

# **BANANA AND STAR SHAPED LIQUID CRYSTALLINE OLIGO-(PHENYLENEVINYLENE)S**

**A Thesis Submitted Towards Partial Fulfillment of  
BS-MS Dual Degree Programme**



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15<sup>th</sup> April 2011

**CERTIFICATE**

This is to certify that the work embodied in the thesis entitled “**BANANA AND STAR SHAPED LIQUID CRYSTALLINE OLIGO (PHENYLENEVINYLENE)s**” has been carried out by **Mr. Harpreet Singh** under my supervision at the Department of Chemistry, Indian Institute of Science Education and Research (IISER), Pune and the same has not been submitted elsewhere for any other degree.

Date:

Place: Pune

**Dr. M. Jayakannan**

(Thesis Supervisor)

*Dedicated to My Beloved Parents .....*

## **DECLARATION**

I hereby declare that the matter embodied in the report entitled “**BANANA AND STAR SHAPED LIQUID CRYSTALLINE OLIGO (PHENYLENEVINYLENE)s**” are the results of the investigations carried out by me at the Department of Chemistry, Indian Institute of Science Education and Research-Pune (IISERP), Pune, under the supervision of Dr. M. Jayakannan and the same has not been submitted elsewhere for any other degree.

**Place:** Pune

April 2011

**Harpreet singh**

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*“Beside a good researcher Jayakannan is a good human being, friendly in nature, perfect family man and good team leader. I must say I was lucky to get a project guide like him. The values which I got from him will stand with me throughout my life.”*

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I bow down to my grandfather, father, mother for their moral encouragement, loving care and trust throughout my degree.

*Harpreet singh*

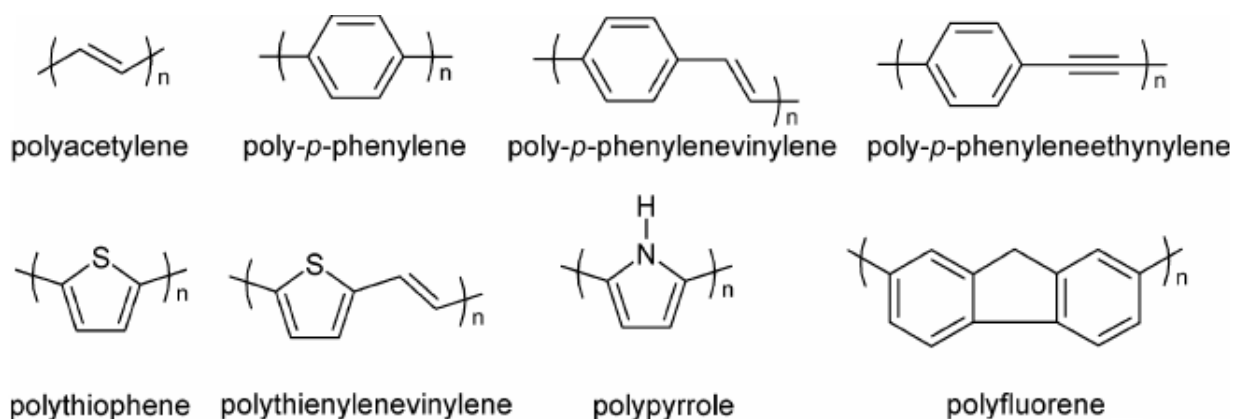
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# **INTRODUCTION**

## 1.1 Introduction to conducting polymer and oligomer

Polymers were well known for their insulating properties, mechanical strength and processability. A new idea, which was given by the pioneer work of three eminent professors Alan Mac Diarmid, Alan J. Heeger and Hideki Shirakawa in 1977 that, “polymer can be conductive” given a new vision to the researcher to look at the polymers from a different angle.<sup>1-2</sup> Polymer which passes electric current are called conducting polymer. All conducting polymers have a basic  $\pi$ -conjugate system having alternative single and double bond (or triple bond).



**Figure 1.1:** Chemical structures of several conjugated polymers

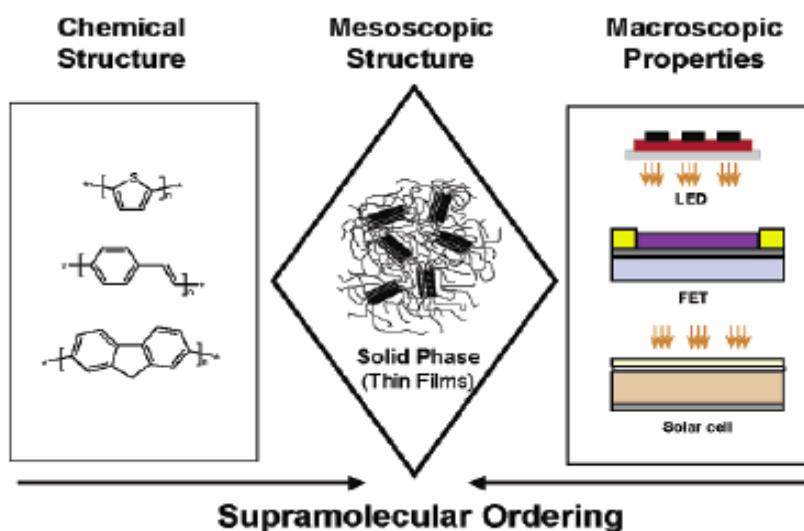
The discovery of polymeric light emitting diodes in 1990 by Cambridge group had given an introduction of  $\pi$ -conjugated system to electronics devices and the dream to arrive at molecular electronics based on this systems.<sup>3-6</sup> The unique combination of structural, mechanical, photonic, and electric properties made these classes of materials attractive for plastic lasers, chemical sensors, LEDs and photovoltaic cells.<sup>7-10</sup>

The performance of organic devices is mainly determined by chemical structure, purity and supramolecular self-organizations. The importance of control on structure at every structural packing order is by far the most delicate for semiconducting polymer. Going from isolated chain to an intermolecular packing order is required for conduction in a microcrystalline or mesoscopic phase. To arrive at controlled microcrystallinity it is necessary to have solubilizing group. A

number of ways to control the solubility are well known by putting a long alkyl chain. The versatility of substituted conjugated polymer has led to tunable physical properties like color, emission, efficiency etc.<sup>11</sup> Side chain variation on the polymer backbone has been studied in



terms of electronics effect and related to morphology and charge carrier mobility.<sup>12-16</sup> For instance, bulky alkyl substituent's directly linked to the conjugate rod hampers a planar conformation.<sup>17-20</sup> System employing liner or branched side chain substituent have been compared base on their photo physics and charge transport, the linear substituent showing emission at higher wavelength due to formation of  $\pi$ -stacked aggregates while the branched substituent show blue shifted emission lacking higher order.<sup>21</sup> The effects of the chemical composition of conjugated polymers on the supramolecular organization, i.e., the morphology of the active layer, are of major concern to further optimize the performance of the devices.



**Figure 1.2.** Schematic representation on how the properties of optoelectronic devices such as LEDs, FETs, and solar cells are related to chemical structure and supramolecular organization

In an engineering approach, variations in processing conditions<sup>22</sup> of the conjugated polymeric materials have realized tremendous progress in controlling the morphology of the active layer, also by introduction of alignment layers<sup>23-24</sup> and thermal<sup>25-28</sup> and mechanical

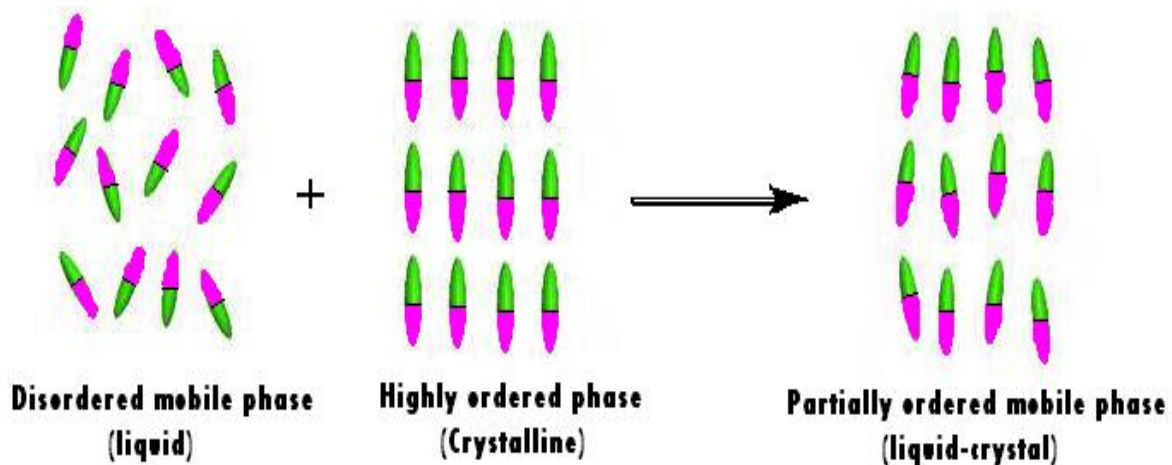
treatments. Nonetheless, most polymeric films are highly amorphous and inhomogeneous, resulting in small domains of 15-30 nm for polyfluorenes<sup>29</sup>, while for polypyridylvinylene<sup>30</sup>, polythiophenen<sup>31</sup> and poly-*p*-phenylenevinylene<sup>32</sup> partially aligned regions of the film of typically 200- 300 nm in size are found. However, dimensions of devices are roughly in the

micrometer regime. Therefore, additional features to control the morphology of the active layers are highly requested to improve performance.

Although  $\pi$ -conjugated polymers are easy to process by technique like Ink-jet printing<sup>33</sup>, it is rather difficult to get a desired morphology or self-organized state due to anisotropy in the inter chain interaction. It is already established that photo physical properties of a  $\pi$ -conjugated systems almost invariant above 5-6 repeating units of the polymer chain. Therefore, small molecules can be used as a building block for electronic devices which may have similar feature of those obtained from high molecular weight polymers. Further high luminescence characteristic, thermal and optical stability, solubility in organic solvent, thin film forming tendency, easy synthesis and purification are some advantage of small molecules over the polymers.

## **1.2. Molecular self organization of $\pi$ -conjugated materials.**

Self assembly approach can be adopted to obtain the supramolecular structures based on small molecules for practical application or desire properties.<sup>34-36</sup> The macroscopic outcome of the self-assembly at the molecular level is routinely visualized as organo or hydro gel, viscous liquid and three dimensional ordered liquid-crystals. Liquid crystals are partly ordered materials having properties of both solid and liquid phases. Their molecules are often shaped like rods or plates or some other forms that encourage them to align collectively along a certain direction. The order of liquid crystals can be manipulated with mechanical, magnetic or electric forces. When liquid crystals subjected to thermal, electric, and magnetic fields, they behave in unique ways that their several distinct optical properties exhibit interesting changes. The temperature sensing and color changing abilities of liquid crystals make them suitable for use in a wide range of thermometers and novelty applications as clothing, and advertising specialties. Liquid crystal colors can change through the visible color spectrum with a temperature change of only two degrees C. Liquid crystalline materials are generally divided into two categories.



**Figure 1.6.** *Schematic diagram of liquid crystal*

- (1) *Thermotropic liquid crystal*
- (2) *Lyotropic liquid crystal*
- (3) *Metallotropic liquid crystal*

Thermotropic and lyotropic LCs consist of organic molecules. Thermotropic LCs exhibit a phase transition into the LC phase as temperature is changed. Lyotropic LCs exhibit phase transitions as a function of both temperature and concentration of the LC molecules in a solvent (typically water). Metallotropic LCs are composed of both organic and inorganic molecules; their LC transition depends not only on temperature and concentration, but also on the inorganic-organic composition ratio. Molecular self assembly is obtained using the weak interaction forces such as weak  $\pi$ - $\pi$  interaction, hydrogen bond and van der Waals forces. Process to get the self assembled oligomer is totally depend on the nature of interaction and the shape of molecule which is used as a building block for supramolecular structure. In the self-assembly of  $\pi$ -conjugated oligomers different specific interactions work simultaneously and the strength of the overall binding is the result of many co-operative process. Oligophenylenevinylene (OPV)<sup>37</sup>, oligophenylene<sup>38</sup>, oligothiophene<sup>39</sup>, oligofluorenes<sup>40</sup>, and oligophenyleneethylene<sup>41</sup> chromophores were reported for self-organization in  $\pi$ -conjugated materials. In this literature

surveys, the examples are common only for OPVs based system, since this study is also aimed to new OPVs self organized systems.

To get self organized supramolecular structures efforts have been taken using hydrogen bonding, and metal ion interaction in addition to  $\pi$ - $\pi$  stacking and the resultant structures were tested for electronic devices. The hydrogen bonding is a special class of dipole-dipole interaction and is predominantly an electrostatic interaction between a weak acidic donor and an acceptor atom that has a lone pair of electron with distance separation of  $\sim 3 \text{ \AA}$ . Hydrogen bonds are ideal secondary interactions to construct supramolecular architectures since these are highly selective and directional. In nature, beautiful examples of these properties are present in DNA and proteins. Hydrogen bonds have also been used to position  $\pi$ -conjugated molecules in self-assembled architecture multiple hydrogen-bonding interactions were introduced in OPV system to create organization structure, sheets and wires.

The thermotropic liquid crystalline properties of a series of organic semiconductors that are chiral and achiral oligo(p-phenylenevinylene)s (OPVs) equipped with hydrogen bonding arrays were reported by E. W. Meijer et. al.<sup>42</sup> In which they have investigated the influence of the length of the rigid and flexible segments, branched side chains and the hydrogen bonding array on the bulk supramolecular organization. The OPVs are functionalized with hydrogen bonding diaminotriazine or ureidotriazine units. Furthermore, the lengths of the rigid OPV backbone and the flexible trialkoxybenzene end groups were changed. The self-assembly of the OPV molecules has already been reported at a solid-liquid interface and in solution showing that diaminotriazine OPVs form hydrogen bonded hexameric rosettes while the ureidotriazine derivatives form hydrogen bonded dimers. These hydrogen bonded rosettes and dimers subsequently self-assemble into columnar stacks in solution. Ajayghosh and co-workers have reported  $\pi$ -conjugate organogels from self assembled oligophenylenevinylenes see figure 1.5. The fiber like morphology of the OPV xerogel are a result of multilayer lamellar assemblies of molecules through  $\pi$ - $\pi$  stacking.<sup>(43)</sup>

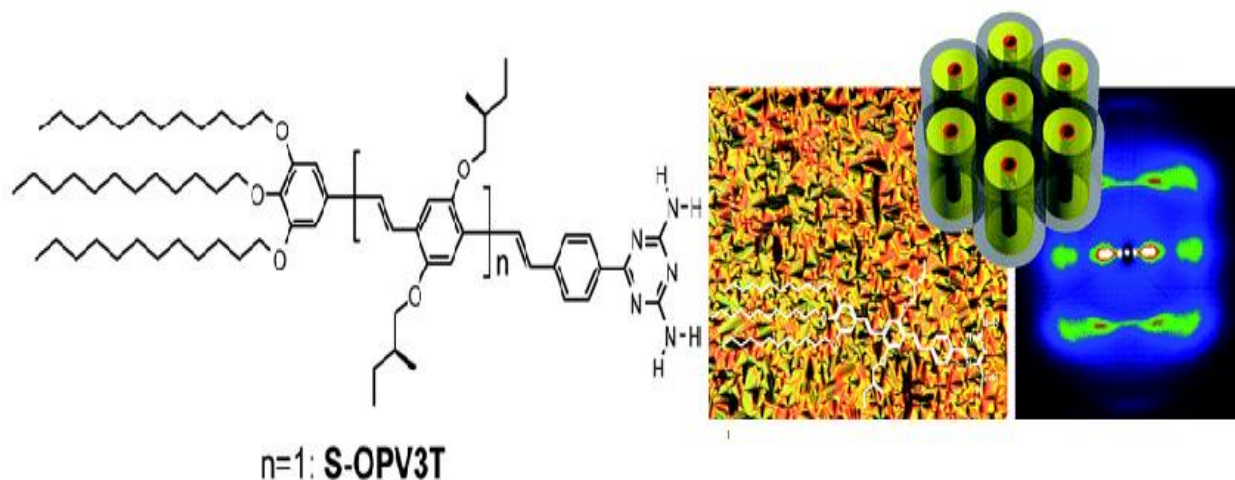


Figure 1.4. Schematic illustration of the columnar superstructure (intracolumnar packing of individual molecules is neglected). (Adopted from ref. 42)

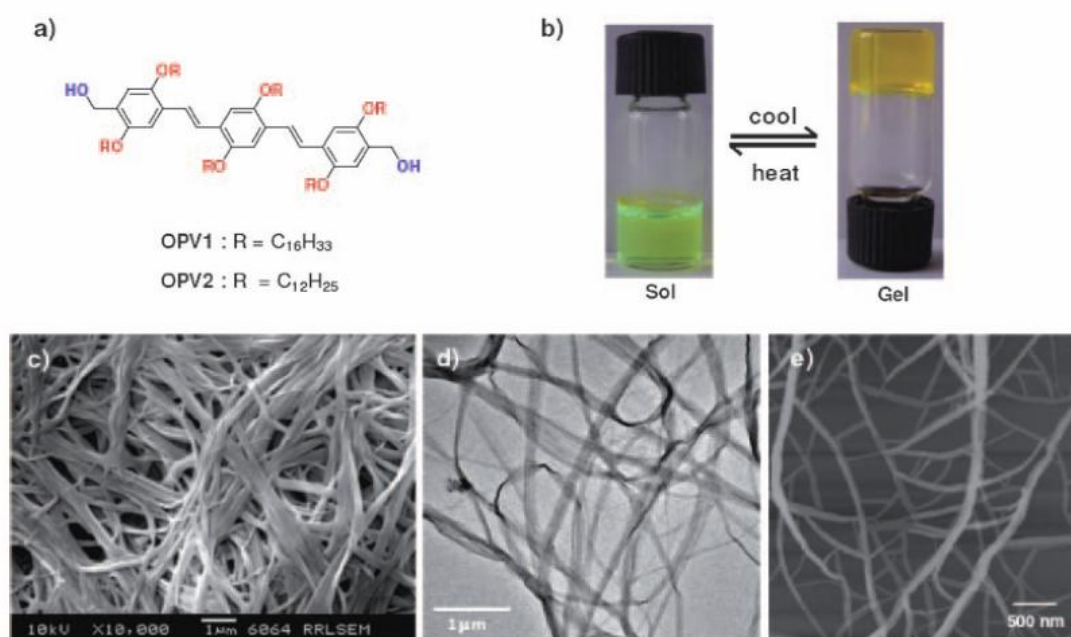
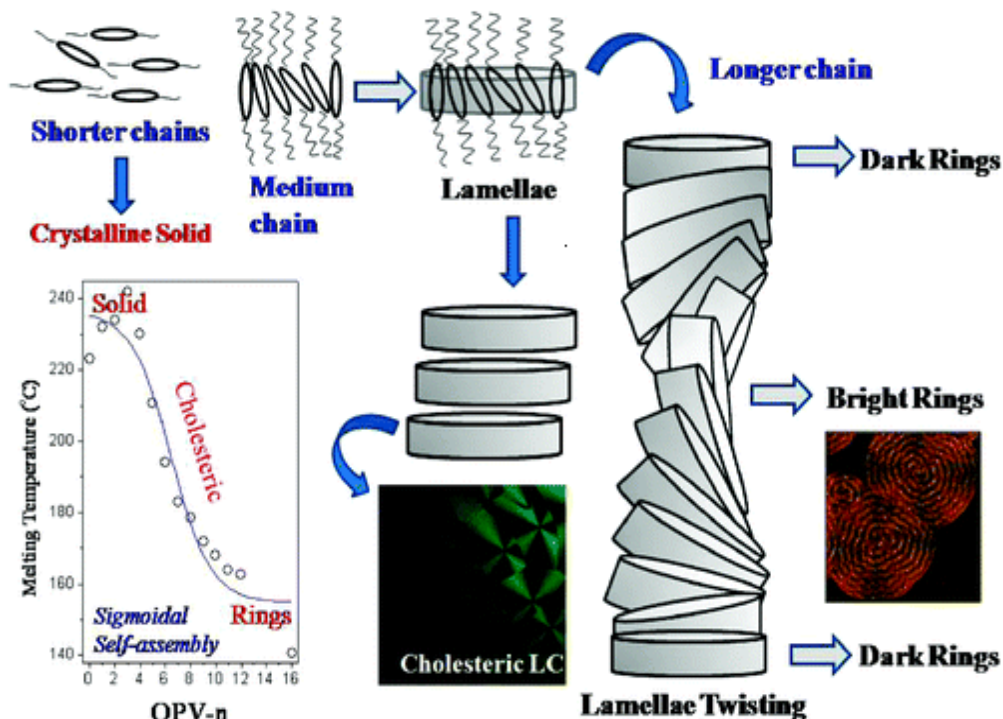


Figure 1.5. self assembly of OPVs based gels via supramolecular interactions. (Adopted from ref. 43)

The development of supramolecular  $\pi$ -conjugated materials via molecular self-organization is an active area of research due to their potential application in optoelectronics, chemical and bio-sensors. The liquid crystalline materials are particularly important since self-organized structures could be obtained via solvent free melt crystallization process and possessed potential for large scale processability in electronic devices. Recently, Meijer and co-workers

reported OPV terminated poly (propylene imine) dendrimers that are liquid crystalline and the mesophase window was found to increase with higher generation.<sup>44</sup> Maddux et al. had developed an orthogonal approach for LC-OPVs and studied the effect of increase in the chain length on the LC transition.<sup>45</sup> Few reports were also known for studying the effect of alkyl side chains or fluoro-substitution on the LC properties of OPVs.<sup>46,47</sup> He et al. and Gu et al. were demonstrated that liquid crystalline OPVs can enhance the photoluminescence and electroluminescence properties to a great extent.<sup>29</sup>

Main aim of introducing hydrogen bond or metal-ion interaction was to strengthen the existing  $\pi$ - $\pi$  stacking. With advantage that these forces provide strength to supramolecular structures, it had some disadvantages like hydrogen bonding unit or metal-ion unit in  $\pi$ -cojugated molecules behaved as insulting matrix which hamper the efficiency of electronic devices.<sup>50</sup> It has



**Figure 1.3.** Sigmoidal plot of OPVs and the proposed mechanism for the self-organization of OPV chromophores in cholesteric LC phase and ring-banded structures. (Adopted from ref. 51).

been now widely recognized that retaining of the aromatic  $\pi$ - $\pi$  stacking among the building blocks without compromising on the molecular self-assembly is very much essential for the success of these materials in electronic devices. Alkyl chains assisted self-organization based on weak van der Waals forces is another important secondary interaction; however, it was not

exploited for self-assembly in  $\pi$ -conjugated materials. From our group S. R. Amrutha *et al.* and Mahima *et al.* utilize weak van der Waals forces to self organize OPV chromophores in the LC-phases. New series of bulky oligophenylenevinylenes (OPVs) bearing tricyclodecanemethylene (TCD) unit in the aromatic  $\pi$ - core with flexible long methylene chains ( $n= 0$  to 12 and 16) in the longitudinal position were designed and synthesized.<sup>51,52</sup> Polarized light microscopic analysis confirmed the formation of cholestric liquid crystalline (LC) phases of fan shaped textures with focal conics in OPVs with  $5 \leq n \leq 9$ . OPVs with longer alkyl chains (OPV-10 to OPV-12) produced birefringence pattern consisting of dark and bright ring banded supra-structures. The melting temperature followed a sigmoidal trend indicating the transformation of molecular self organization in OPVs from solid to ring banded supra-structures via cholestric LC intermediates. At longer alkyl chain length, the stronger van der Waals interactions among the alkyl chains translate the mesogenic effect across the lamella; as a consequence, the lamellae undergo twisted self-organization along the radial growth direction of the spherulites to produce bright and dark bands.

### **1.3. Aim of Thesis work:**

It is very evident from the above literature survey that the molecular self-organization of OPV chromophores and their LC-properties are very important topic of research. However, up to our knowledge, no effort has been taken to trace the effect of non-linear structural aspects of chromophores on their thermotropic LC behaviors. Non-linear molecular architectures like banana shaped or branched star shaped chromophores are investigated in other types of material science, however, not explored in the area of  $\pi$ -conjugated materials. Non-linear chromophores are particular important since they could bring different types of molecular packing and opto electronic properties which is neither known nor available at present in the  $\pi$ -conjugated material system. In this thesis, new class of bent shaped or banana shaped and star shaped liquid crystalline OPVs are designed and synthesized for the above purpose. The OPV molecules were designed in such a way that they possessed only aromatic  $\pi$ -stacking and van der Waals interactions. This facilitate us to understand the role of non-linear structures on the molecular packing of  $\pi$ -conjugated chromophores in thermotropic LC phases. Both 1,4 (para-) and 1,3 (meta-) distyrl chemical linkages are chosen as rigid aromatic core and flexible chains are

designed based on either renewable resource cardanol, pentadecylphenol, or dodecyl alkyl units. It was found that the structure of the OPV molecules play a major role on the determination of their LC-properties and their photophysical characteristics. In a nut shell, the work presented in this thesis provides a new scientific insight into the molecular packing of  $\pi$ -conjugated chromophores, more specifically banana or star shaped OPVs, which are potential candidates for opto electronic applications such as LEDs and photovoltaics.



# **EXPERIMENTAL SECTION**

## 2. Experimental Methods

**2.1. Materials:** 3-Pentadecylphenol, p-methoxyphenol, p-methylphenol, 2-bromoethanol, 4-hydroxybenzaldehyde,  $\text{LiAlH}_4$ , triethylphosphite, and potassium tert-butoxide in 2M THF solution were purchased from Aldrich chemicals. P-Formaldehyde, N,N-dimethylaniline,  $\text{SOCl}_2$ , HBr in glacial acetic acid,  $\text{K}_2\text{CO}_3$ , KOH, KI, cardanol and all other reagents and solvents were purchased locally and purified following the standard procedure.

**2.2. General Procedures:**  $^1\text{H}$  and  $^{13}\text{C}$  NMR were recorded using a 400 MHz JEOL NMR spectrometer. All NMR spectra were recorded in  $\text{CDCl}_3$  containing TMS as internal standard. Infrared spectra were recorded using a Thermo-Scientific Nicolet 6700 FT-IR spectrometer with the solid state. The mass of all the OPVs was determined by using the Applied Biosystems 4800 PLUS MALDI TOF/TOF analyzer. The samples were dissolved in dichloromethane and R-cyano-4-hydroxycinnamic acid was used as the matrix. The purity of all OPVs was further checked by gel permeation chromatographic (GPC) analysis, which was performed using a Viscotek VE 1122 pump, Viscotek VE 3580 RI detector, and Viscotek VE 3210 UV/vis detector in tetrahydrofuran (THF) using polystyrene as standards. Thermal analyses of all the OPVs were performed using a TA Q20 differential scanning calorimeter (DSC). The instrument was calibrated with indium standards. All the OPVs were heated to melt before recording their thermograms to remove their previous thermal history. OPVs were heated and cooled at  $10^\circ\text{C}/\text{min}$  under a nitrogen atmosphere and their thermograms were recorded. To study the different LC phases as shown by different OPVs, we used a LIECA DM2500 P polarized light microscope equipped with Linkam TMS 94 heating and freezing stage connected to a Linkam TMS 600 temperature programmer. Variable temperature X-ray diffraction patterns were recorded using Philip X'pert Pro powder X-ray diffractometer with a copper target. The system consisted of a rotating anode generator with a copper target and a wide angle powder goniometer fitted with a high temperature attachment. Spectra were recorded using Cu KR radiation in the range of  $2\theta$  )  $3\text{-}50^\circ$  at a heating and cooling rate of  $10^\circ\text{C}/\text{min}$ . The absorption and emission studies were done by a Perkin-Elmer Lambda 45 UV-Visible spectrophotometer and SPEX Fluorolog HORIBA JOBIN VYON fluorescence spectrophotometer with a double-grating 0.22 m Spex1680 monochromator and a 450W Xe lamp as the excitation source at room temperature. The solution spectra were recorded in THF and for solid state spectra of OPVs, thin films were prepared by drop casting THF solution on quartz substrates. The concentrations of the OPVs and standard

solution were adjusted in such a way to obtain the absorbance equal to 0.1 for the determination of quantum yield.

### 2.3. Synthesis of intermediate compounds and OPVs

**2.3.1. Synthesis of 2-(3-pentadecylphenoxy)ethanol (1).** 3-Pentadecylphenol (15.0 g, 49.25 mmol) was added to a stirred solution of KOH (5.5 g, 98.50 mmol) in a mixture of ethanol (45 mL) and distilled water (45 mL) at room temperature in nitrogen atmosphere. 2-Bromoethanol (9.2g (5.24 mL), 73.80 mmol) was added drop wise to this solution. After the completion of addition, the reaction mixture was refluxed for 6 hr. It was allowed to cool at room temperature and poured into water (100 mL) and extracted with ethyl acetate. Organic layer was washed with NaOH, brine solution and dried over sodium sulphate. After solvent was evaporated, the product was obtained as white crystalline solid. Yield = 16.1 g (94 %).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 7.18 ppm (t, 1H, Ar-H), 6.75 ppm (m, 3H, Ar-H), 4.07 ppm (t, 2H, Ar-OCH<sub>2</sub>), 3.94 ppm (t, 2H, CH<sub>2</sub>-OH), 2.56 ppm (t, 2H, Ar-CH<sub>2</sub>), 2.5-0.88 ppm (m, 29H, Aliphatic H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 158.66, 144.87, 129.31, 121.42, 114.89, 111.51, 66.07, 61.64, 36.11, 32.02, 31.50, 29.78, 29.62, 29.46, 22.80 and 14.22. FT-IR ( $\text{cm}^{-1}$ ): 3367(C-OH), 2913, 2847, 1596, 1486, 1459, 1374, 1309, 1264, 1174, 1085, 1048, 1003, 957, 901, 879 and 860.

**2.3.2. Synthesis of 1-(2-chloroethoxy)-3-pentadecylbenzene (4).** Compound 1 (5.0 g, 14.30 mmol) and N,N-dimethylaniline (1.74 g, 14.30 mmol) were taken in RB flask and kept under ice cold condition. A solution of  $\text{SOCl}_2$  (3.42 g, 28.70 mmol) in chloroform (5mL) was added drop wise; the color of reaction mixture was turned into dark red. It was refluxed for 4 hr and cooled to room temperature. It was poured into water (100 mL) in conc.HCl (25 mL). The compound was extracted with dichloromethane, dried over sodium sulphate and the solvent was evaporated to get product. Further purification was done by passing through silica gel column using 100% petroleum ether as solvent. Yield = 4.9 g (94 %).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz): 7.18 ppm (t, 1H, Ar-H), 6.75 ppm (m, 3H, Ar-H), 4.21 ppm (t, 2H, Ar-OCH<sub>2</sub>), 3.80 ppm (t, 2H, CH<sub>2</sub>-Cl), 2.56 ppm (t, 2H, Ar-CH<sub>2</sub>), 2.5-0.88 ppm (m, 29H, Aliphatic H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 158.25, 144.94, 129.34, 121.69, 115.09, 111.60, 67.94, 42.07, 36.10, 32.03, 31.49, 29.78, 29.70, 29.62, 29.48, 29.44, 22.81 and 14.22. FT-IR ( $\text{cm}^{-1}$ ): 2914, 2849, 1585, 1449, 11291, 1156, 1084, 1264, 1044, 1085, 957, 901, 879 and 860.

**2.3.3. Synthesis of 4-(2-(3-pentadecylphenoxy)ethoxy)benzaldehyde (PDP-CHO):** 4-hydroxybenzaldehyde (1.19 g, 9.82 mmol) and potassium carbonate (4.07 g, 29.5 mmol) and

catalytic amount of KI were taken with DMF (30 mL) in two neck RBF under nitrogen atmosphere and refluxed for 1 hr. Compound 4 (3.0 g, 8.20 mmol) was added and the reaction mixture was refluxed for 12 h and cooled to room temperature, extracted with ethyl acetate and the organic layer was washed with 10% NaOH. Purification was done by column chromatography in ethyl acetate and pet ether (3% v/v). Yield = 3.1 g (84 %).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 9.89 ppm (s, 1H, Ar-CHO), 7.84 ppm (d, 2H, Ar-H), 7.19 ppm (t, 1H, Ar-H), 7.05 ppm (d, 2H, Ar-H), 6.77 ppm (m, 3H, Ar-H), 4.37 ppm (m, 4H, Ar-OCH<sub>2</sub>), 2.55 ppm (t, 2H, Ar-CH<sub>2</sub>), 2.00-0.88 ppm (m, 29H, Aliphatic H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 190.92 (Ar-CHO), 163.76, 158.49, 144.92, 132.09, 130.28, 129.34, 121.59, 111.54, 66.95, 66.14, 36.10, 32.02, 31.49, 29.69, 29.61, 29.46, 29.43, 22.79 and 14.23. FT-IR ( $\text{cm}^{-1}$ ): 2916, 2848, 1682, 1597, 1452, 1241, 1162, 1067, 969 and 834.

**2.3.4. Synthesis of 2-(2,4-bis(bromomethyl)-5-pentadecylphenoxy)ethanol (2).** Compound 1 (5.0g, 14.3 mmol) and p-HCHO (1.72 g, 57.4 mmol) were taken in glacial acetic acid (40 mL) and HBr in glacial acetic acid (30-33 wt%), (14.4 mL) was added to it using a pressure equalizing funnel. The reaction mixture was then refluxed for 8 hours, cooled to room temperature and poured into large amount of water. The precipitate was repeatedly washed with cold water until the filtrate become neutral. This white solid was filtered to obtain pure product. Yield = 3.1 g (84 %).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 7.30 ppm (s, 1H, Ar-H), 6.67 ppm (s, 1H, Ar-H), 4.50 ppm (s, 4H, Ar-CH<sub>2</sub>-Br), 4.49 ppm (t, 2H, Ar-OCH<sub>2</sub>), 4.03 ppm (t, 2H, Ar-OCH<sub>2</sub>CH<sub>2</sub>OH), 2.68 ppm (t, 2H, Ar-CH<sub>2</sub>), 2-0.92 ppm (m, 52H, aliphatic H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 171.11, 156.68, 144.75, 133.23, 128.20, 124.56, 113.21, 66.52, 62.55, 32.87, 32.02, 31.08, 29.78, 29.68, 29.60, 29.46, 28.40, 22.79, 21.04 and 14.23. FT-IR ( $\text{cm}^{-1}$ ): 2914, 2849, 1582, 1449, 1291, 1156, 1084, 1044, 868, 771 and 688.

**2.3.5. Synthesis of 2-(2,4-dimethyl-5-pentadecylphenoxy)ethanol (3).** Compound 2 (6.0 g, 11.27 mmol) was taken in dry THF (60 mL) and kept under nitrogen.  $\text{LiAlH}_4$  (0.64 g, 16.91 mmol) was added in portions at 0° C and stirred the mixture for 6 h. Reaction mixture was quenched with 10% HCl solution until it became acidic. THF was removed and extraction was done using pet ether as solvent. The organic layer was separated, washed with water, brine solution and dried over sodium sulphate. On concentration white color solid was obtained as product. Yield = 4.0 g (95%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 6.9 ppm (s, 1H, Ar-H), 6.62 ppm (s, 1H, Ar-H), 4.6 (t, 2H, Ar-OCH<sub>2</sub>), 3.95 ppm (t, 2H, CH<sub>2</sub>-OH), 2.52 ppm (t, 2H, Ar-CH<sub>2</sub>),

2.20 ppm (s, 3H, Ar-CH<sub>3</sub>), 2.17 ppm (s, 3H, Ar-CH<sub>3</sub>), 2.00-0.88 ppm (m, 29H, Aliphatic H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ:154.78, 139.60, 132.65, 128.03, 123.90, 112.68, 69.67, 61.86, 33.60, 32.03, 30.70, 29.78, 29.46, 22.80, 18.35, 15.73 and 14.22. FT-IR (cm<sup>-1</sup>): 3303, 2917, 2850, 1612, 1507, 1458, 1373, 1311, 1260, 1208, 1078, 1044, 912 and 848.

**2.3.6. Synthesis of 1-(2-chloroethoxy)-2,4-dimethyl-5-pentadecylbenzene (5).** compound **3** (10.0 g, 26.59 mmol) and N,N-dimethylaniline (3.23 g, 26.59 mmol) were taken in 100 mL RB flask and kept under ice cold condition. A solution of SOCl<sub>2</sub> (6.33 g, 53.19 mmol) in chloroform (5mL) was added drop wise, the color of reaction mixture turned into dark red. It was refluxed for 4 h and cooled to room temperature. It was poured into water (200 mL) in HCl (50 mL). The compound was extracted with dichloromethane, dried over sodium sulphate and the solvent was evaporated to obtained product. Further purification was done by silica gel column chromatography. Yield = 8.9 g (85 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ: 6.91 ppm (s, 1H, Ar-**H**), 6.60 ppm (s, 1H, Ar-**H**), 4.21 (t, 2H, Ar-OCH<sub>2</sub>), 3.80 ppm (t, 2H, CH<sub>2</sub>-Cl), 2.53 ppm (t, 2H, Ar-CH<sub>2</sub>), 2.21 ppm (s, 3H, Ar-CH<sub>3</sub>), 2.19 ppm (s, 3H, Ar-CH<sub>3</sub>), 2.00-0.88 ppm (m, 29H, Aliphatic **H**). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ:154.48, 139.54, 132.73, 128.32, 124.39, 112.91, 68.68, 42.32, 33.59, 32.03, 30.69, 29.80, 29.69, 29.48, 22.81, 18.38, 15.63 and 14.24. FT-IR (cm<sup>-1</sup>): 2917, 2851, 1508, 1460, 1260, 1208, 1102 and 881.

**2.3.7. Synthesis of 4-(2-(2,4-dimethyl-5-pentadecylphenoxy)ethoxy)benzaldehyde (DM-PDP-CHO).** 4-hydroxybenzaldehyde (4.02 g, 32.90 mmol) and potassium carbonate (13.66 g, 98.80 mmol) and catalytic amount of KI were taken with DMF (60 mL) in two neck RBF under nitrogen atmosphere and refluxed for 1 hr. Compound **5** (8.0 g, 20.30 mmol) was added and the reaction mixture was refluxed for 12 h and cooled to room temperature, extracted with ethyl acetate and the organic layer was washed with 10% NaOH. Purification was done by column chromatography in ethyl acetate and pet ether (3% v/v). Yield = 8.2 g (70 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ: 9.89 ppm (s, 1H, Ar-CHO), 7.84 ppm (d, 2H, Ar-**H**), 7.06 ppm (d, 2H, Ar-**H**), 6.90 ppm (s, 1H, Ar-**H**), 6.65 ppm (s, 1H, Ar-**H**), 4.35 ppm (m, 4H, Ar-OCH<sub>2</sub>), 2.52 ppm (t, 2H, Ar-CH<sub>2</sub>), 2.19 ppm (s, 3H, Ar-CH<sub>3</sub>), 2.13 ppm (s, 3H, Ar-CH<sub>3</sub>), 2.00-0.88 ppm (m, 29H, Aliphatic **H**). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ:190.90 (Ar-CHO), 163.93, 154.76, 139.55, 132.71, 132.08, 130.21, 128.25, 124.29, 115.03, 112.87, 67.13, 67.03, 33.61, 32.02, 30.71, 29.79, 29.69, 29.46, 22.08, 18.37, 15.72 and 14.23. FT-IR (cm<sup>-1</sup>): 2914, 2848, 2729, 1695, 1597, 1507, 1401, 1257, 1208, 1158, 1093, 1052, 937, 879 and 823.

**2.3.8. Synthesis of 2-(3-(pentadec-8-enyl)phenoxy)ethanol (6).** Cardanol (10.0 g, 33.33 mmol) was added to a stirred solution of NaOH (2.64 g, 66.66 mmol) in a mixture of ethanol (45 mL) and 50 ml distilled water at room temperature under nitrogen atmosphere. 2-Bromoethanol (6.2g (3.50 mL), 73.80 mmol) was added drop wise. After the completion of addition, the reaction mixture was refluxed for 6 hr. It was allowed to cool at room temperature and poured into water (100 mL) and extracted with ethyl acetate. Organic layer was washed with NaOH, brine solution and dried over sodium sulphate. After solvent was evaporated, the product was obtained as white crystalline solid. Yield = 10.2 g (91%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ: 7.17ppm (m, 1H, Ar-H), 6.74 ppm (m, 3H, Ar-H), 5.34 ppm (m, 2H, -CH=CH-) 4.05 ppm (t, 2H, Ar-OCH<sub>2</sub>), 3.94 ppm (t, 2H, CH<sub>2</sub>-OH), 2.56 ppm (t, 2H, Ar-CH<sub>2</sub>), 2.5-0.88 ppm (m, 25H, Aliphatic H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 Hz) δ: 158.70, 144.79, 130.05, 129.9, 129.33, 121.41, 114.89, 111.53, 69.12, 61.58, 36.12, 31.92, 31.52, 29.87, 29.54, 29.44, 29.35, 29.12, 27.31, 22.80 and 14.26. FT-IR (cm<sup>-1</sup>): 3362, 2922, 28.53, 2362, 1588, 1486, 1450, 1372, 1258, 1159, 1077, 1048, 963 and 898.

**2.3.9. Synthesis of 1-(2-chloroethoxy)-3-(pentadec-8-enyl)benzene (7).** compound **6** (8.40g, 24.20 mmol) and N,N-dimethylaniline (2.93 g, 24.20 mmol) were taken in 100 mL RB flask and kept under ice cold condition. A solution of SOCl<sub>2</sub> (3.42 g, 28.70 mmol) in chloroform (10 mL) was added drop wise, the color of reaction mixture turned into dark red. It was refluxed for 4 h and cooled to room temperature. It was poured into water (100 mL) in HCl (25 mL). The compound was extracted with dichloromethane, dried over sodium sulphate and the solvent was evaporated to obtained product. Further purification was done by silica gel column chromatography. Yield = 7.2 g (81.5%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 Hz) δ: 7.17ppm (m, 1H, Ar-H), 6.74 ppm (m, 3H, Ar-H), 5.34 ppm (m, 2H, -CH=CH-) 4.20 ppm (t, 2H, Ar-OCH<sub>2</sub>), 3.80 ppm (t, 2H, CH<sub>2</sub>-Cl), 2.56 ppm (t, 2H, Ar-CH<sub>2</sub>), 2.5-0.88 ppm (m, 25H, Aliphatic H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 Hz) δ: 158.32,144.88, 130.08, 129.95,129.39, 121.70, 115.12, 111.62, 67.97, 42.09, 36.15, 31.54, 29.91, 29.80, 29.58, 29.47, 29.39, 29.17, 27.39, 22.85 and 14.37. FT-IR (cm<sup>-1</sup>): 2923, 2853, 1590, 1450, 1254, 1157, 1044, 963 and 896.

**2.3.10. Synthesis of 4-(2-(3-(pentadec-8-enyl)phenoxy)ethoxy)benzaldehyde (Card-CHO).** 4-hydroxybenzaldehyde (2.5 g, 20.6 mmol) and potassium carbonate (8.53 g, 61.73 mmol) and catalytic amount of KI were taken with DMF (50 mL) in two neck RBF under nitrogen atmosphere and refluxed for 1 hr. Compound **7** (5.0 g, 13.72 mmol) was added and the reaction mixture was refluxed for 12 h and cooled to room temperature, extracted with ethyl acetate and

the organic layer was washed with 10% NaOH. Purification was done by column chromatography in ethyl acetate and pet ether (3% v/v). Yield = 5.8 g (94%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ: 9.89 ppm (s, 1H, Ar-CHO), 7.84 ppm (d, 2H, Ar-H), 7.19 ppm (t, 1H, Ar-H), 7.05 ppm (d, 2H, Ar-H), 6.77 ppm (m, 3H, Ar-H), 5.36 (t, 2H, -CH=CH-) 4.37 ppm (m, 4H, Ar-OCH<sub>2</sub>), 2.55 ppm (t, 2H, Ar-CH<sub>2</sub>), 2.00-0.88 ppm (m, 29H, Aliphatic H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ: 190.97 (Ar-CHO), 163.76, 158.50, 144.91, 132.42, 130.25, 129.90, 129.35, 121.59, 111.53 (Ar-C), 66.95 (Ar-OCH<sub>2</sub>), 66.13 (Ar-OCH<sub>2</sub>), 36.10, 32.02, 31.88, 31.50, 29.78, 29.61, 29.44, 29.39, 29.08, 22.87 and 14.23. FT-IR (cm<sup>-1</sup>): 2923, 1690, 1598, 1450, 1247, 1158, 1064, 936 and 832.

**2.3.11. Synthesis of 1,4-dimethoxybenzene (8).** 4-Methoxyphenol (10.0 g, 80.60 mmol) was added to stirred ice cold solution of KOH (6.7 g, 120.9 mmol) in methanol (40 mL) under nitrogen atmosphere. After 15 minutes, dimethylsulphate (17.5 mL) was added drop wise and the reaction mixture was gradually heated to 60°C. It was cooled to room temperature, poured into water and extracted into ethyl acetate. The organic layer was washed with water, 10% NaOH and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After solvent evaporation, white solid was obtained as product. Further purification was done by column chromatography. Yield = 10.1 g (91 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 6.83 ppm (s, 4H, Ar-H), 3.76 ppm (s, 6H, Ar-OCH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 Hz, δ): 153.83, 114.72 and 55.81. FT-IR (cm<sup>-1</sup>): 3010, 2952, 2898, 2830, 2480, 2308, 2054, 1967, 1867, 1636, 1500, 1434, 1293, 1223, 1174, 1116, 1026, 819 and 696.

**2.3.12. Synthesis of 1,4-bis(bromomethyl)-2,5-dimethoxybenzene (9).** 1,4-Dimethoxybenzene (10.0 g, 72.40 mmol) and p-HCHO (8.70 g, 289.80 mmol) were taken in glacial acetic acid (50 mL) and HBr in glacial acetic acid (30-33 wt%), (36.23 mL) was added to it using a pressure equalizing funnel. The reaction mixture was then refluxed for 8 hours, cooled to room temperature and poured into large amount of water. The precipitate was repeatedly washed with cold water until the filtrate become neutral. This white solid was filtered to obtain pure product. Yield = 21.0 g (90%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ: 6.85 ppm (s, 2H, Ar-H), 4.52 ppm (s, 4H, Ar-CH<sub>2</sub>-Br), 3.85 ppm (s, 6H, Ar-OCH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 Hz) δ: 151.32, 127.46, 113.87, 56.31 and 28.69. FT-IR (cm<sup>-1</sup>): 2973, 1504, 1401, 1224, 1036, 875 and 717.

**2.3.13. Synthesis of tetraethyl (2,5-dimethoxy-1,4-phenylene)bis(methylene)diphosphonate (10).** Compound **9** (10.0 g, 30.86 mmol) and triethyl phosphite (10 mL) were refluxed at 150 °C for 12 hr. The excess triethyl phosphite was removed by vacuum distillation and the white solid

was obtained as product. The white solid product was purified by repeated washing with hexane. Yield = 13.2 g (97%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 7.16 ppm (s, 1H, Ar-H), 6.62 ppm (s, 1H, Ar-H), 3.98 ppm (m, 8H, -P-OCH<sub>2</sub>), 3.77 ppm (s, 6H, Ar-OCH<sub>3</sub>), 3.19 ppm (d, 4H, Ar-CH<sub>2</sub>-P), 1.21 ppm (t, 12H, -CH<sub>2</sub>-CH<sub>3</sub>).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$ : 151.08, 119.5, 114.10, 61.93, 56.20, 27.23, 25.84 and 16.41. FT-IR ( $\text{cm}^{-1}$ ): 2981, 2897, 2831, 1516, 1472, 1407, 1391, 1265, 1218, 1157, 1110, 1026, 960, 879 and 814.

**2.3.14. Synthesis of 1-methoxy-4-methylbenzene (11).** p-Cresol (25.0 g, 23.10 mmol) was added to stirred ice cold solution of KOH (19.44 g, 34.70 mmol) in methanol (40 mL) under nitrogen atmosphere. After 15 minutes, dimethylsulphate (33.61 mL) was added drop wise and the reaction mixture was gradually heated to 60°C. It was cooled to room temperature, poured into water and extracted into ethyl acetate. The organic layer was washed with water, 10% NaOH and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After solvent evaporation, white solid was obtained as product. Further purification was done by column chromatography. Yield = 23.4 g (83%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz),  $\delta$ : 7.10 ppm (d, 2H, Ar-H), 6.81 ppm (d, 2H, Ar-H), 3.78 ppm (s, 3H, Ar-OCH<sub>3</sub>), 2.3 ppm (s, 3H, Ar-CH<sub>3</sub>).

**2.3.15. Synthesis of 1,3-bis(bromomethyl)-2-methoxy-5-methylbenzene (12).** Compound **11** (20.0 g, 16.3 mmol) and p-HCHO (19.67 g, 65.5 mmol) were taken in glacial acetic acid (70 mL) and HBr in glacial acetic acid (30-33 wt%), (82.5 mL) was added to it using a pressure equalizing funnel. The reaction mixture was then refluxed for 8 hours, cooled to room temperature and poured into large amount of water. The precipitate was repeatedly washed with cold water until the filtrate become neutral. This white solid was filtered to obtain pure product. Yield = 29.0 g (60 %).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 7.15 ppm (s, 2H, Ar-H), 4.51 ppm (s, 4H, Ar-CH<sub>2</sub>-Br), 3.98 ppm (s, 3H, Ar-OCH<sub>3</sub>), 2.28 ppm (s, 3H, Ar-CH<sub>3</sub>).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz,  $\delta$ )  $\delta$ : 154.43, 134.76, 131.56, 62.33, 27.81, and 20.71. FT-IR ( $\text{cm}^{-1}$ ): 2916, 2849, 1612, 1464, 1330, 1272, 1198, 1108 and 722.

**2.3.16. Synthesis of tetraethyl (2-methoxy-5-methyl-1,3-phenylene)bis(methylene)diphosphonate (13).** Compound **12** (5.0 g, 16.34 mmol) and triethyl phosphite (5.7 g, 34.32 mmol) were heated at 150 °C and excess triethyl phosphite was removed by under high vacuum. The resultant crude was obtained as thick yellow oil. Yield = 6.2 g (90 %).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 7.10 ppm (s, 2H, Ar-H), 4.00 ppm (m, 8H, -P-OCH<sub>2</sub>), 3.74 ppm (s, 3H, Ar-OCH<sub>3</sub>), 3.14 ppm (d, 4H, Ar-CH<sub>2</sub>-P), 2.23 ppm (s, 3H, Ar-CH<sub>3</sub>), 1.21 ppm (t, 12H, -P-OCH<sub>2</sub>-CH<sub>3</sub>).  $^{13}\text{C}$



NMR (CDCl<sub>3</sub>, 100 Hz,)  $\delta$ : 154.53, 133.52, 130.85, 124.76, 62.11, 27.60, 20.87 and 16.36. FT-IR (cm<sup>-1</sup>): 3010, 2952, 2898, 2830, 24.80, 2054, 1967, 1867, 1636, 1500, 1434, 1293, 1223, 1223, 1174, 1116, 1026, 819 and 696.

**2.3.17. Synthesis 1-(dodecyloxy)-3-pentadecylbenzene (14).** 3-Pentadecylphenol (15.0 g, 49.30 mmol) was added to stirred solution of KOH (11.0 g, 197.20 mmol) in DMSO (150 mL) at room temperature under N<sub>2</sub>. After 15 minutes, 1-Bromododecane (13.6g, 54.20 mmol) was added slowly and the reaction mixture was stirred for 8 h. The reaction mixture was extracted by ethyl acetate, organic layer was washed with water, 10% NaOH solution and dried over sodium sulphate. After solvent evaporation, crude product was obtained as thick oil which was further purified by column chromatography using pet ether. Yield = 20.8 g (89%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.21 ppm (t, 1H, Ar-**H**), 6.77 ppm (m, 3H, Ar-**H**), 3.98 ppm (t, 2H, Ar-O**CH**<sub>2</sub>), 2.6 ppm (t, 2H, Ar-**CH**<sub>2</sub>), 2-0.92 ppm (m, 52H, aliphatic-**H**). <sup>13</sup>C NMR (CDCl<sub>3</sub> 100 MHz)  $\delta$ :159.20, 144.64, 129.15, 120.72, 114.86, 111.41 (Ar-C), 67.89, 36.13, 32.02, 31.51, 29.77, 29.62, 29.46, 26.18, 22.79 and 14.22. FT-IR (cm<sup>-1</sup>): 2924, 2853, 1590, 1459, 1260, 1158, 1044, 871, 774, 722 and 694.

**2.3.18. Synthesis of 1,5-bis(bromomethyl)-2-(dodecyloxy)-4-pentadecylbenzene (15).** Compound **14** (13.0 g, 27.00 mmol) was added to p-formaldehyde (3.24 g, 18.00 mmol) in a stirred solution of acetic acid (75 mL) at room temperature under N<sub>2</sub> atmosphere. HBr solution in glacial acetic acid (13.75 mL) (30-33 wt %) was added drop wise. After the addition was completed, the reaction mixture was gradually heated to 80°C and stirred for 10 h. It was cooled to room temperature, poured into ice cold water and extracted with ethyl acetate. Organic layer was washed with 10% NaOH followed by brine and dried over sodium sulphate. After evaporation crude was brown sticky solid. Yield = 16.3 g (92%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 Hz,  $\delta$ ): 7.23 ppm (s, 1H, Ar-**H**), 6.73 ppm (s, 1H, Ar-**H**), 4.5 ppm (s, 4H, Ar-**CH**<sub>2</sub>-Br), 4.03 ppm (t, 2H, Ar-O**CH**<sub>2</sub>), 2.6 ppm (t, 2H, Ar-**CH**<sub>2</sub>), 2-0.92 ppm (m, 52H, aliphatic **H**). <sup>13</sup>C NMR (CDCl<sub>3</sub>):157.40, 144.68, 133.08, 127.20, 124.17, 112.94, 68.37, 32.90, 32.02, 31.08, 29.77, 29.69, 29.60, 29.45, 29.28, 28.77, 29.15, 22.79 and 14.22. FT-IR (cm<sup>-1</sup>): 2916, 2849, 1612, 1464, 1330, 1272, 1198, 1108 and 772.

**2.3.19. Synthesis of tetraethyl(4-(dodecyloxy)-6-pentadecyl-1,3-phenylene)bis(methylene) diphosphonate (16).** Compound **15** (3.0 g, 4.50 mmol) and triethyl phosphite (1.6 g, 9.57 mmol) were heated at 150 °C and excess triethyl phosphite was removed by under high vacuum. The

resultant crude was obtained as thick yellow oil. Yield = 3.2g (94%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 7.16 ppm (s, 1H, Ar-**H**), 6.59 ppm (s, 1H, Ar-**H**), 3.97 ppm (m, 8H, -P-OCH<sub>2</sub>), 3.90 ppm (t, 2H, Ar-OCH<sub>2</sub>), 3.16 ppm (d, 2H, Ar-CH<sub>2</sub>-P), 3.07 ppm (d, 2H, Ar-CH<sub>2</sub>-P), 2.60 ppm (t, 2H, Ar-CH<sub>2</sub>), 2.5-0.88 ppm (m, 51H, aliphatic **H**) <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 Hz, δ): 155.71, 141.65, 133.33, 120.83, 117.73, 112.50, 68.30, 62.11, 33.30, 31.98, 30.89, 30.44, 29.75, 26.20, 22.75, 16.45 and 14.18. FT-IR (cm<sup>-1</sup>): 2923, 2854, 1507, 1465, 1391, 1247, 1194, 1160, 1024, 955, 840, 780, 722 and 694.

**2.3.20. Synthesis of 1,4-bis((E)-4-(2-(3-pentadecylphenoxy)ethoxy)styryl)-2,5-dimethoxy benzene (PDP-pOPV).** Compound **10** (0.2 g, 1.44 mmol) and (**PDP-CHO**) (1.44 g, 3.17 mmol) in dry THF (30mL), potassium *tert*-butoxide (8.7mL, 1M THF) was added in ice cold condition under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 12 h. It was poured into methanol and then precipitate was filtered and dried. Further purification was done by silica gel chromatography in dichloromethane/pet ether mixture (12% v/v). Yield = 1.21 g (81%). <sup>1</sup>H- NMR (CDCl<sub>3</sub>, 400MHz) δ: 7.48 ppm (d, 4H, Ar-**H**), 7.34 ppm (d, 2H, Ar-CH=CH-), 7.18 ppm (t, 2H, Ar-**H**), 7.10 ppm (d, 2H, Ar-**H**), 7.05 ppm (d, 2H, Ar-CH=CH-), 6.93 ppm (d, 4H, Ar-**H**), 6.78 ppm (m, 6H, Ar-**H**), 4.32 ppm (t, 8H, Ar-OCH<sub>2</sub>), 3.90 ppm (s, 6H, Ar-OCH<sub>3</sub>), 2.56 ppm (t, 4H, Ar-CH<sub>2</sub>), 2-0.88 ppm (m, 58H, aliphatic **H**). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz) δ: 158.68, 158.33, 151.40, 144.83, 131.14, 129.28, 128.33, 127.88, 126.55, 121.36, 115.07, 114.91, 111.59, 108.92, 66.68, 66.40, 56.42, 36.12, 32.03, 31.51, 29.80, 29.70, 29.64, 29.47, 22.80 and 14.25. FT-IR (cm-1): 2916, 2848, 1599, 1459, 1238, 1167, 1046, 968, 851, 776, 720, 689 and 625. (MW = 1035.52): M<sup>+</sup> = 1034.56.

**2.3.21. Synthesis of 1,4-bis((1E,25E)-4-(2-(3-((E)-pentadec-8-enyl)phenoxy)ethoxy)styryl)-2,5-dimethoxybenzene (CAR-pOPV).** Compound **10** (0.20 g, 1.44 mmol), **CAR-CHO** (1.43 g, 3.17 mmol) and potassium *tert*-butoxide (8.7 mL, 1 M THF) were used for the synthesis following the procedure explain in **PDP-pOPV** synthesis part. Yield = 1.2 g (80%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz) δ: 7.48 ppm (d, 4H, Ar-**H**), 7.34 ppm (d, 2H, Ar-CH=CH-), 7.18 ppm (t, 2H, Ar-**H**), 7.09 ppm (d, 2H, Ar-**H**), 7.05 ppm (d, 2H, Ar-CH=CH-), 6.93 ppm (d, 4H, Ar-**H**), 6.77 ppm (m, 6H, Ar-**H**), 5.33 ppm (m, 2H, R-CH=CH), 4.32 ppm (t, 8H, Ar-OCH<sub>2</sub>), 3.90 ppm (s, 6H, Ar-OCH<sub>3</sub>), 2.56 ppm (t, 4H, Ar-CH<sub>2</sub>), 2-0.88 ppm (m, 54H, aliphatic **H**). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz) δ:158.68, 158.32, 151.40, 144.82, 131.14, 129.28, 128.32, 127.88, 126.55, 121.41, 121.36, 115.06, 114.90, 111.59, 108.91, 66.68, 66.40, 56.43, 36.10, 32.69, 32.02, 31.49, 29.79,

29.44, 22.79 and 14.23. FT-IR (cm<sup>-1</sup>): 2920, 2849, 1603, 1506, 1458, 1409, 1243, 1207, 1178, 1041, 970, 921, 850, 771 and 623. (MW = 1031.53): M<sup>+</sup> = 1030.66.

**2.3.22. Synthesis of 1-(2-(4-((1E,8E)-4-((E)-4-(2-(2,4-dimethyl-5-pentadecylphenoxy)ethoxy)styryl)-2,5-dimethoxystyryl)phenoxy)ethoxy)-2,4-dimethyl-5-pentadecylbenzene (DM-PDP-pOPV).** Compound **10** (0.20 g, 1.44 mmol), **DM-PDP-CHO** (1.52 g, 3.17 mmol) and potassium *tert*-butoxide (8.7 mL, 1 M THF) were used for the synthesis following the procedure explain in **PDP-pOPV** synthesis part. Yield = 1.26 g (80%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz) δ: 7.48 ppm (d, 4H, Ar-**H**), 7.34 ppm (d, 2H, Ar-CH=CH-), 7.10 ppm (s, 2H, Ar-**H**), 7.05 ppm (d, 2H, Ar-CH=CH-), 6.94 ppm (d, 4H, Ar-**H**), 6.89 ppm (s, 2H, Ar-**H**), 6.65 ppm (s, 2H, Ar-**H**), 4.32 ppm (m, 8H, Ar-OCH<sub>2</sub>), 3.90 ppm (s, 6H, Ar-OCH<sub>3</sub>), 2.51 ppm (t, 4H, Ar-CH<sub>2</sub>), 2.19 ppm (s, 6H, Ar-CH<sub>3</sub>), 2.15 ppm (s, 6H, Ar-CH<sub>3</sub>), 2-0.88 ppm (m, 58H, aliphatic **H**). <sup>13</sup>C-NMR(CDCl<sub>3</sub>, 100 MHz) δ: 154.93, 151.40, 139.48, 132.62, 131.07, 128.33, 128.01, 127.86, 126.55, 124.33, 121.30, 114.95, 112.92, 108.92, 67.26, 66.89, 56.43, 33.60, 32.01, 31.59, 30.70, 30.20, 29.79, 29.69, 29.46, 22.79, 18.37, 15.74 and 13.23. FT-IR (cm<sup>-1</sup>): 2919, 2851, 1603, 1506, 1458, 1409, 1243, 1207, 1178, 1041, 970, 921 and 850 and 721. (MW = 1091.62): M<sup>+</sup> = 1090.72.

**2.3.23. Synthesis of 1,4-bis((E)-4-(dodecyloxy)styryl)-2,5-dimethoxybenzene (DD-pOPV).** Compound **10** (0.20 g, 1.44 mmol), **DD-CHO** (0.92 g, 3.17 mmol) and potassium *tert*-butoxide (8.6 mL, 1 M THF) were used for the synthesis following the procedure explain in **PDP-pOPV** synthesis part. Yield = 0.97 g (95%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz) δ: 7.46 ppm (d, 4H, Ar-**H**), 7.33 ppm (d, 2H, Ar-CH=CH-), 7.09 (s, 2H, Ar-**H**), 7.04 ppm (d, 2H, Ar-CH=CH-), 6.87 ppm (d, 2H, Ar-**H**), 3.96 ppm (t, 4H, Ar-OCH<sub>2</sub>), 3.90 ppm (s, 6H, Ar-OCH<sub>3</sub>), 2-0.88 ppm (m, 46H, Aliphatic **H**). <sup>13</sup>C-NMR(CDCl<sub>3</sub>, 100 MHz) δ: 158.85, 151.38, 130.55, 128.43, 127.83, 126.56, 120.99, 114.71, 108.90, 68.13, 56.45, 32.02, 29.77, 29.45, 29.37, 26.14, 22.08 and 14.23. FT-IR (cm<sup>-1</sup>): 2919, 2850, 1603, 1511, 1404, 1250, 1208, 1041, 961, 847, 810 and 724. (MW = 711.07). m/z = 710. 75.

**2.3.24. Synthesis of 1,3-bis((E)-4-(2-(3-pentadecylphenoxy)ethoxy)styryl)-2-methoxy-5-methylbenzene (PDP-mOPV).** Compound **13** (0.20 g, 0.473 mmol), **PDP-CHO** (0.45 g, 0.994 mmol) and potassium *tert*-butoxide (2.8 mL, 1 M THF) were used for the synthesis following the procedure explain in **PDP-pOPV** synthesis part. Yield = 0.42 g (87%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz) δ: 7.48 ppm (d, 4H, Ar-**H**), 7.32 ppm (s, 2H, Ar-**H**), 7.28 ppm (d, 2H, Ar-CH=CH-), 7.18 ppm (t, 2H, Ar-**H**), 7.07 ppm (d, 2H, Ar-CH=CH-), 6.95 ppm (d, 4H, Ar-**H**), 6.77 ppm (m,

6H, Ar-**H**), 4.32 ppm (s, 8H, Ar-OCH<sub>2</sub>), 3.75 ppm (s, 3H, Ar-OCH<sub>3</sub>), 2.56 ppm (t, 4H, Ar-CH<sub>2</sub>), 2.36 ppm (s, 3H, Ar-CH<sub>3</sub>), 2-0.88 ppm (m, 58H, Aliphatic **H**). <sup>13</sup>C-NMR(CDCl<sub>3</sub>, 100 MHz) δ: 158.67, 158.45, 153.55, 148.85, 144.82, 133.72, 130.99, 129.27, 127.90, 125.69, 121.42, 121.30, 115.05, 114.97, 111.61, 66.73, 66.40, 62.15, 36.10, 32.01, 31.48, 29.68, 29.62, 29.45, 22.78, 21.25 and 14.22. FT-IR (cm<sup>-1</sup>): 2917, 1850, 1605, 1510, 1455, 1248, 1157, 1070, 969 and 773. (MW = 1019.52): M<sup>+</sup> = 1018.66

**2.3.25. Synthesis of 1,3-bis((E)-4-(2-(2,4-dimethyl-5-pentadecylphenoxy)ethoxy) styryl)-2-methoxy-5-methylbenzene (DM-PDP-mOPV).** Compound **13** (0.50 g, 1.18 mmol), **DM-PDP-CHO** (1.25 g, 2.60 mmol) and potassium *tert*-butoxide (7.1 mL, 1 M THF) were used for the synthesis following the procedure explain in **PDP-pOPV** synthesis part. Yield = 1.1 g (86%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz) δ: 7.48 ppm (d, 4H, Ar-**H**), 7.33 ppm (s, 2H, Ar-**H**), 7.28 ppm (d, 2H, Ar-CH=CH-), 7.07 ppm (d, 2H, Ar-CH=CH-), 6.96 ppm (d, 4H, Ar-**H**), 6.89 ppm (s, 2H, Ar-**H**), 6.66 ppm (s, 2H, Ar-**H**), 4.32 ppm (s, 8H, Ar-OCH<sub>2</sub>), 3.75 ppm (s, 3H, Ar-OCH<sub>3</sub>), 2.51 ppm (t, 4H, Ar-CH<sub>2</sub>), 2.36 ppm (s, 3H, Ar-CH<sub>3</sub>), 2.19 ppm (s, 6H, Ar-CH<sub>3</sub>), 2.15 ppm (s, 6H, Ar-CH<sub>3</sub>), 2-0.88 ppm (m, 58H, Aliphatic **H**). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz) δ:158.60, 154.93, 153.54, 139.48, 133.71, 132.01, 129.22, 128.03, 127.89, 125.67, 124.34, 121.26, 115.02, 112.95, 67.26, 62.13, 33.60, 32.02, 30.70, 29.79, 29.75, 29.46, 22.79, 21.25, 18.37, 15.74 and 14.23. FT-IR (cm<sup>-1</sup>): 2918, 2850, 1605, 1507, 1458, 1246, 1207, 1174, 1103, 943 and 818. (MW = 1075.63): M<sup>+</sup> = 1074.80.

**2.3.26. Synthesis of 1,3-bis((E)-4-(dodecyloxy)styryl)-2-methoxy-5-methylbenzene (DD-mOPV).** Compound **13** (0.50 g, 1.18 mmol), **DD-CHO** (0.76 g, 2.60 mmol) and potassium *tert*-butoxide (7.1 mL, 1 M THF) were used for the synthesis following the procedure explain in **PDP-pOPV** synthesis part. Yield = 0.8 g (98 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz) δ: 7.46 ppm (d, 4H, Ar-**H**), 7.31 ppm (s, 2H, Ar-**H**), 7.26 ppm (d, 2H, Ar-CH=CH-), 7.06 ppm (d, 2H, Ar-CH=CH-), 6.88 ppm (d, 4H, Ar-**H**), 3.96 ppm (t, 4H, Ar-CH<sub>2</sub>), 3.74 ppm (s, 3H, Ar-OCH<sub>3</sub>), 2.35 ppm (s, 3H, Ar-CH<sub>3</sub>), 2-0.88 ppm (m, 46H, Aliphatic **H**). <sup>13</sup>C-NMR(CDCl<sub>3</sub>, 100 MHz) δ: 158.97, 153.46, 133.69, 131.07, 130.39, 129.32, 127.85, 125.56, 120.95, 114.77, 68.18, 62.10, 32.01, 29.69, 29.45, 29.35, 26.13, 22.78, 21.25 and 14.22. FT-IR (KBr, cm<sup>-1</sup>): 2918, 2849, 1603, 1506, 1245, 1166, 1018, 966, 811 and 720. (MW = 695.07): M<sup>+</sup> = 694.52

**2.3.27. 4,4'-(1E,1'E)-2,2'-(4-(dodecyloxy)-6-pentadecyl-1,3-phenylene)bis(ethene-2,1-diyl)bis**

**(2-(3-pentadecylphenoxy)ethoxy)benzene (Star-PDP-mOPV).** Compound **16** (0.50 g, 0.64 mmol), **PDP-CHO** (0.64 g, 1.42 mmol) and potassium *tert*-butoxide (3.8 mL, 1 M THF) were used for the synthesis following the procedure explain in **PDP-pOPV** synthesis part. Yield = 0.81 g (92%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz) δ: 7.8-6.66 ppm (m, 22H, Ar-**H** and vinylic **H**), 4.32 ppm (s, 8H, Ar-**CH**<sub>2</sub>), 4.01 ppm (t, 2H, Ar-O**CH**<sub>2</sub>), 2.69 ppm (t, 2H, Ar-**CH**<sub>2</sub>), 2.56 ppm (t, 4H, Ar-**CH**<sub>2</sub>), 2-0.88 ppm (m, 112H, aliphatic **H**). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz) δ: 158.69, 158.13, 155.90, 144.81, 131.53, 129.26, 127.70, 127.58, 123.67, 121.40, 115.06, 114.96, 113.22, 111.60, 68.63, 66.68, 66.41, 36.11, 32.01, 31.49, 29.79, 29.62, 29.46, 26.32, 22.78 and 4.22. FT-IR (cm<sup>-1</sup>): 2917, 2850, 1606, 1580, 1512, 1451, 1372, 1290, 1250, 1181, 1154, 1073, 971, 935, 861, 813, 777, 722, 692 and 637. (MW = 1370.24): M<sup>+</sup> = 1369.04.

**2.3.28. 5,5'-(2,2'-(4,4'-(1E,1'E)-2,2'-(4-(dodecyloxy)-6-pentadecyl-1,3-phenylene)bis(ethene-2,1-diyl)bis(4,1-phenylene))bis(oxy)bis(ethane-2,1-diyl))bis(oxy)bis(2,4-dimethyl-1-pentadecylbenzene) (Star-DM-PDP-mOPV).** Compound **16** (0.50 g, 0.64 mmol), **DM-PDP-CHO** (0.68 g, 1.42 mmol) and potassium *tert*-butoxide (3.8 mL, 1 M THF) were used for the synthesis following the procedure explain in **PDP-pOPV** synthesis part. Yield = 0.85 g (92%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz) δ: 7.76-6.66 ppm (m, 18H, Ar-**H** and vinylic **H**), 4.32 ppm (m, 8H, Ar-O**CH**<sub>2</sub>), 4.02 ppm (t, 2H, Ar-O**CH**<sub>2</sub>), 2.70 ppm (t, 2H, Ar-**CH**<sub>2</sub>), 2.54 ppm (t, 4H, Ar-**CH**<sub>2</sub>), 2.19 ppm (s, 6H, Ar-**CH**<sub>3</sub>), 2.16 ppm (s, 6H, Ar-**CH**<sub>3</sub>), 2-0.88 ppm (m, 112H, aliphatic **H**). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz) δ: 158.29, 155.96, 154.96, 141.18, 139.48, 132.62, 131.48, 131.32, 128.61, 127.99, 127.70, 127.70, 127.58, 124.35, 124.22, 123.66, 115.01, 114.93, 113.24, 112.93 (Ar-C), 68.64, 67.27, 66.90, 33.82, 33.62, 32.03, 31.32, 30.72, 29.81, 29.77, 29.56, 29.48, 26.33, 22.81, 18.38, 15.75 and 14.23. FT-IR (cm<sup>-1</sup>): 2918, 2850, 1606, 1580, 1510, 1461, 1372, 1249, 1205, 1177, 1101, 1074, 1037, 968, 940, 830, 811, 778, 721, 692 and 637. (MW = 1426.29): M<sup>+</sup> = 1425.17.

**2.3.29. 4,4'-(1E,1'E)-2,2'-(4-(dodecyloxy)-6-pentadecyl-1,3-phenylene)bis(ethene-2,1-diyl)bis(dodecyloxy)benzene (Star-DD-mOPV).** Compound **16** (0.50 g, 0.65 mmol), **DD-CHO** (0.41 g, 1.42 mmol) and potassium *tert*-butoxide (3.8 mL, 1 M THF) were used for the synthesis following the procedure explain in **PDP-pOPV** synthesis part. Yield = 0.43 g (63%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz) δ: 7.76-6.66 ppm (m, 14H, Ar-**H** and vinylic **H**), 3.97 ppm (m, 6H, Ar-

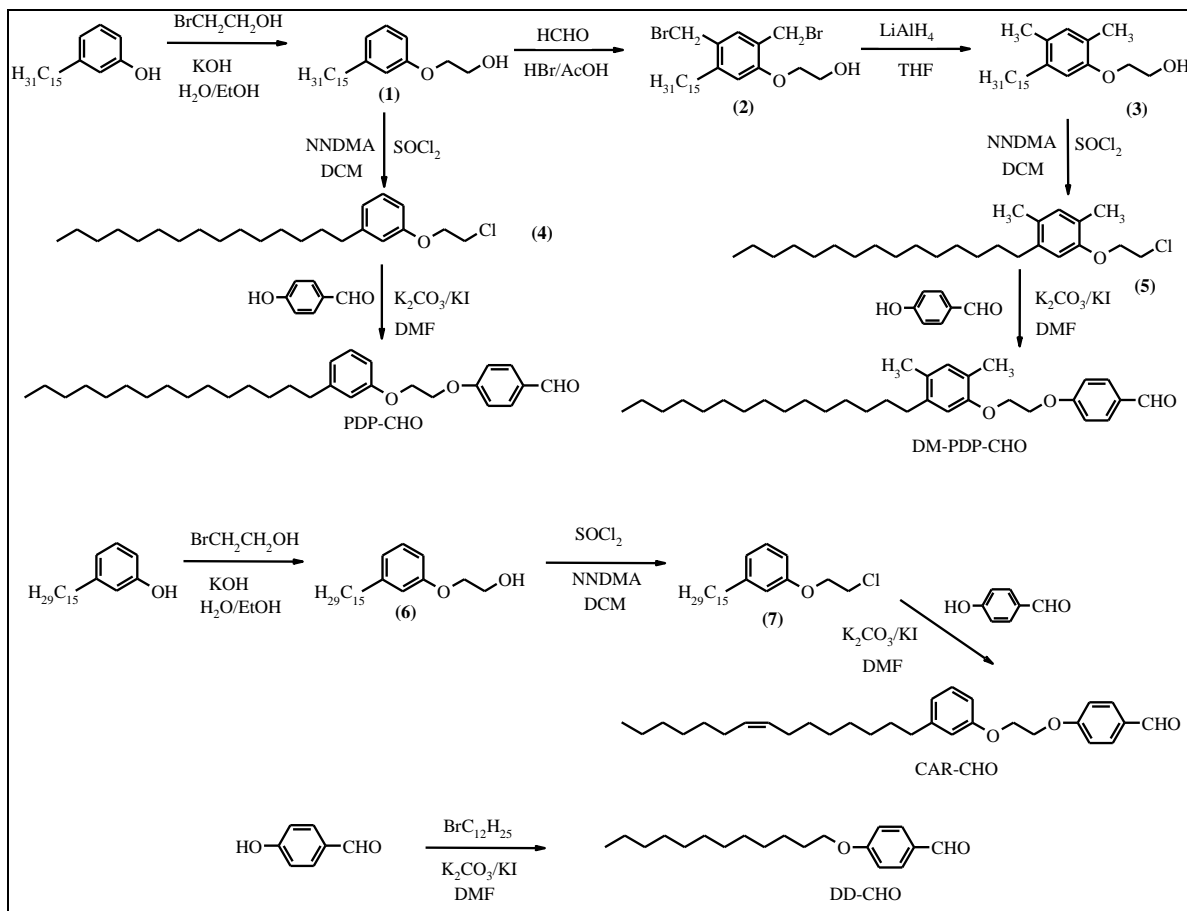
OCH<sub>2</sub>), 2.70 ppm (t, 2H, Ar-CH<sub>2</sub>), 2-0.88 ppm (m, 98H, aliphatic H). <sup>13</sup>C-NMR(CDCl<sub>3</sub>, 100 MHz) δ: 158.65, 155.83, 141.05, 130.94, 130.77, 128.68, 128.13, 127.87, 127.66, 127.53, 124.88, 123.91, 123.59, 114.76, 114.68, 113.23, 68.63, 68.13, 33.81, 32.03, 29.82, 29.77, 29.61, 29.46, 29.39, 29.34, 26.15, 22.80 and 14.23. FT-IR (cm<sup>-1</sup>): 2918, 2849, 1607, 1574, 1510, 1468, 1421, 1391, 1302, 1269, 1243, 1192, 1174, 1099, 1033, 962, 849, 816, 759, 721, 683 and 615 (MW = 1045.73): M<sup>+</sup> = 1044.92.

## **Results and Discussion**

### 3.0. Results and Discussions

#### 3.1. Synthesis of Banana and Star shaped OPVs.

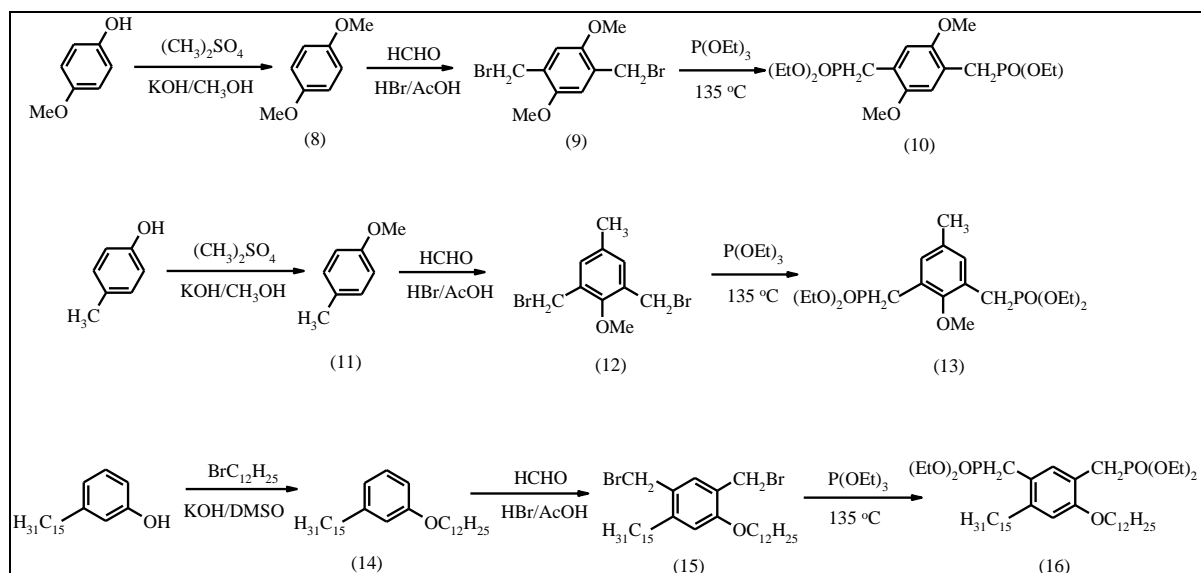
Long alkyl chain substituted aldehydes were synthesized by various steps and given in scheme 1. 3-pentadecylphenol was reacted with 2-bromoethanol in the presence of KOH as a



**Scheme 1.** Synthetic outline for long alkyl chain substituted aldehydes.

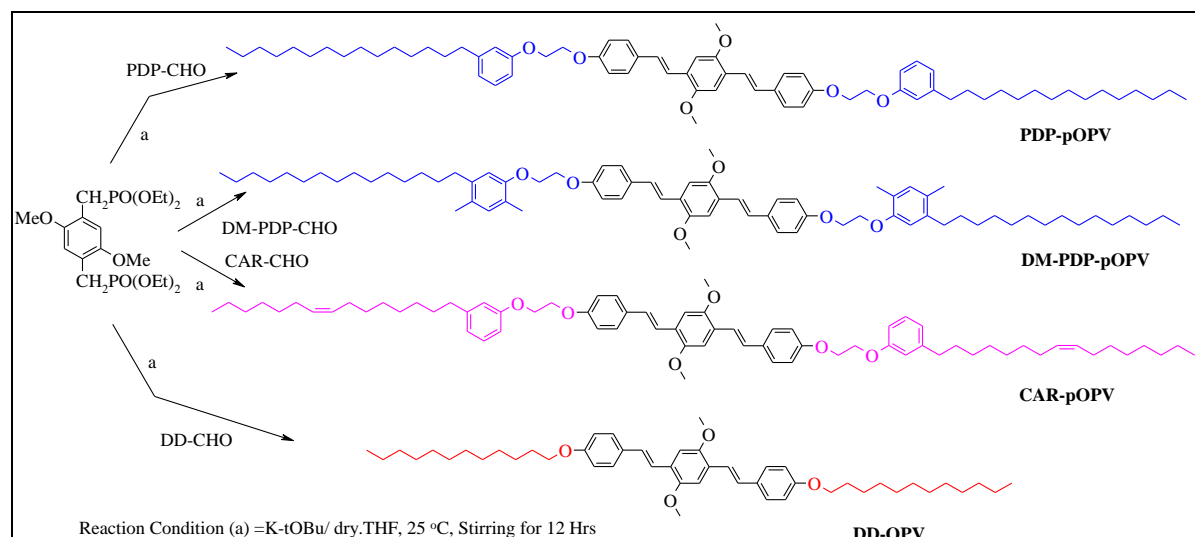
base in  $\text{H}_2\text{O}/\text{EtOH}$  solvent medium to give 2-(3-pentadecylphenoxy)ethanol (**1**). The compound **1** was bisbromomethylated using paraformaldehyde in the presence of HBr in AcOH to yield 2-(2,4-bis(bromomethyl)-5-pentadecylphenoxy)ethanol (**2**). The compound was further reduced using  $\text{LiAlH}_4$  as reducing agent in dry THF solvent to obtained **3**. 2-(2,4-dimethyl-5-pentadecylphenoxy)ethanol (**3**) was reacted with  $\text{SOCl}_2$  in the presence of N,N-dimethylaniline as base in DCM to give compound 1-(2-chloroethoxy)-2,4-dimethyl-5-pentadecylbenzene(**5**). The compound **5** was further reacted with 4-hydroxy benzaldehyde using  $\text{K}_2\text{CO}_3$  in DMF solvent to get aldehyde monomer 4-(2-(2,4-dimethyl-5-pentadecylphenoxy)ethoxy)benzaldehyde (**DM-PDP-CHO**). Similarly aliphatic alcohol group of **1** was reacted with  $\text{SOCl}_2$  using N,N-





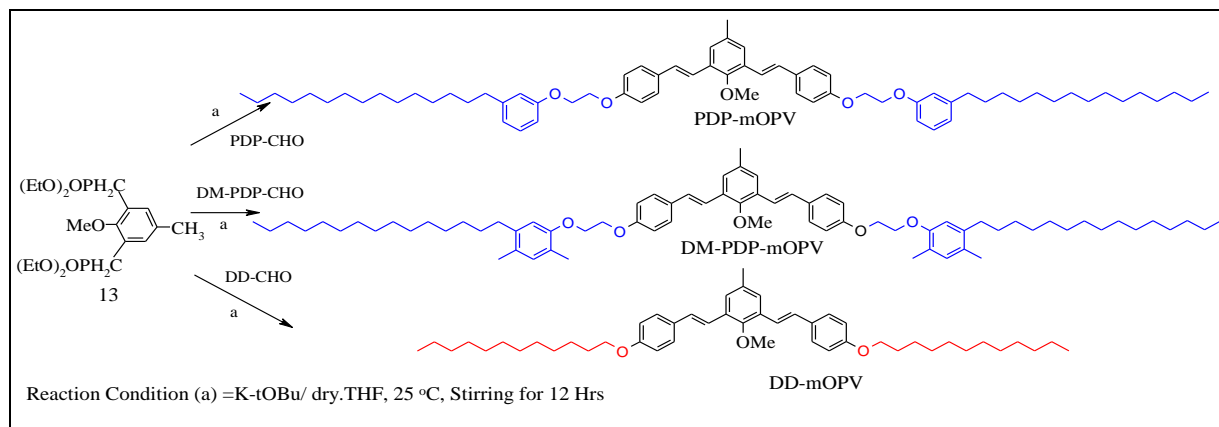
**Scheme 2.** Synthetic outline for bisphosphonate esters dimethylaniline (NNDMA) as base in DCM medium to give 1-(2-chloroethoxy)-3-pentadecylbenzene(4). 4-(2-(3-pentadecylphenoxy)ethoxy)benzaldehyde (**PDP-CHO**) was obtained by the reacting of compound 4 with 4-hydroxy benzaldehyde in  $K_2CO_3$ /DMF reaction condition with catalytic amount of KI. Renewable resource cardanol was subjected to various reactions as described above (compound 6 and compound 7) for producing of (E)-4-(2-(3-(pentadec-8-enyl)phenoxy)ethoxy)benzaldehyde (**CAR-CHO**). Similarly 4-hydroxybenzaldehyde was substituted with 12-bromododecane in the presence of  $K_2CO_3$ / DMF conditions to get 4-(dodecyloxy)benzaldehyde (**DD-CHO**). Synthetic scheme of 1,4 and 1,3 linked phenyl bisphonate esters were given in scheme 2. p-phenylene bisphonate ester was synthesized from commercially available p-methoxyphenol. p-Methoxyphenol and p-cresol was reacted with  $Me_2SO_4$  to yield 1,4-dimethoxybenzene (**8**) and 1-methoxy-4-methylbenzene (**11**) respectively. The compound 8 was further subjected to bisbromomethylation in the presence of paraformaldehyde to get 1,4-bis(bromomethyl)-2,5-dimethoxybenzene (**9**). Similarly the compound **11** was subjected bisbromomethylation reaction to obtain solid 1,3-bis(bromomethyl)-2-methoxy-5-methylbenzene (**12**). Bisbromomethylated compound 9 and compound 11 was

reacted with triethylphosphite at 120°C to give tetraethyl (2,5-dimethoxy-1,4-phenylene)bis



**Scheme 3.** Synthetic outline for banana shaped OPVs.

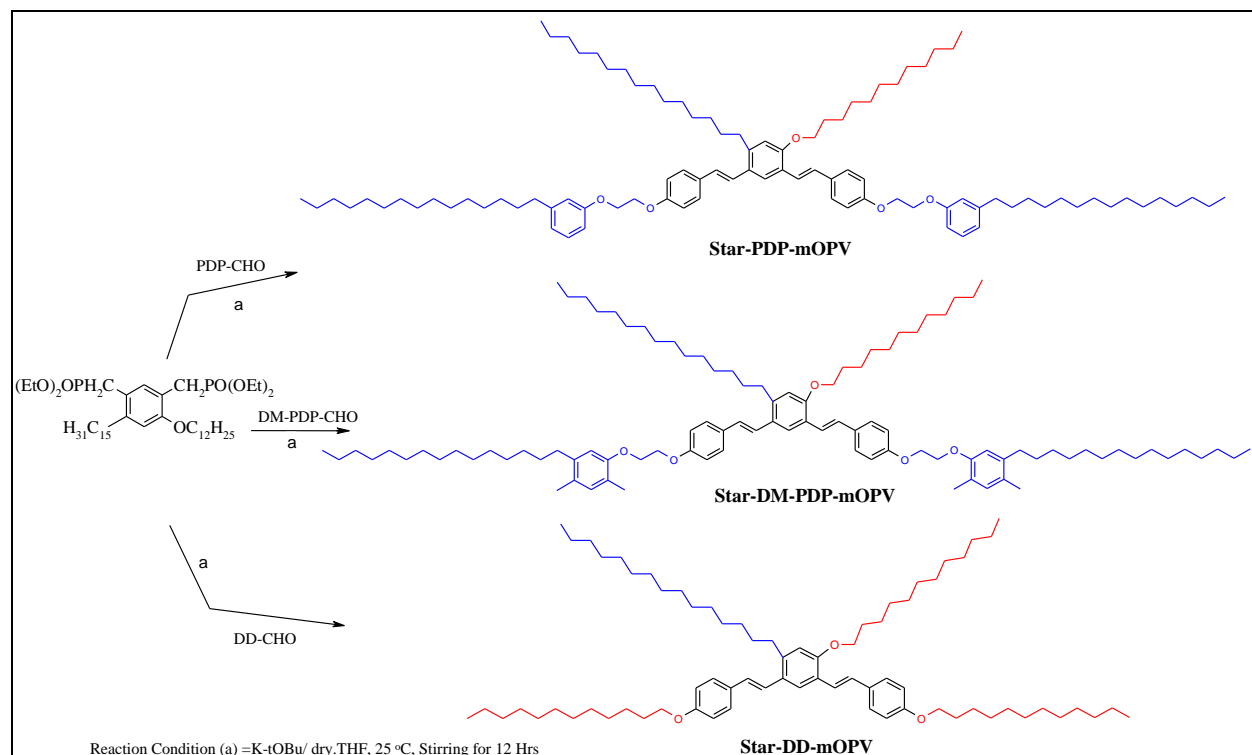
(methylene)diphosphonate (**10**) and tetraethyl (2-methoxy-5-methyl-1,3-phenylene)bis(methylene)diphosphonate (**12**) respectively. Long alkyl chain containing 3-pentadecylphenol was substituted with 1-bromododecane using Williamson ether synthesis method using KOH/DMSO conditions to obtained 1-(dodecyloxy)-3-pentadecylbenzene (**14**).



**Scheme 4.** Synthetic route for synthesis of *m*-OPVs.

The compound **14** was refluxed with paraformaldehyde/ HBr in glacial HOAc conditions to get subsequent product 1,5-bis(bromomethyl)-2-(dodecyloxy)-4-pentadecylbenzene (**15**) which was further converted into bisphosphate ester (tetraethyl (4-(dodecyloxy)-6-pentadecyl-1,3-phenylene)bis(methylene)diphosphonate(**16**)) by reacting with triethylphosphite at above mentioned conditions. All the OPVs were synthesized by following wittig - horner reactions as

shown in schemes 3, 4 and 5. Bisphosphate esters were reacted with various types of long alkyl chain substituted aldehydes to obtain banana shape, star shape and meta OPVs. The compound



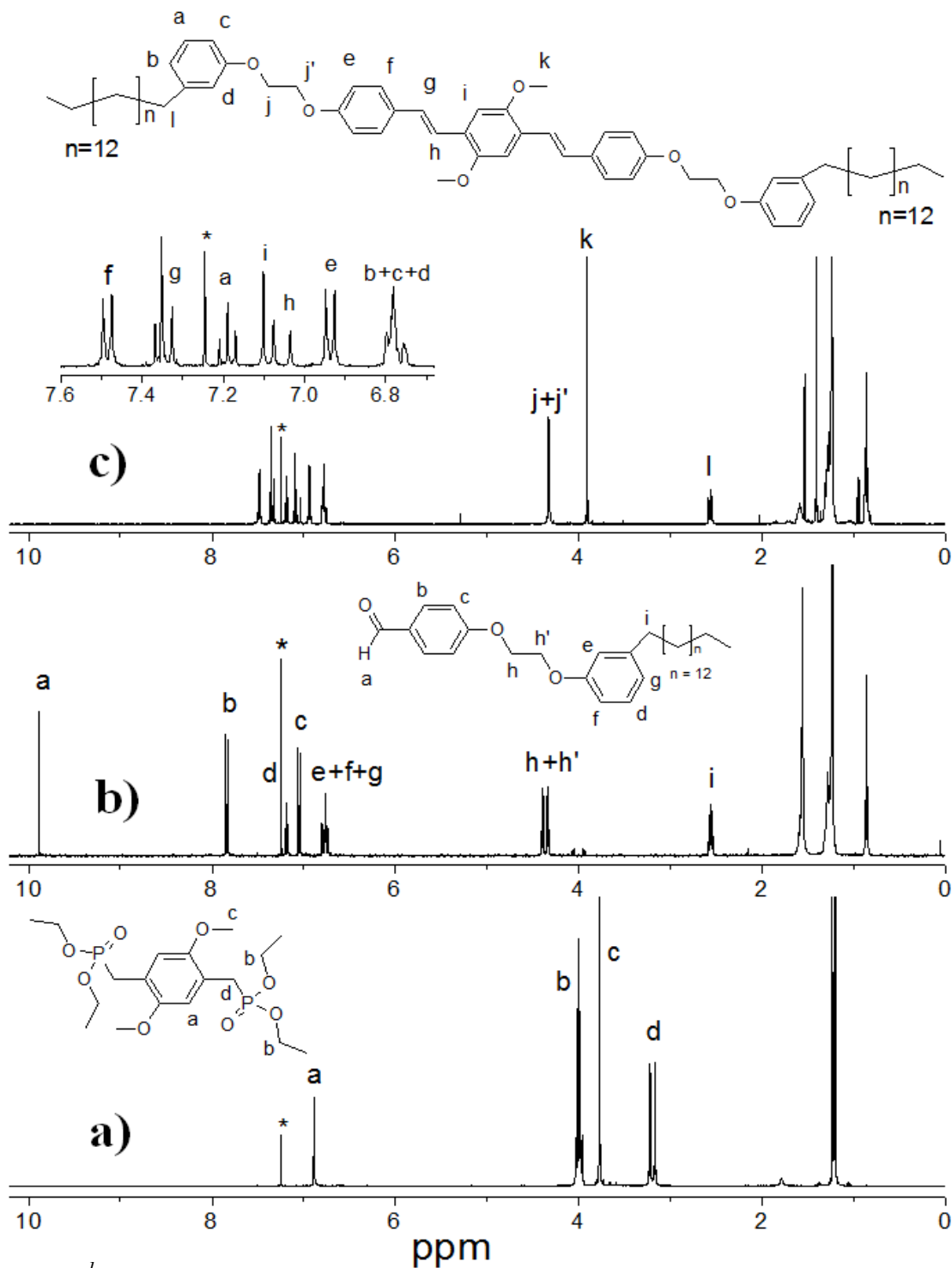
**Scheme 5.** Synthetic route for star shape OPVs.

**10** was reacted with various long alkyl chain substituted aldehydes such as **PDP-CHO**, **DM-PDP-CHO**, **CAR-CHO** and **DD-CHO** in the presence of K<sup>+</sup>OBU<sup>-</sup> as base using THF to give banana shaped p-OPVs such as 1,4-bis((E)-4-(2-(3-pentadecylphenoxy)ethoxy)styryl)-2,5-dimethoxybenzene (**PDP-pOPV**), 1-(2-(4-((1E,8E)-4-((E)-4-(2-(2,4-dimethyl-5-pentadecylphenoxy)ethoxy)styryl)-2,5-dimethoxystyryl)phenoxy) ethoxy)-2,4-dimethyl-5-pentadecylbenzene (**DM-PDP-pOPV**), 1,4-bis((1E,25E)-4-(2-(3-((E)-pentadec-8-enyl)phenoxy)ethoxy)styryl)-2,5-dimethoxybenzene (**CAR-pOPV**) and 1,4-bis((E)-4-(dodecyloxy)styryl)-2,5-dimethoxybenzene (**DD-pOPV**) respectively. Similarly banana shaped m-OPVs and star shaped OPVs were synthesized from tetraethyl (2-methoxy-5-methyl-1,3-phenylene)bis(methylene)diphosphate (**13**) and tetraethyl (4-(dodecyloxy)-6-pentadecyl-1,3-phenylene)bis(methylene)diphosphate (**16**) were shown in scheme 4 and 5 respectively. Long alkyl chain containing aldehydes **PDP-CHO**, **DM-PDP-CHO** and **DD-CHO** and bisphosphate ester **13** were reacted using potassium tert-butoxide as base to give 1,3-bis((E)-4-(2-(3-pentadecylphenoxy)ethoxy)styryl)-2-methoxy-5-methylbenzene (**PDP-mOPV**), 1,3-

bis((E)-4-(2-(2,4-dimethyl-5-pentadecylphenoxy)ethoxy) styryl)-2-methoxy-5-methylbenzene (**DM-PDP-mOPV**), 1,3-bis((E)-4-(dodecyloxy)styryl)-2-methoxy-5-methylbenzene (**DD-mOPV**). Star shaped OPVs were also synthesized by following above procedures from tetraethyl (4-(dodecyloxy)-6-pentadecyl-1,3-phenylene)bis(methylene)diphosphonate (**16**) which is outlined in scheme 5.

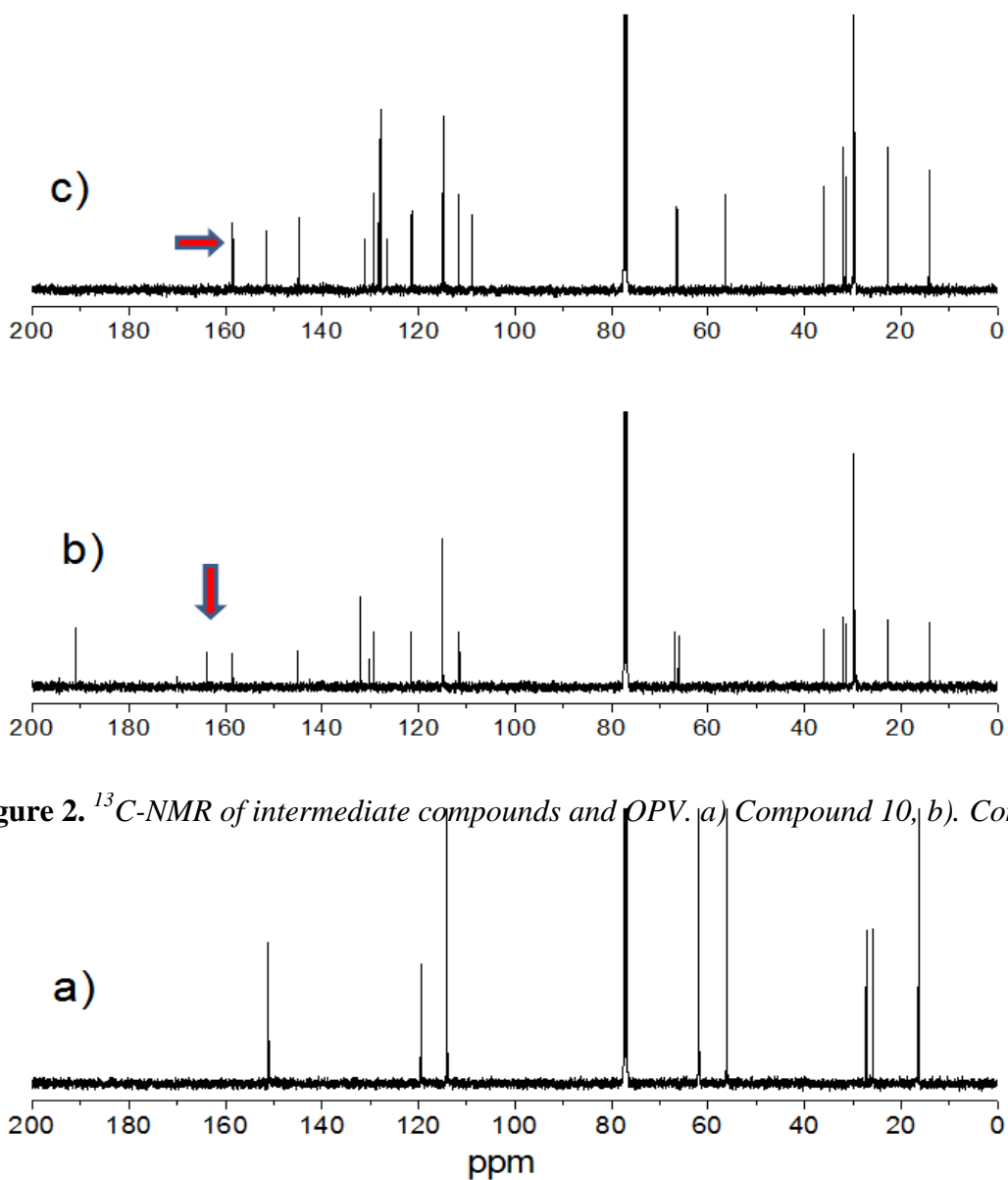
### 3.2. Structural characterization of OPVs.

The structures of the compounds and OPVs were analysed by  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , FT-IR, and MALDI-TOF TOF analysis. The purity of the OPVs was confirmed by GPC technique.  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra of PDP-pOPV was explained elaborately by comparing with spectra of bisphosphonate ester (**10**) and 4-alkoxy benzaldehyde derivative of 3-pentadecylphenol (**PDP-CHO**). The  $^1\text{H-NMR}$  spectra of compound 10, compound PDP-CHO and PDP-OPV are shown in figure 1 and the different types of aromatic and alkoxy protons are assigned and labeled as shown in figure 1. In figure 1a, peak is appeared at 6.88 ppm corresponding to aromatic proton and other peaks corresponding to  $\text{PO}(\text{OCH}_2\text{CH}_3)$ ,  $\text{Ar-OCH}_3$ ,  $\text{Ar-CH}_2\text{PO}(\text{OCH}_2\text{CH}_3)_2$  and  $\text{Ar-CH}_2\text{PO}(\text{OCH}_2\text{CH}_3)_2$  protons are appeared at 4.01 ppm, 3.76 ppm, 3.19 ppm and 1.21 ppm respectively. Similarly 4-(2-(2,4-dimethyl-5-pentadecylphenoxy)ethoxy)benzaldehyde (**PDP-CHO**) showed peaks at 9.87 ppm, 7.82 ppm and 7.04 ppm corresponds to  $\text{Ar-CHO}$ , and  $\text{Ar-H}$  protons of 4-alkoxybenzaldehyde unit as well as aromatic protons belongs to 3-pentadecyl unit at 7.18 ppm and 6.76 ppm respectively (see figure 1b). The peaks appeared at 4.39 ppm - 4.32 ppm, 2.55 ppm and 1.59 ppm - 0.87 ppm are assigned to  $\text{Ar-OCH}_2$ ,  $\text{Ar-CH}_2$  and aliphatic H respect in the 3-pentadecyl unit. In figure 1c, the protons corresponding to the aromatic and vinylic units were appeared as multiplet at 6.75-7.50 ppm and aromatic peaks matched with the expected structure (shown as inset figure).  $\text{Ar-OCH}_2$ ,  $\text{Ar-OCH}_3$  and pentadecyl chain protons compounds and OPV were recorded in  $\text{CDCl}_3$  and shown in figure 2. It is clearly indicate that three different types



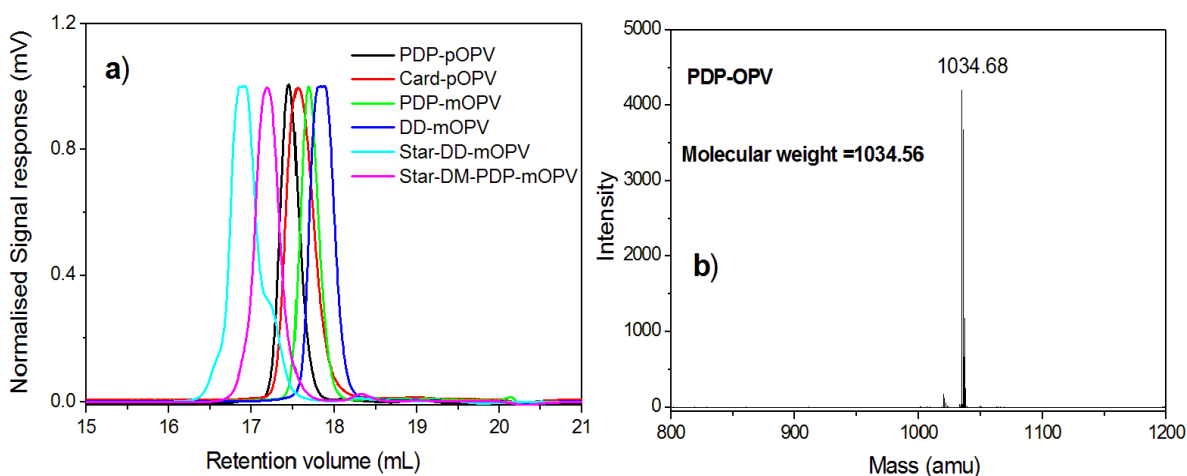
**Figure 1.**  $^1\text{H-NMR}$  of intermediate compounds and OPV. a) Compound 10, b). Compound PDP-CHO, c). PDP-pOPV.

compounds and OPV were recorded in  $\text{CDCl}_3$  and shown in figure 2. It is clearly indicate that three different types of carbon atoms present in the compound **10**.  $^{13}\text{C}$ -NMR spectrum of the pentadecylphenol derivative of 4-hydroxybenzaldehyde shows peak at 190.02 ppm corresponding to the carbonyl carbon of the aldehyde moiety and 10 number of carbon peaks were



appeared at 110-165 ppm in figure 2b. The remaining carbon peaks were exactly matched with expected number carbon atoms present in the system. After wittig condensation reaction,

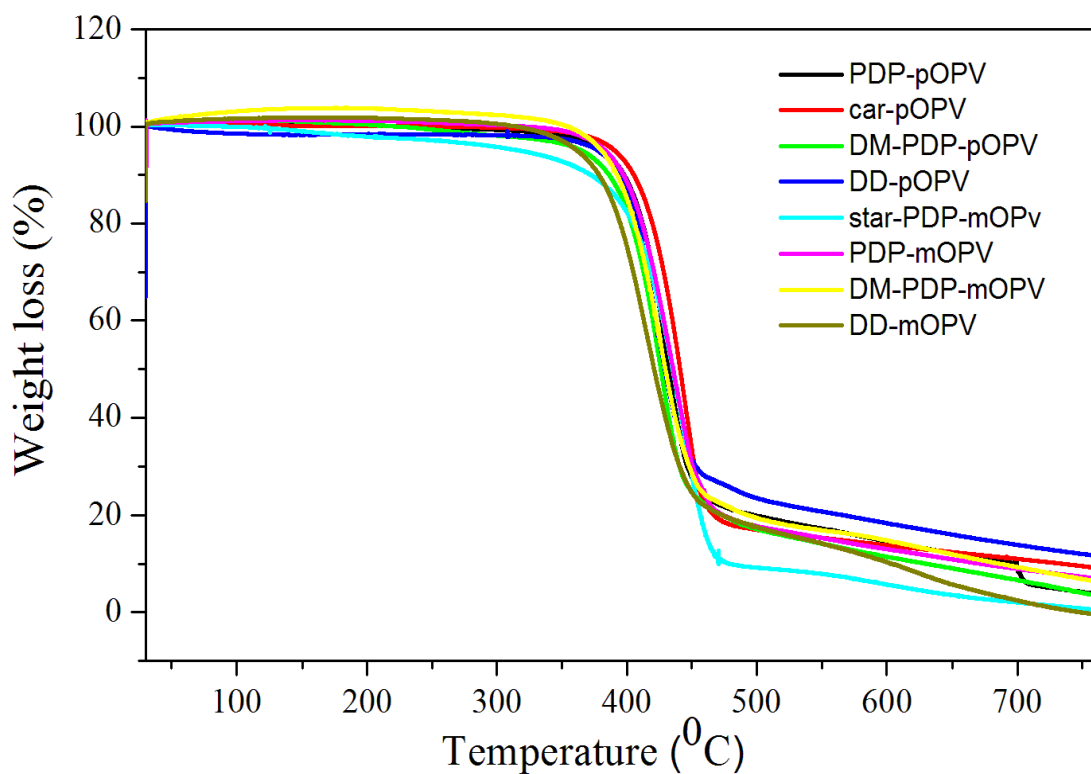
carbonyl carbon of aldehyde group at 190 ppm is completely vanished and new more number aromatic carbon peaks were appeared in the aromatic region from 160- 110 ppm in PDP-OPV. As expected, the peak at 164.12 ppm corresponds to aldehyde containing carbon atom completely is shifted to 159.05 ppm in  $^{13}\text{C}$ -NMR spectra of PDP-OPV, indicated by arrow. These results confirmed the structure of the OPV molecules. The molecular mass of OPVs were determined by MALDI-TOF TOF analysis and their purities of OPVs were confirmed by gel permeation chromatography are shown in figure 3. MALDI-TOF spectrum of one PDP-OPV and GPC chromatogram of the few represented OPVs are shown in the figure 3. GPC chromatogram of OPVs showed as single peak indicating that all synthesized OPVs are highly pure. The MALDI-TOF TOF spectrum of the PDP-OPV showed molecular ion peak at 1034.68 and it is exactly matching with their expected mass of OPV.



**Figure 3.** GPC chromatogram of OPVs and MALDI-TOF TOF spectrum of PDP-pOPV.

### 3.3. Thermal stability and liquid crystalline properties of OPVs.

Thermal stability of the all OPVs was analyzed by thermogravimetric analysis (TGA) and their TGA plots are shown in figure 4. TGA plot of all OPVs showed that good thermal stability with onset degradation temperature upto 350°C. All solid OPV samples were subjected for differential scanning calorimetry (DSC) for tracing their thermal transitions (liquid crystalline). The heating and cooling cycle of DSC thermograms are shown in figure 5. Because of semi solid in nature, DSC analysis could not able to perform for Star-DD-mOPV and Star-DM-PDP-mOPV



**Figure 4.** TGA thermogram of all OPVs.

samples. In figure 5, no melting peak was observed for DM-PDP-mOPV indicating its amorphous nature. DSC thermogram of Car-pOPV and PDP-mOPV showed single melting and crystallize peaks like normal crystallization solids in heating cycle and cooling cycles. PDP-pOPV, DM-PDP-pOPV, DD-pOPV, star-PDP-mOPV and DD-mOPV have shown two types

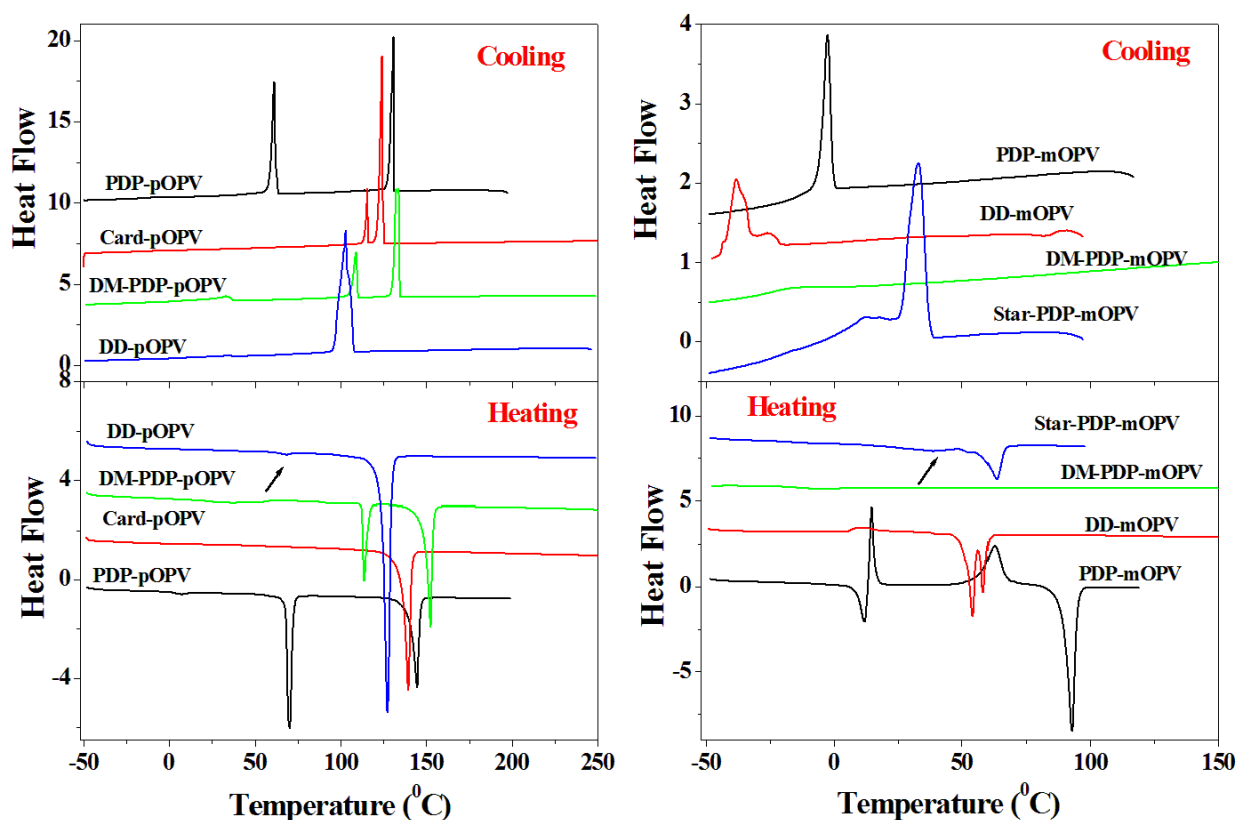
**Table 1.** Mass, thermal decomposition temperature and GPC chromatogram.



Sample	Compound mass (amu)	MALDI-TOF (amu)	Td <sub>onset</sub> (in °C)	GPC chromatogram
PDP-p-OPV	1035.52	1034.56	403	Single
CAR-p-OPV	1031.53	1030.66	414	Single
DM-PDP-p-OPV	1091.62	1090.72	396	Single
DD-p-OPV	711.07	710.75	382	Single
PDP-m-OPV	1019.52	1018.66	399	Single
DM-PDP-m-OPV	1075.63	1074.80.	388	Single
DD-m-OPV	695.07	694.52	376	Single
STAR-PDP-OPV	1370.24	1369.04	405	Single

of

thermal transitions in DSC profiles while heating/cooling cycle. This is typical DSC



thermograms for thermotropic liquid crystalline material behavior. Crystal to liquid and liquid

crystal to isotropic transition were appeared as weak peak at lower temperature and strong peak at higher temperature respectively in heating cycle. Similarly two peaks were appeared in

cooling cycle corresponds to isotropic to LC (first peak) and LC-crystalline (second peak) transitions. In the case of PDP-pOPV, cooling DSC plot showed first peak at 130 °C and second peak at 61 °C which are assigned to isotropic to LC and LC to crystalline transitions, respectively. In melting and cooling cycle, liquid crystalline behavior was observed in DM-PDP-pOPV. But the crystal to liquid crystal and liquid crystal to crystal transitions were happened above 100 °C as compared to PDP-pOPV. In figure 5, dodecyl substituted DD-pOPV also showed isotropic to liquid crystalline transition peak at 103 °C and weak LC-crystalline transition peak at 30 °C in cooling cycle which is typical liquid crystalline behavior. In heating and cooling cycle, the lower temperature liquid crystalline window was obtained for DM-PDP-pOPV

**Table 2.** *Enthalpy and entropy of crystallisation and melting transitions for LC OPV samples.*

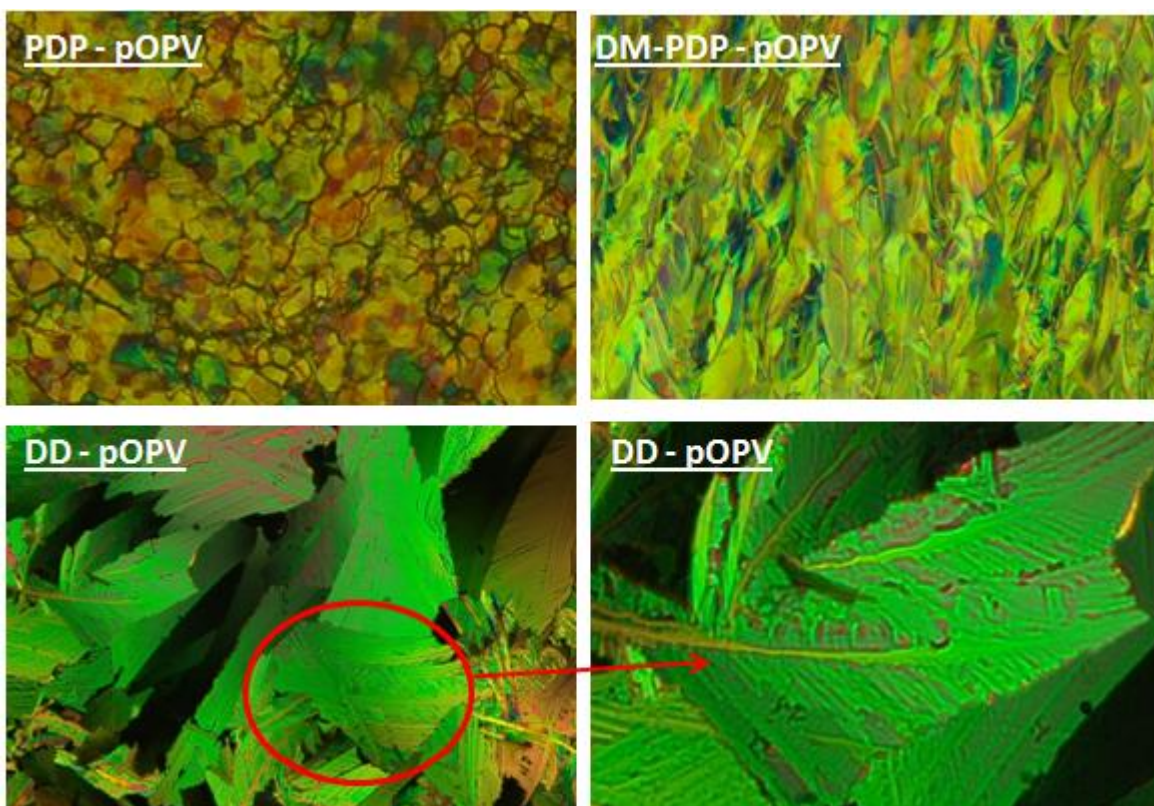
Compound	Cooling Isotropic-LC			Heating LC- isotropic		
	T <sub>c</sub> (in K)	ΔH (KJ/mol)	ΔS (KJ/mol)/ T	T <sub>m</sub> (in K)	ΔH (KJ/mol)	ΔS (J/mol)/T
PDP-pOPV	403	59	147	417	57	136
DM-PDP-pOPV	406	58	143	425	57	135
DD-pOPV	375	83	222	400	84	211
Star-PDP-mOPV	305	41	135	331	35	103
DD-mOPV	304	2	7	337	3	7

and DD-pOPV samples. Interestingly, PDP-pOPV shows LC behavior with larger liquid crystalline temperature window (69 °C) as compared to DM-PDP-pOPV and DD-pOPV. The LC temperature window of PDP-pOPV, DM-PDP-pOPV and DD-pOPV samples was obtained as 39, 59 and 74 degree in heating cycles and as 70, 25 and 69 degree in cooling cycles, respectively. Star shaped pentadecyl phenol derivatized Star-PDP-mOPV and dodecyloxy substituted DD-mOPV were exhibited LC characteristic two transitions peak in the heating as well as cooling cycle, but the transitions were observed at below 100 °C than other LC samples. In the heating cycle of Star-PDP-mOPV, the first peak at 39 °C was assigned to crystal to LC transition and second peak at 64 °C was assigned to LC to isotropic transition. The DSC plots of the DD-mOPV has exhibited liquid crystalline character from the melt to cooling which has two closely spaced exotherms corresponding to the isotropic -LC (31 °C) and LC-crystalline (16 °C) transitions. Very interesting trend could be observed in DSC thermograms of LC samples, one is

LC active window decreased from 25-70 to 16-20 degree (mOPVs) in the cooling cycle and tendency for OPVs to become LC also decreased with changing of rigid backbone from 1,4 linkage to 1,3 linkage in the middle ring without changing the long side chain. Moreover, LC temperature window of dodecyl substituted OPVs is lower than other OPVs, indicating that the dodecyl substitution leads to less crystalline nature in the OPVs. The enthalpies and entropies for melting and crystallization transitions were determined and summarized in table 2. Enthalpy and entropies value for PDP-pOPV and DM-PDP-pOPV are high in cooling and heating. DD-pOPV showed highest enthalpy and entropy value in cooling cycle and melting cycle compared to other OPVs. The highly packed structure needs more energy for the melting (endothermic) and similarly releases more energy (exothermic) while crystallizing compared to weakly packed molecules.

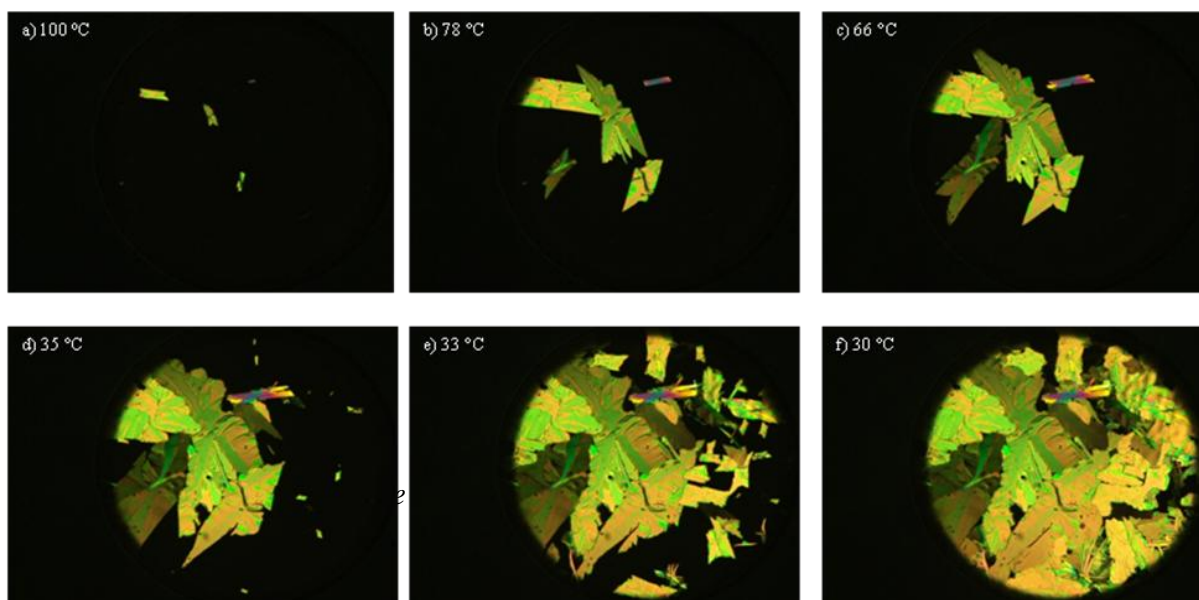
### 3.4. Polarizing Light Microscope Analysis.

LC textures of the all OPVs were studied by using polarized light microscope attached with temperature controllable hot stage. Small amount of powder OPV samples were placed in



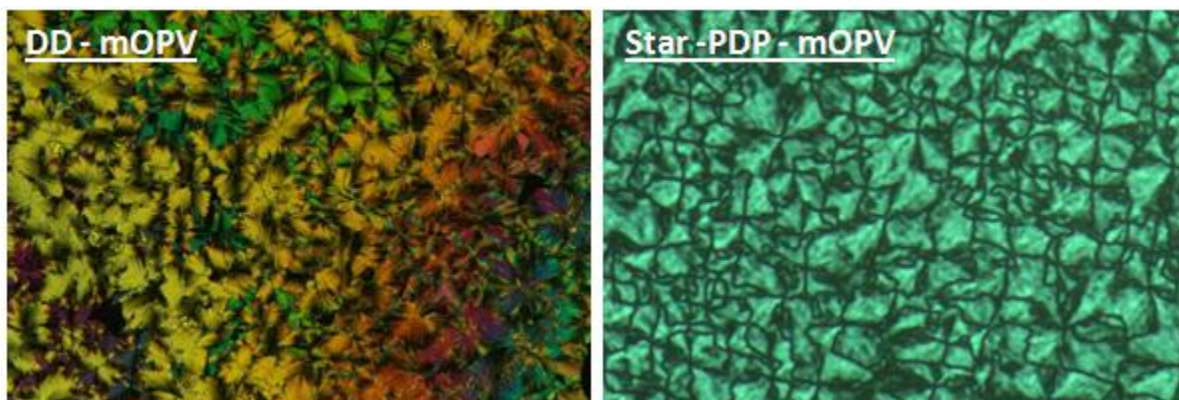
**Figure 6.** *Liquid crystalline textures of pOPVs.*

glass cover slides and melted by heating at 10 °C/min, maintained isothermally at 20 °C above their isotropic temperature for 2-3 min and subsequently cooled at 10 °/min to capture the image using camera. Liquid crystalline morphologies of the OPVs are shown in figure 6. The banana shaped exhibiting focal conics phase textures was observed for pentadecyl phenol substituted PDP-pOPV and DM-PDP-pOPV (side chain containing dimethyl derivatized pentadecyl phenol) produced very interesting banana shaped mosaic texture. The LC texture of DD-pOPV was found very beautiful banana leaf shaped texture with consisting of randomly grown mosaic



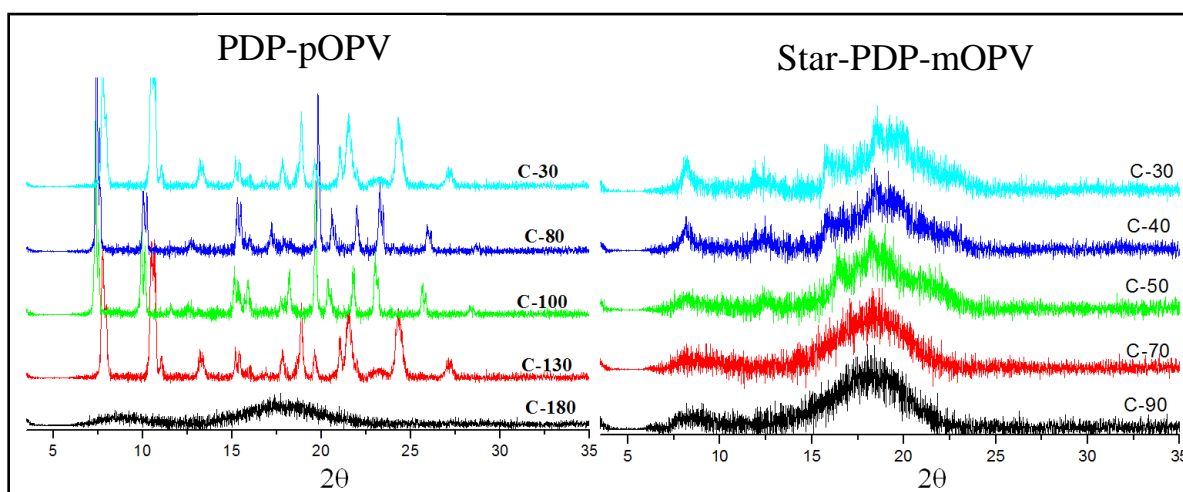
**Figure 7.** *Temperature dependent Liquid crystalline textures of DD-OPVs.*

plates. The gradual growth of banana leaf phase LC texture was captured for DD-pOPV and showed both fully grown leaves and the new born nucleation in figure 7. Thread like nematic and smectic LC phase texture were found in Star-PDP-mOPV and DD-mOPV respectively, shown in figure 8. Uniform thread like texture was seen throughout the Star-PDP-mOPV sample. Upon shining polarized light birefringence pattern consisting of concentric dark and bright flowers were observed in DD-mOPV. In the OPVs having identical aromatic  $\pi$ -core with 1,4 linkage



(para counterpart), LC morphology was transformed from focal conic mosaic to banana shaped mosaic to banana leaf mosaic with changing the side side chain substitution from pentadecyl phenol to dimethyl substituted pentadecyl phenol to dodecyl unit. The transformation in the LC texture was obtained in OPVs having similar rigid aromatic core, indicating that determination of molecular self-organization during the crystallization process is highly depend on van der waals interactions among the alkyl side chain in the OPV chromophores. Shape of the conjugated aromatic core is also **Figure 8. PDA images of OPV organization in OPVs** clearly reflected in Star-PDP-mOPV and DD-mOPV.

### 3.5. Wide Angle X-ray Diffraction studies.



**Figure 9.** Temperature dependent XRD data OPVs.

To identify the lamellar mesophases, variable temperate X-ray diffraction analysis was performed for PDP-pOPV and Star-PDP-mOPV samples and their respective diffractions patterns are shown in figure 8. PDP-pOPV showed multiple sharp crystalline peaks corresponding to a highly crystalline state at room temperature (powder sample). Though Star-PDP-mOPV showed LC behaviors, weak multiple crystalline peaks were observed in room temperature. The powder samples were heated to melt (180 °C for PDP-pOPV and 90 °C for Star-PDP-mOPV) and subsequently cooled to the desired LC active temperature. The crystalline



peaks were started to disappear completely in the isotropic region and upon cooling from melt, the peaks re-appeared. The temperature dependent X-ray study revealed that the molecular self-organization is completely reversible in the repetitive heating/cooling cycles as like PLM and DSC analysis. In the higher angle region, bunch of peaks (strong peaks in PDP-pOPV and weak peaks in Star-PDP-mOPV) are appeared in the higher angle region from  $2\theta = 15 - 25$  ( $d = 4-6 \text{ \AA}$ ) corresponded to aromatic core packing. Three lower angle ( $2\theta < 15$ ) peaks were appearing at  $2\theta = 7.5, 10.6, 13.2$  in PDP-pOPV, but in the case of Star-PDP-mOPV, two weak peaks are seen at  $2\theta = 8.4$  and  $11.7$ .

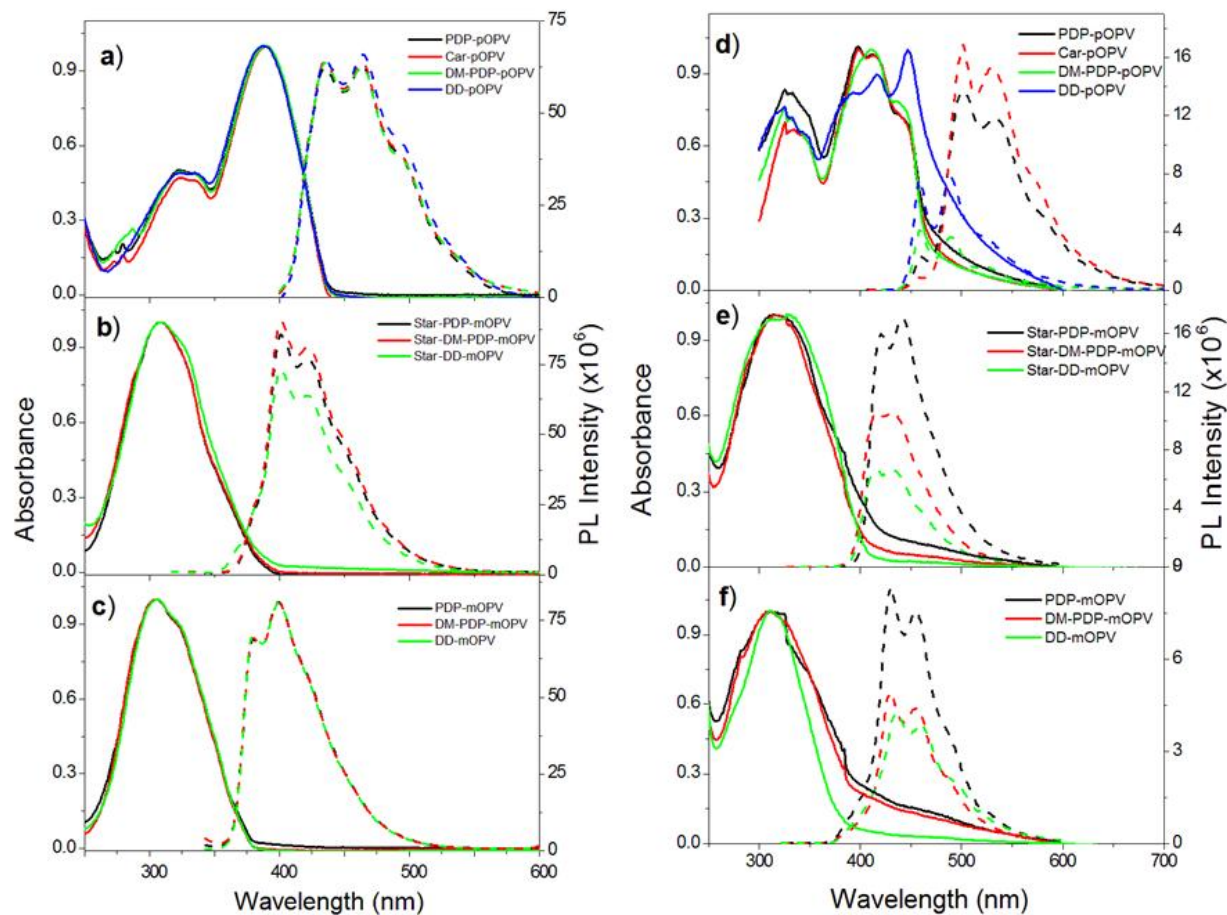
**Table 3.** *Quantum yield, absorbance and emission maxima of OPVs (solution and film state).*

Sample	In soln. (nm) <sup>a</sup>			In film (nm) <sup>c</sup>	
	$\lambda_{\text{Abs}}$	$\lambda_{\text{Em}}$	$\phi_{\text{FL}}^b$	$\lambda_{\text{Abs}}$	$\lambda_{\text{Em}}$
PDP-p-OPV	389	464	0.64	398	501
CAR-p-OPV	389	463	0.65	398	501
DM-PDP-p-OPV	389	463	0.61	411	458
DD-p-OPV	389	456	0.68	447	458
PDP-m-OPV	308	401	0.40	315	441
DM-PDP-m-OPV	308	401	0.42	329	414
DD-m-OPV	308	401	0.42	315	413
STAR-PDP-OPV	304	400	0.46	312	429
STAR-DM-PDP-OPV	304	400	0.44	312	429
STAR-DD-OPV	304	400	0.36	312	435

### 3.6. Photophysical studies.

Highly luminescent  $\pi$ -conjugated aromatic core containing OPVs were subjected for photophysical studies to study role of  $\pi$ - $\pi$  stacking and van der Waals interaction for molecular self-organization. The concentrations of the OPVs and standard solution were adjusted in such a way to obtain the absorbance equal to 0.1 for the determination of quantum yield. All p-OPVs showed absorption and emission maxima at 388 and 465 nm respectively in THF solutions. Absorption and emission maxima were obtained as 310 and 402 nm for Star-mOPVs and mOPVs showed absorption and emission peaks at 306 and 400 nm respectively. It is clearly indicating that solution absorption and emission spectra of OPVs did not show any shift in maxima with change of side chain substitutions. The quantum yield of the OPVs were

determined using quinine sulfate (in 0.1 N conc.  $H_2SO_4$ ) by following the equation:  $\phi_s = \phi_r (F_s A_r / F_r A_s) (n_r / n_s)^2$  where  $\phi_s$  is the fluorescent quantum yield, F is the area of the emission, n is the refractive index of the solvent, and A is the absorbance of the solution at the exciting wavelength. The relative quantum yield of the pOPVs were obtained as approximately 0.6 in THF solution indicate that quantum yield of the OPVs did not change much with changing the



**Figure 10.** Absorbance and emission spectra of OPVs in THF solution(a, b and c) and solid state (c,d and e)

side chain substitutions. Lower quantum yield were observed for mOPVs (approximately 0.4) compared to pOPVs and it is almost same for different side chain substituted meta linked OPVs. It is indicating that quantum yield of conjugated aromatic chromophore in THF solutions did not affected by varying the different alkyl chain. The solid films were recorded for m-OPVs were drop casted on quartz plate. In solid state absorbance and emission spectra, red shift was observed as compared to solution state and quenching occurred in emission properties. But absorption

spectra have not shown any difference in the absorption maxima with changing of alkyl side chain substitution in the conjugated aromatic core of OPVs. However, effective shift was observed in emission spectra with variation of alkyl side chain in the conjugated aromatic core of OPVs. The highly packed structures were expected to have strong  $\pi$ -overlapping among the OPV-chromophores, which led to blue shift in their emission spectra. This may be due to molecular aggregation in the  $\pi$ -conjugated aromatic core of OPVs. In the emission maxima of pOPVs, PDP-pOPV and Car-pPDP in solid state were almost 41 nm red shifted compared to other pOPVs. Similarly emission spectrum of PDP-mOPV and DM-PDP-mOPV showed maximum peak at 455 nm and DD-mOPV showed 5 nm red shift as compared to other PDP-mOPV and DM-PDP-mOPV.



## **CONCLUSIONS**

#### 4. Conclusions.

In this thesis, new series of banana and star shaped  $\pi$ -conjugated oligophenylenevinylenes based on para and meta linked aromatic core are developed. Variable long alkyl chain containing commercially available compounds such as 3-pentadecylphenol, cardanol and dodecane were utilized as long flexible chain in longitudinal position of OPVs to study the role of aromatic  $\pi$ -stacking and van der Waals interactions on the molecular self-assembly. The significance of the present investigation are as follows: (i) a new banana and star shaped molecular structure for liquid crystalline OPV chromophore was developed based on rigid aromatic  $\pi$ -core (1,4 and 1,3 linkage) with long flexible chains to produce five different types of liquid crystalline materials. (ii) Changing of rigid backbone from 1,4 linkage to 1,3 linkage in the middle ring without changing the long side chain, LC active window decreased from 25-70 to 16-20 degree (mOPVs) in the cooling cycle and tendency for OPVs to become LC also decreased (iii) in cooling and heating cycle, highest enthalpy and entropies value were obtained for PDP-pOPV and DM-PDP-pOPV compared to mOPVs (iv) cardanol substituted OPVs showed crystalline properties (v) The banana shaped exhibiting focal conics phase textures was observed for pentadecylphenol substituted PDP-pOPV and DM-PDP-pOPV (side chain containing dimethyl derivatized pentadecylphenol) produced very interesting banana shaped mosaic texture. (vi) DD-pOPV was found as very beautiful banana leaf shaped texture with consisting of randomly grown mosaic plates. (vii) Threat like nematic and smectic LC phase texture were found to respective Star-PDP-mOPV and DD-mOPV samples. (viii) in the present design, OPV mesogens possessed a fixed aromatic  $\pi$ -core with changing alkyl side chain as well as changing of middle ring of aromatic core from 1,4 to 1,3 linkage with fixed alkyl side chain, and therefore, aromatic  $\pi$ - $\pi$  stacking and alkyl chain van der Waals interactions account for transformation of LC textures. (ix) The temperature dependent PLM analyses showed the gradual growth banana leaf shaped texture with mosaic plates in cooling cycle. (xii) The lamellar ordering of the OPV molecules showed sharp peaks in the X-ray diffraction patterns at low angle region and they were reproducible in the repetitive heating/cooling cycles. (xiii) the solution state photophysical studies of OPVs revealed that no change was occur in the absorption and emission maxima with the variation in the alkyl chain lengths (xiv) Highest quantum yield was obtained for pOPVs as compared to mOPVs (xv) solid state emission spectra were showed drastic change in the emission maxima and emission intensity with variation of alkyl side chain.

PDP-pOPV and Car-pPDP in solid state showed almost 41 nm red shift in emission maxima compared to other pOPVs. The approach demonstrated here, allows one to synthesize and manipulate the liquid crystallinity, solid state ordering, molecular self-assembly and photophysical characteristics in  $\pi$ -conjugated chromophores, which have continuous demand in the electronic industry. Further, the liquid crystalline materials are produced in an eco-friendly solvent free self-organization via melt crystallization process and bear potential for large scale processing applications.

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