Chapter 5      Summary and Conclusions

The thesis entitled ‘Novel Bulky π-conjugated Poly(p-phenylenevinylene)s and their Oligomers for Enhanced Luminescent Applications’ is dealt with the design and development of novel bulky PPVs and their structurally similar oligomers for different applications in opto-electronics. New bulky tricyclodecane (TCD) substituted poly(p-phenylenevinylene)s (PPVs) were synthesized through halo-precursor route for controlling π-stacked induced aggregates to attain improved solid state photoluminescence. Two series of bulky copolymers (MTCD-x and BTCD-x series) were prepared by varying the entire composition range from 0 to 100 % and the NMR signals of the structurally similar OPVs were utilized to determine the compositions. The copolymerization effects on the thermal and photophysical properties were investigated and the copolymer composition has been proven to be a very crucial parameter for correlating the structural and photo-physical properties of the polymers. The rigid bulky-PPV polymers follow Flory-Fox trend for the glass transition and showed photoluminescence enhancement 4-5 times higher than that of MEH-PPV. The absolute solid state quantum yield of the OPVs determined by diffuse reflectance technique suggested that the bulky substitution increases the solid state quantum efficiency of the MEH-OPV from 27 % to 82 % which directly give evidence for highly luminescence behaviour of the bulky π-conjugated polymers.

Further, the origin of the molecular aggregates was probed by spectroscopic studies (absorption, excitation and emission) and it revealed that excluding the solvent effects, structural configuration of the polymeric backbone also play an important role in enhancing the solid state luminescent intensity. The solvent induced aggregation studies have proven that the addition of methanol (poor solvent) into the polymer solutions in THF (good solvent), drastically affect both the absorption maxima as well as luminescent intensity. Comparative studies have shown that the MEH-PPV chains experience more π-aggregation compared to that of the bulky PPV chains in BTCD-60. Temperature dependant studies have demonstrated that MEH-PPV chains
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undergo more aggregation (15 nm) in the cooling cycle compared to that of BTCD-60 (10 nm). The solvent and temperature dependant studies performed on the oligomers supported the fact that the bulky unit separates the interchain distance for the enhanced luminescence properties. Polymer-oligomer binary blends were synthesized and the studies revealed that the bulky OPV (BTCD-OPV) increases the emission of the PPV chain via both energy transfer and inter chain separation processes. Decay lifetime measurements of the binary blends further support the efficient energy transfer from the OPV to the PPV backbone resulting in the enhanced emission properties. Therefore, the bulky substitution in the PPV or in the oligomer separates inter-chain or inter-molecular distance more efficiently leading to the improved photo-luminescent properties.

To trace the role of structure on the thermotropic liquid crystalline behaviour, a series of bulky and non-bulky conjugated oligophenylenvinlylenes were designed. BTCD-OPV, TDD-OPV and BTCD-BDD-OPV have shown thermotropic LC behaviours upon cooling from isotropic melt. Among the three OPVs, BTCD-BDD-OPV was found to show a unique ring banded morphology, which is the first example of the ring banded structures in π-conjugated materials. The planarity of π-conjugated backbone is found to be the essential factor for the long range lamellae ordering of liquid crystalline mesogens for ring banded morphology. The sharp peaks in the X-ray diffraction patterns at low angle region and its reproducibility in the repetitive heating/cooling cycles demonstrates the lamellar aggregation of the OPV molecules. Long range amplitude of the lamellar twisting could be observed in the electron microscopic images as helically self-organized micro-crystals. The non-isothermal or isothermal crystallization processes have less influence on the nature of the ring banded morphological development; however, these conditions control the number of rings or layers in each spherulite. Luminescent ring banded structures can be achieved by exciting the OPVs with suitable light source. The existence of strong π-π interactions in the
OPVs which are the main driving force for the self-organization process were successfully demonstrated by photophysical experiments like excitation, emission, and time dependent fluorescence decay. Therefore, it was showed that the size, shape and nature of the pendant groups attached in the OPV backbone is a crucial factor for inducing liquid crystallinity and also tuning wide LC temperature window. Hence, the present work established that tricyclodecanemethanol (TCD-OH) is an effective structure directing unit for achieving highly luminescent materials and liquid crystalline phases compared to that of normal alkyl chains.

The bulky approach demonstrated that highly luminescent polymers and oligomers can be prepared for different applications such as optoelectronics. The bulky approach of PPVs explored here can be extended other polymeric systems to produce highly luminescent materials. The new way of patterning micrometer range ring structures via melt crystallization process is expected to be cheaper and clean way to process electronically important OPV based \(\pi\)-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 behaviour of conjugated segments through melt crystallization processes.