Chapter 4

Supramolecular Ring Banded Bulky Liquid Crystalline Oligo-phenylenevinylenes
4.1. Introduction

Crystallization and melting are two most important phenomena found in solids and semi-crystalline polymers which explain the transitions between random and ordered phases. Generally, the crystallization phenomena occur in three stages, namely, nucleation, growth and perfection. This can be compared with a chain polymerization reaction in the case of polymers, which consists of initiation, propagation and termination steps.\textsuperscript{1} Eventhough a few reports are available for crystal perfection, one of the widely observed features in the morphology of the crystalline material (including polymers) is the appearance of micrometer range spherulites.\textsuperscript{2} The mechanism of spherulitic formation involves (i) the induction of nucleation (ii) crystal growth and (iii) the intersection of the neighboring nuclei. Usually, the intersection between the two crystal nuclei is straight since the rates of the crystal growth are same. The fast growth of crystals from the melt produces the highly ordered structures called spherulites. Therefore, ‘the spherulites are found to be the aggregates of polyhedral crystals or dendrites growing out of a common nucleus’.\textsuperscript{1} Liquid crystalline (LC) materials are other classes of crystalline solids and their morphologies, in general, are completely different from normal spherulites depending on their LC state such as nematic, smectic and cholesteric, etc.\textsuperscript{3} A new type of spherulitic structures with ring bands was reported in commercial semi-crystalline polymers and liquid crystalline materials while they crystallize from the molten state (see scheme 4.1).\textsuperscript{4-6} Keith and Padden was the first to propose a classical mechanism behind the formation of ring banded spherulites which is attributed to the periodic twisting of the lamellae by surface tension and plate reorientation.\textsuperscript{7-11} After that a lot of research works have proven that the origin of the ring banded structure is due to the periodic twisting of lamellar crystals along the radial growth direction of the spherulites.\textsuperscript{12-15} However, according to many reports the lamellar twisting phenomenon was correlated to surface stress,\textsuperscript{6} chain folding-direction to the crystal growth,\textsuperscript{16} periodic change of concentration gradient \textsuperscript{17} and also to the rejection of amorphous polymer
chains from the crystal fronts of polymer binary blends. Though the twisting of lamellar crystals mechanism was widely accepted in all these cases, there seems to be no correlation between the structure of the materials (polymers or small molecules) and appearance of ring banded crystalline structures.

![Scheme 4.1. Examples of ring banded spherulites. Optical images of poly(trimethylene terephthalate) samples (adapted from ref. 6) and some of the commercial polymers showing ring banded structures.](image)

One of the significant properties of the liquid crystalline π-conjugated materials is that their supramolecular organization will lead to a long range order and can be used in different applications such as light emitting diodes, photovoltaic cells, field-effective transistors, chemical and bio-sensors, etc. In phenylenevinylene, both thermotropic and lyotropic behaviors were reported and these properties found to enhance the charge transporting ability several orders of magnitude greater than that from simple solvent casted film (see scheme 2). Recently Li et al. have reported that the attachment of the biphenyloxyl or cyclohexylphenoxy mesogenic units to poly(2,3-diphenylphenylenevinylene)s exhibits thermotropic liquid crystalline phases (see scheme 4.2). The polymers showed green-blue PL and EL and they can be aligned by rubbing treatment to give a linearly dichroic PL with a dichroic ratio of 2.1. Akagi et al. also reported side chain liquid crystalline PPVs which showed enhancement in the electrical conductivity and electrical anisotropy for the aligned polymer film after rubbing treatments (see scheme 4.2).
Phenylenevinylene oligomers also showed liquid crystalline characters\textsuperscript{28-30} (see scheme 4.2) and the details are explained in the next sections.

\begin{itemize}
  \item \textbf{OPV-1} (R = C\textsubscript{6}H\textsubscript{13})
  \item \textbf{OPV-2} (R = n-octyl or n-octyloxy)
\end{itemize}

Scheme 4.2. Phenylenevinylenes with liquid crystalline pendants.

However, the tendency of molecules to crystallize easily limits their applications in optoelectronics, since the crystalline nature will destroys the homogeneity of the thin films which will result in electric shorting.\textsuperscript{31} It was found that for improving the device properties, the control of the spatial orientation of the molecules is necessary. Owing to large complexity, oligomers of semiconducting polymers has been utilized as molecular skeletons for self-assembly rather than the large macromolecular (or polymer) chains. Oligo-phenylenevinylenes (OPVs) is one of the widely studied \ensuremath{\pi}-conjugated systems due to their high luminescence and better charge transport properties.\textsuperscript{32} In OPVs, both non-covalent interactions such as hydrogen bonding and \ensuremath{\pi}-\ensuremath{\pi} stacking of aromatic cores have been employed as tools to self-assemble.
molecular building blocks to produce relatively large and defect-free supramolecular architectures (see scheme 4.3).\textsuperscript{28-30}

Scheme 4.3. Schematic illustration of self-organized structures from OPV backbones (Adapted from references 28a-c).

These supramolecular structures were most often visualized as macroscopic properties such as liquid crystalline, viscous mass or reversible/irreversible molecular gels.\textsuperscript{33,34} Jonkheijm et al. reported spectroscopic investigation of hydrogen bonded OPV derivatives and found...
that organized shell of solvent molecules played a major role towards the self-assembly of π-conjugated molecules. Meijer and coworkers explored the modification of OPV backbone with different molecular design strategy to get different phases by self-organization approach for tuning the liquid crystalline properties. 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.

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. Few reports were also known for studying the effect of alkyl side chains or fluoro-substitution on the LC properties of OPVs. He et al. and Gu et al. were demonstrated that liquid crystalline OPVs can enhance the photoluminescence and electroluminescence properties to a great extent. Therefore, taking advantages from all the above factors, it will be interesting and promising to design and develop new oligomers with efficient luminescent and device properties. It was widely seen that most of the conducting polymers or oligomer based LC-materials were generally nematic, smectic or columnar type of LC materials. Up to our knowledge, so far, there has been no report for π-conjugated ring banded supramolecular crystalline or LC materials in the literature. π-Conjugated ring banded supra-structures would be very much promising since patterning of electronic materials could be achieved via a melt crystallization process which will be very new in cleaner process. The idea of studying fundamental phenomena like ring banded structure in a system like luminescent OPV is very stimulating because: (i) it gives a new opportunity to trace the molecular interactions and the factors which directly influence on the mechanism ring banded formation and (ii) the resultant ring banded luminescent materials could be a new entry into opto-electronic materials and may be attractive for newer applications.

In the present chapter, design and synthesis of more than ten different bulky oligo-phenylenevinylene molecules were discussed which are used for
tracing the ring banded structures in liquid crystalline π-conjugated system (see scheme 4.5). All the OPVs have commonly three aromatic units and differed in their nature of the pendants either in the middle or the outer phenyl rings. A new bulky pendant 1,8-tricyclodecanemethylene has been utilized for making the bulky conjugated OPVs. Three OPV molecules were found as thermotropic liquid crystalline and among them BTCD-BDD-OPV showed ring banded supramolecular structure. Both isothermal and non-isothermal crystallization process were employed as tool to study the ring banded structures. Electron microscopic (SEM and TEM) analysis were carried out in the LC-stage frozen samples to identity lamella twisting, and the mechanism of ring banded structures. Variable temperature X-ray diffraction analysis showed fundamental reflections corresponding to the lamella and confirmed their existence in the mechanism of ring banded morphology. Detailed photophysical studies (excitation and emission and time dependent fluorescence -decay) were carried out in both film and LC-frozen sample to trace the role of π-π interactions in OPV mesogens on the ring banded structures. All these studies revealed that BTCD-BDD-OPV molecule has possessed planar structure for strong three dimensional π-π interactions in solid state which is the main driving force for the ring banded π-conjugated liquid crystalline supra-structures.

4.2. Experimental Methods

4.2.1. Materials: 1,8-Tricyclodecanemethanol (TCD) was donated by Celanese Chemicals & Co. and used without further purification. p-Toluenesulfonylchloride, 4-methoxyphenol, hydroquinone, 2-ethylhexylbromide, potassium tert-butoxide (in 1M THF solution) and Quinine sulfate were purchased from Aldrich Chemicals. Sodium salicylate (99.5%) was purchased from Merck chemicals. HBr in glacial acetic acid, paraformaldehyde and all other reagents/solvents were purchased locally and purified by following the standard procedures. 1,4-bis (bromomethyl)-2-methoxy-5-(2-ethylhexyloxy)benzene, 1,4-bis(bromomethyl)-2,5-di(2-
ethylhexyloxy)benzene, 1,4-bis(bromomethyl)-2-methoxy-5-(1,8-tricyclodecanemethyleneoxy) benzene, 1,4-bis(bromomethyl)-2,5-di(1,8-tricyclodecanemethyleneoxy)benzene, 1,4-bis(bromomethyl)-2,5-di(dodecyloxy)benzene and their corresponding ylides were synthesized according to the similar procedures as explained in chapter 2. The detailed synthesis of intermediate molecules and the monomers were given in chapter 2, and the synthetic procedures and the structural data of the OPVs are explained in the experimental section. The synthesis and structural characterization of BTCD-OPV, MTCD-OPV and MEH-OPV were given in chapter 2.

4.2.2. General Procedures: \(^1\)H and \(^13\)C-NMR spectra of the compounds were recorded using 300-MHz Brucker NMR spectrophotometer in CDCl\(_3\), containing small amount of TMS as internal standard. Infrared spectra of the samples were recorded with a Perkin Elmer Fourier transform infrared (FT-IR) spectrophotometer in the solid state. The purity of the compounds was determined by JEOL JSM600 fast atom bombardment (FAB) high-resolution mass spectrometry. The compound was dissolved in CHCl\(_3\) and suspended in 3-nitrobenzylalcohol as a matrix for FAB-Mass measurements. Elemental analysis of the compounds was carried out using Perkin Elmer Series II CHNS/O Analyzer 2400. The purity of samples were analyzed by gel permeation chromatographic (GPC) analysis was performed using Waters 510 pump and detectors of Waters 2487 UV-Vis detector and Waters 410 differential RI detector in tetrahydrofuran (THF) using polystyrene as standards. The thermal stability of the oligophenylenevinylenechains was determined using DTG-60 Shimadzu Thermogravimetric Analyzer at a heating rate of 10 °C/min in nitrogen atmosphere. Thermal analyses of the polymers were performed with a PerkinElmer Pyris-6 differential scanning calorimetry (DSC) instrument under nitrogen, and the instrument was calibrated with indium, tin, and lead standards. All samples were first heated to melt prior to recording their thermograms to remove their previous thermal history and recorded using a heating /cooling rate of 10°C/min under the purge of dry nitrogen. The liquid
crystalline properties of the OPVs were investigated using Nikon HFX 35 A Optiphot 2-Pol polarized light optical microscope equipped with a Linkam THMS 600 heating and freezing stage connected to a Linkam TMS 93 temperature programmer. Fluorescence light microscopy (FLM) was done on a NIKON ECLIPSE E-600 using an excitation filter EX-330-380, EX-410-450 nm, emission filter BA-400 and dichromatic mirror DM-400. LC frozen and powder X-ray Diffraction patterns were recorded by Philips Analytical Diffractometer using CuK-alpha emission. The spectra were recorded in the range of $2\theta = 0-40$ and analyzed using X'pert software. Variable X-ray diffraction studies were performed using a Rigaku Dmax 2500 diffractometer with a copper target. The system consists of a rotating anode generator with a copper target and a wide-angle powder goniometer fitted with a high-temperature attachment. The generator was operated at 40 kV and 100 mA. All the experiments were performed in the reflection mode. The sample holder was a copper block, and the powder sample was filled in the block. The absorption and emission studies were done by a Perkin-Elmer Lambda 35 UV-Visible spectrophotometer and Spex-Fluorolog DM3000F spectrofluorometer with a double grating 0.22-m Spex 1680 monochromator and a 450-W Xe lamp as the excitation source using the front-face mode. The solution spectra were recorded in THF and for the solid state spectra, thin films (10-100 $\mu$M) were prepared by drop casting THF solution on glass substrates. The solution quantum yields of the OPVs were determined using quinine sulfate in 0.1 M H$_2$SO$_4$ ($\phi = 0.546$) as the standard. Photophysical properties of the liquid crystalline samples were done by freezing the samples in the LC state. The fluorescence lifetime was measured using an IBH FlouroCube Time-correlated picosecond single photon counting system (TCSPC). Solutions and films were excited with a pulsed diode laser 401 nm <100 ps pulse duration with a repetition rate of 1 MHz. The detection system consists of a microchannel plate photomultiplier (5000U-09B, Hamamatsu) with a 38.6 ps response time coupled to a monochromator (5000M) and TCSPC electronics (Data Station Hub including Hub-NL, Nano
LED controller and preinstalled Fluorescence Measurement and Analysis Studio (FMAS) software. The fluorescence lifetime values were determined by deconvoluting the data with exponential decay using DAS6 decay analysis software. The quality of the fit has been judged by the fitting parameters such as $\chi^2<1$ as well as the visual inspection of the residuals.

**Synthesis of 1,4-bis-(4-dodecyloxy styryl)-2,5-di(1,8-tricyclocdecane methyleneoxy) benzene (BTCD-BDD-OPV):**

1,4-Bis(bromomethyl)-2,5-di(1,8-tricyclocdecane methyleneoxy)benzene (2.00 g, 3.4 mmol) and triethylphosphite (1.13 g, 6.8 mmol) were heated to 140-150 °C for 12 h under nitrogen atmosphere. Excess triethyl phosphite was removed by vacuum distillation and the resultant ylide 1,4-bis(tricyclocdecane methyleneoxy)-2,5-xlenetetraethyl diphenophonate was obtained as yellow thick oil. $^1$H-NMR (CDCl$_3$, 300MHz): 6.88 (t, 2H, Ar-H), 4.06 (m, 8H, -PO-OCH$_2$), 3.68 (m, 4H, Ar-OCH$_2$), 3.24 (m, 4H, Ar-CH$_2$P), 1.69-1.21 (m, 42H, aliphatic). FT-IR (KBr, cm$^{-1}$): 3445, 2947, 2868, 1681, 1509, 1474, 1415, 1392, 1305, 1245, 1210, 1163, 1094, 1048, 1029,964, 894, 875, 831, 782, 729, 529. To the above-crude product (0.53 g, 0.75 mmol) in 20 mL dry THF, 4-dodecyloxy benzaldehyde (0.55 g, 0.19 mmol) and potassium tert-butoxide (5 mL, 1M THF) were added and the contents were stirred under nitrogen for 24 h at 30 °C. It was poured into methanol and the yellow precipitate formed was filtered and purified by passing through silica gel column using 2.5 % ethyl acetate in hexane as eluent. Yield = 90 %, m.p. = 160-161 0°C. $^1$H-NMR (CDCl$_3$, 300MHz): 7.47-6.88 (m, 14H, Ar-H and vinylic H), 4.00-3.96 (t, 4H, Ar-OCH$_2$-DD), 3.83-3.75 (m, 4H, Ar-OCH$_2$-TCD), 2.41-0.86 (m, 76H, cyclic-H and aliphatic-H). $^{13}$C-NMR (CDCl$_3$, 75MHz): 158.6, 151.0, 130.6, 128.3, 127.5, 126.5, 121.4, 144.5, 110.9 (Ar-C), 73.5 (Ar-OCH$_2$-DD), 67.9 (Ar-OCH$_2$-TCD), 45.6, 45.2, 43.9, 41.2, 34.6, 31.8, 29.5, 29.3, 29.2, 28.9, 27.9, 26.9, 26.4, 25.9, and 22.6 (Cyclic and aliphatic-C). FT-IR (KBr, cm$^{-1}$): 2919, 2850, 1606, 1575, 1511, 1489, 1475, 1423, 1381,
1291, 1243, 1190, 1176, 1008, 971 (HC=CH, trans), 852 (HC=CH, cis), 818, 720. HR-MS (MW: 979.5): m/z = 978.9 (M+). Anal. Calcd. for C₆₈H₉₈O₄: C, 83.38; H, 10.08; Found C, 83.02; H, 10.38.

1,4-bis-(4-dodecyloxy styryl)-2-(1,8-tricyclodecanemethyleneoxy)-5-(methoxy)-benzene (MTCD-BDD-OPV): 1-(methoxy)-4-(tricyclodecanemethyleneoxy)-2,5-xylenetetraethylphosphonate was synthesized as explained for BTCD-BDD-OPV. To the crude ylide (2.20 g, 3.8 mmol) in 50 mL dry THF, 4-dodecyloxy benzaldehyde (2.76 g, 9.5 mmol) and potassium tert-butoxide in (20 mL, 1M THF) were reacted to obtain MTCD-BDD-OPV and the product was purified as described for MTCD-OPV. Yield = 55 %, m.p.= 99-100 °C. ¹H-NMR (CDCl₃, 300MHz) δ: 7.49-7.06 (m, 14H, Ar-H and vinylic H), 3.99-3.95 (t, 4H, Ar-OCH₂-DD), 3.91 (s, 3H, Ar-OCH₃), 3.84-3.76 (m, 2H, Ar-OCH₂-TCD), 2.29-0.86 (m, 61H, cyclic-H and aliphatic-H). ¹³C-NMR (CDCl₃, 75MHz) δ: 158.7, 151.3, 151.1, 130.6, 130.5, 128.4, 128.3, 127.7, 127.6, 126.7, 126.4, 121.5, 120.9, 114.6, 110.6, 109.1 (Ar-C), 73.7 (Ar-OCH₂-DD), 68.0 (Ar-OCH₃), 56.2 (Ar-OCH₂-TCD), 45.3, 44.0, 41.3, 40.3, 34.8, 31.9, 29.7, 29.6, 29.4, 29.3, 29.1, 28.0, 27.0, 26.5, 26.0 and 22.7 (Cyclic and aliphatic C). FT-IR (KBr, cm⁻¹): 2922, 2852, 1604, 1573, 1512, 1471, 1415, 1392, 1347, 1292, 1245, 1204, 1172, 1041, 963 (HC=CH, trans), 851 (HC=CH, cis), 817, 722, 637. HRMS (MW: 845.3): m/z = 844.8 (M⁺). Anal. Calcd. for C₅₈H₈₄O₄: C, 82.41; H, 10.02; Found C, 82.38; H, 10.32.

1,4-bis(dodecyloxy)-2,5-distyrylbenzene (BDD-OPV): 1,4-bis(bromomethyl)-2,5-di(dodecyloxy)benzene (2.00 g, 3.2 mmol) and triethyl phosphite (1.64 g, 6.4 mmol) were heated to 140-150 °C for 12 h under nitrogen atmosphere. Excess triethyl phosphite was removed by vacuum distillation and the resultant ylide 1,4-di(dodecyloxy)-2,5-xylenetetraethylphosphonate was obtained as thick oil. ¹H-NMR (CDCl₃, 300MHz) δ: 6.90 (s, 2H, Ar-H), 4.05 (m, 8H, -PO-OCH₂), 3.92 (m, 4H, Ar-OCH₂), 3.24 (d, 4H, Ar-CH₂P), 1.96-0.85 (m, 58H, aliphatic). The crude ylide
(2.30 g, 3.1 mmol) in 50 ml dry THF, benzaldehyde (2.23 g, 7.7 mmol) and potassium tert-butoxide in (18 mL, 1M THF) were reacted and the product obtained was purified as described for BTCD-OPV. Yield = 46 %, m.p. = 86-87°C. 1H-NMR (CDCl₃, 300MHz) δ: 7.48-7.03 (m, 16H, Ar-H and vinylic H), 4.01-3.96 (t, 4H, Ar-OCH₂), 1.85-0.78 (m, 46H, cyclic-H). 13C-NMR (CDCl₃, 75MHz) δ: 151.4, 151.2, 130.7, 128.4, 128.3, 127.7, 127.6, 126.8, 126.5, 121.5, 121.0, 114.7, 110.8, 109.2 (Ar-C), 73.8 (Ar-OCH₂), 45.7, 45.3, 44.0, 41.3, 40.3, 34.8, 31.9, 29.7, 29.6, 29.4, 29.3, 29.1, 28.0, 27.0, 26.5, 26.0 and 22.6 (Cyclic-C) FT-IR (KBr, cm⁻¹): 3445, 3058, 2921, 2848, 1599, 1490, 1464, 1426, 1386, 1342, 1327, 1256, 1205, 1071, 1044, 999, 963 (HC=CH, trans), 852 (HC=CH, cis), 748, 722, 690. HRMS (MW: 651.04): m/z = 650.72 (M⁺).

Anal. Calcd. for C₄₆H₆₆O₂: C, 84.87; H, 10.22; Found C, 84.11; H, 10.67.

1,4-bis-(4-dodecyloxystyryl)-2,5-di(dodecyloxy)benzene (TDD-OPV): 1,4-di(dodecyl)-2,5-xylenetetraethyldiphosphonate was synthesized as explained for BDD-OPV. The crude ylide (2.30 g, 3.1 mmol) in 50 mL dry THF, 4-dodecyloxybenzaldehyde (2.23 g, 7.7 mmol) and potassium tert-butoxide in (18 mL, 1M THF) were reacted to get TDD-OPV and was purified as explained for BDD-OPV. Yield = 74%, m.p. = 87-88°C. 1H-NMR (CDCl₃, 300MHz) δ: 7.42-6.83 (m, 14H, Ar-H and vinylic H), 4.02-3.91 (m, 8H, Ar-OCH₂-DD), 2.13-0.82 (m, 72H, aliphatic-H). 13C-NMR (CDCl₃, 75MHz) δ: 158.7, 150.9, 130.6, 128.8, 128.2, 127.4, 127.1, 126.8, 121.7, 115.8, 114.8, 114.4, 114.0, 113.8, 113.5, 111.3, 110.4, 109.6 (Ar-C), 69.6, 68.0 (Ar-OCH₂-DD), 32.4, 31.9, 30.2, 29.7, 29.4, 29.3, 29.1, 26.3, 26.1, 23.2 and 22.7 (aliphatic-C). FT-IR (KBr, cm⁻¹): 2922, 2853, 1606, 1512, 1470, 1422, 1378, 1290, 1246, 1190, 1033, 965 (HC=CH, trans), 851 (HC=CH, cis), 821, 721. HRMS (MW: 1019.7): m/z =1018.7 (M⁺). Anal. Calcd. for C₇₀H₁₁₄O₄: C, 82.45; H, 11.27; Found C, 82.65; H, 11.23.

1,4-bis-(4-dodecyloxystyryl)-2-(2-ethylhexyloxy)-5-(methoxy)-benzene (MEH-BDD-OPV): 1-methoxy-4-(2-ethylhexyloxy)-2,5-
xilenetetraethylidiphosphonate was synthesized as explained for MTCD-BDD-OPV. The crude ylide (1.00 g, 1.8 mmol) in 50 mL dry THF, 4-dodecyloxybenzaldehyde (1.14 g, 3.9 mmol) and potassium tert-butoxide in (12 mL, 1M THF) were reacted to obtain MEH-BDD-OPV. It was then precipitated in methanol and the solid was filtered and purified by passing through silica gel column using ethyl acetate and hexane (1:20 v/v) as eluent. Yield = 50%, m.p. = 89-90 °C. $^1$H-NMR (CDCl$_3$, 300MHz) $\delta$: 7.49-6.88 (m, 14H, Ar-H and vinylic H), 4.00-3.93 (m, 6H, Ar-OCH$_2$-DD and Ar- OCH$_2$-EH), 3.91 (s, 3H, Ar- OCH$_3$), 1.81-0.86 (m, 61H, cyclic-H and aliphatic-H). FT-IR (KBr, cm$^{-1}$): 2924, 2852, 1726, 1604, 1572, 1510, 1466, 1417, 1392, 1292, 1245, 1202, 1173, 1042, 964 (HC==CH, trans), 852 (HC==CH, cis), 820, 722. HRMS (MW: 809.3): m/z =808.7 (M$^+$. Anal. Calcd. for C$_{55}$H$_{84}$O$_4$: C, 81.63; H, 10.46. Found C, 81.02; H, 11.75.

1,4-(2-ethylhexyloxy)-2,5-distyrylbenzene (BEH-OPV): 1,4-bis(bromomethyl)-2,5-(2-ethylhexyloxy)benzene (2.00 g, 3.8 mmol) and triethyl phosphite (1.28 g, 7.6 mmol) were heated to 140-150 °C for 12 h under nitrogen atmosphere. Excess triethyl phosphite was removed by vacuum distillation and the resultant ylide 1,4-(2-ethylhexyloxy)-2,5-xilenetetraethylidiphosphonate was obtained as thick oil. $^1$H-NMR (CDCl$_3$, 300MHz)$\delta$: 6.91 (d,2H, Ar-H), 4.04 (m, 8H, -PO-OCH$_2$), 3.80 (d, 4H, Ar-OCH$_2$), 3.24 (d, 4H, Ar-CH$_2$P), 2.07-0.88 (m, 42H, aliphatic). The crude ylide (1.00 g, 1.6 mmol) in 50 mL dry THF, benzaldehyde (0.42 g, 4.0 mmol) and potassium tert-butoxide in (10 mL, 1M THF) were reacted and the product obtained was purified as described for MEH-OPV (in chapter 2). Yield = 85%, m.p. = 63-64 °C. $^1$H-NMR (CDCl$_3$, 300MHz)$\delta$: 7.53-7.07 (m, 16H, Ar-H and vinylic H), 3.96-3.89 (m, 4H, Ar-OCH$_2$), 1.81-0.86 (m, 30H, aliphatic). $^{13}$C-NMR (CDCl$_3$, 75MHz) $\delta$: 151.2, 138.0,129.8, 129.5, 129.2, 128.4, 128.1, 127.8, 127.0, 126.7,126.3, 125.8, 124.0,122.9,111.1, 110.3, 109.4 (Ar-C), 71.7 (Ar-OCH$_2$), 39.8, 30.9, 29.7, 29.3, 24.2, 23.7, 23.1, 13.3, 11.5 and 11.1

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(Cyclic-C) FT-IR (KBr, cm⁻¹): 3027, 2958, 2926, 2858, 1597, 1500, 1464, 1421, 1380, 1257, 1201, 1034, 964(HC=CH, trans), 852 (HC=CH, cis), 803, 752, 693. HRMS (MW: 538.8): m/z =539.0 (M⁺). Anal. Calcd. for C₃₈H₇₀O₂: C, 84.71; H, 9.35. Found C, 84.37; H, 9.70.

1,4-bis-(4-dodecyloxystyryl)-2,5-di(2-ethylhexyloxy)benzene (BEH-BDD-OPV): 1,4-(2-ethylhexyloxy)-2,5-xylene tetraethyldiphosphonate was synthesized as explained for BEH-OPV. The crude ylide (1.00 g, 1.6 mmol) in 50 mL dry THF, 4-dodecyloxybenzaldehyde (1.16 g, 4.0 mmol) and potassium tert-butoxide in (10 mL, 1M THF) were reacted and the product obtained was purified as explained for MEH-BDD-OPV. Yield = 69 %, m.p.= 101-102 °C. ¹H-NMR (CDCl₃, 300MHz)δ: 7.46-6.87 (m, 14H, Ar-H and vinylic H), 4.00-3.93 (m, 8H, Ar-OCH₂-DD and Ar-OCH₂-EH), 1.79-0.88 (m, 76H, cyclic-H and aliphatic-H). ¹³C-NMR (CDCl₃, 75MHz) δ: 158.7, 151.0, 130.6, 128.1, 127.8, 127.3, 127.1, 126.7, 121.6, 121.4, 120.9, 115.8, 115.5, 114.8, 114.5, 113.8, 113.6, 110.8, 109.1, 106.2 (Ar-C), 71.7 (Ar-OCH₂-DD), 68.0 (Ar-OCH₂-EH), 39.8, 31.9, 30.9, 29.6, 29.4, 29.3, 26.0, 24.2, 23.1 and 22.7 (Cyclic-C). FT-IR (KBr, cm⁻¹): 2922, 2857, 1604, 1471, 1388, 1289, 1244, 1199, 1169, 1037, 1015, 965 (HC=CH, trans), 850 (HC=CH, cis), 821, 724. HRMS (MW: 907.5): m/z =907.6 (M⁺). Anal. Calcd. for C₆₂H₉₈O₄: C, 82.06; H, 10.89. Found C, 81.48; H, 10.68.
4.3. Results and Discussion

4.3.1. Synthesis and Structural Characterization

A series of oligo-phenylenevinylene (OPVs) based on 1,8-tricyclocdecane-methylene (TCD), 2-ethylhexyl and dodecyl pendants were synthesized by following the Wittig-Horner reaction as shown in scheme 4.4 and the structures are given in scheme 4.5.

![Scheme 4.4. Synthesis of OPVs](image)

The bis-alkoxy coupled product (1) was refluxed with HBr in acetic acid and \( p \)-HCHO to get the bisbromomethylated compound (2), which upon treatment with triethylphosphite to obtain the corresponding ylide (3). The ylide was then reacted with benzaldehyde or 4-dodecyloxy benzaldehyde to yield ten different types oligo-phenylenevinylene (see scheme 4.4 and 4.5). For simplicity, the OPVs were labeled as XXX-YYY-OPV, where XXX and YYY are corresponding to the alkoxy substitutions at middle and outer phenyl groups, respectively. For instance BTCD-BDD-OPV represents the bis-TCD substitution in the middle ring and dodecyl chains at the outer phenyl rings. The structures of the OPVs were confirmed by \(^1\)H-NMR, \(^13\)C-NMR, FT-IR, and VT-NMRF. 

\[ \text{NIIST} \]
elemental analysis and high resolution mass spectrometry and the data are explained in the experimental section.

Scheme 4.5. Chemical structures of the OPVs.

The $^1$H-NMR spectrum of BTCD-BDD-OPV is shown in figure 4.1 (spectra of MTCD-OPV and BTCD-OPV are given in chapter 2) and the different types of aromatic and alkoxy protons are assigned and labeled as shown in figure 4.1. In figure 4.1a, the Ar-OCH$_2$-TCD protons (type-b) in appeared as a multiplet at 3.83-3.75 ppm and another peak corresponding to the Ar-OCH$_2$- protons (type-a) of the dodecyl part appeared at 4.00-3.96 ppm. The chemical shifts in the $^1$H-NMR spectra of OPVs clearly indicate that the Ar-
OCH₂- protons are highly sensitive to their structural difference. The aromatic region of BTCD-BDD-OPV is expanded and shown in figure 4.1b. The well resolved and highly separated peaks of BTCD-BDD-OPV may be due to their bulky and rigid nature which gives more planarity to the backbone.

![Figure 4.1. ¹ H-NMR spectra of BTCD-BDD-OPV (a) and its expanded aromatic region (b).](image)

The structure of the double bonds (cis and trans of vinylene double bonds) in the phenylenevinylene backbone were identified by infrared spectra (FT-IR) recorded in KBr pellets (see figure 4.2). The FT-IR spectra of OPVs showed characteristic absorption bands at 2960, 2925 cm⁻¹ (C-H stretching of the aliphatic units), 1605, 1500, 1450 cm⁻¹ (C-H, aromatic ring), 1250, 1205 (C-O ether linkage), 965 cm⁻¹ (trans HC=CH) and 855 cm⁻¹ (cis HC=CH)
vinylene C-H out-of-plane- bending and the values are matching with literature reports.\textsuperscript{42}

The thermal stability of the OPVs was analyzed by TGA and it was found that all the OPVs exhibit good thermal stability and they have the onset of degradation around 300 °C (see figure 4.3). It is also noticed that the dodecyl substitution increases the thermal degradation temperature compared to the OPVs without dodecyl chains.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{FT-IR_spectra.png}
\caption{FT-IR spectra of the OPVs.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{TGA_plots.png}
\caption{TGA plots of the oligo-phenylenevinylenes}
\end{figure}
4.3.2. Liquid Crystalline Properties

All the OPVs were subjected to differential scanning calorimetry (DSC) to study the thermal transitions in the heating/cooling cycles. MEH-OPV, BEH-OPV and MTCD-OPV were found sluggish to crystallize and obtained as amorphous solids. BDD-OPV, MEH-BDD-OPV, BEH-BDD-OPV and MTCD-BDD-OPV have shown crystallization peak and melting transitions in the cooling/heating cycles like normal crystalline solids (see figure 4.4).

![DSC plots of the non-LC oligo-phenylenevinylenes](image)

Figure 4.4. DSC plots of the non-LC oligo-phenylenevinylenes

Interestingly, BTCD-OPV, TDD-OPV and BTCD-BDD-OPV have shown typical DSC thermograms corresponding to thermotropic LC behavior. The DSC thermograms of these LC-OPVs were given in figure 4.5 and the data are summarized in table 4.1. The DSC plots of the BTCD-OPV has exhibited...
liquid crystalline features upon cooling from the melt which has two closely spaced exotherms corresponding to the isotropic -LC (162°C) and LC-crystalline (156°C) transitions. On subsequent heating two peaks were observed corresponding to a weak crystal -LC (at 176°C) and strong LC-isotropic (at 225°C) transitions.

![DSC Thermograms](image)

**Figure 4.5. DSC Thermograms of LC-OPVs under 10°min heating/cooling.**

Tetra dodecyl substituted TDD-OPV was also showed LC behavior in the cooling/heating cycles, but the transitions were observed at much lower temperature region (<100°C) compared to that of BTCD-OPV. Interestingly, BTCD-BDD-OPV exhibits LC properties in the temperature range in between their homo-counterparts BTCD-OPV and TDD-OPV (see figure 4.5). The liquid crystalline temperature window (temperature range in which they exhibit LC behaviors) in the cooling cycles was obtained as 6, 10 and 62 degrees for
the BTCD-OPV, TDD-OPV and BTCD-BDD-OPV, respectively. Similarly, in the heating cycles the window was obtained as 56, 20 and 109 degrees for the sample OPV samples. The enthalpies of cooling and heating cycles (see table 4.1) have indicated that the dodecyl substitution leads to less crystalline nature in the OPVs and the trend was found in the decreasing order for TDD-OPV<BTCD-BDD-OPV<BTCD-OPV. The overall DSC analysis revealed that BTCD-BDD-OPV is very good LC materials and possess large temperature LC window both in cooling and heating cycles. It is very important to note that the LC behavior of OPVs are not easily predictable and highly dependent on the types of rigid or flexible side chains attached on the middle and outer aromatic rings.

Table 4.1. DSC data of liquid crystalline OPVs

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cooling (^a)</th>
<th>Heating (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Iso- LC</td>
<td>LC- Crys.</td>
</tr>
<tr>
<td></td>
<td>(T_c) (\text{OC})</td>
<td>(\Delta H) (\text{J/g})</td>
</tr>
<tr>
<td>BTCD-OPV</td>
<td>159</td>
<td>-58.0 (together)</td>
</tr>
<tr>
<td>BTCD-BDD-OPV</td>
<td>110</td>
<td>-50.4</td>
</tr>
<tr>
<td>TDD-OPV</td>
<td>71</td>
<td>-28.6</td>
</tr>
</tbody>
</table>

\(^a\) Temperature and enthalpy data of the OPVs in the cooling and heating cycles, determined from the DSC analysis.

4.3.3. Ring Banded Spherulites: Polarized Light Microscopic Analysis

Liquid crystalline morphology of the OPVs was studied using polarized light microscope (PLM) attached with temperature programmable hot stage. All compounds were heated to melt at 10 °C/min and kept isothermally 20 °C above their isotropic temperature for 2-3 min and subsequently cooled to room temperature at 10° C/min. PLM images of BTCD-BDD-OPV are shown in figure 4.6. While cooling from the melt, BTCD-BDD-OPV showed a rhythmic growth of spherulitic ring bands. The pattern grows slowly with decrease in the temperature and the texture remains unchanged up to room temperature. It is
also important to note that with decrease in temperature, new nucleating sites were also created and the crystal growth occurred in almost identical ring banded pattern in all nucleating sites. The dark and bright bands in the PLM patterns are more or like spiral rather than concentric rings. The band widths of the bright and dark bands were determined to be 18.2 (±1.0) and 16.7 (±1.8) μm, respectively.

Figure 4.6. PLM images of BTCD-BDD-OPV at 10 °C/min cooling from isotropic stage.
The images of the other two LC OPVs BTCD-OPV and TDD-OPV (see figure 4.7) revealed that the narrow LC window (< 10 °C) hampered the morphological development.

Figure 4.7. PLM images of TDD-OPV and BTCD-OPV upon cooling from the isotropic melt.
Since the crystallization process from the molten stage highly dependent on the cooling conditions, it is very important to study these effects on the ring banded structure formation. To investigate the effect of cooling rates (non-isothermal crystallization) and crystallization residence time (isothermal crystallization), the sample was subjected to isothermal/non-isothermal kinetics by both DSC as well as PLM. Non-isothermal crystallization was carried out at different cooling rates ranging from 2, 5, 8, 10 and 20°C/min in both DSC and PLM. The DSC plots as well as their thermal data are given as figure 4.8 and table 4.2 respectively.

![Figure 4.8: DSC plots for the non-isothermal crystallization process.](image)

### Table 4.2: Non-isothermal properties of oligo-phenylenevinylene

<table>
<thead>
<tr>
<th>Cooling rate (°C)</th>
<th>$T_c$ (°C)$^a$</th>
<th>$\Delta H_{iso-LC}^a$ (J/g)</th>
<th>$\Delta H_{LC-Cry}^a$ (J/g)</th>
<th>Total $\Delta H^b$ (J/g)</th>
<th>No. of nucleating sites (10X)</th>
<th>Width of bright bands (μm)</th>
<th>Width of dark bands (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>116</td>
<td>-57.2</td>
<td>-4.3</td>
<td>-61.5</td>
<td>1</td>
<td>28.7 ± 3.4</td>
<td>29.0 ± 2.5</td>
</tr>
<tr>
<td>5</td>
<td>113</td>
<td>-52.9</td>
<td>-5.9</td>
<td>-58.8</td>
<td>7</td>
<td>24.0 ± 2.4</td>
<td>18.9 ± 2.2</td>
</tr>
<tr>
<td>8</td>
<td>111</td>
<td>-52.2</td>
<td>-6.6</td>
<td>-58.8</td>
<td>14</td>
<td>20.0 ± 1.8</td>
<td>17.9 ± 2.5</td>
</tr>
<tr>
<td>10</td>
<td>110</td>
<td>-50.4</td>
<td>-5.2</td>
<td>-55.6</td>
<td>16</td>
<td>18.2 ± 1.0</td>
<td>16.7 ± 1.8</td>
</tr>
<tr>
<td>20</td>
<td>105</td>
<td>-49.2</td>
<td>-5.3</td>
<td>-54.5</td>
<td>25</td>
<td>17.8 ± 2.0</td>
<td>14.2 ± 1.7</td>
</tr>
</tbody>
</table>

(a) Obtained from the DSC analysis  
(b) From the PLM studies.
PLM images of the BTCD-BDD-OPV under different cooling rates are shown in figure 4.9.

*Non-isothermal Crystallization, 2° min*

126 °C  
125 °C  
124 °C

*Non-isothermal Crystallization, 5° min*

119 °C  
115 °C  
110 °C

*Non-isothermal Crystallization, 10° min*

119 °C  
115 °C  
108 °C

*Non-isothermal Crystallization, 20° min*

119 °C  
115 °C  
109 °C

*Figure 4.9. PLM images of BTCD-BDD-OPV at different cooling rates.*

Each time fresh samples were loaded and the images were captured at 10X magnification for qualitative comparison of the data. At 2 °/min, only one nucleating site could be observable (nucleated in a site away from the lens frame) and the layer of ring bands expanded with decrease in temperature. It is
very important to note that there is no new nucleating site is appeared till the end of crystallization. At higher cooling rates (20 °C/min), both new nucleating sites as well as the expansion of ring bands of existing ones were noticed.

Isothermal crystallization was also performed at crystallization temperature, \( T_c = 115, \) 120 and 125 °C. The sample was rapidly cooled (30°C/min) from the melt to desired \( T_c \) and allowed to crystallize isothermally (\( T_c \) was chosen based on DSC analysis). The DSC plots and the data of the isothermal crystallization process are given in figure 4.10 and table 4.3.

![DSC plots for the isothermal crystallization process](image)

**Figure 4.10.** DSC plots for the isothermal crystallization process.

**Table 4.3. Isothermal properties of oligo-phenylenevinylene**

<table>
<thead>
<tr>
<th>( T_{is0}(^\circ C) )</th>
<th>( \Delta H_{Cry}^a ) (J/g)</th>
<th>Width of bright bands (μm) ( ^b )</th>
<th>Width of dark bands (μm) ( ^b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>115</td>
<td>-31.6</td>
<td>26.9(±2.9)</td>
<td>18.2(±1.6)</td>
</tr>
<tr>
<td>120</td>
<td>-45.7</td>
<td>21.8(±4.7)</td>
<td>26.2(±2.7)</td>
</tr>
<tr>
<td>125</td>
<td>-59.8</td>
<td>36.4(±4.6)</td>
<td>30.2(±3.7)</td>
</tr>
</tbody>
</table>

* Obtained from the DSC analysis
* From the PLM studies.
At $T_c=125 \, ^\circ C$, crystallization starts after $\sim 2$ minutes and only a single nuclei was initiated. Over a period of time, the ring banded structures grow in the entire frame with multiple layers. At lower $T_c= 115 \, ^\circ C$, the samples produce large number of nucleating sites and results in the formation of banded structures with fewer rings (see PLM images in figure 4.11).

**Figure 4.11**. PLM images of BTCD-BDD-OPV in the isothermal crystallization process.

Various parameters from the above crystallization process such as crystallization temperature ($T_c$), enthalpy ($\Delta H_c$ of Isotropic-to-LC), number of
nucleating sites and average width of the dark and bright bands were plotted against the cooling rates and shown in see figure 4.12. The DSC data at different cooling rates (from 2 to 20 °C/min) indicate both the enthalpies of crystallization as well as T_c decreases with increase in cooling rate. The spherulites were less ordered with 3-4 ring bands at 20 °C/min compared to a highly crystalline large ring banded structure at slow cooling rate (at 2 °C/min). The number of nucleating sites (NS) increases with the increasing in cooling rates, which account for the less ordered crystalline domains (low enthalpy values). This can be explained that at slower cooling rate the melt experience less stress by external stimuli and the crystal growth produce highly crystalline domains. A similar observation could also be seen for the isothermal crystallization depending upon their T_c (see figure 4.11 and table 4.3). As expected, at higher T_c, the sample follows the trend observed at slow cooling rate in the non-isothermal process.

![Figure 4.12. Plots of crystallization parameters with cooling rates. (NS=nucleating sites).](image-url)
The average widths of the bands were calculated from the PLM images. The band width increases with decrease in cooling rate indicating that at slow cooling rates, the crystalline domains has high tendency for alignment to produce thick ring bands. Therefore, using the current approach, one can pattern the conjugated crystalline molecules, particularly OPVs, either with large ring bands from single nucleation or multiple small rings depending upon the $T_c$ or cooling rates employed in the isothermal or non-isothermal processes, respectively. Therefore, the banded ring structures observed in the BTCD-BDD-OPV is not merely an artifact rather than reproducible phenomena in the LC phase irrespective of the different types of crystallization processes (isothermal or non-isothermal). These crystallization experiments indicated that one can pattern the conjugated material with desired number of rings by simply adapting different cooling rates or crystallizing at different $T_c$.

It is generally believed that the ring-banded structures are occurred due to the periodic twisting of lamellar crystals along the radial growth direction of the spherulites.\textsuperscript{11-13} To understand the mechanism of the ring banded structures in OPVs, isothermally crystallized sample of BTCD-BDD-OPV at $T_c=120$ °C was closely observed (see images in figure 4.13). It is obviously clear from the images that the formation of ring banded spherulites can be noticed starting from the nucleation process. Two nucleation positions (site 1 and 2) were clearly visible in the image and site-1 was closely monitored to observe the ring structure formation. The nucleation has occurred instantaneously and needle like crystal starts grow radially from the centre. It forms a disc like first stage bands around the nucleating site. With increasing time, the ring bands are expanded with two, three rings and so on. Typically, in the liquid crystalline sample, the molecules or group of molecules act as mesogens, which facilitate molecular orientation for LC-phase. Therefore, the continuous upward diffusion of mesogens to the front crystalline phase creates the depletion region (valleys). The artificial density gradient arose by the moment of mesogens generate density gradient which further facilitates the movement of more
molecules far from the growth site for the formation of the second ring band. This pattern of process repeats as much as times possible with alternative ridge and valleys until interrupt by the neighboring crystal growth (in this case site-2).

![Image of ring banded structures](image)

**Figure 4.13.** Formation of the ring banded structures of BTCD-BDD-OPV starting from two nucleation sites (The nucleation site 1 is expanded as shown in inset and the PLM images shown here are of the isothermally crystallized sample at 120 °C).

The size of the banded spherulites is in micrometer range, and therefore, the samples were subjected to scanning and transmission electron microscopic analysis for understanding the nucleation and growth. For SEM analysis, the sample was prepared in hot stage (at 10 °C/min) under the polarizing microscope and a portion of the sample (with ring banded structures) was carefully transferred into the SEM stud. The sample for TEM analysis was prepared by placing a pinch of sample on formerly coated TEM grid in a DSC pan and subjected to heating/cooling cycles corresponding as shown in figure 4.5. SEM and TEM images of the samples are shown in figure 4.14. SEM image of the LC frozen sample has 300 nm widths and few micrometers long twisted and aggregated micron size crystals. The closer observation of the twist revealed...
that the micro-crystals are self-organized together and twisted along the axis of the rotation. The average sizes of the crystals were determined as 230-300 nm with length up to 0.4-0.5 μM. TEM image of the LC-frozen sample is also confirming the presence of twisted micro-crystalline solids. The contrast difference along the axis of the aggregated crystals confirmed that the helical phase orientation of crystals.

Figure 4.14. PLM (a), SEM (b), and TEM (c) images of BTCD-BDD-OPV in the LC frozen state.
Electron microscopic images directly evident that LC mesogens aggregated to produce micro-meter size crystals, which undergo twisted helical assemblies. The long range ordering of these helical (or twisted) assemblies (in sub-micron level) leads to the formation of supra-ring structures in the PLM image (in 20 micron level). Despite, both electron microscope techniques confirmed the existence of twisted crystalline alignments in the band ring spherulites, the lamella twisting at molecular (or mesogen) level could not be observable due to size limitation.

4.3.4. X-ray Diffraction and Energy Minimization Studies

To identify the lamellar mesophases, the sample BTCD-BDD-OPV was subjected to X-ray diffraction studies both in powder, LC-frozen and variable temperate X-ray analysis. The X-ray diffractions patterns are shown in figure 4.15 and 4.16.

![X-ray diffraction pattern of BTCD-BDD-OPV at 30 °C](image)

Figure 4.15. X-ray diffraction pattern of BTCD-BDD-OPV at 30 °C

The powder sample showed multiple sharp crystalline peaks with respect to highly crystalline state. A bunch of peaks appeared in the higher angle region from $2\theta = 15 - 25$ ($d = 4-6$ Å) which are corresponding to aromatic ring packing. In the low angle region ($2\theta > 15$), three peaks at $2\theta = 3.26, 6.32$ and 12.7 were clearly visible. The d-spacing values of these
reflections were corresponding to 27.07, 13.97 and 6.92 Å with regular periodicity. The intense sharp peak at 27.07 Å assigned to the fundamental 001 plane the lamellar structure and two other less intensity peaks at 13.97 and 6.92 Å were assigned to higher order reflections of 002 and 003 in the lamellae. The presence of these fundamental peaks at the low angle region clearly evident the existence of the lamellar structure in the molecule. The sample was heated to melt (T_m = 160 °C) and subsequently cooled at 10 °C/min to obtain ring banded structures (confirmed by PLM). The frozen LC- sample was then subjected to X-ray analysis and the pattern is shown in figure 4.15. After melt crystallization, the intensity of the peaks at higher angle region is reduced significantly; however, the fundamental reflections at the lower angle in the lamellar phase were un-altered. The sample was further subjected to variable temperature X-ray analysis heating/cooling from 30 to 170 °C in the LC active temperature window (see figure 4.16).

Upon heating (see figure 4.16), the transformation of mesophase has influenced on the crystalline peaks are slowly starts to disappeared. In the isotropic region (at 160-170 °C), the sample was completely melted and all the
crystalline peaks were vanished. In the subsequent cooling cycle, the three fundamental peaks at 27.07, 13.97 and 6.92 Å were re-appeared. These detailed X-ray analysis revealed that the lamellar structure in the molecule is reproducible in repetitive heating/cooling conditions. All our attempts to grow single crystal for BTCD-BDD-OPV molecule was so far not successful (currently also attempts are going on), and therefore, the energy minimization for the molecular structure was obtained using ChemBio 3D ultra 11.0 (molecular mechanics-2). Typically, unsubstituted or substituted OPVs are non-planar structure, in which at least one of the phenyl rings tilted from the OPV \(\pi\)-conjugated backbone (see for OPVs in figure 4.17). This distortion arises mainly because of the steric hindrance induced by the vinylene hydrogen with the aromatic protons in the outer phenyl rings.

![Energy minimized models of the OPVs](image)

*Figure 4.17. Energy minimized models of the OPVs (obtained from ChemDraw Bio 3D ultra 11.0(MM2) programmes).*
Gill et al. had solved the single crystal structure for octyl- substituted OPV and they had confirmed the tilting of $\pi$-conjugated segments due to steric hindrance.\textsuperscript{47, 48} It supports that the energy minimized structures of OPVs were well in accordance with the OPV crystal structure and good enough to compare their structural different on LC properties. Interestingly, energy minimized structure of BTCD-BDD-OPV was found completely different from the other OPVs and its $\pi$-conjugated backbone has existed as perfectly planar (see figure 4.18).

Figure 4.18. Energy minimized structure of BTCD-BDD-OPV and mechanism for the ring banded supra-structures.

The bulky TCD units in the central aromatic rings occupy both the sides of the conjugated backbone and tilted the outer phenyl rings to the same plane of the central aromatic core. Structurally similar other two liquid crystalline
molecules BTCD-OPV and TDD-OPV posses distorted π-conjugated backbone as similar to common OPV molecules, which could be the reason for their failure to show the ring banded structures.

The dimensions of the BTCD-BDD-OPV were obtained from the energy minimized structure and shown in figure 4.18. A model for the BTCD-BDD-OPV molecular packing is constructed based on the energy minimized structure, fundamental lamellae reflections in the x-ray diffractions, electron microscopic images and shown in figure 4.18. The OPV molecule has planar conjugated backbone with two TCD units placed on the either side of the π-backbone and the dodecyl chains were projected outward. The rigid central aromatic core and long alkoxy chains makes these molecules behave as a typical liquid crystalline mesogens. The close packing of these mesogens creates lamellar structure with spacing of 28.5 Å, which is almost matching with that the d-spacing (27.07 Å) first sharp fundamental reflection at 2θ = 3.26 (see figure 4.15) (values are within the acceptable experimental variation). This gives clearly evidence for the existence of lamellar structures in the liquid crystalline BTCD-BDD-OPV. The interlayer distance in the aromatic core 2θ = 15 – 25 (d = 4-6 Å), which is much larger than reported for π-stacking.43-45 This may be due to the presence of two large bulky TCD units positioned at the either side of the π-conjugated backbone. Usually the aromatic π-core interactions are expected in the range of 3.0 Å,25 however, recently Gill et al.48 reported much larger interlayer distance (3.77 Å) in their octyloxy substituted OPVs due to strong steric hindrance. Therefore, it may be assumed that TCD-is much more bulky than octyloxy pendants and expected to show more steric hindrance for larger interlayer distance of ~ 4 Å in BTCD-BDD-OPV. However, more structure analysis like single crystal study is required to confirm the above observation. Nevertheless, X-ray analysis data had been widely utilized to calculate the inter-layer distance in self-assembled system, and therefore, we feel that the interlayer distances reported in the current one may not deviated far from the original value. Based on the above data and
morphological analysis of LC phases by PLM, SEM and TEM, we postulate the following mechanism for ring bonded structures in OPV as shown in figure 4.18. The following steps are involved in the formation ring banded structures: (i) the crystallization starts from the nucleation (evident from figure 4.13), (ii) the planar BTCD-BDD-OPV mesogens self-organized form lamella (evident from XRD), (iii) the strong aromatic interactions in the OPV backbone induce long range twisted lamellar aggregates which results in the growth of helical micro-crystalline arrangements (evident by SEM and TEM) and (iv) the banded ring structures in PLM is the consequence diffusion of these micro-crystalline domains in the LC phase to the crystal front. The comparison of the sizes of the molecular mesogens (from XRD, width = ~ 28.5 Å = 2.85 nm) and ring banded structures (from PLM, width = ~20 μM) revealed that each ring may contain more than 100-1000 molecules in the width and millions in the twisted length. Therefore, the formation of ring banded structures in the current system has originated from the molecular aggregation at the mesogens level which leads to macroscopically banded structures. The present investigation directly provide experimental evidence for the mechanism proposed by Keith and Padden i.e, "the ring bonded structures was attributed to periodic twisting of lamellar crystals along the radical growth direction of the spherulites". To our knowledge, this is the first ring banded structures observed in the any types of conducting materials.

4.3.5. Photophysical Properties

Eventhough the present mechanism provides the insight into the ring banded structures, the aggregation of lamella was not very clear from the microscopic based model. Unlike other banded ring structures (in commercial polymers), in the present system, the LC mesogen bears an photoactive OPV conjugated units, and therefore, photophysical characterization such as excitation, emission and fluorescence decay profile could also be employed as tools to trace the π-stacking phenomena at the lamellar structures (at molecular
level). Photophysical properties of the OPVs were studied in solution (in THF, see figure 4.19), solvent caste film and also frozen liquid crystalline solids.

Figure 4.19. Absorption and emission spectra of the OPVs in THF.

Solid films of the OPVs were caste on the glass plate and the emission and excitation spectra of the BTCD-OPV, TDD-OPV, and BTCD-BDD-OPV are given in figure 4.20. The excitation and emission spectra of the BTCD-BDD-OPV in film (see figure 4.20) were almost 40 nm red shifted compared to BTCD-OPV and TDD-OPV. The small peak at 452 nm in the excitation spectrum of TDD-OPV is corresponding to the transitions from the –OR in the outer phenyl rings (see other examples in figure 4.21). The BTCD-BDD-OPV has also showed an additional peak at 470 nm in the excitation spectrum corresponding to the presence of strong π-aggregation. The excitation spectra of LC-frozen samples showed further red-shift compared to films and shift was found much larger for BTDC-BDD-OPV compared to all the samples. This may be due to the planarity of the conjugated segment in the BTCD-BDD-OPV molecule compared to other OPVs (see figure 4.18).
Chapter 4  
Liquid Crystalline Banded Spherulites

Figure 4.20. Excitation and emission (excited at 400 nm) spectra of BTCD-BDD-OPV. Solid line (film with 0.1 O.D.) and dotted line (LC frozen).

Figure 4.21. Excitation spectra of the OPVs in film. (The spectra are collected at the respective emission maxima).
Thin layer of ring banded structures were prepared on a glass plate for BTCD-BDD-OPV by heating/cooling under the PLM (similarly for BTCD-OPV and TDD-OPV). The sample was subjected to fluorescence microscopic analysis with excitation light source using 410-450 nm and 330-380 nm. The FL-microscope (FLM) image is shown in figure 4.22. It was found that the concentric bands observed in the PLM are exactly reflecting in the FLM also. The results confirmed the reproducibility of different microscopic techniques in attaining the banded ring structures.

Scheme 4.22. The banded structures excited with light of different wavelengths.

The ring banded morphology is appeared as green color with respect to the emission color of the OPV-units. It clearly evident the ring banded structures is luminescent under photo excitation. The emission spectra of film and LC-frozen of BTCD-BDD-OPV was found largely red-shifted (as notice in the excitation spectra) and provide additional proof for strong \( \pi \)-aggregation compared to other OPVs. It is well-known that molecular aggregation in \( \pi \)-conjugated chains expected to quench luminescence properties.\(^{49, 50}\) Therefore, one would expect a significant difference in the emission decay profile among these samples. Time dependent fluorescence decay measurements for BTCD-BDD-OPV and BTCD-OPV in film were carried out by exciting with 401 LED laser light source. The fluorescence decay profiles were shown in figure 4.23. It revealed that the strongly aggregated BTCD-BDD-OPV molecules showed faster decay profile compared to that of BTCD-OPV. The life time values were obtained as \( \tau_1 = 0.18 \, \text{ns} \) and \( \tau_2 = 1.25 \, \text{ns} \) for BTCD-BDD-OPV and \( \tau_1 = 1.25 \, \text{ns} \) and \( \tau_2 = 4.02 \, \text{ns} \) for BTCD-OPV.\(^{51, 52}\) The highly aggregated BTCD-BDD-OPV
showed the faster fluorescence decay with less life time compared to weakly aggregated BTCD-OPV.

![Decay lifetime profiles of BTCD-OPV and BTCD-BDD-OPV in film.](image)

Further to trace the π-induced molecular interactions and its role on the self-assembly, both BTCD-BDD-OPV and TDD-OPV were subjected to concentration dependant $^1$H-NMR (using 500 MHz) and photophysical studies in chloroform solution. The concentrations of the samples were varied from 50 mg to 2 mg in 0.5 mL of CDCl$_3$ (from $1 \times 10^{-1}$ to $4 \times 10^{-3}$ M$^{-1}$) for $^1$H-NMR analysis. $^1$H-NMR spectra (see figure 4.24) of these samples did not show any significant features for concentration variation in both aromatic units and aliphatic dodecyl chains, and therefore, we could not infer any useful information from NMR studies. The samples were subjected to photophysical studies by varying the optical density from 0.1 to 2.0 (from $5 \times 10^{-5}$ to $0.3 \times 10^{-5}$ M$^{-1}$) in chloroform.
Figure 4.24. Expanded aromatic region of the $^1$HNMR spectra of BTCD-BDD-OPV at different concentrations.

The excitation and emission spectra of these samples were shown in the figure 4.25.

Figure 4.25. Excitation and emission spectra of BTCD-BDD-OPV and TDD-OPV at different concentrations in CHCl$_3$ (Optical density (O. D) is given, $\varepsilon$ of BTCD-BDD-OPV = $47 \times 10^3$ M$^{-1}$ cm$^{-1}$ and $\varepsilon$ of TDD-OPV = $36 \times 10^3$ M$^{-1}$ cm$^{-1}$).
It is very interesting to note that at higher concentrations, the sample BTCD-BDD-OPV showed the formation of a new peak at 468 nm corresponding to the molecularly aggregated species. On the other hand the peak is essentially absent in TDD-OPV in almost all concentrations. The peak intensity ratio \( \frac{I_{468}}{I_{395}} \) was plotted for both the samples with concentration (figure 4.26) and the plots confirmed that the BTCD-BDD-OPV molecule possessed a strong \( \pi \)-interaction in the molecular level at higher concentration. The strong \( \pi \)-interaction in the OPV units shifts the BTCD-BDD-OPV emission spectra towards red-region compared to that of the TDD-OPV. Since the molecular vicinity of the conjugated backbone are very close to each other at higher concentration in solution, the nature of aggregated OPV species (at high concentration) are almost similar to that of solid state properties (in LC stage and thin films). Therefore, the concentration dependant photophysical studies directly provide evidence for the strong \( \pi \)-\( \pi \) interactions in BTCD-BDD-OPV and supports the mechanism of the self-organization proposed in the figure 4.18.

![Figure 4.26. Plot of intensity ratio \( \frac{I_{468}}{I_{395}} \) versus concentration](image)

More detailed studies using optically active side chains in the BTCD-OPV mesogens will provide more insight into the twisting phenomena. It is very important to add that the proposed mechanism for the ring banded
structures is very much suitable for OPVs and for other types of conjugated materials, but may not be relevant to commercial thermoplastic polymers like polyesters. It is also not possible to rule out that a similar molecular interactions at the lamellar level may also exist in systems like polyesters, however, the lack of availability of optical probe like OPV limit their fundamental understanding. In the present investigation, for the first time, it has been utilized the aromatic $\pi$-interactions as a self-organization tool to produce supramolecular ring banded structures, particularly, in liquid crystalline oligophenylenevinylenes.
4.4. Conclusion

In this chapter, we have designed and developed a series of bulky and non-bulky conjugated oligo-phenylenevinylene for tracing the role of structure on the thermotropic liquid crystalline behavior. Interestingly, BTCD-OPV, TDD-OPV and BTCD-BDD-OPV have shown thermotropic LC behaviors upon cooling from isotropic melt. Among the three, BTCD-BDD-OPV was found to show a unique ring banded morphology, which is a first example in \( \pi \)-conjugated materials. The most important finding in the current approach may be listed as: (i) Planarity of \( \pi \)-conjugated backbone is very much essential for long range lamellae ordering of liquid crystalline mesogens for ring banded morphology, (ii) The lamellar aggregation of the OPV molecules produce sharp peaks in the X-ray diffraction patterns at low angle region and they were reproducible in the repetitive heating/cooling cycles, (iii) Long range amplitude of the lamellar twisting could be observed in the electron microscopic images as helically self-organized micro-crystals, (iv) Nature of the ring banded morphological development was less influenced by the non-isothermal or isothermal crystallization process, however, these conditions influence on the number of rings or layers in each spherulites, (v) Luminescent ring banded structures can be obtained by exciting the OPVs with suitable light source, (vi) Photophysical experiments like excitation, emission, and time dependent fluorescence decay were successfully utilized to prove that existence of strong \( \pi-\pi \) interactions the OPVs is the main driving force for the self-organization process, and, (vii) Size and shape of the pendants attached in the OPV backbone is a crucial factor for inducing liquid crystallinity and also tuning wide LC temperature window.

Therefore, tricyclodecanemethanol (TCD-OH) is proven to be an effective structure directing unit for LC-phases compared to that of normal alkyl chains. The current system directly provides experimental evidence of the lamellar twisting mechanism proposed by Keith and Padden based on computational simulation and microscopes. Hence, here, we have successfully
shown a new way to pattern micrometer range ring structures via melt crystallization process, which is expected to be cheaper and clean way to process electronically important OPV based π-conjugated materials. The approach could be expanded for the wide range of other classes of conjugated materials and it may open new opportunities for patterning and understanding the self-organization behavior of conjugated segments through melt crystallization processes.
4.5. References

Chapter 4

Liquid Crystalline Banded Spherulites


