorption and emission spectra (in solution) of all OPVs discussed in this work.

Table 1
Quantum yields and absorption-emission maxima for synthesized OPV.

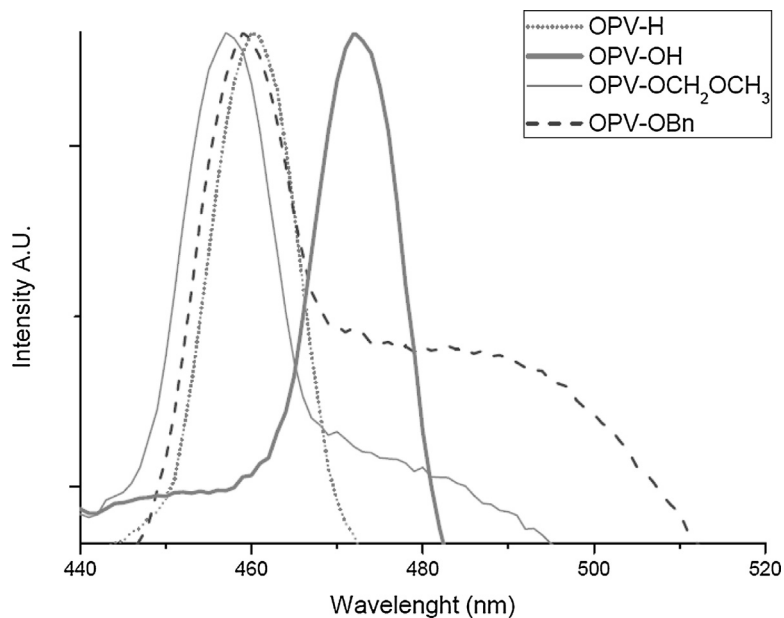|	UV (max, nm)	FL (max, nm)	Solid-state FL (max, nm)	Quantum yield (ϕ_{FL})
OPV—H (**1**)	373	429	460	0.210
OPV—OH (**2**)	425	500	472	0.593
OPV—OCH$_2$—OCH$_3$ (**3**)	304	455	457	0.519
OPV—OBn (**4**)	307	459	459	0.445

Fig. 3. Emission spectra of the OPVs as crystalline solids.

presence of bulky side substituents like —OCH₂—OCH₃ and —OBn decrease the interactions between the chromophores and results in little or no shift in the emission spectra. The total absence of substituents in OPV—H (**1**) allows strong inter-chromophore interaction that result in a large red shift in the emission. On the other hand, the unexpected blue shift in OPV—OH (**2**) could be due to a combination of effects. Hydrogen-bonding between the —OH and —COOH groups may lead to tighter crystal packing and stronger inter-chromophore interactions. Additionally, packing in the solid state may increase the torsional angle between the planes of the aromatic rings, which decreases the orbital overlap and blue-shifts the band.

The results obtained from quantum yield measurements confirm the strong influence of the electron-donating substituents on the electronic properties of the OPVs. In particular, OPV—OH exhibits the highest fluorescence quantum yield. Upon comparing the quantum yields of these OPVs with that of others previously reported it is clear that this series of dicarboxylic-terminated OPVs have highly desirable optical properties. Additionally, their potential for further structural modification and for use as linkers for synthesizing fluorescent MOFs makes them very attractive for optoelectronic and sensing applications.

4. Conclusions

Six novel OPVs – three acids and three esters – were synthesized using an adaptation of the Mizoroki–Heck reaction that offers high yield with lower-cost reagents and better control of the stereochemistry of the products. Higher yields were obtained from the C—C coupling step for two of the previously reported molecules, OPV—ester—H (**11**) and OPV—H (**1**). The optoelectronic characterization of the acid–OPVs shows that the substituents on the central ring strongly affect the electronic properties of the conjugated system. Each of the molecules is highly fluorescent in both solution and the solid state. These findings indicate that OPVs of this type could be engineered to create new fluorescence linkers for synthesizing optoelectronically active MOFs, including MOF-based chemosensors. Work in this direction is currently underway in our laboratories.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.synthmet.2015.07.024.

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