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# One-pot synthesis and study of spectroscopic properties of oligo (phenylenevinylene)s

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# ABSTRACT

Two series of OPVs (oligo(phenylenevinylene)), that is, ((1E,1'E)-(2,5-dimethoxy-1,4-phenylene)bis (ethene-2,1-diyl))dibenzene derivatives and 4-((*E*)-4-((*E*)-styryl)styryl)pyridine derivatives with different functional groups of varying electronic properties have been synthesized by one-pot Wittig–Heck methodology. The synthesized derivatives have been studied for their optical properties. Amongst them the ((1E,1'E)-(2,5-dimethoxy-1,4-phenylene)bis(ethene-2,1-diyl))dibenzene derivatives with appropriate changes in the end group showed a significant impact on the UV absorption and emission spectra. Particularly **NO<sub>2</sub>–OPV** showed distinct solvatochromism in the wavelength range of 218 nm in different solvents. Whereas 4-((*E*)-4-((*E*)-styryl)styryl)pyridine derivatives showed clear acidochromism which can be detected visually as well as spectroscopically.

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A variety of conjugated molecules have been studied for their wide range of applications in different fields. Molecules with  $\pi$ -conjugation are capable of allowing the mobility of electrons through continuous delocalization due to their structural and orbital arrangements.<sup>1</sup> Amongst the conjugated molecules, oligo (phenylenevinylene) (OPVs), representing the model class of compounds of poly(phenylenevinylene) (PPV), have been extensively studied due to their high stability and good luminescent efficiency. These  $\pi$ -conjugated molecules are investigated at length for their absorption and fluorescence behaviour, and can be tuned by chemical functionalization and external control (e.g., solvent, temperature, pH). Further modulation of the optoelectronic properties of OPVs is possible by introducing different substituents which are capable of other interactions such as hydrogen bonding and  $\pi$ - $\pi$ stacking leading to applications in various fields. The optical and electronic properties of these molecules strongly depend on structural features and hence can be modulated by variations in conjugation length<sup>2-4</sup> and donor-acceptor strengths.<sup>2a,4b,5</sup> These molecular systems have gained great interest owing to their potential application in fields, such as organic light emitting diodes (OLED),<sup>6,7</sup> field effect transistors (FETs),<sup>8,9</sup> nonlinear optical devices,<sup>10,11</sup> solar cells<sup>12,13</sup> and chemical sensors.<sup>14–18</sup> The oligo (phenylenevinylene) (OPV)-based materials have received a great deal of attention, due to their specific photophysical properties and high quantum yields.<sup>19,20</sup>

Owing to the importance of this class of compounds, many methods are known for the synthesis of oligo(phenylene-vinylene)s. Generally the conjugation in the molecule is built by condensation reactions namely Wittig, Knoevenagel, Perkin etc., or by metal mediated coupling reactions such as Mizoroki–Heck or Sonogashira reactions.

One-pot synthesis is referred to a protocol, comprising of several simultaneous synthetic steps. More than often the combination of these operations results in lesser consumption of reagents required for reactions and work-up. This technique can effectively reduce reaction time, may avoid purification of unstable, toxic, or volatile intermediates, and generally support concept of green synthesis. Recently several procedures have been developed for making useful molecules and intermediates by adopting one-pot or domino or tandem synthetic schemes.<sup>21</sup> As part of our interest in the synthesis of conjugated molecules from readily available materials we have developed one-pot dehydrohalogenation-Heck or Wittig-Heck,<sup>22</sup> Wittig-Suzuki,<sup>23</sup> and oxidation-Wittig-Heck<sup>24</sup> reaction protocols. In this Letter we further present one-pot Wittig-Heck methodology to synthesize ((1E,1'E)-(2,5-dimethoxy-1,4-phenylene)bis(ethene-2,1-diyl))dibenzene derivatives and 4-((E)-4-((E)-styryl)styryl) pyridine derivatives (OPVs) where different functional group of varying electronic properties can be easily introduced. The OPVs which mainly differ in the end group can exhibit considerably different physical and optical properties.

Amongst ((1E,1'E)-(2,5-dimethoxy-1,4-phenylene)bis-(ethene-2,1-diyl))dibenzene derivatives we have synthesized seven compounds,**OPV 1–7**, by the given one-pot procedure. The synthesis





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Scheme 1. One-pot Wittig-Heck synthetic methodology for the preparation of OPV 1-7.



Scheme 2. One-pot Wittig-Heck synthetic methodology for the preparation of OPV 8.



Scheme 3. One-pot Wittig-Heck methodology for the synthesis of OPV 9-11.

begins with the Wittig reaction of 4-substituted benzaldehydes **1a–1g** with methyltriphenylphosphonium iodide **2** resulting in situ generation of 4-substituted styrene which will eventually undergo Mizoroki–Heck reaction with 1,4-diiodo-2,5-dimethoxybenzene **3** in the same pot to give the final products (**OPV 1–7**) (Scheme 1).

In the similar manner **OPV 8** was synthesized using 4-bromo benzyltriphenylphosphonium bromide **4** which can undergo

in situ Wittig reaction with 2,5-dimethoxyterephthalaldehyde **5** and Mizoroki–Heck reaction with 4-vinyl pyridine **6** giving the final product (**OPV 8**) (Scheme 2).

On the other hand OPVs **9**, **10** and **11** were synthesized from 4bromobenzyltriphenylphosphonium bromide **4**. This undergoes in situ Wittig reaction with substituted aldehydes (**1a**, **1e**, **7**) followed by one-pot Mizoroki–Heck reaction with vinyl pyridine **6** furnishing pyridine terminated OPVs (Scheme 3).

## Photophysical properties of OPV 1-7

Initially we studied **OPVs 1–7** by UV–visible and florescence spectroscopy as they are structurally similar to two methoxy substituents at 2 and 5 positions of the central ring. The only difference is the terminal functional group which shows distinct variation in its optical properties. It is established that OPVs having Z–Z, Z–E and E–E stereochemistry have distinctly different optical and physical properties.<sup>25</sup> We have determined that all the OPVs in our study are of E–E isomers as established by <sup>1</sup>H NMR analysis. We have studied the UV–Visible absorbance and florescence emission of



Figure 1. (a) UV-Visible spectra for OPV 1-7. (b) PL spectra for OPV 1-7.



Figure 2. (a) UV-Visible and (b) PL spectra of NO<sub>2</sub>-OPV in different solvents.



Figure 3. Emission spectra for OPVs (a) 8, (b) 9, (c) 10 and (d) 11.

solution of **OPV 1–7** in toluene and the observed two characteristic broad absorption peaks for all the compounds attribute to different electronic transitions (Fig. 1). All the compounds showed higher energy band around 330 nm, whereas it shifted to 350 nm in **OPV 5** with electronegative nitro end group. Another absorption band, that is, lower energy band varied from around 390 nm for most OPVs. It was seen at 420 nm for **OPV 6** with the presence of -N  $(CH_3)_2$  end group and 431 nm for the **OPV 5** with  $-NO_2$  moiety. Hence it can be concluded that with only the end group modification of **OPVs** showed the  $\lambda_{max}$  over the range of 41 nm. The emission spectra for all these compounds in toluene also showed distinct variation with the change in the end group functionality. These changes result due to dipole–dipole interactions between solvent and OPVs as well as due to aggregation.<sup>26</sup> It was observed that all

#### Table 1

Absorption and emission values for pyridine terminated OPVs

OPV	$\lambda_{\max}$ (nm)	$\lambda_{max}$ after protonation (nm)	$\lambda_{\rm em} (\rm nm)$	$\lambda_{\rm em}$ after protonation (nm)	Shift in emission peak (nm)
8	352, 408	427	480	618	138
9	318, 332	368	421	496	75
10	364	417	455	604	149
11	316, 366	376	508	517	9

the OPVs except the one with  $-NO_2$  end group showed vibronic features (due to distinct transitions associated with a typical C–C stretching motion strongly coupled to the electronic system) suggesting the dominance of single molecule species. Also the absence of such vibronic features in OPVs containing  $-NO_2$  indicate to the presence of highly aggregated species in solution.<sup>26</sup>

Further spectral examination indicates that the  $\lambda_{em}$  for **OPV 1–7** varied in the range of 64 nm, that is, from 442 nm to 506 nm. The Stoke shifts for most OPVs were around 52 nm whereas the NO2-**OPV** showed distinctly high  $\lambda_{em}$  at 506 nm with the Stoke shift of 75 nm. Another important observation about the NO<sub>2</sub>-OPV was seen in its solvatochromism. The sample of NO<sub>2</sub>-OPV dissolved in different solvents such as toluene, chloroform, tetrahydrofuran, dichlorobenzene, acetonitrile, dimethylsulfoxide were evaluated to measure the absorption as well as emission of these solutions. The absorption peak varied over a range of 42 nm, between 390 and 432 nm for different solvents. But in case of emission the role of solvent was prominent as the emission ranged spanned over 218 nm, that is, from 432 nm in methanol to 650 nm in acetonitrile and DMSO, see Figure 2. Such strong solvatochromism can be attributed to combination of electrostatic OPV-solvent interactions, intramolecular charge transfer and aggregate formation in solution.<sup>26</sup> Solvent stabilization of intramolecular charge transfer in the excited state also leads to such high solvatochromism.

# Photophysical properties of OPV 8-11

The presence of terminal pyridine group in OPV 8-11 was explored using its pyridyl ring that can prove to be an active site for the protonation and hence can drastically alter the absorption and emission of the compound. The pyridine terminated OPVs 8-**11** were spectroscopically studied for their protonation behaviour. All the pyridine terminated compounds were readily soluble in organic solvents. They were highly fluorescent in diluted solutions and display a spectral sensitivity to pH in absorption spectra as well as in fluorescence spectra at the low concentration range of 0.01 mM. All the compounds exhibit highly pH-dependent absorption and emission. The absorption spectrum of pyridine terminated OPVs showed a strong absorption in the range of 300-400 nm. The absorption near 300 nm can be assigned to  $\pi$ - $\pi$ \* electronic transition while the absorption band near 400 nm can be due to  $n-\pi^*$ transition. All the pyridine terminated OPVs showed a clear bathochromic shift on addition of HCl. This acid-induced change is clearly detected visually (blue to orange) as well as studied by measuring its absorbance and emission in methanol by addition of methanolic HCl solution. The absorption and emission change is reversible, as the blue emission of free sample can be fully restored on the addition of ammonia. The pH-dependent change can be readily attributed to the protonation-deprotonation process of the terminal pyridine groups, which allows the reversible inter-conversion between the cationic and neutral forms of OPVs. The quinonoid form formed due to the protonation of pyridine nitrogen, absorbs at higher wavelength as compared to the benzenoid form. The changes of these compounds occur in the visible range, making it suitable for applications as visually sensing material. Solution of **OPV 8** shows absorption at 352 and 408 nm which is red shifted on acidification with dilute methanolic HCl and the new absorption band appears as a broad peak at 427 nm. Further in order to study the substituent effect we have systematically studied **OPV 9–11** with electron releasing and electron withdrawing substituents. **OPV 9** (R = H) showed absorption at 318 and 332 nm which after protonation shifted to 368 nm. Also the **OPV 10** with –OMe functional group absorbs at 364 nm whereas **OPV 11** with chromophoric –NO<sub>2</sub> group shows absorption peaks at 316 and 366 nm. Upon protonation the absorption peak of **OPV 10** shifts from 364 to 417 nm, such high bathochromic shift can be attributed to the presence of electron releasing –OMe group which can stabilize the pyridyl nitrogen after protonation. In case of **11** ( $R = NO_2$ ) protonation leads to a smaller bathochromic shift, that is, from 366 to 376 nm due to the presence of electron withdrawing –NO<sub>2</sub> group.

The emission spectra of all the pyridine terminated **OPVs** showed emission peak in the visible region of electromagnetic spectrum and showed a bathochromic shift after protonation. The **OPV 8** shows a clear emission band at 480 nm which quickly disappears on protonation with methanolic HCl and a new band appears at 618 nm. Such a large bathochromic shift can be attributed to the long conjugation of  $\pi$ -bond across the pyridine nitrogen and the electron donating –OMe group. The OPV **9**, **10** and **11** show an emission band at 421, 455 and 508 nm, respectively, and after protonation new band appears at 496, 604 and 517 nm, respectively.

It is observed that there was 75 nm bathochromic shift in **OPV 9** whereas 149 nm bathochromic shift was observed in the case of **OPV 10** with –OMe substitution where the positive charge of protonated pyridine will be stabilized by the push–pull mechanism. On the other hand the **OPV 11** showed only 9 nm shift due to the presence of electron withdrawing –NO<sub>2</sub> group. Florescence spectra for **OPV 9**, **10** and **11** are shown in Figure 3. The absorption and emission wavelengths are summarized in Table 1.

Hence, in this Letter we have presented the synthesis of oligo (phenylenevinylene)s by one-pot Wittig–Heck methodology in good yields.<sup>27</sup> The OPVs with different substituents showed varying optical properties depending on the end group substituents. The OPV– $NO_2$  showed solvatochromism with the wavelength range of 218 nm in different solvents. The pyridine terminated OPVs showed acidochromism which was studied spectroscopically.

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# Supplementary data

Supplementary data (characterization data and copies of the spectra) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2015.10.033.

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- 27. Typical procedure for the synthesis of **OPVs** General procedure for the synthesis of **OPV 1–7**:

Synthesis of 4,4'-((2,5-dimethoxy-1,4-phenylene)bis(ethene-2,1-diyl)dibenzene OPV 1

A two neck round bottom flask was charged with 1, 4-diiodo dimethoxy

benzene (0.2 g, 0.512 mmol), methyl triphenylphosphine iodide (0.416, 0.102 mmol), benzaldehyde (0.108 g, 0.102 mmol), K<sub>2</sub>CO<sub>3</sub> (0.496 g, 0.358 mmol), palladium acetate (0.0011 g, 0.00512 mmol), dpp (0.0042 g, 0.0102 mmol), TBAB (0.066 g, 0.205 mmol) in *N*,*N*-dimethyl acetamide (10 mL) and was stirred at 140 °C under N<sub>2</sub> atmosphere for 24 h. The cooled mixture was then poured in water (100 mL) and extracted with ethyl acetate (3 × 50 mL). The organic layer was washed with water (2 × 20 mL) and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography on silica gel and petroleum ether–ethyl acetate mixture as eluent to give pure product as pale yellow solid (0.144 g, 82.3%). Melting point: 176 °C (Lit. 28 177–178 °C).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.58 (d, *J* = 7.2 Hz, 2H, aromatic protons of terminal benzene ring), 7.52 (d, *J* = 16.4 Hz, 1H, *E* olefinic protons), 7.37–7.41 (m, aromatic protons of terminal benzene rings), 7.26–7.30 (m, aromatic protons of terminal benzene rings), 7.17 (s, aromatic protons of tetra substituted benzene ring), 7.15 (d, *J* = 16.4 Hz, 1H, *E* olefinic protons), 3.96 (s, 3H).

Synthesis of 4,4'-((1E,1'E)-(((1E,1'E)-(2,5-dimethoxy-1,4-phenylene)bis(ethene-2,1-diyl))bis(4,1-phenylene))bis(ethene-2,1-diyl))dipyridine **OPV 8** 

A two neck round bottom flask was charged with 2,5-dimethoxyterephthalaldehyde (0.150 g, 0.773 mmol), 4-bromo benzyl triphenylphosphine bromide (0.792 g, 1.546 mmol), 4-vinyl pyridine (0.178 g, 1.546 mmol), K<sub>2</sub>CO<sub>3</sub> (0.854 g, 6.180 mmol), palladium acetate (0.0034 g, 0.0154 mmol), dppp (0.0095 g, 0.023 mmol), TBAB (0.049 g, 0.154 mmol) in *NN*-dimethyl acetamide (10 mL) and was stirred at 140°C under N<sub>2</sub> atmosphere for 24 h. The cooled mixture was then poured in water (100 mL) and extracted with ethyl acetate ( $3 \times 50$  mL). The organic layer was washed with water ( $2 \times 20$  mL) and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography on silica gel and petroleum ether–ethyl acetate mixture as eluent to give pure product as orange solid (0.336 g, 79.40%).

Melting point: >250 °C (d) (Lit. 29)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.60 (d, *J* = 6 Hz, 4H), 7.64–7.30 (m, 14H), 7.18– 7.14 (m, 4H), 7.10–7.018 (m, 4H), 3.96 (s, 6H).

- General procedure for the synthesis of **OPV 9–11**:
- Synthesis of 4-((E)-4-((E)-styryl)styryl)pyridine OPV 9

A two neck round bottom flask was charged with, 4-bromo benzyl triphenylphosphine bromide (0.500 g, 0.976 mmol), benzaldehyde (0.124 g, 1.171 mmol), 4-vinyl pyridine (0.122 g, 1.171 mmol),  $K_2CO_3$  (0.539 g, 3.90 mmol), palladium acetate (0.0021 g, 0.00976 mmol), dpp (0.0060 g, 0.014 mmol), TBAB (0.031 g, 0.097 mmol) in *N*,*N*-dimethyl acetamide (10 mL) and was stirred at 140 °C under N<sub>2</sub> atmosphere for 24 h. The cooled mixture was then poured in water (100 mL) and extracted with ethyl acetate ( $3 \times 50$  mL). The organic layer was washed with water ( $2 \times 20$  mL) and dried over anhydrous sodium sulfate. The solution was purified by column chromatography on silica gel and petroleum ether–ethyl acetate mixture as eluent to give pure product as yellow solid (0.229 g, 85%). Melting point: 280°C (Lit. 30 283–284 °C).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.60 (d, *J* = 6.0 Hz, 2H), 7.61–7.51 (m, 6H), 7.41–7.30 (m, 6H), 7.19 (d, *J* = 16.4 Hz, 1H), 7.13 (d, *J* = 16.4 Hz, 1H), 7.05 (d, *J* = 16.4 Hz, 1H).

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