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Phenylenevinylene oligomers by Mizoroki-Heck cross coupling reaction. Structural and optoelectronic characterization

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ABSTRACT

In order to study the effect of the molecular structure on the optical properties of totally *trans-trans* phenylenevinylene oligomers (OPVs), sixteen 1,4-distyrylbenzene derivatives (**1a-i** and **2a-g**) functionalized with different electron-donating (ED) and electron-withdrawing (EW) groups were synthesized by the Mizoroki-Heck cross coupling reaction in moderate to good yields (40–95%). The implemented methodology, with a small modification previously reported by our group, allows obtaining the desired vinyl configuration as well as one novel OPV compound (**1h**). After structural characterization by several techniques (e.g. FTIR, ^{1}H, ^{13}C and Solid-State NMR), particular emphasis was placed upon the investigation of their optical properties by UV–vis and fluorescence spectroscopies. The results showed that, with only one exception, the ED and EW groups at the ends of OPV systems lead to a bathochromic shift. This effect is intensified with the introduction of methoxy groups on the central ring. Consistent with these, the HOMO-LUMO gaps (ΔE) decreases as the strength of ED and EW substituents increases. The ED and EW substituents also lead to a decrease in the Φ_f values. This contribution in the area of organic electronics can be used as a reference to better select the most appropriate technological application for each OPV and this can be extrapolated to their respective structurally analogous segmented polymer.

1. Introduction

In the field of polymer electronics, poly(phenylenevinylene) (PPV) and poly(phenyleneacetylene) (PPA) systems have attracted considerable attention because of their remarkable optical and electronic properties. Due to their structural similarities and specially by using their structurally analogous oligomers, these two electronically conjugated systems have allowed making very interesting comparisons between their physicochemical properties, which has led to comparative studies of chemical stability [1] and studies on the formation of cyclic systems with applications in sensing and electronic transport [2–5]. Despite the very good structural stability shown by these cyclic systems, the tension of the ring caused by the twists in the vinyl bonds produce a detrimental in terms of electronic conjugation, especially in PPVs [6]. Although our research interest includes these two electronic systems, this work have been focused on phenylene vinylene derivatives since the presence of double bonds between the aromatic rings in PPVs instead of triple bonds in PPAs, allows us to continue the studies on the influence of the configuration (*cis* or *trans*, *syn* and *anti*) on the optoelectronic properties and its implication over the desired technologic application [7]. In 1970, Hörhold et al. [8] reported the optoelectronic properties of one of the first PPVs. Twenty years later, Burroughes et al. [9] demonstrated that PPVs can be used as the active element in organic light-emitting diodes (OLEDs). Since then, phenylenevinylene derivatives have been exploited in many applications ranging from materials science to biomedicine, with notable results in OLEDs [10–13], laser dyes [14], photovoltaic cells [15–17], chemosensors [18,19], linkers for metal organic frameworks (MOFs) [20,21], dendrimers [22,23], photoredox catalysts and photosensitizers [24,25].

Because, PPVs very often are difficult to synthesize and characterize (i.e. poor solubility, heterogeneous structural configuration) [26], oligo phenylenevinylenes (OPVs) have drawn interest as structural models for PPVs. The synthesis of OPVs is much easier; allowing to obtain a large number of well-defined chemical structures with better structural and optoelectronic characterization in a short time, information that can also be used as experimental data in theoretical studies to predict structure-property relationships. Additionally, OPVs act as model compounds to study their

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structural analogue PPVs, especially segmented polymers.

Although many routes have been reported for the synthesis of phenylenevinylene systems, such as Wittig [27–29], Gilch [30], Wessling [31] and Knoevenagel [32,33], these methodologies present some disadvantages like harsh experimental conditions, unwanted byproducts and often producing a mixture of *cis*- and *trans*-isomers. On the other hand, the Mizoroki-Heck reaction is one of the most powerful methods for the formation of C=C bonds under soft reaction conditions, with minimal structural limitations for precursors and yielding all-*trans* vinyl bonds with very few side reactions [34].

In recent years several studies have been reported on the structural and optoelectronic properties of numerous substituted OPVs, with the goal of determining structure-property relationships [34–37]. In order to contribute to the understanding of these technological attractive materials, here we report the synthesis by Mizoroki-Heck cross coupling reaction of a series of OPVs with different ED and EW substituents (Fig. 1) in addition to their structural and optical characterization. Although several of these compounds have been previously reported by other synthetic methodologies, in this contribution they were synthesized for the first time by the Heck reaction, which also made possible to obtain OPV **1h**, a novel compound difficult to synthesize by most commonly used methodologies mentioned above, such as the Wittig reaction. The study of the effects of ED and EW substituent groups on the properties of OPVs will provide insights about the structural features that a phenylenevinylene derivative must have to be valuable in a specific application.

2. Experimental section

2.1. Materials

Aldehydes (**3a-e**), styrene (**4f**), 4-acetoxystyrene (**4g**), 1,4-dimethoxybenzene (**5**), dihalobenzenes (**7a,b**), 4-substituted aryl halides (**8a-d**), methyltriphenylphosphonium bromide, potassium carbonate, bis(dibenzylidene acetone) palladium(0) [Pd(dba)$_2$], triphenylphosphite [P(OPh)$_3$], triethylamine (TEA) and solvents were purchased from Sigma–Aldrich, Alfa Aesar and Merck and were used without further purification. Dimethylformamide (DMF) was dried over anhydrous BaO and stored under nitrogen with molecular sieve until use. Reactions to get **1a-i** and **2a-g** compounds were carried out under nitrogen in tightly capped glass vials with teflon/silicone septum and aluminum caps.

2.2. Techniques

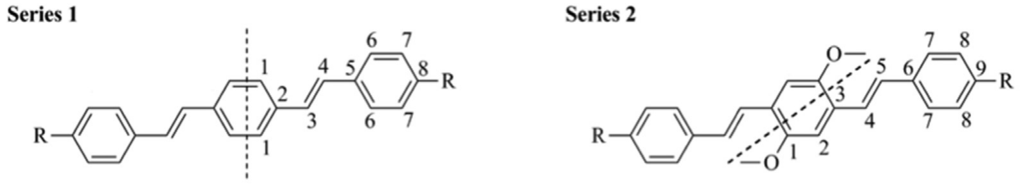
Melting points were determined on a digital melting point apparatus Stuart SMP10 and are uncorrected. FT-IR spectra were recorded on a Shimadzu IR Prestige-21 FT-IR spectrometer in the range of 4000-400 cm^{-1}. Samples were prepared in KBr discs and ATR technique was used for some of them. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded on a Bruker Avance spectrometer using CDCl$_3$ or DMSO-d_6 as solvents with tetramethylsilane (TMS) as internal standard, and KBr was used as filling for solid NMR analysis. Mass spectra were taken on a Bruker UltrafleXtreme™, MALDI-TOF/TOF mass spectrometer, equipped with a 355 nm solid-state Nd:YAG laser. For LDI measurements, 1 μL of a 2.5 mM stock solution of each compound was applied on the target surface and evaluated at 25% of laser fluence. Elemental analysis was performed on a FLASH 2000 elemental analyzer, using the Eager 300 for EA1112 software. UV–vis spectra were measured on a Thermo Scientific Evolution 300 spectrophotometer in DMF solutions. Fluorescence spectroscopy (FS) was performed on a PTI QuantaMaster™ 40 spectrofluorometer in DMF solutions. Fluorescence quantum yields (Φ_f) were determined at λ_{exc} corresponding to the absorption maximums. Quinine sulfate in 0.1 M H_2SO_4 ($\Phi_f = 0.54$) was used as standard for determination of fluorescence quantum yields (Φ_f) at λ_{exc} corresponding to the absorption maximum of series 1 and to the first absorption maximum of series 2 (λ_1). Perylene in ethanol ($\Phi_f = 0.92$) was used as standard for determination of the Φ_f at λ_{exc} corresponding to the second absorption maximum of series 2 (λ_2). The Φ_f of the nitro compound in series 1 (OPV **1b**) was calculated also using perylene as standard.

2.3. Synthesis of starting materials

4-Substituted styrenes (**4a-d**) and 1,4-divinylbenzene (**4e**) were prepared by the Wittig reaction (Scheme 1). The general procedure is as follows: A mixture of methyltriphenylphosphonium bromide (1.05 equivalents) and potassium carbonate (1.6 equivalents) was stirred in 50 mL of 1,4-dioxane under a nitrogen atmosphere at 25 °C for 4 h. The corresponding aldehyde (1 equivalent) previously dissolved in 1,4-dioxane was slowly added to the reaction mixture and allowed to react at 100 °C for 24 h. After cooling to room temperature, the mixture was filtered and the solvent evaporated. The products were purified as colorless oils by silica gel chromatography with hexane or mixtures of heptane:ethyl acetate as eluent. Once synthesized, the styrenes were used immediately to avoid polymerization.

2.3.1. 4-Methoxystyrene (4a)

Obtained as yellow oil with 53% yield from 4-methoxybenzaldehyde (**3a**, 1.8 mL, 14.90 mmol), methyltriphenylphosphonium bromide (5.590 g, 15.65 mmol) and potassium carbonate (3.296 g, 23.84 mmol). ^{1}H NMR (400 MHz, CDCl$_3$):



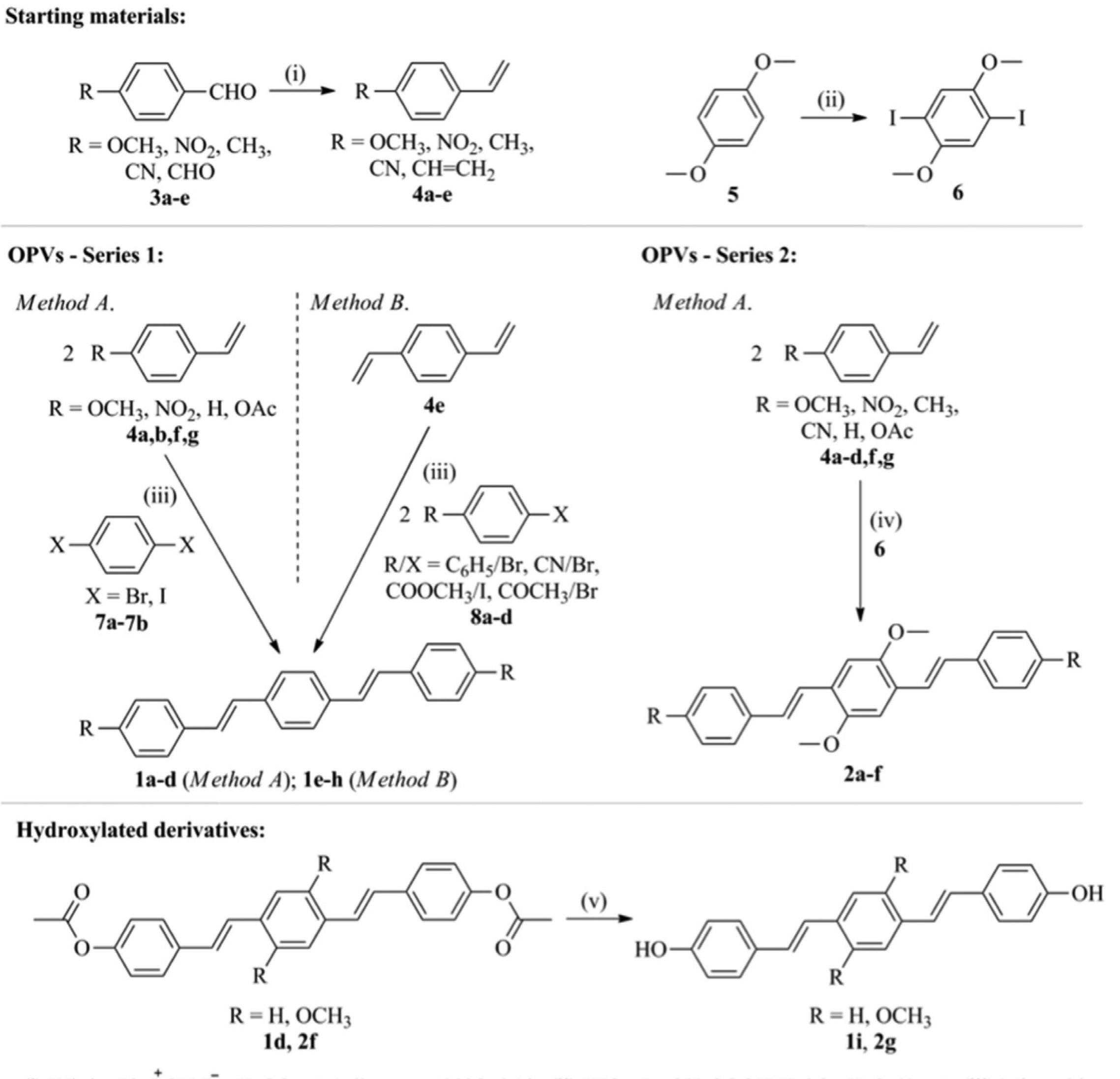
1a-i

2a-g

OPV	R	OPV	R	OPV	R
1a:	-OCH$_3$	**1d:**	-OCOCH$_3$	**1g:**	-COOCH$_3$
1b:	-NO$_2$	**1e:**	-C$_6$H$_5$	**1h:**	-COCH$_3$
1c:	-H	**1f:**	-CN	**1i:**	-OH

OPV	R	OPV	R	OPV	R
2a:	-OCH$_3$	**2d:**	-CN	**2g:**	-OH
2b:	-NO$_2$	**2e:**	-H		
2c:	-CH$_3$	**2f:**	-OCOCH$_3$		

Fig. 1. Chemical structure of the synthesized OPV systems (**1a-i** and **2a-g**).



(i) Wittig: $Ph_3\overset{+}{P}CH_3\overset{-}{Br}$, K_2CO_3, 1,4-dioxane, 100°C, 24 h. **(ii)** KIO_3, I_2, $CH_3COOH:H_2SO_4:H_2O$ 60:1:5. **(iii)** Mizoroki-Heck, Series 1: $Pd(dba)_2$, $P(OPh)_3$, Et_3N, dry DMF, 120°C, 48 h. **(iv)** Mizoroki-Heck, Series 2: $Pd(dba)_2$, $P(OPh)_3$, Et_3N, 1,4-dioxane, 100°C, 24 h. **(v)** Base-catalyzed hydrolysis: From "acetylated" derivatives, KOH, MeOH, 70°C, 3 h.

Scheme 1. Synthetic routes to OPVs **1a-i** and **2a-g**.

δ 3.80 (s, 3H, OCH_3), 5.12 (dd, 1H, H-1a, $J = 10$ Hz), 5.61 (dd, 1H, H-1b, $J = 17.6$ Hz), 6.65 (dd, 1H, H-2, $J_1 = 10{,}9$ Hz, $J_2 = 17.6$ Hz), 6.86 (d, 2H, H-5, $J = 8{,}8$ Hz), 7.34 (d, 2H, H-4, $J = 8{,}6$ Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.27, 111.56, 136.20, 130.40, 127.37, 113.88, 159.34 ppm.

2.3.2. 4-Nitrostyrene (*4b*)

Obtained as deep yellow oil with 89% yield from 4-nitrobenzaldehyde (**3b**, 2.026 g, 13.41 mmol), methyltriphenylphosphonium bromide (5.029 g, 14.08 mmol) and potassium carbonate (2.965 g, 21.45 mmol). ^1H NMR (400 MHz, $CDCl_3$): δ 5.52 (dd, 1H, H-1a), 5.95 (dd, 1H, H-1b), 6.78 (dd, 1H, H-2, $J_1 = 10{,}9$ Hz, $J_2 = 17.6$ Hz), 7.54 (d, 2H, H-4, $J = 8{,}7$ Hz), 8.19 (d, 2H, H-5, $J = 8{,}8$ Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 118.63, 134.97, 143.82, 123.96, 126.82, 147.15 ppm.

2.3.3. 4-Methylstyrene (*4c*)

Obtained as colorless oil with 33% yield from 4-tolualdehyde (**3c**, 2 mL, 16.92 mmol), methyltriphenylphosphonium bromine (6.347, 17.77 mmol) and potassium carbonate (3.742 g, 27.08 mmol). ^1H NMR (400 MHz, $CDCl_3$): δ 2.30 (s, 3H, CH_3), 5.18 (dd, 1H, H-1a, $J = 10.9$ Hz), 5.69 (dd, 1H, H-1b, $J = 17.6$ Hz), 6.69 (dd, 1H, H-2, $J_1 = 10{,}9$ Hz, $J_2 = 17.6$ Hz), 7.13 (d, 2H, H-5, $J = 7{,}9$ Hz), 7.31 (d, 2H, H-4, $J = 8{,}1$ Hz) ppm.

2.3.4. 4-Cyanostyrene (*4d*)

Obtained as colorless oil with 60% yield from 4-formylbenzonitrile (**3d**, 2.030 g, 15.48 mmol), methyltriphenylphosphonium bromine (5.808 g, 16.26 mmol) and potassium carbonate (3.424 g, 24.77 mmol). ^1H NMR (400 MHz, $CDCl_3$): δ 5.37 (dd, 1H, H-1a, $J = 10.9$ Hz), 5.80 (dd, 1H, H-1b, $J = 17.6$ Hz), 6.65 (dd, 1H, H-2, $J = 17.6$ Hz), 7.40 (d, 2H, H-4, $J = 8{,}3$ Hz), 7,53 (d, 2H, H-5, $J = 8{,}3$ Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 117.74, 135.36, 141.90, 126.75, 132.39, 111.12, 118.91 ppm.

2.3.5. 1,4-Divinylbenzene (*4e*)

Obtained as colorless oil with 70% yield from terephthalaldehyde (**3e**, 2.060 g, 15.36 mmol), methyltriphenylphosphonium bromide (11.25 g, 31.49 mmol) and potassium carbonate (5.52 g, 39.94 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.24 (dd, 2H, H-1a, J = 10.8 Hz), 5.75 (dd, 2H, H-1b, J = 17.6 Hz), 6.70 (dd, 2H, H-2, J = 17.6 Hz), 7.38 (s, 4H, H-4) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 113.74, 136.49, 137.14, 126.40 ppm.

*2.3.6. 1,4-Diiodo-2,5-dimethoxybenzene (**6**) was synthesized as follows*

1,4-dimethoxybenzene (**5**, 5.314 g, 38.46 mmol), iodine-resublimed crystals (11.715 g, 46.16 mmol) and potassium iodate (4.116 g, 19.23 mmol) were dissolved in 131 mL of CH_3COOH:H_2SO_4:H_2O (120:1:10). The reaction mixture was allowed to stir under reflux for 24 h to obtain a dark reddish solution. After this, 200 mL of a saturated solution of sodium sulfite was added inducing precipitation of the product. The pale yellow solid formed was filtered and washed with sodium sulfite, ethanol and chloroform to give a bright white powder (77% yield). m,p.: 173–175 °C; Lit 171–174 °C [38]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.76 (s, 6H, OCH_3), 7.12 (s, 2H, H-3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 67.85, 164.15, 96.21, 132.41 ppm.

*2.4. Synthesis of oligo(phenylene vinylene)s **1a-i** and **2a-g***

The OPV synthesis was done following two different pathways according to the Mizoroki-Heck reaction (Scheme 1). First; by the coupling between 4-substituted styrenes and dibromo or diiodobenzenes (Method A, Scheme 1), and second; the reaction between 4-substituted bromo or iodobenzenes with 1,4-divinylbenzene (Method B, Scheme 1).

The general procedure is as follows: 2.05 equivalents of the corresponding styrene and 1 equivalent of 1,4-dibromo or 1,4-diiodobenzene (Method A, to OPVs **1a-d** and **2a-f**) or 2.05 equivalents of the appropriate aryl halide and 1 equivalent of 1,4-divinylbenzene (Method B, to OPVs **1e-h**), were placed in a 10 mL headspace crimp vial equipped with a magnetic stir bar. Then, for both methods, it was added 0.01 equivalents (1 mol%) of $Pd(dba)_2$, 0.1 equivalents (10 mol%) of $P(OPh)_3$ and 5 equivalents of TEA. The vial was sealed with a PTFE/silicone septum with aluminum cap and purged-saturated with N_2, then 2 mL of solvent was injected (dry DMF for OPVs-series 1 and 1,4-dioxane for OPVs-series 2, Scheme 1) and the system was purged once again with N_2. The reaction mixture was vigorously stirred at 110 °C during 48 h for OPVs-series 1 and 24 h for OPVs-series 2. After finished, highly fluorescent solid products were obtained.

The hydroxylated OPVs **1i** and **2g** were obtained by a base-catalyzed hydrolysis (10 equivalents of KOH in methanol) from 1 equivalent of acetylated derivatives **1d** and **2f.** As work-up, the reaction mixture from each hydrolysis was dropwise added over HCl 2 M to induce precipitation of the products.

The OPVs purification was performed according to their solubility. OPVs-series 1, which had greater difficulties to dissolve in most common organic solvents, were washed with chloroform and ethanol. Additionally, compounds **1c**, **1f** and **1h** were recrystallizated from chloroform and OPVs **1a**, **1b** and **1d** from DMF. The OPVs-series 2 were precipitated from their reaction mixture with ethanol or water, the solids were filtered and dissolved in chloroform and they were passed through celite to finally get fluorescent solids after concentration by rotary evaporation.

*2.4.1. 1,4-Bis[(E)-2-(4-methoxyphenyl)ethenyl]benzene (**1a**)*

Obtained as a light green powder with 65% yield from 4-methoxystyrene (**4a**, 0.8 mL, 5.98 mmol) and 1,4-dibromobenzene (**7a**, 0.688 g, 2.92 mmol). m.p.: 296–300 °C; Lit. 310–311 °C [39]. FT-IR (KBr): $\bar{\upsilon}$ 3019 (=C–H), 2955, 2837 (CH_3), 1603, 1573, 1515, 1465 (C=C), 1252, 1029 (C–O–C), 969 (HC=CH *trans*), 835 cm^{-1}(*para*-substitution). ^{13}C Solid-State NMR (Solid + KBr): δ 130.64 (C-1 and C-6), 135.89 (C-2), 117.69 (C-3), 110.27 (C-4), 159.27 (C-5), 127.42 (C-7), 123.76 (C-8), 54.59 (OCH_3) ppm. MALDI-MS: Calc. for $C_{24}H_{22}O_2$: 342.16; found: 342.16. Anal. Calc. For $C_{24}H_{22}O_2$: C, 84.18; H, 6.48; O, 9.34. Found: C, 83.24; H, 6.49; O, 10.24.

*2.4.2. 1,4-Bis[(E)-2-(4-nitrophenyl)ethenyl]benzene (**1b**)*

Obtained as an orange powder with 59% yield from 4-nitrostyrene (**4b**, 0.821 g, 5.50 mmol) and 1,4-dibromobenzene (**7a**, 0.633 g, 2.68 mmol). m.p.: 292–294 °C; Lit. 288–290 °C [27]. FT-IR (ATR): $\bar{\upsilon}$ 2922 (=C–H), 1631, 1589 (C=C Ar), 1508, 1335 (NO_2), 960 (HC=CH *trans*), 847 cm^{-1}(*para*-substitution). ^{13}C Solid-State NMR (Solid + KBr): δ 130.33 (C-1 and C-6), 134.90 (C-2), 124.72 (C-3 and C-4), 143.72 (C-5), 122.62 (C-7), 145.83 (C-8) ppm. MALDI-MS: Calc. for $C_{22}H_{16}N_2O_4$: 372.11; found: 372.15. Anal. Calc. For $C_{22}H_{16}N_2O_4$: C, 70.96; H, 4.33; N, 7.52; O, 17.19. Found: C, 69.65; H, 4.61; N, 7.25; O, 17.49.

*2.4.3. 1,4-Bis[(E)-2-phenylethenyl]benzene (**1c**)*

Obtained as a light green solid with 85% yield from styrene (**4f**, 0.8 mL, 7.23 mmol) and 1,4-dibromobenzene (**7a**, 0.835 g, 3.54 mmol). m.p.: 254–258 °C; Lit. 254 °C [36]. FT-IR (KBr): $\bar{\upsilon}$ 3024 (=C–H), 1595, 1561, 1510, 1484, 1446 (C=C), 968 (HC=CH *trans*), 814 (*para*-substitution), 690 cm^{-1}(mono-substitution). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (d, 4H, H-3 and H-4), 7.53 (d, 8H, H-1 and H-6 overlap), 7.37 (t, 4H, H-7), 7.26 (t, H-8) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 126.85 (C-1), 136.71 (C-2), 128.59 (C-3), 128.27 (C-4), 137.33 (C-5), 126.52 (C-6), 128.71 (C-7), 127.65 (C-8) ppm. MALDI-MS: Calc. for $C_{22}H_{18}$: 282,141; found: 282,148. Anal. Calc. For $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 92.17; H, 6.28.

*2.4.4. 1,4-Bis[(E)-2-(4-acethoxyphenyl)ethenyl]benzene (**1d**)*

Obtained as a light green powder with 71% yield from 4-acetoxystyrene (**4g**, 0.79 mL, 5.14 mmol) and 1,4-diiodobenzene (**7b**, 0.828 g, 2.51 mmol). m.p.: 300–302 °C; Lit. 298–302 °C [40]. FT-IR (ATR): $\bar{\upsilon}$ 3026 (=C–H), 2931 (CH_3), 1757 (C=O), 1670, 1514, 1502 (C=C Ar), 1209, 1165 (C–O–C), 968 (HC=CH *trans*), 844 cm^{-1}(*para*-substitution). ^{13}C Solid-State NMR (Solid + KBr): δ 134.52 (C-1), 131.42 (C-2), 127.07 (C-3 and C-4), 130.53 (C-5), 123.75 (C-6), 121.91 (C-7), 149.67 (C-8), 18.80 (CH_3), 169.86 (C=O) ppm. MALDI-MS: Calc. for $C_{26}H_{22}O_4$: 398.15; found: 398.22. Anal. Calc. For $C_{26}H_{22}O_4$: C, 78.37; H, 5.57; O, 16.06. Found: C, 76.27; H, 5.37; O, 15.59.

*2.4.5. 1,4-Bis[(E)-2-(4-biphenyl)ethenyl]benzene (**1e**)*

Obtained as a green bright powder with 54% yield from 4-bromobiphenyl (**8a**, 1.099 g, 4.71 mmol) and 1,4-divinylbenzene (**4e**, 0.299 g, 2.30 mmol). m.p.: >300 °C; Lit. > 320 °C [41]. FT-IR (KBr): $\bar{\upsilon}$ 3021 (=C–H), 1601, 1579, 1560, 1508 (C=C), 971 (HC=CH *trans*), 839 (*para*-substitution), 718 cm^{-1}(mono-substitution). ^{13}C Solid-State NMR (Solid + KBr): δ 135.05 (C-1, C-2, C-5, C-8, C*i*, C*m*), 125.67 (C-3, C-4, C-6, C-7, C*o*, C*p*) ppm. MALDI-MS: Calc. for $C_{34}H_{26}$: 434.20; found: 434.18. Anal. Calc. For $C_{34}H_{26}$: C, 93.97; H, 6.03. Found: C, 91.66; H, 6.38.

*2.4.6. 1,4-Bis[(E)-2-(4-cyanophenyl)ethenyl]benzene (**1f**)*

Obtained as a yellow powder with 90% yield from 4-bromobenzonitrile (**8b**, 1.123 g, 6.16 mmol) and 1,4-divinylbenzene (**4e**, 0.392 g, 3.01 mmol). m.p.: 274–276 °C; Lit. 279–281 °C [42]. FT-IR (KBr): $\bar{\upsilon}$ 3026 (=C–H), 2216 (C≡N), 1630, 1596, 1499 (C=C), 958 (HC=CH *trans*), 830 cm^{-1}(*para*-substitution). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (s, 4H, H-1), 7.13 (d, J_{trans} = 16.3 Hz, 2H, H-3), 7.22 (d, J_{trans} = 16.3 Hz, 2H, H-4), 7.60 (d, 4H, H-6), 7.65 (d, 4H, H-7) ppm. ^{13}C NMR (100 MHz, $CDCl_3$):

δ 126.92 (C-1), 110.78 (C-2), 127.19 (C-3), 131.67 (C-4), 136.60 (C-5), 127.41 (C-6), 132.55 (C-7), 141.65 (C-8), 118.99 (CN) ppm. MALDI-MS: Calc. for $C_{24}H_{16}N_2$: 332.131; found: 332.145. Anal. Calc. For $C_{24}H_{16}N_2$: C, 86.72; H, 4.85; N, 8.43. Found: C, 85.30; H, 4.87; N, 8.42.

*2.4.7. 1,4-Bis[(E)-2-(4-methoxycarbonylphenyl)ethenyl]benzene (**1g**)*

Obtained as a light green powder with 71% yield from methyl 4-iodobenzoate (**8c**, 1.348 g, 5.14 mmol) and 1,4-divinylbenzene (**4e**, 0.327 g, 2.51 mmol). m.p.: >300 °C; Lit. > 321 °C [43]. FT-IR (KBr): ῡ 3019 (=C–H), 2954 (CH_3), 1721 (C=O), 1679, 1646, 1607, 1566 (C=C Ar), 1282, 1108 (C–O–C), 962 (HC=CH *trans*), 813 cm^{-1}(*para*-substitution). ^{13}C Solid-State NMR (Solid + KBr): δ 130.06 (C-1 and C-6), 134.90 (C-2), 122.52 (C-3 and C-4), 137.63 (C-5), 128.20 (C-7), 128.68 (C-8), 53.37 (OCH_3), 164.77 (C=O) ppm. MALDI-MS: Calc. for $C_{26}H_{22}O_4$: 398.152; found: 398.149. Anal. Calc. For $C_{26}H_{22}O_4$: C, 78.37; H, 5.57; O, 16.06. Found: C, 76.97; H, 5.53; O, 16.27.

*2.4.8. 1,4-Bis[(E)-2-(4-acetylphenyl)ethenyl]benzene (**1h**)*

Obtained as a pale yellow powder with 58% yield from 4-bromoacetophenone (**8d**, 1.113 g, 5.59 mmol) and 1,4-divinylbenzene (**4e**, 0.355 g, 2.73 mmol). m.p.: 296–298 °C. FT-IR (KBr): ῡ 3022 (=C–H), 1672 (C=O), 1609, 1551, 1514 (C=C), 964 (HC=CH *trans*), 837 cm^{-1}(*para*-substitution). ^{13}C Solid-State NMR (Solid + KBr): δ 127.44 (C-1 and C-6), 134.77 (C-2), 123.93 (C-3 and C-4), 136.33 (C-5), 129.60 (C-7), 137.17 (C-8), 25.18 (CH_3), 197.38 (C=O) ppm. MALDI-MS: Calc. for $C_{26}H_{22}O_2$: 366.162; found: 366.211. Anal. Calc. For $C_{26}H_{22}O_2$: C, 85.22; H, 6.05; O, 8.73. Found: C, 84.34; H, 6.02; O, 8.67.

*2.4.9. 1,4-Bis[(E)-2-(4-hydroxyphenyl)ethenyl]benzene (**1i**)*

Obtained as a green powder with 85% yield from **1d** (0.3 g, 0.75 mmol) and KOH (0.422 g, 7.53 mmol) in MeOH (3 mL). m.p.: >300 °C; Lit. 300 °C [44]. FT-IR (ATR): ῡ 3308 (O–H), 3020 (=C–H), 1603, 1591, 1502, 1452 (C=C Ar), 1385 (C–O), 1250 (C–O), 964 (HC=CH *trans*), 833 cm^{-1}(*para*-substitution). ^1H NMR (400 MHz, DMSO-d_6): δ 7.52 (s, 4H, H-1), 7.15 (d, J_{trans} = 16.4 Hz, 2H, H-3), 7.01 (d, J_{trans} = 16.4 Hz, 2H, H-4), 7.43 (d, J_{ortho} = 8.59 Hz, 4H, H-6), 6.78 (d, J_{ortho} = 8.5 Hz, 4H, H-7) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 126.82 (C-1), 136.81 (C-2), 128.57 (C-3), 125.38 (C-4), 157.77 (C-5), 128.28 (C-6), 116.07 (C-7), 128.73 (C-8) ppm. MALDI-MS: Calc. for $C_{22}H_{18}O_2$: 314.131; found: 314.133. Anal. Calc. For $C_{22}H_{18}O_2$: C, 84.05; H, 5.77; O, 10.18. Found: C, 80.18; H, 5.80; O, 12.02.

*2.4.10. 1,4-Bis[(E)-2-(4-dimethoxyphenyl)ethenyl]-2,5-dimethoxybenzene (**2a**)*

Obtained as a yellow powder with 40% yield from 4-methoxystyrene (**4a**, 0.67 mL, 5.09 mmol) and 1,4-diiodo-2,5-dimethoxybenzene (**6**, 0.969 g, 2.48 mmol). m.p. 212–214 °C; Lit. 209–210 °C [45]. FT-IR (ATR): ῡ 3059 (=C–H Ar), 2908, 2833 (CH_3), 1600, 1573, 1510, 1464 (C=C Ar), 1249, 1043, 1030 (C–O–C), 966 (HC=CH *trans*), 821 cm^{-1}(*para*-substitution). ^1H NMR (400 MHz, $CDCl_3$): δ 3.92 (s, 6H, CH_3–O, terminal rings), 3.83 (s, 6H, CH_3–O, central ring), 7.11 (s, 2H, H-2), 7.35 (d, J_{trans} = 16.4 Hz, 2H, H-4), 7.06 (d, J_{trans} = 16.4 Hz, 2H, H-5), 7.49 (d, J_{ortho} = 8.7 Hz, 4H, H-7), 6.90 (d, J_{ortho} = 8.7 Hz, 4H, H-8) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.40 (CH_3–O, terminal rings), 55.33 (CH_3–O, central ring), 151.38 (C-1), 108.97 (C-2), 126.55 (C-3), 121.18 (C-4), 128.33 (C-5), 130.75 (C-6), 127.78 (C-7), 114.10 (C-8), 159.21 (C-9) ppm. MALDI-MS: Calc. for $C_{26}H_{26}O_4$: 402.183; found: 403.23. Anal. Calc. For $C_{26}H_{26}O_4$: C, 77.59; H, 6.51; O, 15.90. Found: C, 75.62; H, 6.38; O, 16.01.

*2.4.11. 2,5-Dimethoxy-1,4-bis[(E)-2-(4-nitrophenyl)ethenyl] benzene (**2b**)*

Obtained as a red powder with 95% yield from 4-nitrostyrene (**4b**, 0.707 g, 4.74 mmol) and 1,4-diiodo-2,5-dimethoxybenzene (**6**, 0.902 g, 2.31 mmol). m.p. 272–274 °C; Lit. 274–278 °C [45]. FT-IR (ATR): ῡ 3067 (=C–H Ar), 2924, 2839 (CH_3), 1587, 1466 (C=C Ar), 1512, 1333 (NO_2), 1211 (C–O–C), 964 (HC=CH *trans*), 827 cm^{-1}(*para*-substitution). ^1H NMR (400 MHz, DMSO-d_6): δ 3.50 (s, 6H, CH_3–O), 7.00 (s, 2H, H-2), 7.11 (d, J_{trans} = 16.5 Hz, 2H, H-4), 7.23 (d, J_{trans} = 16.5 Hz, 2H, H-5), 7.41 (d, J_{ortho} = 8.9 Hz, 4H, H-7), 7.80 (d, J_{ortho} = 8.9 Hz, 4H, H-8) ppm. ^{13}C Solid-State NMR (Solid + KBr): δ 143.06 (C-1), 104.80 (C-2), 123.71 (C-3 and C-7), 120.72 (C-4), 129.25 (C-5), 145.78 (C-6), 126.18 (C-8), 151.24 (C-9), 52.93 (CH_3O) ppm. MALDI-MS: Calc. for $C_{24}H_{20}N_2O_6$: 432.132; found: 432.157. Anal. Calc. For $C_{24}H_{20}N_2O_6$: C, 66.66; H, 4.66; O, 22.20; N, 6.48. Found: C, 64.10; H, 4.87; O, 22.87; N, 6.16.

*2.4.12. 2,5-Dimethoxy-1,4-bis[(E)-2-(4-methylphenyl)ethenyl] benzene (**2c**)*

Obtained as a yellow powder with 53% yield from 4-methylstyrene (**4c**, 0.654 g, 5.53 mmol) and 1,4-diiodo-2,5-dimethoxybenzene (**6**, 1.052 g, 2.70 mmol). m.p. 183–185 °C; Lit. 176–178 °C [45]. FT-IR (ATR): ῡ 3049 (=C–H Ar), 2912, 2829 (CH_3), 1514, 1493, 1460 (C=C Ar), 1259, 1047 (C–O–C), 962 (HC=CH *trans*), 846 cm^{-1} (*para*-substitution). ^1H NMR (400 MHz, $CDCl_3$): δ 2.29 (s, 6H, CH_3), 3.85 (s, 6H, CH_3–O), 7.05 (s, 2H, H-2), 7.37 (m, 6H, H-4, H-7), 7.02 (d, J_{trans} = 16.5 Hz, 2H, H-5), 7.09 (d, J_{ortho} = 7.9 Hz, 4H, H-8) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.26 (CH_3), 56.41 (CH_3–O), 137.33 (C-1), 109.12 (C-2), 126.62 (C-3), 122.24 (C-4), 128.81 (C-5), 135.10 (C-6), 129.35 (C-7), 126.51 (C-8), 151.49 (C-9) ppm. MALDI-MS: Calc. for $C_{26}H_{26}O_2$: 370.193; found: 370.196. Anal. Calc. For $C_{26}H_{26}O_2$: C, 84.29; H, 7.07; O, 8.64. Found: C, 83.42; H, 7.13; O, 8.45.

*2.4.13. 1,4-Bis[(E)-2-(4-cyanophenyl)ethenyl]-2,5-dimethoxybenzene (**2d**)*

Obtained as a yellow powder with 75% yield from 4-cyanostyrene (**4d**, 0.67 mL, 5.22 mmol) and 1,4-diiodo-2,5-dimethoxybenzene (**6**, 0.993 g, 2.55 mmol). m.p. 284–286 °C; Lit. 297 °C [46]. FT-IR (ATR): ῡ 3055 (=C–H Ar), 2993, 2835 (CH_3), 2220 (C≡N), 1597, 1493, 1465 (C=C Ar), 1209 (C–O–C), 956 (HC=CH *trans*), 815 cm^{-1} (*para*-substitution). ^1H NMR (400 MHz, $CDCl_3$): δ 3.95 (s, 6H, CH_3–O), 7.13 (s, 2H, H-2 overlap), 7.13 (d, 2H, H-4 overlap), 7.59 (d, J_{trans} = 16.4 Hz, 2H, H-5), 7.63 (d, 8H, H-7, H-8) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.26 (CH_3–O), 110.49 (C-1), 109.29 (C-2), 126.49 (C-3), 126.81 (C-4), 127.47 (C-5), 142.22 (C-6), 126.96 (C-7), 132.48 (C-8), 151.81 (C-9), 119.10 (CN) ppm. MALDI-MS: Calc. for $C_{26}H_{20}N_2O_2$: 392.152; found: 392.169. Anal. Calc. For $C_{26}H_{20}N_2O_2$: C, 79.57; H, 5.14; O, 8.15; N, 7.14. Found: C, 78.27; H, 5.23; O, 8.29; N, 7.21.

*2.4.14. 2,5-Dimethoxy-1,4-bis[(E)-2-phenylethenyl]benzene (**2e**)*

Obtained as a yellow powder with 45% yield from styrene (**4f**, 0.69 mL, 5.98 mmol) and 1,4-diiodo-2,5-dimethoxybenzene (**6**, 1.139 g, 2.92 mmol). m.p.: 178–180 °C; Lit. 177–178 °C [45]. FT-IR (ATR): ῡ 3057 (=C–H), 2933, 2827 (CH_3), 1595, 1498, 1460 (C=C Ar), 1259, 1047 (C–O–C), 960 (HC=CH *trans*), 750 cm^{-1} (mono-substitution). ^1H NMR (400 MHz, $CDCl_3$): δ 3.86 (s, 6H, CH_3–O), 7.07 (s, 2H, H-2 overlap), 7.42 (d, J_{trans} = 16.5 Hz, 2H, H-4), 7.05 (d, J_{trans} = 16.3 Hz, 2H, H-5 overlap), 7.49 (d, J_{ortho} = 7.3 Hz, 4H, H-7), 7.29 (t, 4H, H-8), 7.18 (t, 2H, H-9) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.39 (CH_3–O), 151.54 (C-1), 109.18 (C-2), 123.24 (C-3), 127.49 (C-4, C-5), 137.84 (C-6), 128.64 (C-7), 126.60 (C-8), 128.97 (C-9) ppm. MALDI-MS: Calc. for $C_{24}H_{22}O_2$: 342.162; found: 342.211. Anal. Calc. For $C_{24}H_{22}O_2$: C, 84.18; H, 6.48; O, 9.34. Found: C, 82.46; H, 6.53; O, 9.51.

2.4.15. 1,4-Bis[(E)-2-(4-acetoxyphenyl)ethenyl]-2,5-dimethoxybenzene (**2f**)

Obtained as a yellow powder with 58% yield from 4-acetoxystyrene (**4g**, 0.68 mL, 4.47 mmol) and 1,4-diiodo-2,5-dimethoxybenzene (**6**, 0.850 g, 2.18 mmol). m.p. 220–222 °C; Lit. 231 °C [47]. FT-IR (ATR): ū 3004 (=C–H Ar), 2932 (CH_3), 1754 (C=O), 1617, 1504 (C=C Ar), 1214 (C–O–C methoxy), 1197 (C–O–C ester), 969 (HC=CH *trans*), 828 (*para*-substitution) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.31 (s, 6H, CH_3–C=O), 3.92 (s, 6H, CH_3–O), 7.10 (m, 8H, H-2, H-5, H-8), 7.43 (d, $J_{trans} = 16.5$ Hz, 2H, H-4), 7.55 (d, $J_{ortho} = 8.5$ Hz, 4H, H-7) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.18 (CH_3C=O), 56.37 (CH_3–O), 169.50 (C=O), 149.97 (C-1), 109.15 (C-2), 126.52 (C-3), 127.95 (C-4), 123.40 (C-5), 135.67 (C-6), 127.49 (C-7), 121.74 (C-8), 151.53 (C-9) ppm. MALDI-MS: Calc. for $C_{28}H_{26}O_6$: 458.173; found: 458.226. Anal. Calc. For $C_{28}H_{26}O_6$: C, 73.35; H, 5.72; O, 20.94. Found: C, 72.20; H, 5.67; O, 20.32.

2.4.16. 1,4-Bis[(E)-2-(4-hydroxyphenyl)ethenyl]-2,5-dimethoxybenzene (**2g**)

Obtained as a yellow powder with 80% yield from **2f** (0.5 g, 1.09 mmol), KOH (0.617 g, 10.99 mmol) and MeOH (5 mL). m.p.: 294–296 °C; Lit. 302 °C [47]. FT-IR (ATR): ū 3363 (O–H), 3000 (=C–H), 1604, 1585, 1514, 1494 (C=C Ar), 1354 (C–OH), 1259 (C–OH), 1024 (C–O–C), 958 (HC=CH *trans*), 821 cm^{-1}(*para*-substitution). ^1H NMR (400 MHz, DMSO-d_6): δ 3.88 (s, 6H, CH_3–O), 7.20 (s, 2H, H-2), 7.22 (d, 4H, H-4 and H-5), 7.40 (d, $J_{ortho} = 8.5$ Hz, 4H, H-7), 6.78 (d, $J_{ortho} = 8.5$ Hz, 4H, H-8), 9.59 (s, 2H, OH) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 56.60 (CH_3–O), 151.18 (C-1), 109.18 (C-2), 66.82 (C-3), 129.12 (C-4), 119.78 (C-5), 128.19 (C-6), 129.09 (C-7), 116.09 (C-8), 157.70 (C-9) ppm. MALDI-MS: Calc. for $C_{24}H_{22}O_4$: 374.152; found: 374.183. Anal. Calc. For $C_{24}H_{22}O_4$: C, 76.99; H, 5.92; O, 17.09. Found: C, 72.41; H, 5.81; O, 18.78.

3. Results and discussion

3.1. Synthesis and characterization of oligomer structure

Because 4-substituited styrenes are not readily available due to their tendency to polymerize during purification, transport or storage, they were synthesized by the Wittig reaction and once obtained they were used immediately in the Mizoroki-Heck reaction. As shown in Scheme 1, two different paths can be used to accomplish the reaction. In the first case (method A) an excess of 4-substituted styrene was used, while in the second case (method B) the excess was for the 4-halobenzene. In both cases, the excess of terminal rings precursors was given to try to ensure that di-coupling products were preferentially obtained and not those of a single coupling.

In this work, we used a modification of the classic Mizoroki-Heck methodology using triphenylphosphite [$P(OPh)_3$] instead of triphenylphosphine (PPh_3), which has been proved previously to be more efficient [48]. In general, the sixteen oligomers were obtained with high to moderate yields with a stereoselectivity towards compounds with totally *trans-trans* configuration. The high stereoselectivity during the formation of the vinyl bonds in the products was confirmed by FT-IR (presence of bands between 980 and 958 cm^{-1}, corresponding to *trans*-HC=CH vibrations and absence of bands from 730 to 665 cm^{-1}, corresponding to *cis*-HC=CH vibrations) and by ^1H NMR; the proton-proton coupling constants "*J*" in vinyl bonds was found between 12 and 18 Hz, which is typical for bonds in *trans* configuration.

To emphasize the importance of the pure *trans*-configuration in the vinyl bonds of OPV systems for some specific applications, it has been reported that compounds with *trans*-configuration adopts a more-planar conformation, which is beneficial for the electronic conjugation and promotes the improvement of the photoluminescence intensity [49]. On the other hand, *cis*-conformation leads to structural torsions which decrease the electron cloud density on the olefinic segments leading to small blue shifts in the absorption spectrum, affecting the molar absorption coefficients, and fluorescence properties compared with the *trans*-conformation [50].

As it was mentioned above, most of the compounds synthesized here have already been reported in the literature, mainly by Wittig and Horner-Wadsworth-Emmons (HWE) reactions, which produce mixtures of *cis-cis* and *cis-trans* OPV isomers. However, the implementation of additional procedures could be necessary in order to obtain the *trans* product, if this configuration is required. Some examples are the modification of the original Wittig reaction [28], the isomerization reaction using hot iodine solution [39], photoisomerization [51] or the use of additional steps to separate the isomers [36]. However, the extra steps reduce the yield of the final product, increase the probability of impurities and increase costs of the process.

Besides the advantage of yielding products with pure *trans*-configuration, the methodology used allows to synthesize the novel OPV **1h** (R = $-COCH_3$) from the corresponding ketone derivative (4-bromoacetophenone) and 1,4-divinylbenzene. Which by other methodologies, like the Wittig reaction (using the proper precursors) may generate several products by a competing reactions or the need of extra synthetic steps like protection-deprotection of carbonyls. As drawback, it was found that series 1 compounds have very limited solubility in most common solvents, making very difficult the purification and characterization processes and also the optoelectronics measurements that require the preparation of solutions with well-established concentrations.

3.2. Optoelectronic properties of oligomers

In order to characterize the effect of electron-donating (ED) and electron-withdrawing (EW) groups on the photophysical properties, the synthesized OPVs were studied by UV–vis and FS techniques. Fig. 2 shows the normalized absorption and emission spectra of OPVs **1a-i** (Fig. 2, left) and **2a-g** (Fig. 2, right) in DMF (1×10^{-5} M), ordered by their increase in the bathochromic shift. The UV–vis absorption (λ_{abs}), molar attenuation coefficient (ε), HOMO-LUMO gap (ΔE), photoluminescence emission (λ_{em}) and fluorescence quantum yields (Φ_f) are summarized in Table 1.

Despite the poor solubility of series 1 compounds, efforts were made in order to obtain the required concentration for optoelectronic analysis, and it was made applying ultrasonic and heating techniques. The HOMO-LUMO gaps (ΔE) were determined from the analysis of the absorption edge according to the equation $\sigma \cdot h\nu = A \cdot (h\nu - \Delta E)^{1/2}$, where σ is the absorption coefficient, h is the Planck constant, ν is the frequency of light and A is the absorbance. By drawing the $(h\nu A)^2$ vs $h\nu$ curves and extending the linearity edge of absorbance to the intersect with the energy axis, the ΔE value is obtained [52,53]. The fluorescence quantum yields (Φ_f) were calculated according to a method described in the literature [54], using the following equation:

$$\Phi_{f(OPV)} = \Phi_{f(ST)} \frac{f_{(ST)}}{f_{(OPV)}} \frac{F_{(OPV)}}{F_{(ST)}} \left(\frac{\eta_{(OPV)}}{\eta_{(ST)}} \right)^2$$

where $\Phi_{f(OPV)}$ and $\Phi_{f(ST)}$ are the fluorescence quantum yield of the sample and of standard, respectively (the subscript f describe fluorescence). $f_{(OPV)}$ and $f_{(ST)}$ are the absorption factors, the fraction

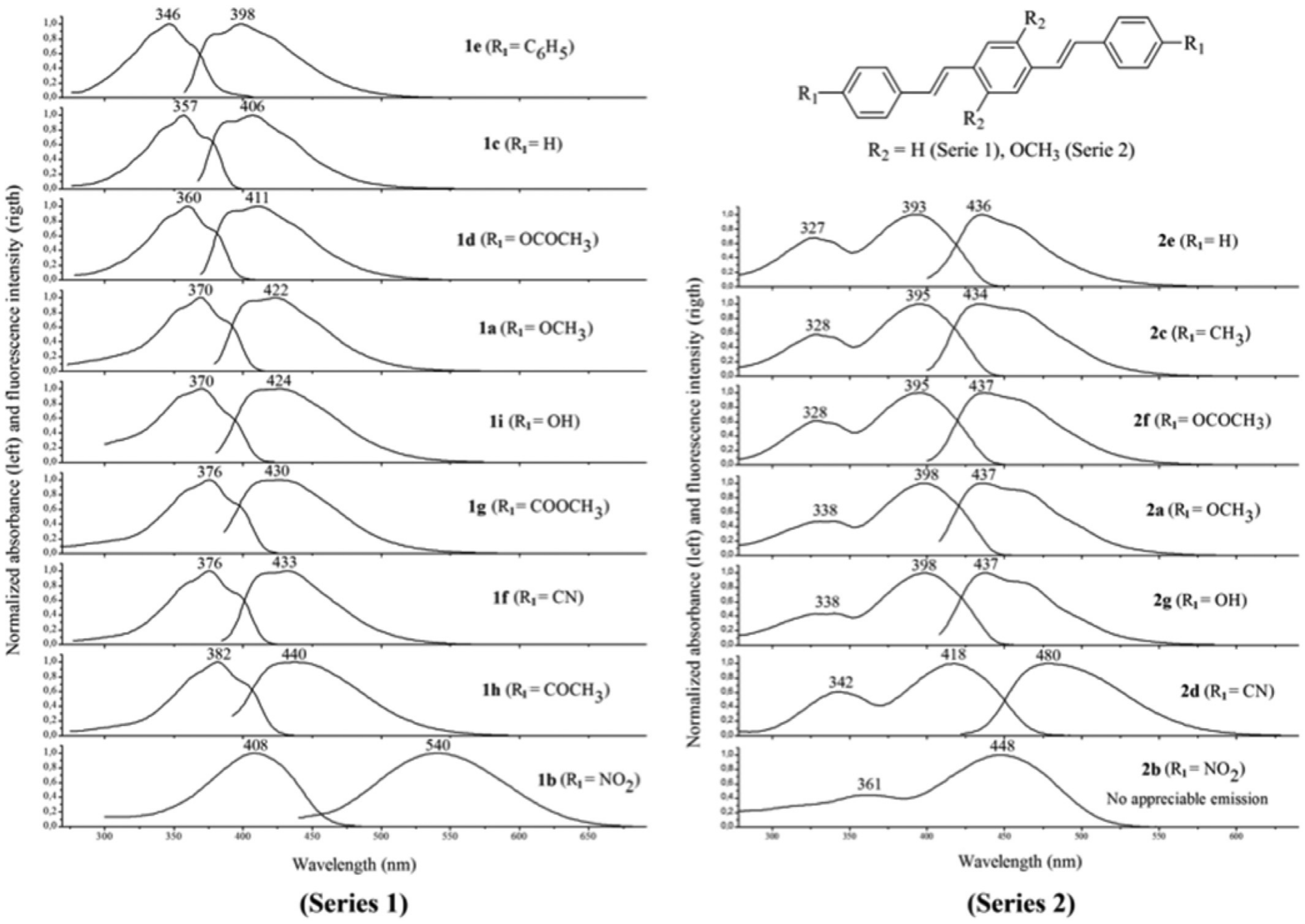


Fig. 2. Normalized absorption and emission spectra of the OPVs **1a-i** (series 1) and **2a-g** (series 2) in DMF, ordered by their bathochromic effect.

of the light impinging on the sample that is absorbed: $f_{(OPV)} = 1{-}10^{-A(OPV)}$ and $f_{(ST)} = 1{-}10^{-A(ST)}$. $F_{(OPV)}$ y $F_{(ST)}$ are the integrated intensities (areas under the emission curve) of sample and standard spectra, respectively. $\eta_{(OPV)}$ y $\eta_{(ST)}$ are the refractive indices of the solvent used in the sample and reference solutions, respectively.

The absorption spectra in series 1 and 2 (Fig. 2) showed that both ED and EW groups at the two ends of the OPV structure leads to a bathochromic shift compared with the OPV with hydrogen atoms in that positions (OPVs **1c** and **2e**). Similar effect is observed in the emission spectra. This trend is observed for most of the substituents, except for the compound **1e** (R = $-C_6H_5$), where the phenyl group caused a hypsochromic effect, might be due to the extended electronic conjugation of the biphenyl system.

Disregarding the exception presented by compound **1e**, the ED and EW groups generally have a red shift that is more intensified with EW groups. The same behavior has been reported in similar studies of OPVs with ED and/or EW substituents on terminal rings [35–37]. It has been shown that the trend depends on the ED or EW strength of the substituents. In this work, it was observed that the ED groups studied have a moderate effect on the bathochromic shift and this shift increases with the increase of electron donating strength of the substituent in the order $-OCOCH_3 < -OCH_3 < -OH$ for series 1, and $-CH_3 < -OCOCH_3 < -OCH_3 < -OH$ for series 2. On the other hand, the bathochromic effect is intensified by the presence of the EW groups, and the trend also is related with the EW strength of the substituents with the order $-COOCH_3 < -CN < -COCH_3 < -NO_2$ for series 1, and $-CN < -NO_2$ for series 2.

In series 1, the OPV **1d**, substituted with acetoxy groups (R = $-OCOCH_3$) is a constitutional isomer of **1g** (R = $-COOCH_3$). The direct interaction between the oxygen and the benzene ring over **1d** produce a small red shift effect (3 nm in UV–vis and 5 nm in FS with respect to unsubstituted OPV **1c**), which become much greater by changing the oxygen by carbonyl group on OPV **1g** (19 nm in UV–vis and 24 nm in FS with respect to unsubstituted OPV **1c**), suggesting that EW substituents have a greater bathochromic effect than ED substituents. This also is corroborated for series 2; the presence of the acetoxy group on OPV **2f** produce a slight bathochromic shift compared to the reference compound **2e**.

The ED groups over OPVs of series 1 have similar effects. The OPVs **1a** (R = $-OCH_3$) and **1i** (R = $-OH$), have both the same shift of 13 nm in UV–vis and shifts of 16 and 18 nm in FS, respectively. The bathochromic effect produce by EW groups in OPV systems is very similar for the compounds **1g** (R = $-COOCH_3$) and **1f** (R = $-CN$), both with a shift of 19 nm in UV–vis and of 24 and 27 nm in FS, respectively.

For OPV **1h** (R = $-COCH_3$) it was found that the ketone substituent presents one of the largest bathochromic shifts (25 nm in UV–vis and 34 nm in FS), due possibly to the formation of a larger electronic conjugation favored by the inductive effect over the benzene by the carbonyl group directly attached to it. This also could explain the largest bathochromic effect in the series 1 given by the nitro group in OPV **1b** (R = $-NO_2$) with a red shift of 51 nm in

Table 1
Photophysical data for OPVs **1a-i** and **2a-g** in DMF (1×10^{-5} M).

OPV	λ_{abs} (nm)	ε ($Lmol^{-1}cm^{-1}$)	ΔE (eV)	λ_{em} (nm)	Φ_f[a]
1a	355 (sh)	–	3.08	404 (sh)	–
R = OCH_3	370 (max)	51,800		422 (max)	0.66
	387 (sh)	–			–
1b	408 (max)	58,800	2.75	540 (max)	0.06[b]
R = NO_2)					
1c	343 (sh)	–	3.20	388 (sh)	–
R = H	357 (max)	62,000		406 (max)	0.86
	375 (sh)	–			–
1d	346 (sh)	–	3.17	392 (sh)	–
R = $OCOCH_3$	360 (max)	60,400		411 (max)	0.80
	378 (sh)	–			–
1e	346 (max)	49,500	3.28	380 (sh)	0.72
R = C_6H_5	363 (sh)	–		398 (max)	–
1f	360 (sh)	–	3.03	418 (sh)	–
R = CN	376 (max)	55,400		433 (max)	0.60
	395 (sh)	–			–
1g	360 (sh)	–	3.01	430 (max)	–
R = $COOCH_3$	376 (max)	72,600			0.63
	396 (sh)	–			–
1h	367 (sh)	–	2.97	440 (max)	–
R = $COCH_3$	382 (max)	73,300			0.64
	400 (sh)	–			–
1i	357 (sh)	–	3.06	424 (max)	–
R = OH	370 (max)	49,700			0.70
	390 (sh)	–			–
2a	$\lambda_1 = 338$	26,600	2.85	437 (max)	0.48
R = OCH_3	$\lambda_2 = 398$	54,000		461 (sh)	0.85[b]
2b	$\lambda_1 = 361$	17,300	2.50	N/A[c]	N/A[c]
R = NO_2	$\lambda_2 = 448$	38,600			
2c	$\lambda_1 = 328$	32,700	2.88	434 (max)	0.50
R = CH_3	$\lambda_2 = 395$	56,400		460 (sh)	0.95[b]
2d	$\lambda_1 = 342$	13,400	2.71	480 (max)	0.45
R = CN	$\lambda_2 = 418$	21,900			0.53[b]
2e	$\lambda_1 = 327$	18,400	2.89	436 (max)	0.86
R = H	$\lambda_2 = 393$	27,300		458 (sh)	0.94[b]
2f	$\lambda_1 = 328$	26,600	2.88	437 (max)	0.56
R = $OCOCH_3$	$\lambda_2 = 395$	43,400		461 (sh)	0.92[b]
2g	$\lambda_1 = 338$	13,400	2.85	437 (max)	0.55
R = OH	$\lambda_2 = 398$	30,200		462 (sh)	0.88[b]

[a] Quinine sulfate was used as standard for determination of fluorescence quantum yields (Φ_f) at λ_{exc} corresponding to the absorption maximum of series 1 and to the first absorption maximum of series 2 (λ_1).

[b] Perylene was used as standard for determination of Φ_f at λ_{exc} corresponding to the absorption maximum of OPV **1b** and to the second absorption maximum of series 2 (λ_2).

[c] No appreciable emission in DMF. sh: shoulder; max: wavelength of maximum absorption.

UV–vis and 134 nm in FS, such effect changes the absorption and emission properties of the OPV from the ultraviolet region to the visible region of the electromagnetic spectrum.

The shifts in the wavelength generated by ED groups in compounds of series 2 are smaller with respect to the reference compound in this series (OPV **2e**). The shifts obtained for OPVs **2c** (R = $-CH_3$) and **2f** (R = $-OCOCH_3$) are very small and similar, with shifts of 1 and 2 nm for absorption wavelengths λ_1 and λ_2 respectively, and shifts of -2 and 1 nm in the emission spectrum, respectively. The red shift increases slightly when increasing the ED ability in the OPVs **2a** (R = $-OCH_3$) and **2g** (R = $-OH$) with shifts in the absorption spectrum of 11 nm (λ_1) and 5 nm (λ_2) and only of 1 nm in the emission spectrum.

The shift tends to increase with strongly EW groups in series 2. For OPV **2d** (R = $-CN$) shifts of 15 nm (λ_1) and 25 nm (λ_2) in the UV–vis and 44 nm in the FS spectrum were obtained.

As in series 1, the OPV with nitro groups of series 2 (compound **2b**), possess the highest bathochromic effect. Although this OPV did not show appreciable emission in solution (DMF), the absorption spectrum showed the greatest shift with values of 34 nm (λ_1) and 55 nm (λ_2). Interestingly, this compound also presents a particular behavior, in solvents like acetonitrile or DMF shows a negligible emission; in chloroform a weak orange emission above 600 nm, while in diethyl ether and toluene present moderate emission at 530 nm. Recently it was reported that the emission of **2b** changes from 432 to 650 nm with solvents such as methanol, toluene, chloroform, THF, dichlorobenzene, acetonitrile and DMSO [34].

Although the shift of ED and EW groups seems to be lower in OPVs of series 2 that in the series 1 with respect to unsubstituted OPVs for each series, it is important to note that the absorption and emission wavelengths of OPVs in series 2 are more shifted toward the visible region, indicating that the presence of two ED methoxy groups over the central ring strongly increases the bathochromic shift of OPVs. Comparing the reference compounds in each series, it is clear that the methoxy groups in the central ring of the OPV **2e** produce a large bathochromic shift of 36 nm in the UV–vis and 30 nm in the FS spectra with respect to unsubstituted OPV **1c**. A similar study reported by Chaieb, also showed that the introduction of electron donating groups on the central ring leads to a red shift [36].

The bathochromic effect of the methoxy groups at the central ring also shows that by comparing compounds substituted with acetoxy groups in series 1 and 2, compounds **1d** and **2f**, the methoxy groups generate a shift of 35 nm in the absorption spectrum and 26 nm in the emission spectrum, values that are comparable but lower than those generated for methoxy groups in the reference compounds **2e** and **1c**.

When the terminal groups are ED, the bathochromic effect of the methoxy groups in the central ring tends to be lower; compound **2a** (R = $-OCH_3$) with shifts of 28 nm in the UV–vis and 15 nm in the FS spectra compared to **1a** (R = $-OCH_3$). Another example is OPV **2g** (R = −OH) with shifts of 28 nm in the UV–vis and 13 nm in the FS spectrum compared to **1i** (R = −OH). When the terminal groups are EW, the bathochromic effect due to the methoxy groups in the central ring tends to increase; OPVs **2d** (R = −CN), shifts 42 nm in the absorption spectrum and 47 nm in the emission spectrum compared to **1f** (R = −CN) and **2b** (R = $-NO_2$), with shifts of 40 nm in the UV–vis with respect to **1b** (R = $-NO_2$). These results show that the bathochromic shift caused by the methoxy groups at the central ring is influenced by the presence of other ED or EW substituents at the end rings of the molecule, suggesting a change on the electronic environment of the PV system.

The effect of the position of methoxy groups over the red shift was also evaluated by comparing the displacements caused by these groups in isomers **1a** (OCH_3 groups at the end rings) and **2e** (OCH_3 groups at the central ring). The shift generated by methoxy groups in the OPV **1a** is 13 nm in UV–vis and 16 nm in FS with respect to unsubstituted compound **1c** (R = H), while the shift caused for methoxy groups in the compound **2e** is much higher, 36 nm in UV–vis and 30 nm in FS versus **1c**, which might indicate that the presence of two methoxy groups over the same ring strongly intensifies the red shift.

With respect to the molar attenuation coefficient (ε), no clear trends were observed (Table 1). OPVs of series 2 showed values of ε lower than those obtained for OPVs of series 1. The ΔE values obtained (see Table 1) shows that the energy gap decreases according to the following trend: $C_6H_5 > -H > -OCOCH_3 > -OCH_3 > -OH > -CN > -COOCH_3 > -COCH_3 > -NO_2$ (series 1) and $-H > -OCOCH_3, -CH_3 > -OCH_3, -OH > -CN > -NO_2$ (series 2).

The EW groups in the OPV system lead to smaller ΔE values, being the lowest the $-NO_2$ (2.75 eV for OPV **1b**; 2.50 eV for OPV **2b**). The ED groups also contribute to decrease the ΔE with respect to unsubstituted OPVs, once again with the exception of OPV substituted with phenyl rings (OPV **1e**), which in this case presents the greatest EΔ(3.28 eV). The trend shows that ΔE decrease with the increase of ED and EW strength of the substituents, in agreement with the increase in the bathochromic shift. This is reasonable, considering that the increase in wavelength implies a decrease in energy required for excitation. The same trend was found by Wu and coworkers for OPVs substituted with other ED groups [35]. The ΔE values obtained for OPVs of series 2 are much lower than obtained for OPVs of series 1, which indicate that the introduction of methoxy groups in central ring favors the reduction of the energy gap.

Furthermore, regarding the fluorescence quantum yields (Φ_f), it is noted that for series 1 both ED and EW groups leads to a decrease in the Φ_f values compared to the unsubstituted compound **1c**, according to the order: $H > -OCOCH_3 > -C_6H_5 > -OH > -OCH_3 > -COCH_3 > -COOCH_3 > -CN$. Although there is no clear trend, it was observed that ED groups such as $-OCOCH_3$, $-C_6H_5$, −OH and $-OCH_3$ reduce the quantum yield relative to the reference OPV **1c** from 0.86 to 0.80, 0.72, 0.70 and 0.66 respectively. This decrease is intensified with EW groups such as $-COCH_3$, $-COOCH_3$ and −CN up to values of 0.64, 0.63 and 0.60 respectively. Chaieb and coworkers also found a similar trend; high values of Φ_f for OPVs with ED groups and low values for OPVs with EW substituents [36].

In the case of OPVs of series 2, similar to that found for series 1, the presence of ED and EW groups at the end rings leads to a decrease in the Φ_f value relative to the reference OPV **2e**. The Φ_f values calculated at the λ_{exc} of the first absorption maximum (λ_1) exhibit a trend of $-H > -OCOCH_3 > -OH > -CH_3 > -OCH_3 > -CN$. The ED and EW substituent reduce the Φ_f value from 0.86 to 0.45. When the Φ_f values are measured at the λ_{exc} of the second absorption maximum (λ_2) similar trend was observed: $-CH_3 > H > OCOCH_3 > OH > OCH_3 > CN$. In this case, the quantum yields obtained for OPVs with methyl and hydrogen atoms at the end rings were quite similar and the same trend in decrease of Φ_f with the presence of substituents was found. The lower Φ_f value obtained for the cyano compound regards to the absence of emission of the nitro-compound (OPV **2b**) also corroborate that the EW groups have the biggest effect over the decrease of Φ_f values related with ED substituents.

From this study, it can be inferred that the phenylenevinylene type systems possess valuable optoelectronic properties, which can be adjusted with the inclusion of substituents with strongly ED and/or EW nature. The inclusion of these groups in the structure of PV derivatives produces a bathochromic shift while leads to a decrease in the ΔE values. This could be quite beneficial when the goal is to take advantage of renewable sources such as solar energy to excite molecules in order to make them useful in various applications (i.e. as organic photo-redox catalysts, components in the active layer of photovoltaic cells, conductive materials, etc.). It was also noticed that unsubstituted OPVs exhibit excellent fluorescence quantum yields. The inclusion of ED groups such as acetoxy, hydroxyl, phenyl, methyl and methoxy, improve the absorption and emission properties but with a decrease in quantum yields. Nevertheless, these remain high, making these systems potential candidates for applications in OLEDs and laser dyes.

4. Conclusions

Sixteen model OPVs were synthesized by Mizoroki-Heck cross coupling reaction. The methodology reported could be used as synthetic route for phenylenevinylene systems with highly desired functional groups in their molecular structure, with high stereoselectivity to *trans-trans* configuration of the vinyl bonds and allowing the synthesis of compounds that present difficulties to be obtained by other synthetic methodologies. The optoelectronic study in DMF solutions showed that ED and EW groups at the end rings lead a red shift in absorption and emission spectrums, with a magnitude that depends of the electronic strength of the substituents. In addition, inclusion of methoxy groups at the central rings increases the red shift into the visible region of the electromagnetic spectrum. However, ΔE values decrease with increasing of ED and EW strength of the substituents. Properties like molar attenuation coefficient and fluorescence quantum yield were calculated without a clear trend. Nevertheless it was found that ED and EW substituents decrease the Φ_f values with respect to unsubstituted OPVs.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.molstruc.2016.12.032.

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