



## 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, ((1*E*,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 ((1*E*,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>

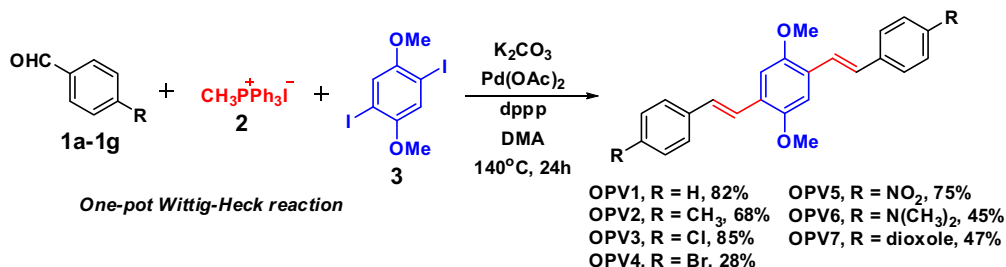
Owing to the importance of this class of compounds, many methods are known for the synthesis of oligo(phenylenevinylene)s. Generally the conjugation in the molecule is built by condensation reactions namely Wittig, Knoevenagel, Perkin etc., or by metal mediated coupling reactions such as Mizoroki–Heck 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 ((1*E*,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.

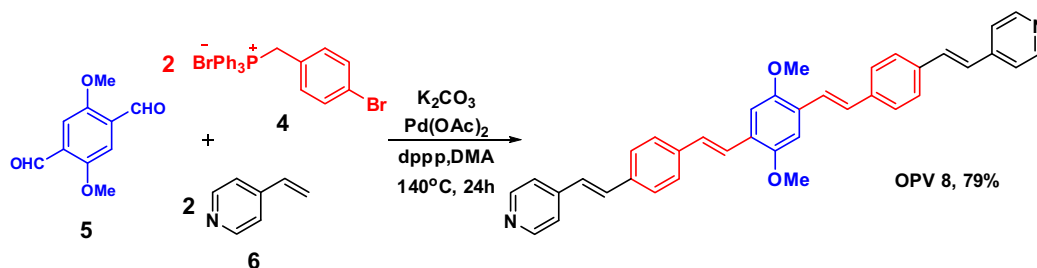
Amongst ((1*E*,1'*E*)-(2,5-dimethoxy-1,4-phenylene)bis(ethene-2,1-diyl))dibenzene derivatives we have synthesized seven compounds, **OPV 1–7**, by the given one-pot procedure. The synthesis

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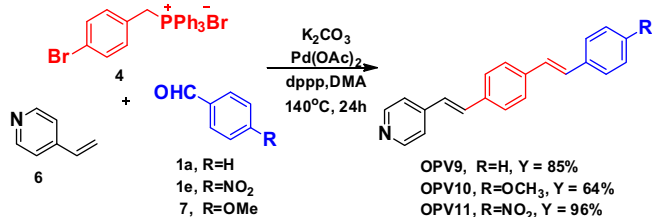
E-mail address: [avbedekar@yahoo.co.in](mailto:avbedekar@yahoo.co.in) (A.V. Bedekar).



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-diodo-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-bromobenzyltriphenylphosphonium 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 4-bromobenzyltriphenylphosphonium 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 fluorescence 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 fluorescence emission of

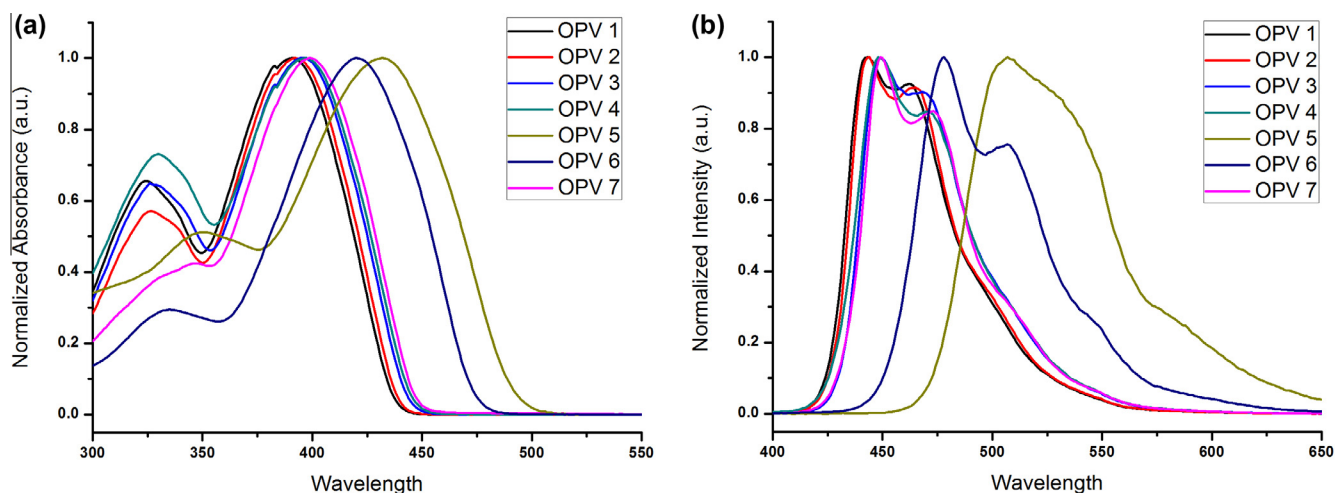


Figure 1. (a) UV-Visible spectra for OPV 1–7. (b) PL spectra for OPV 1–7.

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