Chapter 1

Introduction and Literature Survey
1.1. General Introduction to Organic Semiconductors

Organic electronics has emerged as a vibrant field of research and development, and technology. An organic semiconductor is an organic material with semiconductor properties, that is, with an electrical conductivity between that of insulators and metals. This means the traditional (semi)conducting inorganic materials such as silicon, copper or metal oxides are replaced by organic materials (small molecules, oligomers or polymers). In comparison to the inorganic counterparts, organic materials possess reduced conducting properties, but they exhibit a lot of advantages that enable novel applications, such as organic devices on flexible or transparent foils. The fabrication of organic devices is simple: the organic material is deposited on top of a transparent electrode and eventually a cathode is evaporated. The final device is extremely thin and thus lightweight. Generally there are two competing processing technologies: (1) gas-phase deposition (such as thermal evaporation of small molecules) and (2) solution-based methods (such as printing of “organic inks”). Whereas the first method allows for easy processing of several materials on top of each other, the second promises cost-effective and fast production. Organic electronics is still a young field of technology including devices such as organic field effect transistors (OFETs), organic solar cells (OSC) or organic light-emitting diodes (OLEDs). These devices enable new applications and design possibilities, for example in the field of portable electronics, large area lighting, flexible displays or energy production.

1.2. Organic photovoltaic Materials

The need to develop inexpensive renewable energy sources stimulates scientific research for efficient, low-cost photovoltaic devices. Currently, most commercial solar cells are made from a refined, highly purified silicon crystal, similar to the material used in the manufacture of integrated circuits and computer chips (wafer silicon). The high cost of these silicon solar cells and their complex production process has generated interest in developing alternative photovoltaic technologies. Organic solar cell technology is a promising candidate for the solar energy conversion compared to its inorganic counterparts due to its low cost, light weight, and potential use in flexible devices. Like inorganic PVs, organic devices are made by creating interfaces of an electron-rich material (p-type) with an electron-poor material (n-type). The bulk heterojunction (BHJ) solar cell has become one of the most successful device structures developed to date. In this device structure, the blend of donor and.
acceptor or donor-acceptor polymer is used as active layer. The chemical structure of various conjugated polymers and oligomers commonly used in organic solar cell have been summarized in the scheme 1.1.8

Scheme 1.1. Various conjugated polymers and oligomers used in organic solar cells (Adapted from Chem. Rev. 2007, 107, 1324-1338).

Important representatives of hole conducting semiconductors are phthalocyanines, pentacene, oligothiophene, oligofluorene, oligo(phenylenevinylene), derivatives of thiophene chains such as poly(3-hexyl thiophene), derivatives of phenylenevinylene backbones such as poly[2-methoxy-5-(3,7-dimethyloctyloxy)]-1,4-phenylenevinylene) (MDMO-PPV) and derivatives of fluorene backbones such as (poly(9,9′-dioctylfluorene-co-bis- N,N′-(4-butylohlphenyl)-1,4-phenylenediamine) (PFB) etc.8 Much of the focus has been on the development of p-type semiconductors that have seen a dramatic rise in performance over the last decade. Much less attention has been devoted to electron transporting materials. The reported n-type organic semiconductors are PCBM (phenyl-C_{61}-butyric acid methyl ester), perylenebisimide, naphthalanebisimide and perfluoropentacene etc. The most used acceptor material in organic solar cells is PCBM, which is soluble in organic solvents.16,17 The success
of PCBM as a champion acceptor for OSCs is due to its ability to accept electrons from
semiconducting polymers at ultrafast time scales, and the nano-scale interpenetrating network
that it forms with these polymers. However, PCBM suffers from disadvantages including
high energy costs for material production and poor absorption in the visible spectrum.
Perylene and naphthalene bisimides (PBI/NBI) have been attracting considerable attention as
good n-type organic semiconductors because of its out-standing photophysical properties,
thermal stability, and ability to self-organize.  

1.3. Operating principles of organic solar cell

This section will deal with the material and device requirement for one of the organic
photovoltaic device i.e solar cell. The process of conversion of light into electricity by an
organic solar cell can be described by the following steps: absorption of a photon leading to
the formation of an excited state, that is, the bound electron-hole pair (exciton) creation;
exciton diffusion to a region where exciton dissociation, that is, charge separation occurs; and
charge transport within the organic semiconductor to the respective electrodes. The photo-
induced charge transfer from poly(p-phenylenevinylene) (PPV) (donor) to C\textsubscript{60} (acceptor) is
depicted schematically in figure 1.1 together with the energetic description.

![Figure 1.1. Illustration of the photo-induced charge transfer (left) with a sketch of the energy level scheme (right). After excitation in the PPV polymer, the electron is transferred to the C\textsubscript{60} due to its higher electron affinity (Adapted from J. Mater. Res. 2004, 19, 1924-1945).](image)

Donor and acceptor molecules must be well-mixed in bulk heterojunctions on the
length scale of 10-20 nm in each domain because exciton recombination significantly
increases when the domain sizes of the donor or acceptor materials exceed the exciton
diffusion length. The charge carrier mobilities of crystalline organic semiconductors are higher than amorphous semiconductors because of strong π-π interactions. But, the photovoltaic properties of crystalline conjugated polymers with higher carrier mobilities are not always good due to macrophase separation of the active layers during post-fabrication treatment process. Active layers consist of conjugated polymers as donors and fullerenes as acceptors often form complicated morphologies that typically arise from limited polymer:fullerene miscibility, resulting in phase-separated polymer and fullerene-rich domains. An active layer incorporating phase-separated domains in a solar cell can affect the device performance because these domains provide not only interfaces for charge separation of photogenerated excitons but also percolation pathways for charge carrier transport to the respective electrodes. The former requires a fine dispersion of fullerene units in the polymer, due to the short exciton diffusion length in the polymer (≤ 10 nm), while the latter requires fullerene domain to form complementary interpenetrating networks for charge transport to the respective electrodes to avoid charge recombination.

Figure 1.2. (a) Bright-field TEM image of a thermally annealed P3HT:PCBM film. The scale bar is 200 nm (Adapted from Nano Lett. 2009, 9, 507-513); (b) schematic drawings of the hierarchical structure in the nanometer-scale morphology in pristine and annealed P3HT:PCBM films (Adapted from Adv. Mater. 2009, 21, 1323-1338).

Figure 1.2 (a) shows the bright-field TEM image of an annealed regioregular poly(3-hexyl thiophene) (P3HT):PCBM photoactive layer; the P3HT fibers and PCBM-rich domains are clearly discernable as bright and dark regions, respectively, because of their different densities. Figure 1.2 (b) shows a schematic drawing of a hierarchical P3HT:PCBM
microstructure.\textsuperscript{33} In a pristine film, the fullerene moieties can disperse individually or form aggregated domains intercalated between P3HT lamellae and amorphous polymer chains. The sizes of the aggregated fullerene and P3HT lamellae domains show increase after thermal annealing. One way to overcome these drawbacks is by covalently linking the donor (D) and acceptor (A) in a single polymer chain.\textsuperscript{35-38} The covalent bond enables a predefined control over the characteristic distance between donor and acceptor and thereby the extent of phase separation.

Polymers are attractive for organic photovoltaics because thin films of these materials can be obtained through simple solution techniques such as drop casting, spin-coating and ink printing etc. But the mobilities are usually lower than the small molecules due to the poor molecular ordering and low crystallinity obtained by the solution techniques.\textsuperscript{39-41} Therefore, apart from designing suitable chemical structures, self-organization of molecules in the solid state remains a major challenge before π-conjugated organic materials can be utilized for actual application in molecular electronics.

1.4. Self-assembly of Organic Semiconductors

Self-assembled supramolecular structures of π-conjugated molecular building blocks are a promising class of materials to improve the solid-state organization of future optoelectronic materials.\textsuperscript{42-45} Over the past decade, several noncovalent interactions such as hydrogen bonding, electrostatic interactions, π-π stacking, dipolar interactions, chirality, and so forth, have been identified as enabling the construction of various hierarchical architecture from specially engineered small molecule building blocks.\textsuperscript{46-49} Oligofluorenes, oligothiophenes, oligophenlenes and oligophenylenevinylenes were reported for chiral self-organization in π-conjugated materials.\textsuperscript{50-52} High luminescent characteristics, thermal and optical stability, film forming tendency and solubility in organic solvents make oligo(p-phenylenevinylene) (OPV) chromophore very unique compared to other ‘p’ type π-conjugates.\textsuperscript{53, 54}

The self organization of oligo(p-phenylenevinylene) (OPV) chromophore via hydrogen bonding, π-π stacking and metal-ion interactions etc has been reported and the resultant structure were tested successfully as active layer in electronic devices.\textsuperscript{55, 56} Meijer and co-workers have made significant contributions to the helical self-assembly of π-conjugated oligomers derived from phenylenevinylenes, where the chirality of the attached side chains was translated to the conjugated oligomer backbone at a supramolecular level.\textsuperscript{57,}
They reported the synthesis and characterization of three hydrogen-bonded oligo(p-phenylenevinylene)s, OPV3, OPV4, and OPV5, that differed in conjugation length [figure 1.3 (a)]. All three compounds possessed chiral side chains, long aliphatic chains, and an ureido-s-triazine hydrogen bonding unit. $^1$H NMR and photophysical measurements showed that the OPV oligomers grew hierarchically in an apolar solvent; initially, dimers were formed by hydrogen bonds that subsequently developed into stacks by $\pi-\pi$ interactions of the phenylenevinylene backbone with induced helicity via the chiral side chains [figure 1.3 (b)].

Figure 1.3. (a) Molecular structures of OPV3, OPV4, and OPV5 as calculated by molecular dynamics and subsequent energy minimization at 300 K for 50 ps; (b) self-assembled helical columnar architectures at low temperatures simulated for stacked OPV4 dimers (Adapted from J. Am. Chem. Soc. 2003, 125, 15941-15949).

Ajayaghosh and co-workers described the hierarchical growth of left-handed helical nanostructures of chiral oligo(p-phenylenevinylene)s (OPVs). Three different OPVs with remote chiral handles, C-OPV1, C-OPV2, and C-OPV3 were prepared and the structures of the molecules are shown in figure 1.4 (a). C-OPV2, with hexadecyl side chains, was able to form stable aggregates in solution (as evident from optical studies). C-OPV1, with dodecyl side chains, was found to be a better gelator than C-OPV2, and formed a yellow fluorescent gel in nonpolar solvents, such as dodecane, heptane, and cyclohexane [figure 1.4 (b)]. However, C-OPV3, which is substituted with six chiral side chains, failed to form a gel in any of the solvents. AFM analysis of the C-OPV1 gel from dodecane ($6.5 \times 10^{-3}$ M) clearly showed the formation of entangled left-handed-helical coiled-coil fibers of 50-100 nm in
diameter [figure 1.4 (c)]. Careful analysis of a single fiber showed the morphology of a left-handed coiled-coil rope of approximately 90 nm width and 11 nm height [figure 1.4 (d)]. These observations point towards a hierarchical self-organization of the C-OPV1 into coiled-coil aggregates of nanometer dimensions.

Figure 1.4. (a) Structures of chiral OPV derivatives; (b) photograph of the gel from C-OPV1 in dodecane solution (6 x 10^{-3} M); (c) dense network of helical fibers and (d) single left-handed coiled-coil rope of the C-OPV1 (Adapted from Angew. Chem. Int. Ed. 2004, 43, 3421-3425).

A different approach towards helical system is to use host-guest chemistry to induce tunable chirality to the achiral host by specific recognition of appropriate chiral guest molecules. S. J. George and co-workers reported the adenosine phosphate induced one-dimensional (1D) self-assembly and the resultant supra-molecular chirality of naphthalenebiimide (NBI) amphiphiles i.e. NDPA-Amph and NDPA-Bola [figure 1.5 (a)].

Extensive studies on molecular phosphate sensors suggested that the dipicolylethylenediamine-zinc complex (DPA-Zn) motif can specifically bind to various adenosine phosphates with high association constants. Hence they designed NBI amphiphiles substituted with DPA-Zn motifs, in order to promote guest induced self-assembly and chiral induction through specific binding interactions. The binding of multivalent chiral phosphates resulted in high chiral order, as evident from the excitonic, bisignated circular dichroism signals, in the resulting NBI assemblies. Transmission Electron Microscopy (TEM) imaging of NDPA-Amph (70% water in THF, 7 x 10^{-5} M) assemblies with 0.5 equivalents of ADP, stained with uranyl acetate showed the formation of 1D nanofibers with a uniform diameter of 8 nm [figure 1.5 (b) and (c)]. TEM analysis of NDPA-Bola/ADP co-assemblies revealed the formation of fibers with 4 nm diameter, suggesting
that they were constructed from single NBI π-stacked columns with bound adenosine phosphates on both DPA-Zn sites.

**Figure 1.5.** (a) Molecular structures of **NDPA-Bola** and **NDPA-Amph**; (b) and (c) TEM images (7 x 10⁻⁵ M solution) of **NDPA-Amph**/0.5 equivalents of ADP (70% water in THF). Inset of (c) shows the schematic of the corresponding helical stack (Adapted from Chem. Commun. 2012, 48, 10948-10950).

Another category that has received lot of attention is the helical self-assembly of the achiral π-conjugated oligomers by the chiral peptide segments.⁶²-⁶⁴ R. J. Kumar and co-workers determined the ability of semiconductors templated by α-helical polypeptides to form higher order structures and the charge carrier properties of the supramolecular assemblies.⁶⁴ L-lysine was functionalized with a sexithiophene organic semiconductor unit via iterative Suzuki coupling and the click reaction. The resultant amino acid was incorporated into a homopolypeptide by ring-opening polymerization of an amino acid N-carboxyanhydride and the structure of the polymer is shown in figure 1.6. Spectroscopic investigation of the polypeptide revealed that it adopted an α-helical secondary structure in organic solvents that underwent hierarchical self-assembly to form higher order structures as shown in figure 1.6. In cyclohexane, the polymer formed organogels at 2% (w/v). Organic photovoltaic and organic field effect transistor devices were fabricated by deposition of the PCBM blended active layer from chlorobenzene at concentrations shown to induce self-assembly of the polymer. Compared with control compounds, these devices showed significantly greater hole mobility, short circuit current, and efficiency.

Though, supra-molecular assemblies have been obtained by different approaches, all of them are synthetically challenging. Hence, construction of highly ordered solid state
structures of π-conjugates by using a simple approach is still a challenging problem to be addressed.

![Chemical Structure](image1.png)

**Figure 1.6.** Self-organization of polymer as visualized by negative staining (uranyl acetate in EtOH) TEM of samples deposited from solutions in cyclohexane; (a)-(d) 2.1 x 10^5 M; (e) and (f) 1.0 x 10^5 M. Scale bar (a), (b): 500 nm; (c), (d): 200 nm; (e), (f): 500 nm (Adapted from J. Am. Chem. Soc. 2011, 133, 8564-8573).

### 1.5. Highly Fluorescent 1D Nanostructures of Organic Semiconductors

Inorganic nanowires have been extensively investigated for the linear optical properties, which can potentially be employed in various nanodevice applications including laser, waveguide, and polarized emission. The same research has been much less advanced for the organic counterparts. The device application concerned with the linear optical properties, particularly those based on fluorescence emission, demands that the organic nanomaterials thus fabricated be highly fluorescent. Although various small molecules, oligomers and conjugated polymers have been fabricated into 1D nanostructure, most of the π-conjugated molecules lose their strong fluorescence upon being assembled into the solid state. The challenge is thus to find building-block molecules that are not only suited for fabrication into 1D structure but also, enable strong fluorescence in the solid state.

Several classes of organic materials with high p-type charge carrier mobility have been known for long time; their n-type counterparts have become available only recently. Perylenebisimides (PBI) is the basis for a class of n-type chromophores exhibiting relatively
high electron mobility, large molar absorption coefficients, fluorescence quantum yield as well as good thermal and photochemical stabilities.\textsuperscript{18-20} L. Zang and co-workers reported the fabrication of ultralong nanobelts (\(>0.3\) mm) from an asymmetric perylenebisimide derivative, shown in figure 1.7 (a).\textsuperscript{74} The polyoxyethylene side-chain attachment made the molecule highly soluble in hydrophilic solvents such as ethanol. Self-assembly of the nanobelts of this molecule was performed through a solvent exchange processing, in which the molecules were transferred from a “good” solvent (such as ethanol) into a “poor” solvent (such as H\(_2\)O) where the molecules had limited solubility and therefore self-assembled into 1D nanobelts via molecular stacking. Figure 1.7 (b) shows the ultralong nanobelt structure obtained from the self-assembly of this molecule in a 1:1 water:ethanol solvent and figure 1.7 (d) shows the emission photograph taken for the nanobelt suspension (under irradiation of 366 nm UV light), where the fluorescence was quenched as expected.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{(a) Molecular structures of perylenebisimide derivative; (b) SEM image showing the belt morphology and uniform size of the nanobelts; (c) photograph taken for the nanobelts formed and suspended in 1:1 water:ethanol; (d) the emission photograph taken for the same samples under irradiation of a 366 nm UV light (Adapted from J. Am. Chem. Soc. 2007, 129, 7234-7235).}
\end{figure}

F. Würthner and co-workers synthesized a highly fluorescent perylenebisimide based organogelator (PBI1), shown in figure 1.8.\textsuperscript{75} UV/Vis studies revealed more pronounced aggregation in apolar solvents like MCH due to intermolecular \(\pi-\pi\) stacking and hydrogen bonding interactions. On the other hand, in polar solvents like acetone and dioxane, participation of the solvent molecules in hydrogen bonding significantly reduced the aggregation propensity but enforced the gel formation at higher concentrations [figure 1.8 (a)]. Although highly fluorescent organogels can feasibly be fabricated from the PBIs modified with substituents at the bay positions, the twisted conformation of the PBI backbone
distorted the π-π stacking, thus preventing the formation of well-defined nanowires in straight geometry suited for nanodevices fabrication [figure 1.8 (b) and (c)].

\[ \text{Figure 1.8. (a) Photographs of PBI1 in different solvents under a UV lamp (366 nm); (b) and (c) TEM images of PBI1 in MCH (1 \times 10^{-4} \text{ M}) and acetone (1 \times 10^{-3} \text{ M}) respectively (Adapted from Chem. Eur. J. 2008, 14, 8074-8078).} \]

Strong fluorescent nanofibers have recently been fabricated from a half-hydrolyzed PBI modified with branched side-chains in appropriate size (e.g., hexylheptyl) as shown in figure 1.9. This molecule possessed a structure that provided a good balance between the molecular stacking and the fluorescence yield of the materials thus assembled. The former prefers a molecular structure with minimal steric hindrance (usually referring to a small or linear side chain), while the latter favors bulky, branched side chains that may distort the π-π stacking to afford increased fluorescence (by enhancing the low-energy excitonic transition) for the molecular assembly. Figure 1.9 (a) shows the scanning electron microscopy (SEM) image of the nanofibers fabricated from this molecule through a vapor-diffusion (slow solvent exchange) process. The average diameter of the nanofibers is \( \sim 350 \) nm as determined by zoom-in SEM imaging as shown in figure 1.9 (b). These nanofibers demonstrated strong fluorescence with yield \( \sim 15\% \) as depicted in the fluorescence microscopy images [figure 1.9 (c) and (d)], implying a distorted molecular stacking that is usually observed for the PBIs modified with branched side chains. However, the nanofibers fabricated were highly curved and entangled together, probably because of the asymmetric structure of the molecules. Although the entangled nanofibers demonstrated potential applications in fluorescence
sensing of gaseous reagents, the curved shape made them less suited for application in 1D confined optical nanodevice.

Figure 1.9. (a) SEM image of the nanofibril film deposited on a glass slide; (b) zoom-in SEM image of the nanofibril film; (c) and (d) bright-field and fluorescence optical microscopy image of a nanofibril film respectively (Adapted from Nano Lett. 2008, 8, 2219-2223).

L. Zang and co-workers recently reported the fabrication of well-defined nanobelts from the flip-flap stacking of a cyclohexyl substituted molecule, CH-PTCDI, as shown in figure 1.10 (a). The nanobelts demonstrated long, straight belt-like morphology with length of hundreds of micrometers and width of 250-1500 nm [figure 1.10 (b)]. In contrast to the weak fluorescence emission (with quantum yield <1%) previously observed for the self-assembled materials of PBIs, which mostly adopted the translated stacking, these nanobelts demonstrated dramatically increased emission (with quantum yield of ca. 17%), which could easily be imaged with a fluorescence microscope [figure 1.10 (c)]. The increased fluorescence of these new nanobelts is attributed to the flip-flap stacking mode, which was believed to be effective for enhancing the fluorescence by strengthening the low-energy excitonic transition.

Even though well-defined highly fluorescent 1D nanostructure has been recently fabricated from various symmetric and asymmetric PBIs, there is no such 1D self-assembly reported for PBI based polymers. PBI small molecules possess specific electronic and optical properties due to their well-defined chemical structure. However, the material properties of small molecules are generally secondary to those of their polymeric analogues, since entanglements of macromolecular chains, which are responsible for the typical polymer properties, are lacking. Hence more intellectual input is required for developing fluorescent
1D nanostructure from PBI based polymers which would be really promising for many applications.

![Molecular structure of CH-PTCDI](image)

**Figure 1.10.** Molecular structure of CH-PTCDI; (b) large area SEM image showing the long nanobelts deposited on a glass slide; (c) fluorescence microscopy image of nanobelts cast on glass slide (Adapted from Chem. Mater. 2009, 21, 2930-2934).

1.6. **Photo-induced Energy- and Electron-Transfer in Donor-Acceptor System**

Energy- and electron-transfer processes between a donor and an acceptor play a fundamental role in most of the applications such as OLEDs and solar cells as well as in basic biological process such as photosynthesis.\(^{78\text{-}82}\) Therefore, a systematic design and study of tailor-made donor-bridge-acceptor (DBA) model systems are required for understanding these key processes. Photo-induced energy transfer between donor and acceptor was studied as early as 1940.\(^{83,84}\) The nonradiative energy transfer due to dipole-dipole interactions in donor-acceptor mixtures and bridged systems within a range of about 10 nm can be explained by Förster transfer. Here, the rate of energy transfer \((k_T)\) is extremely dependent on the distance \(R\) between the moieties \((k_T \propto R^{-6})\). Photo-induced electron transfer was also reported in different types of donor-acceptor systems.

Thelakkat and co-workers have reported the photo-induced energy- and electron-transfer in DBA molecule containing tetraphenylbenzidine (TPD) and perylenebisimide (PBI).\(^{85}\) The structure of the molecule is shown in figure 1.11. The energy transfer efficiencies in DBA determined using different methods such as (i) decrease in donor lifetime, (ii) decrease in donor fluorescence intensity, and (iii) increase in acceptor fluorescence intensity lie close to >90%. The schematic representation of the photo-induced energy- and electron-transfer observed in DBA molecule is shown in figure 1.11 (d) and (e).
In figure 1.11 (d), the energy is transferred from the excited D to A and figure 1.11 (e) depicts one of the possible channels of concurring charge-transfer processes after the direct excitation of A. The influence of linking D and A on the energy transfer process from D to A was investigated by comparing the fluorescence spectra of DBA and a blend of donor (TPD) and acceptor (PBI). They found that the fluorescence lifetime of pure donor, donor in the presence of acceptor, and donor in DBA decreases from 0.85 to 0.57 ns and finally to extremely short values of even below 80 ps, respectively. Thus, the linkage of D and A has a drastic influence on energy transfer dynamics in DBA.

![Chemical structures of (a) tetraphenylbenzidine (TPD), (b) perylenebisimide (PBI), (c) DBA molecule containing tetraphenylbenzidine and perylenebisimide; (d) Energy transfer from donor to acceptor after excitation of the donor at 349 nm and (e) one possible channel of electron transfer and fluorescence quenching of acceptor after direct excitation of acceptor at 525 nm (Adapted from Chem. Mater. 2007, 19, 88-94).](image)

Both oligo(p-phenylenevinylene) (OPV) and perylenebisimide (PBI) chromophores have been utilized in bulk-heterojunction like solar cell configurations as donor and acceptor materials, but their combination has received little attention. E. W. Meijer and co-workers have synthesized two copolymers consisting of alternating oligo(p-phenylenevinylene) (OPV) donor and perylenebisimide (PBI) acceptor chromophores by using a Suzuki polycondensation reaction. The copolymers differed by the length of the saturated spacer that connected the OPV and PBI units, as shown in scheme 1.2. Photo-induced singlet energy transfer and photo-induced charge separation in these polychromophores have been studied in solution and in the solid state via photoluminescence and femtosecond pump-probe spectroscopy. In both polymers, a photo-induced electron transfer occurs within a few picoseconds after excitation of the OPV or the PBI chromophore. The differences in rate
constants for the electron- and energy-transfer processes were discussed on the basis of correlated quantum-chemical calculations and in terms of conformational preferences and folding of the two polymers. In solution, the lifetime of the charge-separated state is longer than in the films where geminate recombination is much faster.

![Scheme 1.2. The Structure of alternating copolymers containing OPV and PBI (P1 and P2).](image)

R. A. J. Janssen and co-workers have synthesized two new donor-acceptor copolymers that consist of an enantiomerically pure oligo(p-phenylenevinylene) main chain with dangling perylenebisimides by using a Suzuki cross-coupling polymerization as shown in scheme 1.3. Absorption and circular dichroism spectroscopy revealed that the transition dipole moments of the donor in the main chain and the dangling acceptor moieties of the copolymers were coupled and in a helical orientation in solution, even at elevated temperatures. A strong fluorescence quenching of both chromophores indicated an efficient photo-induced charge transfer after photo-excitation of either donor or acceptor. The formation and recombination kinetics of the charge-separated state were investigated in detail with femtosecond and near-steady-state photo-induced absorption spectroscopy. The optical characteristics indicated a short distance and appreciable interaction between the electron-rich donor chain and the dangling electron-poor acceptor chromophores.

Although research on the photo-induced energy- and electron-transfer in copolymer containing OPV and PBI chromophores have been done, the systematic study of the factors influencing the photo-induced energy- and electron-transfer in OPV-PBI copolymer is a missing link in the literature.
1.7. Reactive Blending

The important bottleneck in the development of suitable polymeric materials for photovoltaic applications is the lack of an easy synthetic process. The technology of polymer blends has been one of the major areas of research and development in polymer science in the past three decades. The advantages of polymer blends versus developing new polymeric structures have been well-documented. The ability to combine existing polymers into new compositions offers the advantage of reduced research and development expense compared to the development of new monomers and polymers to yield a similar property profile. An additional advantage is the much lower capital expense involved with scale-up and commercialization. Another specific advantage of polymer blends versus new monomer/polymer composition is that blends can often offer property profile combinations not easily obtained with new polymeric structures. An inherent property of condensation polymers is their ability to react with each other. The presence of groups like ester, amide, urethane, and other similar types, as well as carboxylic, amine, etc., groups in the polymers makes the post reaction possible. Interchange reactions take place at elevated temperatures (most frequently in the melt) between functional groups belonging to molecules with different degree of polymerization or different chemical compositions. Most prominent examples are polyesters, polycarbonates and polyamides, where interchange reactions are best studied and understood.
Polyesters and polycarbonates are mostly used for engineering thermoplastics because of their excellent mechanical and thermal properties. Bisphenol A polycarbonate (PC)/polyester blends are among the most widely studied polymer blend systems industrially and academically. Because PC and polyester have common ester linkages in the backbone, ester-carbonate exchange (transesterification) occurs during their high-temperature melt blending. M. Jayakannan and P. Anilkumar investigated the reactive blending of bisphenol A polycarbonate (PC) with poly(1,4-cyclohexanediol-1,4-cyclohexanedicarboxylate) (PCCD) using a new high-temperature solution-blending methodology. The blending was carried out at very high concentrations at high temperatures. This approach had many advantages over conventional melt blending, such as independence from the polymer properties ($T_g$, $T_m$, and $T_c$ and crystallization temperature) and flow behaviors. The ester-carbonate exchange reaction in the blends was studied with $^1$H NMR and Fourier transform infrared (FT-IR). The ester-carbonate exchange reaction in the PC/PCCD blends leads to four major types of new linkages, two corresponding to new esters and two corresponding to new carbonates, as shown in scheme 1.4. Model blending reactions based on acidolysis, alcoholysis, and transesterification reactions were carried out to study the effect of PCCD end groups on PC/PCCD reactive blending. These model reactions revealed that the reactive blending was affected by both alcoholysis and transesterification, whereas acidolysis was absent. This may be due to the poor nucleophilicity of aliphatic acids toward the aromatic polycarbonates.

1.8. Conclusions and Aims of the Thesis

Ease of synthesis and film-forming ability or ease of processability is very important properties that are highly desirable in organic semiconducting materials. Reasonably high molecular weight is a prerequisite for polymeric semiconducting materials to attain this goal of easy processability. However, unlike acrylic or vinylic polymers where this is true, in main-chain semiconducting polymers, the π-π stacking interaction of the aromatic core results in reduced solubility and hence reduced solution processability. The π-π stacking interaction is a major hurdle to develop film-forming polymers especially for n-type semiconducting materials like perylene and naphthalene bisimides (PBI/NBI). Therefore, the synthesis of high molecular weight solution processable semiconducting polymers by using a simple approach is very challenging. This thesis work is focused on design and development of new solution processable semiconducting polymers and their supramolecular organization in the solid state. The important aspects of the thesis are:

1. Demonstrate a successful strategy for the synthesis of donor-acceptor semiconducting polymers.
2. Chirality induced helical self-assembly of π-conjugated material has been studied.
3. A simple approach for the fabrication of highly fluorescent semiconducting polymer into 1D elongated fiber over a large scale has been developed.
4. The photo-induced energy- and electron-transfer in random copolyester containing oligo (p-phenylenevinylene) and perylenebisimide were investigated.

In the second chapter, we have demonstrated a successful strategy for the incorporation of fluorescent chromophores such as OPV and PBI into the backbone of poly(1,4-cyclohexylenedimethylene-1,4-cyclohexanedicarboxylate) (PCCD). These polymers possessed the required thin film processability for potential application in organic photovoltaic devices. The third chapter deals with chiral polyester induced solid state helical self-assembly of oligo(p-phenylenevinylene) (OPV) chromophore. In the fourth chapter, synthesis of highly fluorescent n-type organic semiconducting material, which could be fabricated into well-defined nanofibers over a large scale, was investigated. The fifth chapter describes the synthesis of novel copolyesters containing OPV and PBI chromophore by melt polycondensation. Photoinduced energy- and electron-transfer in these polyesters were studied in solution as well as in the solid state. Finally, the overall conclusion of the thesis has been summarized.
1.9. References

13) Brabec, C. J.; Dyakonov, V.; Parisi, J.; Sariciftci, N. S. *Organic Photovoltaics: Concepts and Realization*; Springer, **2003**.
14) Pagliaro, M.; Palmisano, G.; Ciriminna, R. *Flexible Solar Cells*; Wiley-VCH, **2008**.