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# Exploring the nitro group reduction in low-solubility oligo-phenylenevinylene systems: Rapid synthesis of amino derivatives

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#### ABSTRACT

A small series of amino oligo-phenylenevinylenes (OPVs) were successfully synthesized from their nitro-analogs in a rapid, simple, and highly efficient fashion employing a sodium sulfide/pyridine system as a reducing agent. In this research, classic and sustainable reduction methodologies including NH<sub>4</sub>HCO<sub>2</sub>/Zn and a choline chloride/ tin (II) chloride deep eutectic solvent (DES) were also evaluated, showing degradation products, incomplete reactivity, and product isolation difficulties in all cases. The straightforward Na<sub>2</sub>S/pyridine synthetic protocol proved to maintain the *E-E* stereochemistry of the OPV backbone that has been previously assembled by the Mizoroki–Heck cross-coupling reaction. Also, the optoelectronic properties were determined and discussed, considering the amino group insertion in these conjugated systems as a contribution for future construction of novel materials with applications in supramolecular electronics, light harvesting, and photocatalysis.

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#### **KEYWORDS**

Amino phenylenevinylene; Mizoroki–Heck reaction; nitro reduction; optoelectronic properties

#### **GRAPHICAL ABSTRACT**



#### Introduction

The polyphenylenevinylene (PPV) system is considered a promising organic semiconductor material with remarkable optical and electronic properties. Unnumbered applications have been described in light-harvesting,<sup>[1,2]</sup> molecular electronics,<sup>[3,4]</sup> photocatalysis,<sup>[5]</sup> water splitting for hydrogen production,<sup>[6,7]</sup> chemosensors,<sup>[8,9]</sup> among

• Supplemental data for this article can be accessed on the publisher's website.

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others.<sup>[10]</sup> However, on the basis of their length and structural defects concerning heterogeneous geometrical configuration around double bonds, the overall polymer electronic conjugation is compromised. Hence, the oligo-phenylenevinylene (OPV) moiety emerges as a rational model approach offering the possibility to explore by extrapolation the unique optical, electronic and thermal properties of their high molecular weight analogs, overcoming the problems mentioned above and other important solubility issues.<sup>[11]</sup>

Different synthetic approaches, including Gilch,<sup>[12]</sup> Knoevenagel,<sup>[13]</sup> and Wittig<sup>[14]</sup> reactions have been widely used to access the OPV skeleton. More recently, the Wittig-Horner reaction has shown high E-selectivity, facilitating the synthesis of more complex structures such as OPV-hexasubstituted benzenes and OPV-functionalized azafullerenes.<sup>[15,16]</sup> Nevertheless, the Mizoroki-Heck reaction, considered the method of choice for arylation of alkenes, also offers a powerful and convenient strategy to provide pure anti all-trans materials under mild conditions as demonstrated by the efforts made by our research group in terms of efficiency and stereoselectivity improvement.<sup>[17,18]</sup> Alternative and sustainable routes for obtaining anti trans-trans OPVs in high yields have been subjected to recent studies, leading to the development of efficient Pd supported heterogeneous catalytic systems.<sup>[19-21]</sup> It should be disclosed that Pd-coupling reactions employing sterically hindered deactivated bromoarenes (e.g., 1-Bromo-2-nitrobenzene) are considered a synthetic challenge which has been addressed with bulky phosphine ligands, the use of ionic liquids, longer reaction times and high temperatures to support the oxidative addition of the C-X bond.<sup>[22-24]</sup>

On the other hand, supramolecular hydrogen-bonded architectures employing OPVs have also recently attained special recognition for applications in electronic devices. It has been demonstrated that secondary interactions between these  $\pi$ -conjugated systems result in materials with macromolecular improved optical and electronic properties associated with the self-aggregation of their units.<sup>[25]</sup> To achieve larger degrees of supramolecular polymerization, several nitrogen-containing groups (e.g., urea, melamine) have been employed to functionalize the OPV moiety.<sup>[26,27]</sup> Thus, amino OPV derivatives could serve as simple molecular models for conjugated superstructures. Although the preparation of isolated examples of amino OPV derivatives has been carried out by acid hydrolysis<sup>[14]</sup> of amide OPV precursors and reduction from NO<sub>2</sub>-OPVs employing different reducing agents such as SnCl<sub>2</sub><sup>[28,29]</sup> and Na<sub>2</sub>S,<sup>[30,31]</sup> a rational evaluation of the most relevant reaction conditions leading to NH<sub>2</sub>-OPV has not yet been performed from poorly soluble starting materials. Therefore, herein we describe a concise chemical exploration of synthetic features conducted to obtain amino OPV derivatives employing substituted styrenes and aryl bromide-iodide moieties through the Mizoroki-Heck reaction. This, as the basis for the stereoselective (*E*-*E*)  $\pi$ -conjugated backbone construction (Scheme 1), yielding a small series of amino-OPVs expeditiously prepared taking advantage of the best reduction reaction conditions found in this study. Additionally, the optoelectronic characterization, regarding the nature of the nitro and amino substituents and their position around the OPV structure, are examined providing insights for future applications in the field of photoluminescent materials.



Scheme 1. Approaches employed in this work to assemble the amino-OPV backbone

	R + 1	OMe P(PhO) <sub>3</sub> (9 mol%) P(PhO) <sub>3</sub> (9 mol%) Et <sub>3</sub> N (2 eq.) OMe DMF, 24 h, 110 °C R	R
Entry	1 Styrene	2a 3 (R=NO <sub>2</sub> ), 4 (R=NH <sub>2</sub> ), Product	5 (R=NHAc)
1	O <sub>2</sub> N 1a	O <sub>2</sub> N OMe NO <sub>2</sub> O <sub>2</sub> N OMe Sa	80
2	H <sub>2</sub> N <b>1b</b>	H <sub>2</sub> N H <sub>2</sub> H <sub>2</sub> N H <sub>2</sub>	NR
3	AcHN 1c	AcHN OMe NHAC OMe Sa	5 <sup>ª</sup>

Table 1. Preliminary formation of amino and nitro OPV derivatives *via* direct Mizoroki-Heck coupling reaction.

<sup>a</sup>Multiple products formation. NR: no reaction

#### Results

#### Synthesis of nitro-OPVs

Mizoroki-Heck reaction conditions for the preparation of OPVs have been previously optimized by our research group and were employed to successfully provide the desired nitro-OPV model **3a** (Table 1, entry 1).<sup>[32]</sup> Alternatively, preliminary efforts to access amino OPV derivatives also involving direct Mizoroki-Heck coupling reaction of 4-aminostyrene **1b** and 2,5-diiodo-1,4-dimethoxybenzene **2a** (Table 1, entry 2) were unpromising; the use of aminostyrene precursor gave multiple products (as observed by TLC) that were not possible to isolate by column chromatography.

The observed chemical behavior can be attributed to the low stability exhibited by the 4-aminostyrene which probably involves a spontaneous polymerization caused by the nucleophilic attack of the amino group directly on the activated  $\beta$ -position of the double bond generating a zwitterionic propagating species.<sup>[33]</sup> To prevent this, amine protection was carried out by treatment with acetyl chloride. The easily formed *N*-(4vinylphenyl) acetamide **1c** was immediately brought under the same Pd(0)-catalyzed coupling reaction conditions. However, only a 5% of the desired *N*-acetyl OPV derivative **5a** (purified by column chromatography) was obtained among multiple products (Table 1, entry 3). These exploratory outcomes confirmed that aminostyrene derivatives are not suitable substrates to obtain the amino OPV compounds under these reaction conditions. Nevertheless, the successful preparation of the nitro OPV model compound **3a** suggested that a reduction could be a feasible synthetic alternative to amino OPVs.

Having established a convenient route to obtain nitro OPVs, a small library of compounds was prepared employing a combination of styrene and 1,4-dihalide precursors to afford different nitro-substituted OPV on both central and flanking aryl rings (Table 2). All nitro OPV products were obtained as stable solids. Noteworthy, the *trans* stereoselective preparation of compounds **3a** and **3b** was successfully achieved employing the Mizoroki–Heck reaction as an alternative route to classic Wittig conditions, whereas a mixture of *cis* and *trans* isomers was obtained as reported by Saikachi and Muto.<sup>[34]</sup>

No significant yield variation was observed regardless of the electronic and steric nature of the 1,4-dihalide arene precursors. Due to poor solubility of the nitro OPV compounds in the most common deuterated solvents (CDCl<sub>3</sub>, DMSO-d<sub>6</sub>), pyridine- $d_5$  was alternatively employed to obtain the <sup>1</sup>H-NMR spectra in some cases. Compounds **3d** and **3g** were not soluble in any of the available deuterated solvents (pyridine- $d_5$  or DMSO- $d_6$ ), and thus <sup>13</sup>C CP/MAS-NMR was employed as a characterization technique. However, the acquisition of solid-state NMR data was only possible for **3g**.

It should be highlighted that NMR spectroscopy confirms characteristic<sup>[3]</sup> *J* coupling constants ( $\sim$ 16.0 Hz) for the protons on both *E* double bonds of the nitro OPV products, indicating that the symmetry of the substituents in the 1,4-dihalide precursor has no effect on the reaction stereochemical preference. Thus, the unique configuration is a consequence of the employed conditions, being the phosphite ligand responsible for the steric hindrance that promotes control in the orientation of the substrates during the arene-alkene coupling as suggested on previous research results.<sup>[17]</sup>

#### **Reduction of nitro-OPVs**

Initial reduction experiments were carried out employing a solid mixture of ammonium formate and zinc grounded in a mortar, followed by the addition of the nitro OPV **3a** (Table 3, entry 1).<sup>[35]</sup> After 15 min, TLC revealed that no reaction was taking place under these conditions indicating that the use of a grinding auxiliary might be required to enhance the catalytic hydrogen transfer.<sup>[36]</sup> As an attempt to improve the reactivity through a classical approach, methanol, one of the most commonly used solvents for this transformation, was used, followed by the addition of few drops of acetic acid (Table 3, entry 2). The reaction mixture was then heated to reflux; however, no product

	$R_1 \xrightarrow{R_2} R_1 \xrightarrow{R_2} 2 \text{ eq.}$	+ X + X + X + X + X + X + X + X + X + X	$\begin{array}{c} Pd(dba)_2 \\ \hline P(PhO)_3 \\ \hline Et_3N \\ DMF, 110^\circC, 24 h \\ R \\ \end{array} \begin{array}{c} R_2 \\ R_1 \\ \hline R_2 \\ R_4 \\ \hline R_4 \\ \end{array} \begin{array}{c} R_3 \\ R_2 \\ R_4 \\ \hline R_4 \\ \end{array} $	4
Entry	Styrene, 1	Aryl halide, 2	Product, 3	Yield, %
1	O <sub>2</sub> N 1a		O <sub>2</sub> N O <sub>2</sub> O <sub>2</sub> NO <sub>2</sub>	80
2	0 <sub>2</sub> N 1d		O <sub>2</sub> N O <sub>2</sub> N Me <b>3b</b>	69
3	O <sub>2</sub> N CI	OMe OMe 2a		55
4	O <sub>2</sub> N Me <sub>2</sub> N 1g		O <sub>2</sub> N Me <sub>2</sub> N Me <sub>2</sub> N Me <sub>2</sub> N Me	62
5	MeO 1h		Me Meo 3e	87
6	<sup>O<sub>2</sub>N 1d</sup>	Me	NO <sub>2</sub> NO <sub>2</sub> NO <sub>2</sub> NO <sub>2</sub>	56
7	0 <sub>2</sub> N 1d	Me 2b	O <sub>2</sub> N Me Me <b>3g</b>	70
8	O <sub>2</sub> N 1a	2c	O <sub>2</sub> N 3h	40
9	1e	NO <sub>2</sub> Br		37
10	NC 1f	Br 2d	NO <sub>2</sub> CN	50

 Table 2. Pd-catalyzed coupling reaction for direct synthesis of nitro OPV precursors.

	O2N ON	Reaction cond	itions H <sub>2</sub> N ON 4a	le NH	2
Entry	Reducing agent	Solvent	Temperature, °C	Time, h	Yield, %
1	NH <sub>4</sub> HCO <sub>2</sub> /Zn	None <sup>a</sup>	r.t.	0.25	NR
2	NH₄HCO₂/Zn	MeOH/AcOH	118	12	NR
3	SnCl <sub>2</sub> ·H <sub>2</sub> O	EtOH/AcOEt (1:1)	78	8	<5 <sup>b</sup>
4	SnCl <sub>2</sub> ·H <sub>2</sub> O	HCI (37%)	110	1	<5 <sup>b</sup>
5	Na <sub>2</sub> S	Pyridine/HCI (37%)	90	2	<5 <sup>b</sup>
6	Na <sub>2</sub> S	Pyridine	115	0.5	82
7	Na <sub>2</sub> S	1,4-dioxane	100	0.5	22
8	Na <sub>2</sub> S	PEG 600	100	1	18
9	SnCl <sub>2</sub> ·2H <sub>2</sub> O	Choline chloride (DES)	120	4	20



<sup>a</sup>Mechanochemical reaction.

<sup>b</sup>Multiple product formation.

NR: no reaction

formation was observed. These results can be attributed to the poor solubility of the OPV in methanol, preventing the appropriate interaction between reactants in solution.

Then, to improve the OPV solubility,  $SnCl_2$  in a mixture of EtOH/AcOEt was explored (Table 3, entry 3). Although complete solubility of the nitro OPV was reached under reflux conditions, and successful reduction of similar nitro-substituted conjugated systems have been reported,<sup>[28]</sup> conversion of **3a** into the corresponding amino derivative was not observed, and multiple products were formed instead. The same chemical behavior was observed when concentrated HCl (37%) was used as solvent (Table 3, entry 4).

The use of HCl in combination with Na<sub>2</sub>S has been previously reported for selective nitro group reductions.<sup>[30]</sup> However, under these conditions, the model compound **3a** was again converted into multiple products (Table 3, entry 5). An analog methodology involving the use of sodium sulfide/pyridine has already been reported, but its application was limited to a single OPV example.<sup>[31]</sup> Our exploratory synthetic efforts confirmed that this reduction system serves as a rapid and efficient approach toward amino OPV derivatives (Table 3, entry 6). A greener approach exploring the use of watermiscible, less harmful solvents was unsuccessful. 1,4-dioxane, PEG-600, and a choline chloride/tin (II) chloride deep eutectic solvent (DES)<sup>[37]</sup> gave the desired product but in low yields (Table 3, entries 7, 8 and 9). It should be noted that the purification procedure for these last three systems became tedious, considering that an emulsion was formed after pouring the reaction mixture in water, therefore preventing the formation of the solid amino OPV product although TLC indicated reaction completion.

Remarkably, after reaction is complete with the best reaction conditions (Table 3, entry 6), the obtained solid product was recovered by filtration followed by washing cycles with water and a 1:1 water/ethanol mixture. No further purification procedures were required. By evaluating the characteristic coupling constant values observed for vinylic protons, <sup>1</sup>H-NMR spectra confirmed that the *E-E* stereochemistry was maintained (Figure 1).



Figure 1. <sup>1</sup>H-NMR spectrum for compound 4a, aromatic region expansion.

To demonstrate the effectiveness of this synthetic methodology, the best reaction conditions were used to reduce all other nitro substituted OPV systems previously prepared by Mizoroki-Heck reaction (Table 4). Complete reduction of the nitro group was achieved in all cases in moderate to high yields. Reduction of nitro-OPVs 3d and 3g required a minor procedure modification to enhance solubility, and consisted in heating the reacting mixture (OPV 3d/3g, pyridine, and Na<sub>2</sub>S) at 100 °C on a capped vial for 12 h, after which the reaction crude was also poured into water and the target product recovered by filtration. It should be noted that the insertion of other substituents around the OPV scaffold (compounds 4c-e) led to a significant decrease in the reduction reaction yields, although no side-products were observed by TLC. Interestingly, the reduction reaction with OPVs containing the nitro group in the central ring (3i and 3j, Scheme 2) gave a mixture of products as confirmed by MALDI-MS and NMR experiments. Reports indicate that the use of sulfide as a reducing agent for p-substituted nitrobenzenes promotes the formation of azo and azoxy compounds as by-products.<sup>[38]</sup> Upon thorough examination of the MALDI spectrum, a self-radical unimolecular induced fragmentation pattern is observed for all signals due to the presence of the amino group. However, signals at 592 and 502 m/z confirm the presence of the azo compound and its subsequent double bond cleavage product along with the desired amino OPV with the corresponding  $[M+H]^+$  ion signal at 298 m/z (see Supplementary Data).

Despite the efforts that were made to isolate the major amino OPV products **4i** and **4j** *via* recrystallization and purification by column chromatography, HPLC, and NMR results indicate the side-product remains in a 0.28:1 ratio (see Supplementary Data). The formation of the azo compound can be ascribed to the reaction between the nitrosyl reduction intermediate<sup>[39]</sup> and a preformed amine molecule in the medium, as depicted on Scheme 3. The azo dimerization starts with the addition of the amine on the nitrosyl group and then the elimination of water affords the N=N bond.

#### 8 🍝 M. ACELAS ET AL.



#### Table 4. Sodium sulfide/pyridine reduction of other nitro OPV systems.



Scheme 2. Products observed under the evaluated reaction conditions for nitro-OPVs 3i and 3j



Scheme 3. Proposed mechanism of OPV azo-dimerization

Monitoring the reduction of compound 3j by HPLC confirms the coelution of two substances with different UV–Vis absorption spectra (see supplementary data). MALDI-MS showed the  $[M+H]^+$  ion of the expected amino-OPV at 348 m/z as well as other peaks at 590 and 522 that can be assigned to the azo by-product fragmentation ions (see Supplementary Data). It should be highlighted that under the employed reduction conditions, the nitrile group was unaffected, and the formation of possible thioamide-type side-products was not observed in the MS spectrum.<sup>[40]</sup> The overall experimental data show that placing the nitro group in the central ring of the OPV moiety seems to stabilize the reduction nitrosyl intermediate due to the electron-donating character of the styrene substituents, thus favoring the formation of the azo by-product.

#### **Optoelectronic properties of OPVs**

The photophysical properties of compounds 3a-j and 4a-h were studied by UV–Vis and fluorescence spectroscopy to evaluate the effect of the NO<sub>2</sub> and NH<sub>2</sub> groups position around the OPV conjugated scaffold (Figures 2 and 3; Table 5).

Initial spectral examination for all compounds shows a double band absorption caused by the expected  $\pi \rightarrow \pi^*$  electronic transition and the additional  $n \rightarrow \pi^*$  electronic transition. This ascribed to the OMe group in the central ring, and the presence of an additional group containing a heteroatom (OMe and NMe<sub>2</sub>) in the flanking aryl rings, that can be observed for both NO<sub>2</sub> and NH<sub>2</sub> OPVs **3a-e** and **4a-e**. An analog absorption behavior is observed for all other NH<sub>2</sub>-OPVs **4f-h**, where a shoulder associated with the  $n \rightarrow \pi^*$  transition of the amine group is also noticed. The change in the electronic nature of the substituents over the flanking aryl rings indicates that the electron-donating character of the amino group causes a hypsochromic effect for both absorption and emission maxima in all cases, except for compounds **3e** and **4e**, where a redshift of 8 nm is observed in the absorption. This phenomenon can be attributed to the simultaneous presence of a strong electron-donating group and the different position of the nitro group in the aromatic ring. The blueshift is also exhibited when the NO<sub>2</sub> and NH<sub>2</sub> groups are changed from position 4- to position 3-, and from position 3- to position -2, producing a modification on the electronic density of the OPV structure.

For the nitro series, a redshift of 5 and 37 nm in the absorption spectra was observed when Me– (compound 3f) and OMe– (compound 3a) groups are bonded to the central ring compared to the reference structure 3h. Furthermore, the same electronic behavior



Figure 2. Normalized absorption and emission spectra of OPVs 3a-j and 4a-e in MeCN.



Figure 3. Normalized absorption and emission spectra of OPVs 4a-h in MeCN.

is observed when additional groups are bonded to the flanking aryl rings, and the  $NO_2$  is located in position -3, where a redshift of 6 and 8 nm was found for compounds **3c** and **3d**, respectively, in comparison with the reference structure **3h**. Noteworthy, when the nitro group is moved to position 2-, an opposite effect is exhibited with a blueshift of 6 nm for compound **3e**, also employing OPV **3h** as reference.

This trend can be seen for the amino series as well, with a redshift of 3 and 53 nm corresponding to Me (OPV 4f) and -OMe (OPV 4a) substituents, respectively, when

#### 12 🕢 M. ACELAS ET AL.

OPV	$\lambda_{\max}$ (nm)	$\lambda_{\rm em}$ (nm)	$\varepsilon$ (L mol <sup>-1</sup> cm <sup>-1</sup> )	$\Delta E$ (eV)	$\Phi_f$
3a	435	483	92,800	2.45	0.01
	351 <sub>sh</sub>				
3b	396	476	15,900	2.73	_a
	325 <sub>sh</sub>				
3c	404	499	3332	2.69	_ <sup>a</sup>
	330 <sub>sh</sub>				
3d	406	476	3100	2.63	_ <sup>a</sup>
	344 <sub>sh</sub>	497 <sub>sh</sub>			
3e	392	517	19,100	2.77	_ <sup>a</sup>
	328 <sub>sh</sub>	538 <sub>sh</sub>			
3f	403	563	61,750	2.64	0.05
3g	353	475	9200	2.97	_ <sup>a</sup>
3ĥ	398	550	22,300	2.99	0.09
3i	334	408	69,150	3.05	_ <sup>a</sup>
3j	345	521	83,800	2.92	_ <sup>a</sup>
4a	402	468	37,350	2.68	0.26
	326 <sub>sh</sub>	497 <sub>sh</sub>			
4b	392	430	32,700	3.19	0.50
	322 <sub>sh</sub>	454 <sub>sh</sub>			
4c	395	479	8300	2.79	0.42
	326 <sub>sh</sub>	503 <sub>sh</sub>			
4d	404	586	48,200	2.71	0.06
	326 <sub>sh</sub>				
4e	400	486	32,100	2.96	0.37
	324 <sub>sh</sub>	507 <sub>sh</sub>			
4f	379	474	40,600	2.99	0.20
	320 <sub>sh</sub>				
4g	354	459	28,150	3.17	0.31
	279 <sub>sh</sub>				
4h	376	474	45,800	2.99	0.25
	322 <sub>sh</sub>				

Table 5. Photophysical properties for OPVs 3a-j and 4a-h in MeCN.

<sup>a</sup>No appreciable emission.

OPV **4h** is used as reference. This bathochromic effect is also observed when the -OMe group is kept in the central ring, and other substituents are included in the flanking aryl rings, displaying redshifts of 19, 28, and 24 nm for compounds **4c**, **4d**, and **4e**, respectively, compared to OPV **4h**. This absorption pattern is attributed to the increasing electron-donating character of the central ring substituents (H < Me < OMe), inducing a generalized bathochromic effect. Alternatively, when the nitro group is placed on the central ring, compounds **3i** and **3j** exhibit a blue shift of 64 and 53 nm in the absorption spectra compared to reference compound **3h**, respectively.

Regarding the emission spectra, an additional band is observed for all compounds bearing two or more electron-donating groups (compounds 3d, 3e, 4a-c, and 4e) except for compound 4d, where a broad emission band is observed due to overlapping. The insertion of additional electron-donating groups (OMe, NMe<sub>2</sub>, and NH<sub>2</sub>) around the OPV scaffold seems to modify the vibronic states of the molecule, inducing a double band emission. It should be noted that a significant Stokes shift of 182 nm is displayed for compound 4d, ascribed to the contribution of the electron-donating effect of the two substituents in the flanking aryl ring, lowering self-absorption phenomena. However, for compound 4e, a significant decrease in the Stokes shift of 86 nm, suggests that the position of the amino group plays a major role in the OPV energetic levels. Also, a strong bathochromic effect is obtained for the emission spectra when a combination of electron-withdrawing groups (NO<sub>2</sub> and CN) are placed around the OPV skeleton leading to a Stokes shift of 170 nm in compound 3j.

The attenuation coefficients  $\varepsilon$  of 4-nitro (**3a**, **3f**) and 4-amino compounds (**4a**, **4f**) are significantly higher compared to their 3-substituted analogs as a result of a modification on the electronic density on the OPV conjugated backbone. Additionally, the position of the nitro group in OPV **3e**, significantly increases the attenuation coefficient compared to the other 4-substituted OPVs **3c** and **3d**. Interestingly, compound **4c** exhibits the lowest  $\varepsilon$  value among all amino OPV derivatives, possibly due to the presence of the Cl atom and its moderate electron-withdrawing effect. No additional trends regarding this property were observed. It should be disclosed that the attenuation coefficient for compound **3a** had been previously reported in DMF ( $\varepsilon = 38,600 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ).<sup>[32]</sup> However, the difference in the obtained value relies in the strong solvatochromism exhibited by this particular compound considering that, this time, MeCN was used as the solvent.<sup>[41]</sup>

The optical gap  $\Delta E$  showed an increase for the 3-substituted OPVs compared to their 4-substituted analogs. Also, a stronger inductive effect exerted by the central ring substituents is related to a decrease in the  $\Delta E$  value. Compounds 3d and 4d exhibit a higher  $\Delta E$  value compared to the other flanking aryl ring substituted OPVs 3c, 3d, 4c, and 4d. This property can also be attributed to the modification in the position of the nitro and amino group around the OPV scaffold allowing a molecular energy level modulation. Additionally, it can be observed that nitro OPVs have a very low quantum fluorescence yield ( $\Phi_f$ ) associated with the lack of appreciable emission at low absorbance values in most cases. It was only possible to determine the  $\Phi_f$  values for compounds 3a, 3f, and 3h. Alternatively, an increase in the quantum yield is observed for 3-amino OPVs compared to 4-amino compounds. The overall obtained  $\Phi_f$  values indicate that the efficiency of the conversion of absorbed light into emitted light is slightly improved by the reduction of the nitro group in the OPV backbone. Moreover, it was found that compound 4d displayed the lowest  $\Phi_f$  among all other amino OPV derivatives. This observation was attributed to the intramolecular hydrogen bonding between the -NMe<sub>2</sub> and -NH<sub>2</sub> vicinal groups, which generates additional vibronic internal conversion processes, leading to the dissipation of the excitation energy and to the decrease in the radiative relaxation pathway.<sup>[42]</sup> Although the  $\Phi_f$  values for the prepared amino OPVs are not high enough for emissive materials applications, alternative photocatalytic properties can be explored. However, it is expected that their supramolecular selfassembly leads to a significant improvement in their photophysical properties.

#### Conclusions

In summary, we have demonstrated that the preparation of the amino OPV backbone can be achieved *via* Mizoroki–Heck coupling reaction and subsequent reduction of the aromatic nitro group upon treatment with a  $Na_2S$ /pyridine system. This methodology proved to be a convenient strategy for low solubility  $NO_2$ –OPVs when the nitro groups are located on the flanking rings, and serves as an expedite synthetic pathway to design a variety of amino OPV-type building blocks and diversify future development of hydrogen-bonded supramolecular polymers with promising technological applications.

Also, the photophysical properties are reported, indicating a high dependence on the type of substituent (EWG or EDG) and its position around the OPV, as result of the modification in the electron density of the molecule.

# **Experimental part**

# Materials

All reagents were purchased from Merck (Kenilworth, NJ), Alfa Aesar (Haverhill, MA), and Sigma-Aldrich Chemical Co. (St. Louis, MO), and used without further purification. The reaction progress was monitored using thin-layer chromatography on PF254 TLC aluminum sheets from Merck. Column chromatography was performed using silica gel (60-120 mesh). The melting points (uncorrected) were determined using a Stuart SMP10 digital melting point apparatus. IR spectra were recorded on an FTIR Thermo Scientific Nicolet iS10 spectrophotometer coupled to a diamond ATR Smart iTR cell. Mass spectra were collected from m/z 0 to 1000 in reflectron positive ion mode using an UltraFlextreme MALDI-TOF-MS (Bruker, Billerica, MA) with a laser solid source of Nd:YAG and 1000 Hz acquisition frequency employing the laser desorption ionization (LDI) method at a 25% laser fluency. Elemental analyses were performed on a Thermo Scientific analyzer (Flash 2000) and were within  $\pm 0.4$  of theoretical values. NMR spectra (<sup>1</sup>H and <sup>13</sup>C) were measured on a Bruker Ultrashield-400 spectrometer (400 MHz <sup>1</sup>H NMR and 100 MHz <sup>13</sup>C NMR), using CDCl<sub>3</sub>, DMSO-d<sub>6</sub>, methanol-d<sub>4</sub>, pyridine-d<sub>5</sub> or mixtures as solvents and references. J values are reported in Hz; chemical shifts are reported in ppm ( $\delta$ ) relative to the solvent peak (residual CHCl<sub>3</sub> in CDCl<sub>3</sub> at 7.26 ppm for protons, residual DMSO at 2.50 ppm for protons and residual pyridine at 8.74 ppm for protons). Signals were designated as follows: s, singlet; d, doublet; dd, doublet of doublets; ddd, doublet of doublets of doublets; t, triplet; td, triplet of doublets; g, quartet; m, multiplet; br., broad. <sup>13</sup>C CP/MAS-NMR spectra were acquired using a Bruker AVANCE III instrument operating at 9.4T using KBr as filler. The absorption and emission spectra were recorded on  $1 \times 10^{-5}$  M solutions in MeCN using a Thermo Scientific Evolution 300 spectrophotometer and a PTI QuantaMaster<sup>TM</sup> 40 spectrofluorometer. The maxima of absorption  $\lambda_{max}$  and emission  $\lambda_{em}$  were directly obtained from the corresponding spectra. The attenuation coefficient  $\varepsilon$  was obtained from the analysis of OPV solutions in the 2.0-18.0 µM range. The optical HOMO-LUMO gap was calculated using the onset value of the absorption spectrum in the direction of longer wavelengths.<sup>[43]</sup> Finally, the fluorescence quantum yields  $\Phi_f$  were acquired according to the reference method described in the literature using quinine sulfate (in 0.1 M H<sub>2</sub>SO<sub>4</sub>) as standard.<sup>[44]</sup>

# Synthesis

General procedure for the synthesis of nitro oligo-phenylenevinylenes OPVs 3a-3g. To a 10 mL crimp vial equipped with a magnetic stirrer, the corresponding styrene (2.0 mmol), aryl 1,4-dihalide precursor (1.0 mmol), bis(benzylidene)acetone palladium (0) (2.0 mol%) and triphenylphosphite (9.0 mol%) were added. The vial was then sealed with a PTFE septum-aluminum cap followed by purge-saturation with Ar. Dry DMF (3 mL) and triethylamine (2.0 mmol) were subsequently added *via* syringe. The reaction

mixture was stirred at 110 °C for 24 h. After the reaction is complete, the crude was filtered over celite, and precipitation of the product was induced by the addition of cold water (75 mL). Recrystallization from a 2:1 DMF:1,4-dioxane afforded the desired OPVs.

4,4'-((1E,1'E)-(2,5-dimethoxy-1,4-phenylene)bis(ethene-2,1-diyl)) bis(nitrobenzene) 3a. Red solid, mp 275–278 °C; yield 0.259 g (80%) from 1-nitro-4-vinylbenzene (0.240 g, 1.61 mmol), 1,4-diiodo-2,5-dimethoxybenzene (0.314 g, 0.81 mmol), Pd(dba)<sub>2</sub> (18.4 mg, 0.03 mmol), P(PhO)<sub>3</sub> (45.0 mg, 0.145 mmol), and Et<sub>3</sub>N (0.163 g, 1.61 mmol). IR (ATR, cm<sup>-1</sup>): 3068, 2226, 1604, 1506, 1219, 921, 844. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ (ppm): 3.94 (s, 6H), 7.59 (s, 2H), 7.63 (d, J = 16.5 Hz, 2H), 7.73 (d, J = 8.8 Hz, 4H), 7.99 (d, J = 16.5 Hz, 2H), 8.25 (d, J = 8.8 Hz, 4H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ (ppm): 56.6, 110.7, 124.8, 127.8, 128.3, 128.6, 128.7, 130.6, 145.3, 147.4, 152.9. MALDI-MS Calc. for C<sub>24</sub>H<sub>20</sub>N<sub>2</sub>O<sub>6</sub> 432.132; found [M]<sup>+</sup> 432.292. Anal. Calcd for C<sub>24</sub>H<sub>20</sub>N<sub>2</sub>O<sub>6</sub>: C, 66.66; H, 4.66; N, 6.48%. Found: C, 66.81; H, 4.57; N, 6.55%.

General procedure for the synthesis of amino oligo-phenylene vinylene derivatives 4a-e. On a 50 mL round bottom flask equipped with a condenser and a magnetic stirrer, the corresponding OPV (1 mmol) was dissolved in 3.0 mL of pyridine and taken to ebullition. Then, a solution of 6 mmol sodium sulfide hydrate (approx. 60% Na<sub>2</sub>S) in 4 mL of water (approx. 1.5 M) was added while maintaining a gentle reflux. At this point, the color of the reaction mixture changes to dark brown. After the addition is complete, the reaction was stirred and heated at 115 °C for 30 additional minutes. After reaction completion, the crude was poured over 50 mL of cold water. The solid product was filtered before being washed with water (20 mL) and a water/ethanol (1:1) mixture (20 mL). No further purification procedures were required.

4,4'-((1E,1'E)-(2,5-dimethoxy-1,4-phenylene)bis(ethene-2,1-diyl))dianiline 4a. Yellow solid. Yield 0.256 g (82%), mp 189–191 °C. From OPV **3a** (0.327 g, 0.76 mmol) and Na<sub>2</sub>S (0.589 g (60%), 4.53 mmol). IR (ATR, cm<sup>-1</sup>): 3446, 3369, 3213, 3034, 3001, 2954, 1608, 1514, 1207, 1039. <sup>1</sup>H-NMR (400 MHz, Pyridine-d<sub>5</sub>)  $\delta$ (ppm): 3.73 (bs, NH), 3.90 (s, 6 H), 6.67 (d, J = 8.5 Hz, 4H), 7.02 (d, J = 16.4 Hz, 2H), 7.10 (s, 2H), 7.29 (d, J = 16.4 Hz, 2H), 7.37 (d, 8.5 Hz, 4H). 13 C-NMR (100 MHz, Pyridine-d<sub>5</sub>)  $\delta$ (ppm): 56.4, 108.9, 115.2, 119.7, 126.6, 127.8, 128.7, 146.0, 151.3. MALDI-MS Calc. for C<sub>24</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub> 372.183; found [M]<sup>+</sup> 372.316. Anal. Calcd for C<sub>24</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>: C, 77.39; H, 6.49; N, 7.52%. Found: C, 77.04; H, 6.42; N, 7.28%.

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#### **Disclosure statement**

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18 🕢 M. ACELAS ET AL.

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