Molecular Design, Synthesis and Performance Evaluation of Phenothiazine-based Small Molecules for Organic Solar Cells

Srikanth Revoju
To my parents and ammamma
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Abstract

The dual challenge of growing global energy demand and environmental and climatic consequences push us to seek for new alternatives to conventional fossil resources. Photovoltaics offers one of the most promising routes to generate electricity in a clean way. As an emerging technology in photovoltaics, organic solar cells (OSCs) have attracted a great deal of attention owing to their potential low-cost, lightweight, flexibility and solution processability. Although power conversion efficiencies (PCEs) above 12% have been achieved, there is a great interest for new ideal materials to further improve the PCEs and address device durability, which are major concerns for the commercialization of this technology.

The main objective of this thesis is to design and synthesize phenothiazine-based conjugate small molecules and explore their use as electron donor components in OSCs.

In the first project, a small molecule based on cyano-arylenevinylene building block with deep HOMO level has been prepared. Although a high open-circuit voltage of 1.0 V was achieved, the tendency of the small molecule to crystallize at a higher temperature and with time hindered the attainment of an optimal phase morphology required for the achievement of a higher efficiency.

Phenothiazine is a non-planar moiety with unusual “butterfly” type of geometry known to hinder the molecular aggregation and intermolecular excimer. It was envisaged that the bent shape of phenothiazine renders suitable nonplanarity to the small molecules, and by that reduces the risk of excessive aggregation and formation of too large domains of the small molecule in the active layer with fullerene derivatives.

In project 2 and 3, phenothiazine is used as a π-system bridge and as a core unit to construct small molecules based on symmetric and asymmetric frameworks with varying terminal electron-withdrawing groups. The electron-withdrawing property of the terminal units was found to have a significant influence on the optical absorption properties, electronic energy levels, molecular ordering, charge carrier mobility and morphology of the resulting active layers. The dipole moments of small molecules of asymmetric
configuration seemed to be related to the formation of self-assembled dimers or similar aggregates, although no strong correlation with PCE was observed.

In project 4, alkyl solubilizing groups of the central phenothiazine unit of symmetrically configured small molecules are replaced with short glycol (methoxyethoxy ethyl) chain to study the effect on the basic optoelectronic and dielectric properties. As anticipated, glycol substituted small molecules showed higher dielectric constants owing to their flexible C–O units. Although absorption properties are unchanged in solution, a dense π-π stacking was observed in the solid state.

In summary, it is demonstrated that phenothiazine is a promising candidate and worth exploring donor material for OSCs. Its versatility as a π-linker and as a central core unit in symmetric and asymmetric configurations has been explored. The use of nonplanar building blocks such as phenothiazine for the construction of donor materials is an interesting strategy for controlling molecular aggregation and difficult solution processability of small molecules if it is combined with the judiciously designed conjugate backbone.
List of Publications

This thesis is based on following papers, which are referred to in the text by corresponding Roman numerals I-IV.


Author´s Contributions

Paper I
Major part of the synthesis and structural characterization of compounds.

Paper II - IV
Formulated the research problems.
Made all synthesis and structural characterization of compounds.
Performed CV experiments and data interpretation.
Performed significant-to-major part of DFT calculations.
Made significant contribution to the interpretations of the results and to the writing of the manuscripts.

(Solar cell fabrication, photovoltaic studies, XRD and TEM measurements were performed by collaborators, as well as writing the part of the papers that describe those results and interpretations).
# List of Abbreviations

A | acceptor  
---|---
AM | air mass  
AFM | atomic force microscopy  
BDT | benzodithiophene  
BHJ | bulk heterojunction  
CV | cyclic voltammetry  
D | donor  
DFT | density functional theory  
DMF | N,N-dimethylformamide  
dppf | diphenylphosphino ferrocene  
DSC | differential scanning calorimetry  
E<sub>exc</sub> | excitation energy  
E<sub>g</sub> | energy gap  
E<sub>ox</sub> | onset oxidation potential  
EQE | external quantum efficiency  
E<sub>red</sub> | onset reduction potential  
eV | electron volt  
FF | fill factor  
HOMO | highest occupied molecular orbital  
Hz | hertz  
IPCE | incident photon to current conversion efficiency  
ICT | internal charge transfer  
IND | 1,3-indandione  
ITO | indium tin oxide  
J<sub>sc</sub> | short-circuit current density  
J-V | current-voltage  
LUMO | the lowest unoccupied molecular orbital  “MN” | malononitrile  
NMR | nuclear magnetic resonance
OPV  organic photovoltaic
OSC  organic solar cell
PC_{61}BM [6,6]-phenyl-c_{61}-butyric acid methyl ester
PC_{71}BM [6,6]-phenyl-c_{71}-butyric acid methyl ester
PCE  power conversion efficiency
PEDOT:PSS poly(3,4-ethylenedioxythiophene)polystyrene sulfonate
PFN  poly[(9,9-bis(3-(n,n-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)]
PTZ  phenothiazine
P3HT  poly(3-hexylthiophene)
R_s  series resistance
R_{sh}  shunt resistance
SCLC  space charge limited current
SVA  solvent vapour annealing
TDDFT  time-dependent density functional theory
TEM  transmission electron microscopy
THF  tetrahydrofuran
TGA  thermogravimetric analysis
TPA  triphenylamine
TSA  two step-annealing
UV-Vis  ultraviolet-visible
V_{oc}  open circuit voltage
XRD  x-ray diffraction
\varepsilon  molar extinction coefficient
\lambda  wavelength
\mu_{es}  excited state dipole moment
\mu_{gs}  ground state dipole moment
\mu_e  electron mobility
\mu_h  hole mobility
\varepsilon_r  dielectric constant of the material
1 Introduction

1.1 The energy challenge

Global economic and population growth are the major drivers of increasing world energy demand. World’s population is set to increase from 7.6 billion in 2017 to approximately 9.8 billion in 2050. More than half of the anticipated growth in global population is expected to occur in developing nations of Africa and Asia and the living standards in these regions are also expected to rise significantly. World’s total primary energy supply is of 156 PWh in 2014 and is expected to increase up to 244 PWh in 2050. Under these circumstances, providing clean, affordable, and equitable energy to all will be one of society’s foremost challenges for the next half-century. Currently, fossil fuels (coal, oil and gas) derived energy accounts for more than 80% of total primary energy share and are expected to dominate in near future. Dependence on fossil fuels, unfortunately, comes with the serious implications on environment and climate. Combustion of fossil fuels results in the emission of greenhouse gases -mainly carbon dioxide- leading to global warming, ocean acidification, and sea level rise. Carbon dioxide emissions from human activities have grown substantially over the past decade, reaching about 40 Gt CO$_2$ per year in 2013. In order to mitigate greenhouse gas emissions, 195 countries signed the historic Paris climate agreement (COP21) in 2015 and agreed to keep the increase in global average temperature to well below 2°C above pre-industrial levels and endeavour to limit them even more, to 1.5°C. The dual challenge of global energy supply with a simultaneous cut in carbon emissions force us to change our energy habits and move towards more sustainable energy resources. Renewable energy resources can provide sustainable benefits for our climate, our health, and our economy. These resources include wind, biomass, hydro and solar energy. Solar energy is deemed as the largest of all carbon-neutral energy sources with more energy striking our earth in an hour ($4.3 \times 10^{20}$ J) than all of the energy consumed on the planet in an entire year ($4.1 \times 10^{20}$ J).
1.2 Photovoltaics

Photovoltaic (PV) devices represent one of the most promising routes to harvest the solar energy. Conversion of solar radiation into electricity occurs by the photovoltaic effect which was first observed by the French physicist Becquerel in 1839. However, the birth of the modern era solar cells conceived to be 1954, when Chapin et al. reported solar cells based on p-n junctions in single crystal silicon with power conversion efficiencies (PCE) of 5-6% at Bell Laboratories. For many years PV research was mainly directed towards space applications and satellite power. However, following the oil crisis in the 1970s, research on photovoltaics cells gathered momentum and since then tremendous progress has been achieved, which ultimately led to the emergence of new solar technologies. Traditionally, solar cells have been categorized into three generations namely first generation, second generation and the third generation. First generation solar cells are mainly based on single-junction crystalline silicon wafers with typical performances of about 15-20% for commercial ones. Recently, PCEs above 26% are reported in the literature. Although Si solar cells dominate the market with a share of more than 80%, they still suffer from high manufacturing costs and long energy payback time due to the amount of material required and energy intensive production processes. Second generation solar cells are investigated with the aim of reducing costs and material consumption by employing thin film technologies. These are based on thin layers of various semiconductors materials like cadmium telluride (CdTe), copper indium gallium selenide (CIGS) or amorphous silicon (a-Si). These are flexible to some degree and exhibit promising photovoltaic performances of 22.1%, 22.6% and 14% for CdTe, CIGS, and a-Si solar cells, respectively. Although these are cost-effective due to lower material consumption, the production of these solar cells still includes vacuum processes, high-temperature treatments and use of scarce elements. Third generation solar cells are based on devices that can exceed the Shockley–Queisser limit. They include expensive high-performance multi-junction (tandem) solar cells and also emerging solar cells such as quantum dots solar cells (QDSCs), dye-sensitized solar cells (DSSCs), organic solar cells (OSCs) and perovskite solar cells (PSCs). Multi-junction solar cells currently hold the world record in terms of performance with PCE
values of 46%, while emerging technologies have reached efficiencies of 13.4%, 11.9%, 13.1% and 22.1% for QDSCs, DSSCs, OSCs, and PSCs, respectively.\textsuperscript{6,7}

This new generation solar cell technologies are attracting great attention as many of these can be made from solution-processed techniques and their light weight, fabrication on flexible substrates and transparency could give them an advantage over conventional solar cells.\textsuperscript{8, 9} The development of different photovoltaic technologies and their respective growth in highest PCEs from 1977 to 2017 is illustrated in Figure 1.1.

### 1.3 Organic solar cells

The organic solar cell also referred to as organic photovoltaic (OPV) cell, is an emerging technology with the cell typically composed of electron donor (D) and electron acceptor (A) materials sandwiched between two electrodes. OSCs have drawn intense attention from both academic and industrial communities owing to the aforementioned advantages. Many scientific discoveries over the years contributed immensely to the fundamental knowledge of organic semiconductors and development of photovoltaic devices. Although the observation of photoconductivity and the photovoltaic effect in organic molecules dates back to the early 20th century, the major breakthrough was achieved by the introduction of the bilayer heterojunction concept, in which two organic layers with specific electron or hole transporting properties were sandwiched between the electrodes.\textsuperscript{10} In 1986 Tang reported a PCE of about 1% for a bilayer device composed of two vacuum-evaporated organic materials (a phthalocyanine derivative as p-type semiconductor and a perylene derivative as an n-type semiconductor) sandwiched between a transparent conducting oxide and a semi-transparent metal electrode.\textsuperscript{11} In the meantime, the advent high-purity conjugated polymers in the 1990’s allowed the fabrication of OSCs with materials simply processed from solution.\textsuperscript{12} In 1992, the Heeger and Wudl groups observed ultrafast photo-induced electron transfer from the conjugated polymer poly[2-methoxy-5-(2-ethylhexyloxy)]-1,4-phenylenevinylene (MEH-PPV) to fullerene (C\textsubscript{60}), which suggested the use of conjugated polymers as electron donors and fullerene derivatives as electron acceptors in polymer solar cells.\textsuperscript{13} Concurrently, the concept of the bulk heterojunction (BHJ) was introduced by the Heeger and Friend research groups,
Figure 1.1. Certified highest efficiencies for a variety of photovoltaic technologies provided by NREL.
for polymer solar cells using the blended systems of conjugated polymer (donor): fullerene (acceptor) and polymer donor: polymer acceptor, in which a large interface area between donor and acceptor provides pathways for charge generation, separation, and transportation.\textsuperscript{14, 15} Since then, tremendous progress has been achieved in the understanding of fundamental concepts, development of new active layer materials, morphology control and characterization, new device architectures, and interface engineering.\textsuperscript{16–18} As a result, the PCEs of solar cells have increased from 1% in the 1990s to over 13% recently.\textsuperscript{19–24} Working principle, device architecture, photovoltaic parameters and materials and their design principles will be discussed in following sections.

1.4 Working principle of an organic solar cell

The photovoltaic process for OSCs fundamentally differs from that in inorganic photovoltaics with respect to the photogeneration of charge carriers. In inorganic semiconductors, light absorption readily creates free charge carriers (electrons and holes) while in organic semiconductors, due to lower dielectric constants ($\varepsilon_r \sim 2-4$), coulombically bound electron–hole pairs (exciton) are generated.\textsuperscript{25} This difference introduces extra steps in the mechanism of OSCs to dissociate the excitons into free carriers. The process of converting sunlight into electric current in an OSC is accomplished by four successive steps:

1) Absorption of a photon leading to the generation of exciton

2) Exciton diffusion

3) Exciton dissociation

4) Charge transport and charge collection.

The initial step is the absorption of light by the active layer (1), which promotes an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the donor material, resulting in the generation of excitons. The excitons are neutral species with a binding energy of typically 0.3-1 eV.\textsuperscript{17} Next step is exciton diffusion (2). Excitons are generally believed to have diffusion lengths in the sub-20 nm scale.\textsuperscript{12, 16, 17} They need to diffuse to the interface before undergoing undesirable processes such as relaxation, recombination or intersystem
crossing (generates the triplet excited state). Then exciton dissociation (3) occurs when an electron is transferred from the LUMO of the electron donor to the LUMO of an electron acceptor (A). The difference between the electron affinity levels ($\Delta$LUMO) determines the efficiency of this process and the optimum energy difference for effective charge transfer has been empirically found to be $\geq 0.3$ eV.\textsuperscript{10,17} After the charge separation at the D-A interface, holes will transport to the positive electrode and the electrons will transport to the negative electrode through the interpenetrated networks of donor and acceptor, respectively. Finally, the electrons/holes are collected at the corresponding electrodes. The operating mechanism of an OSC is illustrated in Figure 1.2.

![Figure 1.2. The operating mechanism of an organic solar cell.](image)

1.5 Device architecture

Depending on the active layer structure, OSCs can be classified into monolayer solar cells, bilayer solar cells, bulk heterojunction solar cells and tandem solar cells as depicted in Figure 1.3.

1.5.1 Monolayer solar cells

These are the first generation of OSCs based on single organic layers sandwiched between two metal electrodes of different work functions as shown in Figure 1.3a. The performance of these OSCs was generally poor
with efficiencies less than 0.1%, but in the late 1970s, notable PCE value of 0.7% was reported for merocyanine dyes. The built-in potential was derived from either the difference in work function of the electrodes or the formation of a Schottky-barrier between the p-type (hole conducting) organic layer and the metal with the lower work function.

1.5.2 Bilayer solar cells

The next breakthrough was achieved by introducing the concept of a two component donor/acceptor active layer for OSCs that relied on thin layers of thermally evaporated small molecules. Tang in 1986 reported about 1% PCE with a high fill factor of 65% for a bilayer solar cell. In these bilayer structures, due to the shorter diffusion lengths of excitons, only those generated near the donor/acceptor interface lived long enough to dissociate at interface while others underwent charge recombination. Nevertheless, this seminal work represented a major milestone and paved the way for the development of other donor/acceptor type architectures. A typical device structure is shown in Figure 1.3b.

1.5.3 Bulk-heterojunction solar cells

The bulk-heterojunction architecture was first introduced by Yu et al. in 1995 to address the limited exciton diffusion length and low photocurrent in earlier OSC designs. In a typical BHJ structure, as shown in Figure 1.3c, donor and acceptor materials are blended together to form a bicontinuous interpenetrating D-A network with large interfacial areas. Such a bicontinuous nanoscale network results in optimal domain size which is favourable for the efficient exciton diffusion and dissociation. Thus, the performance of BHJ devices is sensitive to the morphology of the blend layer in addition to the opto-electronics properties of materials. However, the formation of BHJ morphology is a complex issue, which is not only influenced by structural features (backbone, substituents, and side chains), miscibility and ratio of donor-acceptor but also by the various device fabrications methods such as choice of solvents, solvent additives, and thermal and solvent annealing. The greater understanding and control of morphology will further enhance the PCEs of blend films. BHJ is considered as the state of the art
active layer morphology today and record efficiencies of 11-13% were achieved.\textsuperscript{19-22}

1.5.4 Tandem solar cells

Single junction solar cells inherently suffer from the low mobility of electrons and holes and relatively narrow absorption spectra of the organic materials ($E_g \sim 1.6-2.0$ eV), leading to low PCEs.\textsuperscript{28} To overcome this, tandem solar cell technology is developed by stacking multiple photoactive layers with complementary absorption properties in series/parallel fashion. Hiramoto \textit{et al.} first reported an organic tandem solar cell with two single cells, connected in series, consisting of metal-free phthalocyanine and a perylene tetracarboxylic derivative separated by a thin interstitial layer of gold.\textsuperscript{29} Since then, tandem organic solar cells using both vacuum and solution processing with better PCEs in comparison to single junction devices have been widely reported.\textsuperscript{23, 24} The general construction of tandem organic solar cell is shown in Figure 1.3d.
One of the most important characterization tools for the evaluation of the photovoltaic performance of a solar cell is the current-voltage (J-V) measurement. The J-V characteristics are monitored under solar irradiation by changing the external load from zero (short-circuit conditions) to infinite load (open-circuit conditions). The following parameters, open-circuit voltage ($V_{oc}$), short-circuit current density ($J_{sc}$), fill factor (FF) and efficiency ($\eta$), could be obtained from a J-V curve (Figure 1.4). Standard illumination is the air mass 1.5 global (AM1.5 G) solar spectrum with an intensity of 1000 W m$^{-2}$ (also denoted as “1 sun”). The sun’s spectrum is termed as AM 1.5 when the sunlight travels through the atmosphere to reach the surface of the earth and makes an angle of 48.2° with the zenith.
1.6.1 Open-circuit voltage

$V_{oc}$ is defined as the maximum output voltage of the solar cell when no current flows through the cell. Numerous studies have demonstrated that $V_{oc}$ of the OSC depends on the energy gap between the HOMO of the donor and the LUMO of the acceptor.\textsuperscript{30, 31} Scharber et al. analysed $V_{oc}$ across a wide range of material combinations and proposed an empirical relationship\textsuperscript{32}:

$$V_{oc} = \left(\frac{1}{q}\right) (|E_{HOMO}| - |E_{LUMO}| - 0.3 \text{ V})$$

where $q$ is the elementary charge, $E_{HOMO}$ is the HOMO level energy of the donor and $E_{LUMO}$ is the LUMO level energy of the acceptor, determined from cyclic voltammetry and absorption spectroscopy. It should be noted that the loss of 0.3 eV is empirical and its origin is still under investigation.\textsuperscript{30, 31}

1.6.2 Short-circuit current

$J_{sc}$ is defined as the maximum output current over an area in the SC when the cell is short-circuited. The short circuit current is affected by various factors such as light absorption, photo-induced exciton generation and transport, the morphology of active layer and active layer/electrode interface structure.\textsuperscript{25}

1.6.3 Fill factor

The FF is defined as the ratio between the maximum power output of the cell ($P_{max} = J_{max} \cdot V_{max}$) and the product $J_{sc} \cdot V_{oc}$. It is a measure of the “squareness” of the $J$–$V$ curve and it represents the “easiness” or “hardness” of the extraction of the photogenerated carriers out of a photovoltaic device, and in an ideal case will have a value of unity (100%).\textsuperscript{33, 34} There are various factors that can influence the FF and also these factors often interact with each other in a complex way, which makes FF the least understood one in the OSCs, comparing to that of $V_{oc}$ and $J_{sc}$. The series resistance ($R_s$) and shunt resistance ($R_{sh}$) are two important factors that affect the FF of a cell. Generally, $R_s$ is originated from the bulk resistances of the active layer and electrodes, and the contact resistance between the active layer and electrodes. The $R_{sh}$ is derived from the current leakage induced by the pinhole in the cell, or the current
leakage from the edge of the device. Besides $R_s$ and $R_{sh}$, competition between recombination and extraction of free charges also determines the FF of OSCs. For achieving high FF, along with very low $R_s$ and very large $R_{sh}$, reduced recombination, a certain degree of crystallinity, and improved nano-scale morphology are required.\textsuperscript{33-34}

$$\text{FF} = \frac{J_{\text{max}} \cdot V_{\text{max}}}{J_{\text{sc}} \cdot V_{\text{oc}}}$$

1.6.4 Power conversion efficiency

The solar cell efficiency is determined by the ratio of the maximum power generated and power of the incident light ($P_{\text{in}} = 1000 \text{ Wm}^{-2}$).

$$\eta = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{J_{\text{sc}} \cdot V_{\text{oc}} \cdot \text{FF}}{P_{\text{in}}}$$

1.6.5 Incident photon to current conversion efficiency

The incident photon to current conversion efficiency (IPCE) is defined by the ratio of the number of electrons generated in a solar cell to the number of photons incident on the photovoltaic device surface at given wavelength under monochromatic illumination. It is equivalent to external quantum efficiency (EQE).

$$\text{IPCE} = \frac{N_{\text{charge}}}{N_{\text{photons}}} = \frac{1240 \cdot J_{\text{sc}}}{\lambda \cdot P_{\text{in}}}$$
Where $J_{sc}$ is the measured photocurrent, $P_{in}$ is the input optical power and $\lambda$ is the wavelength of the incident light. Generally, the IPCE is measured under short-circuit conditions and is graphically displayed versus the corresponding wavelength in a photovoltaic action spectra.

![Graph showing current-voltage curves for dark and light currents in solar cells with the output parameters.]

**Figure 1.4.** The current-voltage curves for dark and light currents in solar cells with the output parameters.

### 1.7 Materials

As mentioned previously, the active layer of the OSC consists of an acceptor material, which is typically a fullerene or non-fullerene derivative, and an electron donor which can either be a polymer or small molecule. The following sections briefly discuss the development of the active layer components of the OSC.

#### 1.7.1 Electron acceptor

After the demonstration of ultrafast photo-induced electron transfer from the donor-type conjugated polymer to fullerenes ($C_{60}$) by Heeger and co-workers in 1992, they have become ubiquitous choice as electron acceptors in OCSs. Among various derivatives, $C_{61}$-butyric-acid-methyl ester ($P_{61}$CBM) and phenyl-$C_{71}$-butyric acid methyl ester ($PC_{71}$BM) are the most common
acceptors for their (i) ability to accept and transport electrons in three dimensions (ii) high electron mobilities, (iii) multiple reversible electrochemical reductions, and (iv) ability to form favourable nanoscale morphology for efficient charge generation, separation and transportation.\textsuperscript{25} However, they suffer from inherent limitations of such as weak absorption in the visible region of the solar spectrum, limited tunability, morphological instability and high costs for production.\textsuperscript{36-38}

Recently, intensive efforts have been directed towards the development of soluble, non-fullerene, organic small molecules commonly referred as non–fullerene acceptors (NFAs) to fabricate BHJ-OSCs. Various NFAs were reported in the literature based on fluorene, dibenzosilole, perylene diimide, naphthalimide diimide, diketopyrrolopyrrole, indacenodithiophene, and indacenodithieno[3,2-b]thiophene moieties with impressive PCEs of > 12\% achieved recently.\textsuperscript{36-38} These developments indicate that NFAs are a potential alternative to fullerene derivatives and further improvement in PCE is quite feasible with continued innovation and research.

1.7.2 Electron donor

1.7.2.1 Polymers

Conjugated polymers were widely investigated as electron donors in OSCs. The development of donor polymers can be roughly divided into three phases from the perspective of the constituting building blocks. Phase one is centered around poly(phenylene vinylene)s (PPV) derivatives such as poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV).\textsuperscript{12, 18, 39} Efficiencies of photovoltaic devices reached around 3\% with PC\textsubscript{60}BM as the electron acceptor, however, large band gap and poor hole conducting properties of the PPV-based derivatives limited further improvement. Then, in phase two, smaller bandgap poly-(thiophene) derivatives such as poly(3-hexylthiophene) (P3HT) were explored.\textsuperscript{12, 18, 39} Optimized P3HT:PCBM BHJ devices exhibited PCE of 5\% mainly due to the higher currents attributed to its lower band gap as well as to its increased π-stacking and crystallinity which yields a higher hole mobility. P3HT is still one of the benchmark materials against which most of the materials, fabrication
methods, and device architectures are compared. In phase three, numerous modern polymers have been reported based on ‘weak donor/strong acceptor’ strategy combining ‘weak donors’ with ‘strong acceptors’ in co-polymers (here, the ‘donor’ and ‘acceptor’ terms refer to the electron affinities of the co-monomers relative to each other and not to be confused with donors and acceptors in OSC devices).\textsuperscript{18, 32, 39, 40} The PCE of polymer solar cells has been progressively improved to 12%, however, several issues related to their synthesis with batch-to-batch variation, such as side length polydispersity, structural defects, and impurities due to difficult purification yet need to be addressed for possible commercialization of polymer OSCs.

1.7.2.2 Small molecules

“Small molecules” recently emerged as promising alternatives to the polymers with attractive features like well-defined molecular structure, definite molecular weight, and high purity without batch to batch variations. Historically, SM-OSCs used to be prepared \textit{via} vacuum deposition due to their low molecular weight. In 2006, Roncali et al. developed a series of tetrahedral-shaped oligothiophene molecular donors that could be solution-processed with PC\textsubscript{61}BM to produce solar cells with a PCE of ~0.2%.\textsuperscript{41} Since then several new classes of small molecule donors with favourable optical and electronic properties have been reported for use in solution processable OSC devices. Recently, PCEs of SM-OSCs reached the range of 11–13% with fullerene and non-fullerene acceptors, this advancement clearly demonstrates the ability of SMs to replace conjugate polymers in the fabrication of high-efficiency BHJ OSCs.\textsuperscript{36-38, 42, 43}

1.8 Molecular design

This section gives an overview of the active layer characteristics required for the high efficiencies and the design principles employed for the synthesis of the novel donor molecules. As mentioned above, the performance of a solar cell is determined by three key parameters; \(J_{sc}\), \(V_{oc}\), and FF, and the goal of the molecular design is to simultaneously optimize all of them and by that
maximize the efficiency. The guiding principles for molecular design can be drawn by understanding the correlation between the solar cell parameters and the donor characteristics. An ideal donor should possess the following intrinsic features, in the active layer: (a) low bandgap with broad and strong absorption in visible and NIR region; (b) suitable LUMO and HOMO energy levels; and (c) high charge carrier mobility, a certain degree of crystallinity, and optimal mixing with the acceptor.

Accordingly, in order to achieve high $J_{sc}$, the active layer should possess low bandgap with broad and intense absorption across the solar cell spectrum as $J_{sc}$ is proportional to the product of spectral absorption breadth and absorption intensity of active layer. The distribution of photon flux as a function of wavelength with maximum intensity in the infrared region of the spectrum is illustrated in Figure 1.44 Theoretically (assuming EQE 100%), a medium bandgap donor material with an absorption onset of 650 nm can reach only $J_{sc}$ of 16.77 mA/cm$^2$ whereas a lower band gap material with 950 nm absorption onset can achieve high $J_{sc}$ of 35.72 mA/cm$^2$. Therefore, lowering the band gap of a donor material is a fundamental characteristic to consider while designing the donor materials for photovoltaic applications.

In addition to the suitable bandgap, frontier energy levels of the donor material (HOMO and LUMO) have to be positioned correctly relative to the acceptors in order to provide sufficient driving force for the exciton dissociation and obtain maximum $V_{oc}$. As described, $V_{oc}$ is empirically related to the energy gap between the HOMO of the donor and the LUMO of the acceptor of the OSC. Finally, the FF depends on the efficient extraction of the photo-generated carrier from the device and is strongly tied to the morphology of the donor:acceptor blend. The bicontinuous interpenetrating D-A network will facilitate the effective charge transport with minimum recombination.
From the above discussion, it is evident that newly designed donors should possess low bandgap and also low lying HOMO levels. Often, a trade-off between $J_{sc}$ and $V_{oc}$ is required because maximization of either one would result in a decrease of the other parameter. For example, drastically lowering the band gap of a donor material should increase the $J_{sc}$ as expected with the concomitant shifting of the HOMO energy level upwards, resulting in a loss of $V_{oc}$ and likely no overall improvement in PCE. The correlation between solar cell parameters and active layer characteristics is illustrated in Figure 1.6. From theoretical calculations, it has been estimated that the optimal bandgap of donor molecules should be around 1.35–1.65 eV with a HOMO level of -5.4 eV.39

Figure 1.5. Photon flux from the sun at the earth's surface (1000 Wm$^{-2}$, AM1.5G) as a function of wavelength. The integral of the curve is shown on the right y-axis as a percentage of the total number of photons and as the obtainable short circuit current density for an absorber material with a step function absorbance at that wavelength. Reprinted with permission from ref 44. Copyright © 2007 Elsevier.
Following subsection ‘Molecular design’ deals with the design principles employed by synthetic chemists to control the electronic characteristics of the donor materials, specifically bandgap and energy levels, through structural modifications. Generally, a conjugated molecular semiconductor can be arbitrarily divided into three constituting structural components: the conjugated backbone, the side chains, and the substituents.

### 1.8.1 Conjugated backbones

Conjugated backbones determine the fundamental optoelectronic properties of the resulting polymers or small molecules. Conjugated systems possess inherent bandgap because of the bond length alternation between single and double bonds in the backbone. Several design principles have been established in order to decrease the band gap of the conjugated molecules. The stabilization of a quinoidal form and the donor-acceptor (D-A) approach are the most commonly employed design strategies.\(^ {18,39}\)

Among two non-degenerate states that exist in aromatic polymers or small molecules, the quinoidal form possesses higher energy but lower band gap than the aromatic form. In the "Quinoid" approach, two aromatic units are

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**Figure 1.6.** The correlation between solar cell output parameters and the active layer characteristics.
fused in a particular geometry to stabilize the quinoidal form. One such example is shown in Figure 1.7a, where the quinoid form is more important than for the thiophene compound without the fused bezenoid ring. Because the aromatic stabilization energy is lower for thiophene (1.26 eV) than for benzene (1.56 eV), the isothianaphthene moiety exhibits further deearomatization of thiophene unit (and consequent aromatization of the benzene unit). Stabilization of quinoidal form not only lowers the bandgap of related conjugated systems but also coplanarizes the backbone.

Another design principle is the “donor-acceptor” or “push–pull” approach, which is by far the most dominant approach used to make low bandgap conjugate polymers or small molecules. The underlying concept is that electron-rich donors and electron-deficient acceptors are incorporated in an alternating fashion into the conjugated backbone, resulting in a compressed band-gap via molecular orbital hybridization and via intramolecular charge transfer. In D-A systems, to a certain degree, HOMO and LUMO energy levels can be individually tuned because LUMO is predominantly located on the acceptor unit whereas HOMO is spread on the donor unit. A simplified molecular orbital interaction diagram for narrowed optical band gap of D–A units is shown in Figure 1.7b.

Figure 1.7. (a) The aromatic and quinoidal forms of poly (isothianaphthene) (b) Simplified molecular orbital hybridization and resulting band gap reduction in D–A conjugate systems.
1.8.2 Side chains

In general, the most direct influence side chains have on conjugated polymers and small molecules is on their solubility characteristics. The side chains render solution processability, which is the key feature for future low-cost mass production of these flexible solar cells. Beyond imparting the solubility to conjugated molecules, side chains can have pronounced impact on material energy levels, charge transport, and active layer morphology.\textsuperscript{45, 46} The type, position, shape (linear or branched) and length of side chain affects the inter- and intramolecular interactions of the conjugate donor, as well as their miscibility with PCBM, thus playing a large role in determining the domain size.

In literature, various kinds of side chains such as alkyl, hybrid (alkoxy, alkylthio, alkylamine or amide acetate), oligoether and fluoroalkyl are explored for the conjugated systems.\textsuperscript{18, 39} Tuning the side chain positions alters the properties of the conjugated polymer or small molecules, however, the positions available for side chains are often limited by the conjugated backbones. In contrast, shape and length offer much versatility. Several investigations have studied the impact of side-chain shape and length and attempted to correlate them with material properties and device performances. In general, larger and branched side chains improve the solubility of polymers or small molecules in common organic solvents, by disturbing \( \pi \)-stacking. However, oversized insulating side chains will introduce too much steric hindrance that may even disturb the conjugation of the backbone and increase the intermolecular \( \pi \) distance, which could thwart the light absorption and charge transport, thus adversely affecting the solar cell properties. Therefore, a delicate balance must be reached.

1.8.3 Substituents

In addition to side-chain modification, substitution of atoms or small groups are generally used as fine-tuning methods to tweak the electronic properties (energy levels, band gap, mobility, dipole moment, etc.) of polymers or small molecules. For examples, fluorine atom can lower both the HOMO and the LUMO energy levels without introducing much steric hindrance.\textsuperscript{18, 39} Additionally, it affects the molecular dipole of the conjugated backbone and promotes noncovalent, intrachain F\( \cdots \)S, F\( \cdots \)H and F\( \cdots \)F interactions to
improve polymer crystallinity. Contrarily, when an \( \pi \)-electron donating substituent (such as alkoxy) is introduced, HOMO level of the material raised, often accompanied by the reduction in the bandgap.

Finally, this brief overview of molecular design illustrates that synergistic balance is required between all the contributing structural features of conjugate systems in order to realise ideal electron donor or acceptors for the organic solar cells.

1.9 Phenothiazine as a building block in OSCs

Since the inception of organic photovoltaics, numerous polymers and small molecules were reported based on various building blocks of electron donating or withdrawing nature, as detailed in the earlier sections. The majority of them share a common feature of possessing a rigid coplanar structure. Such a feature is deemed to enhance electron delocalization and promote cofacial \( \pi \)-\( \pi \) stacking in the solid state, thus benefiting charge transport in the devices. However, it is often accompanied by excessive aggregation and higher order crystallinity, leading to reduced solubility in the processing solvents and adversely effecting charge mobility, eventually resulting in inferior photovoltaic performance.\(^{47, 48}\) This problem can be circumvented by rational design of non-planar building blocks which can introduce judicious conformational twist and reduce the coplanarity of the conjugated backbone. Furthermore, it is expected that a non-planar unit can induce desired aggregation, solution-processability, and film-morphology which are critical for high-performing OSCs.

Phenothiazine (PTZ) is a well-known non-planar heterocyclic electron-rich moiety which contains nitrogen and sulphur.\(^{49}\) The phenylene rings of PTZ are folded along the S···N vector, having the aspect angle of 21° as shown in Figure 1.8. Phenothiazine is exploited as a building block in organic light-emitting diodes, organic thin-film transistors and dye-sensitized solar cells owing to their ability to suppress molecular aggregation due to the butterfly conformation together with good electrochemical and thermal properties, easy tunability, low price and commercial availability.\(^{49}\) However, it has not been fully explored as a building block for OSCs probably due to its non-planar geometry and low hole bulk mobilities.\(^{50}\)
Phenothiazine is typically prepared by the reaction of diphenylamine and sulfur. The PTZ core and its atom numbering are shown in Figure 1.8. Phenothiazine can be functionalized with a variety of substituents at positions N-10, C-2, C-3, C-7 and C-8 to tune its photo-physical and electrochemical properties. The decoration of the N-10 position with alkyl, oligo, aryl or aralkyl renders them solution-processable properties. Position C-3 and C-7 are the most commonly substituted ones which carry the large potential to attach different electron-donating or -withdrawing blocks for affording promising organic semiconductors. Reactions at C-3 and C-7 are typically electrophilic substitution such as formylation and bromination. Mono- or dibromination of PTZ at these positions generates the aryl bromides which in turn participate in palladium-catalyzed (Stille or Suzuki) coupling reactions with aryl-tin or aryl-boron reagents. Furthermore, aromatic S-heterocycles with various sulfur oxidation states (such as sulfide, sulfoxide, and sulfone) could be easily achieved through reduction and oxidation reactions.

Figure 1.8. Chemical structure of phenothiazine and top and side view of DFT optimized geometry structure.
1.9.1 Literature survey

In 2001, Jenekhe et al. first introduced PTZ units in the design of photovoltaic polymers.\textsuperscript{51} They reported the photophysical properties of donor-acceptor type phenothiazine-quinoline copolymers and corresponding oligomers with preliminary photovoltaic results, suggesting the possible use of PTZ for conjugated photovoltaic polymers. Later, in 2006, Shim and coworkers reported the first successful bulk heterojunction photovoltaic devices based on a series of copolymers comprising cyanovinylene-functionalized-phenothiazine and fluorine moieties.\textsuperscript{52} These photovoltaic devices showed PCEs up to 0.53%. Two series of soluble regioregular and regiorandom alternating conjugated copolymers consisting of 10-alkylphenothiazine and bithiophene or 3-pentylthieno[3,2-b]thiophene moieties were synthesized and applied as donors in blend with PC\textsubscript{61}BM for polymer solar cells by Tang et al.\textsuperscript{53} Although open-circuit voltages of up to 0.8 V have been obtained PCEs were poor with maximum being 0.24%. They attributed the poor device performance to the lack of effective absorption of polymers in the near-infrared to red region of the solar spectrum. Further, Lin and Chu’s groups reported narrow-band-gap conjugated copolymers containing arylcyanovinyl-modified-phenothiazine and fluorene.\textsuperscript{54, 55} These polymers showed strong absorptions in the range of 300–800 nm due to the donor-acceptor character of monomers, but only modest PCEs of up to 1.85% were achieved. Besides this, the Lin group also presented a family of soluble donor-acceptor conjugated polymers comprising of the phenothiazine donor and various benzodiazole acceptors units which demonstrated broad absorption in the region of 300–750 nm with optical bandgaps of 1.80–1.93 eV.\textsuperscript{56} The maximum PCEs of 1.20% were obtained with PC\textsubscript{71}BM as an electron acceptor in polymer solar cells. Li and coworkers fabricated all-polymer solar cells based on a polymer blend of poly(3-(10-n-octyl-3-phenothiazine-vinylene)thiophene-co-2,5-thiophene) as donor and poly(1,4-dioctyloxyl-p-2,5-dicyanophenylenevinylene) as acceptor. They observed strong photoluminescence quenching in the polymer blend indicating photoinduced charge transfer between the two polymers. Improvement in the PCEs of photovoltaic devices from 0.41% to 0.8% was observed after thermal annealing of the blend film.\textsuperscript{57} In addition, only a few other copolymers based on phenothiazine have been published for organic photovoltaics with
relatively low efficiencies with the maximum being 1%.\textsuperscript{58,59} In 2012, Kim et al. investigated the effect of insertion of S,S-dioxides into the polymer backbone on optical, electrochemical and photovoltaic characteristics.\textsuperscript{60} They designed two D–A type polymers based on either PTZ or its oxidized analogue phenothiazine and electron-deficient benzothiadiazole. Both polymers showed significant differences in optoelectronic properties. In a conventional architecture, the polymer-based PTZ displayed the superior PCE of 1.69%, while the utilization of its oxidized form showed better performance in inverted solar cells, with a PCE of 1.22%.

Interestingly, phenothiazine-based small molecules have shown better photovoltaic performances in comparison with their counterparts. In 2014, Sun’s group for the first time reported PTZ derivatives as donor materials for the SM-OSCs.\textsuperscript{61} They designed two small molecules named PTZ1 and PTZ2 based on donor-$\pi$-acceptor (D-$\pi$-A) and A-$\pi$-D-$\pi$-A type frameworks with dicyanovinyl as the electron withdrawing end-group, respectively. The small molecule PTZ2 with A-$\pi$-D-$\pi$-A configuration showed a wider response to solar light and had the narrower band gap. Optimized devices based on PTZ2 showed a higher PCE (3.25%) with nearly double $J_{sc}$ (10.3 mA/cm$^2$) compared to that of PTZ1-based devices (1.85%). Later, Li et al. synthesized a D–A–D type small molecule with PTZ as the electron-donor and 5-(2,6-dimethyl-4H-pyran-4-ylidene)-1,3-diethyl-2-thioxo-dihydropyrimidine-4,6(1H,5H)-dione (PD) as the electron-donating unit, and the solution-processed BHJ-OSCs based showed poor PCE of 0.28%.\textsuperscript{62} Similarly, Maglione and coworkers designed and synthesized three low bandgap D–A–D type small molecules by direct heteroarylation.\textsuperscript{63} The PTZ moiety was connected to the electron deficient diketopyrrolopyrrole core unit via three different electron rich heteroarenes, (thiophene, thiazole and thienothiophene) and was used as donor material in blends with PC$_{71}$BM in a BHJ architecture. These devices exhibited rather low hole-mobilities and moderate PCEs of 0.7%, which the authors ascribe to the non-planar structure of the molecular systems. Recently, an A-D-A type small molecule with phenothiazine as the donor, BODIPY as the acceptor, and ethynyl as the bridge was reported by Liao et al.\textsuperscript{64} The small molecule displayed broad optical absorption (320-700nm) with high molar extinction coefficient. The solution-processed BHJ-OSCs exhibited reasonable PCE of 3.33% with a $J_{sc}$ of 9.76 mA/cm$^2$, a $V_{oc}$ of 0.63 V.
and an FF of 54.1% in the optimized conditions. Besides this, Weng et al. synthesized a family of small molecules based on A-D-A and A-D-D-A type frameworks with the PTZ core, where they investigated the correlation between different end groups and their photovoltaic performance in inverted OSCs.\textsuperscript{65} Besides this, the PTZ unit was also explored in donor-acceptor dyads for use as electron acceptors in BHJ-OSCs. In another study, Sharma et al. employed a carbazole–phenothiazine dyad as non-fullerene electron acceptor along with P3HT as a donor for SM-OSCs.\textsuperscript{66} The device efficiency was enhanced from 2.80% to 4.16% when a thin layer of TiO\textsubscript{2} was inserted between the active layer and the Al electrode. The authors attribute it to a more balanced charge transport which increases the charge collection efficiency. Mi et al. and Blanco et al. investigated phenothiazine–fullerene dyads for applications in organic solar cells and moderate PCEs of the range 1.3–3.5% were reported.\textsuperscript{67, 68}

\textbf{1.10 Use of the quantum chemistry calculations in the design of organic compounds for OSCs}

It is far from possible today to \textit{a priori} describe the light absorption capacity, the solid-state structure, rates of electron and hole transfer between molecular interfaces, and other properties of a molecular blend in a SC BHJ, by quantum mechanics (QM) calculations to accurately predict the voltage, electric current and PCE of the SC. Furthermore, it may never be possible to do that to such an accuracy that makes the QM computations a more important part than the trial-and-error testing steps of an OSC device preparation. However, QM electronic structure methods can today give some guidelines in SC research, for example, give ideas for new organic compounds, which also seem to be possible to synthesize in few and cost-effective steps.

In this project, the energy levels of valence electrons, the absorption patterns (absorption spectra) of light in the visible region, and the energies for the excitons of organic compounds have been estimated with the use of QM methods. Hypothetical organic compounds have been devised from the assembly of smaller compounds (molecular groups, ‘building blocks’) in different combinations, and with some driving force from ‘chemical intuition’.

The dominant QM calculation method used has been a density functional theory (DFT) method.\textsuperscript{69, 70} The DFT has become a popular and important
method for calculation of various properties of chemical systems. In contrast to Hartree-Fock (HF) and related \textit{ab initio} methods which rely on the fundamental Hamiltonian and electron wave functions for calculation of molecular orbitals (MOs) and properties, DTF methods calculate the ground state energy and molecular properties from electron density functionals.

Electron correlation is an important part of the molecular energy and is not easy to handle by QM methods. In the HF method, electron repulsion (ER) between electrons with the same spin is treated in the calculations, but ER between an electron and other electrons is described by the repulsion to the average field from the other electrons. Extensions of the HF method (‘post-HF’ methods) take ER into account to various degrees but are increasingly computationally demanding. In the DFT method, which includes several different approaches, the correlation energy is calculated from a density functional, that is, a function of the electron density function for the molecular system. According to DFT, the energy of a system can be calculated from (solely) the electron density distribution. This leads to lower computational requirements for a DFT method. The DFT method uses AO and basis sets in the same way as the HF method, but the self-consistent MOs obtained are in principle not the same as for the HF method. Therefore, important energy levels as those for HOMO and LUMO can differ significantly from a HF and a DFT calculation with the same basis set.

A hybrid DFT method is a method that incorporates an approximate treatment of the Hartree–Fock exact exchange functional to improve the precision of the calculations. The most common hybrid functional for calculations of organic molecules appears to be the B3LYP functional,\textsuperscript{71} often using the 6-31G(d) basis set. The popularity of the B3LYP functional for organic compounds may be because of good agreement with experimental data on geometries. However, it can give less good agreement for properties such as excitation energies and especially those which have a considerable degree of charge-transfer character.\textsuperscript{72} A general disadvantage in comparison with HF methods may be that DFT is less tested against experimental data and that the practitioner, therefore, needs to find reported data for similar compounds or chemical systems for a comparison, to establish the reliability of a chosen DFT method.
Alternatively, some calibration calculations for similar systems with known experimental data should be performed with the selected DFT method and other DFT methods at higher levels of theory. As indicated above, a sometimes mentioned shortcoming of DFT (compared to HF theory) is that the eigenvalues (MO energies) have no physical meaning. However, it has been argued that the eigenvalue corresponding to the ionization potential (IP) and therefore HOMO, should be correct. A linear scaling as a possibility for more quantitative work has also been proposed.\textsuperscript{73}

B3LYP/6-31G(d) calculations were used in this work to estimate MO energies. For prediction of excitation energies (absorption wavelengths), the so-called time-dependent density functional theory (TD-DFT) has been applied.

1.11 Outline of the thesis

This thesis deals with the design and synthesis of phenothiazine-based conjugated systems and evaluation of their performances as donor material in small molecule organic solar cells.

Significant progress in the design and application of conjugated polymers or small molecules over the past years contributed immensely to the development of OSCs. The prevalent conjugated systems share a common feature of planar building blocks with a notion that planarity benefits to form compact configuration, long-range $\pi-\pi$ stacks, and improve the charge mobility in the OSC active layer. However, rigid molecular systems may often be accompanied by improper aggregation behaviour and poor solubility in device processing solvents, which eventually has an adverse effect on the photovoltaic performance. Phenothiazine is a non-planar moiety with unusual “butterfly” type of geometry known to hinder the molecular aggregation and formation of intermolecular excimer. We envisioned that the small molecules with bent phenothiazine possess suitable nonplanarity characteristics and also interact with fullerene derivatives to form suitable nanoscale morphologies. Accordingly, small molecules based on the PTZ unit are designed and applied as electron donors in BHJ-OSCs. The thesis is divided into 5 chapters.
Chapter 2 presents an example of the utility of the cyano-arylenevinylene building block for the construction of donor small molecules along with an example of a BHJ-OSC application.

Chapter 3 explores the influence of varying terminal electron-acceptor groups on the physicochemical and photovoltaic properties in a symmetrical design configuration where the phenothiazine unit is used as π-linker.

Chapter 4 describes design, synthesis and study of optical and electrochemical properties of three asymmetric SMs based on the phenothiazine core and the terminal groups 3-ethylrhodanine, malononitrile and 1,3-indandione.

Chapter 5 focuses on the effect of replacing alkyl solubilizing groups of the phenothiazine core with short methoxyethoxy-ethyl chains on the basic optoelectronic and dielectric properties along with an evaluation of their photovoltaic results.
2 A donor-acceptor-donor small molecule with a high open circuit voltage

2.1 Background

As detailed in the introduction, an ideal donor component of the BHJ-OSC should satisfy certain electronic requirements (such as low band gap for high $J_{sc}$ and suitable energy levels for high $V_{oc}$) and morphological requirements. Over the years, chemists have synthesised several donor materials based on a variety of molecular moieties and structural frameworks in order to realise high efficient OSCs. Consequently, numerous examples of donor materials with decreased band gap and high $J_{sc}$ have been reported. However, donor molecules with a high $V_{oc}$, ideally exceeding 1 V, are comparatively few.

Arylenevinylene based semiconducting polymers and their cyano-substituted derivatives such as poly (cyanoterephthalylidene) (CN-PPV) have been studied extensively for optoelectronics, including the polymer solar cells. Introduction of electron-withdrawing cyano groups into the vinylene moiety of arylenevinylene was found not only to influence the frontier MO energy levels but also affect molecular packing through noncovalent interactions. In this chapter, the utility of cyano-arylenevinylene building block for the construction of donor small molecules is described along with an example of a BHJ-OSC application.

2.2 Design and synthesis

For D–A–D molecular design, we chose the cyano-substituted arylenevinylene derivative (2Z,2′Z)-2,2′-(2,5-bis(octyloxy)-1,4-phenylene)bis(3-(thiophen-2-yl)acrylonitrile), denoted as ZOPTAN, as the central electron accepting unit. This central A unit is chemically connected through its thiophenylene groups to two peripheral triphenylamine (TPA) groups, which act as the internal donor units, to give compound ZOPTAN-TPA, Figure 2.1. Incorporation of the CN group was anticipated to lower the HOMO, while the TPA capping groups were expected to provide efficient hole transport properties.
Figure 2.1. Structural formula of the ZOPTAN-TPA.

The synthetic strategy employed for the synthesis of this target small molecule is shown in Figure 2.2. Hydroquinone was used as starting material, which was alkylated with C₈H₁₇Br in the presence of KOH, and subsequently treated with in situ generated HBr and paraformaldehyde, to give the benzyl bromide derivative 2. Compound 2 was treated with sodium cyanide to obtain 3. Bromination of 4 by N-bromosuccinimide (NBS) afforded 5 which was then reacted with 3 in the presence of catalytic amount of potassium tert-butoxide in methanol to generate precursor ZOPTAN-Br. Bromination of 6 by NBS resulted in 7 which was transformed into the corresponding boronic acid (TPA-B(OH)₂) via lithiation and subsequent quenching with trimethyl borate. Precursors ZOPTAN-Br and TPA-B(OH)₂ were reacted under palladium-mediated Suzuki coupling reaction conditions to prepare the target small molecule ZOPTAN-TPA.
2.3 Material characterization

2.3.1 DFT modelling

Quantum chemical calculations were performed prior to the synthesis of the small molecule to shed light on its HOMO and LUMO energy levels and spatial distributions, as well as the geometry of the ground state. Geometry optimizations were done with the use of the density functional theory (DFT) B3LYP hybrid exchange-correlation functional and the 6-31G(d) basis set. The conformation of lowest energy found by the DFT geometry optimizations has the arrangement of methoxy, nitrile and thiophenylene groups as shown by the ZOPTAN-TPA structure in Figure 2.1. The excitation energy was computed at the CAM-B3LYP/6-31+G(d) level of theory for the conformer of ZOPTAN-TPA.
lowest energy as found by the B3LYP/6-31G(d) geometry optimizations. The calculations showed a singlet transition with $E_{\text{exc}} = 2.7$ eV (452 nm) and the oscillator strength ($f$) of 3.2, described mainly by a HOMO→LUMO transition. For wavelengths above 300 nm, two additional weaker excitations were found, with energies of 3.7 and 4.1 eV, and $f = 0.13$ for both.

The geometry-optimized structure of ZOPTAN-TPA molecule features a large degree of planarity in the ground state, as anticipated for a highly conjugated system. The location of the LUMO (**Figure 2.3a**) on the central ZOPTAN core is in accordance with the expected internal acceptor capability of this unit. A relatively even distribution of HOMO (**Figure 2.3b**) over the conjugated system was observed, suggesting that the hole density will be evenly distributed in both the electronically excited molecule and for the charge-separated hole carrier. The DFT-calculated HOMO and LUMO energy levels and energy gap are given in **Table 2.1**.

### 2.3.2 Optical and electrochemical properties

The optical absorption spectra of a ZOPTAN-TPA in dilute chloroform solution and thin film cast from the chloroform solution are shown in **Figure 2.3c**. The solution spectrum features two broad absorption bands, with peak
wavelengths at $\lambda_{\text{minor}} = 305$ nm and $\lambda_{\text{major}} = 434$ nm. The band at shorter wavelength is assigned to the $\pi-\pi^*$ transition of the conjugated backbone while the other is assigned to the ICT between the donor and acceptor units. The film displays a broader absorption envelope, and a relative increase in magnitude as well as a pronounced red shift of the major absorption peak to $\lambda_{\text{major}} = 492$ nm. The redshifting of ICT bands are generally attributed to the enhanced $\pi-\pi$ stacking interactions and some ordered structure in the solid state.\(^{80}\)

The HOMO and LUMO energy levels of ZOPTAN-TPA were established with cyclic voltammetry (CV) and are compiled in Table 2.1. The LUMO offset between the ZOPTAN-TPA and PC\textsubscript{61}BM acceptor is ca. 0.7 eV, which is larger than the exciton binding energy, suggesting favourable exciton dissociation at the D/A. Further, the difference between the HOMO of the small molecule and LUMO of the PC\textsubscript{61}BM acceptor is noticeably large, ca. 1.5 eV, from which we anticipated the opportunity for a high open circuit voltage for this small molecule.

<table>
<thead>
<tr>
<th>Compound</th>
<th>CV (eV)</th>
<th>DFT (eV)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HOMO</td>
<td>LUMO</td>
<td>HOMO</td>
</tr>
<tr>
<td>ZOPTAN-TPA</td>
<td>5.2</td>
<td>3.0</td>
<td>4.8</td>
</tr>
</tbody>
</table>

ZOPTAN-TPA was thermally characterized with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA showed that the material is stable up to 410° C, whereas DSC revealed that small molecule can crystallize and that its melting point is 145° C. Such thermal characteristics can be considered as sufficient for a solar cell.

### 2.3.3 Photovoltaic properties

The BHJ-OSCs were fabricated with an ITO/PEDOT:PSS anode and an Al cathode sandwiching a PCBM:ZOPTAN-TPA active layer. In order to establish
the appropriate processing conditions for our OSC devices, we have therefore studied the effects of thermal annealing on device performance.

For this study, a PCBM:ZOPTAN-TPA mass ratio of 2:1 and a film thickness of 130 nm were selected. It was found that whereas the FF and the $V_{oc}$ are relatively unaffected by the thermal annealing process, the $J_{sc}$, and thereby the PCE, suffered severely. Following one minute of annealing at 70 °C under the inert N$_2$ atmosphere, the $J_{sc}$ and PCE dropped by 15 % and 19 %, respectively, while a 1 min heat treatment at 90 °C resulted in drops of 26 % and 33 %. AFM studies revealed that with annealing, sharp protruding features appeared in blend film, which increased in size and density with increase of both temperature and annealing time. We attributed them to ZOPTAN-TPA crystals based on i) DCS measurement which indicated that ZOPTAN-TPA is prone to crystallization and ii) X-ray diffraction (XRD) data which revealed distinctive signs of crystallinity in both an annealed ZOPTAN-TPA powder and an annealed spin-cast ZOPTAN-TPA thin film, whereas the ZOPTAN-TPA thin film before annealing appears amorphous (see the paper I SI). AFM micrographs of the same type of PCBM: blend film directly after spin-coating and after a 5 min thermal annealing at 90 °C under N$_2$ atmosphere are shown in Figure 2.4.
Further, the donor to acceptor weight ratio was optimized by varying PCBM:ZOPTAN-TPA mass ratio between 1:2, 1:1, 2:1 and 4:1. The photovoltaic characteristics of non-annealed BHJ devices with different mass ratios are depicted in Table 2.2. In line with our anticipation, a high $V_{oc}$ for all four mass ratios were indeed recorded, with the trend being an increase in $V_{oc}$ with increasing concentration of ZOPTAN-TPA up to a 1:1 mass ratio, for which the highest average value of $V_{oc} = 1.01$ V was measured. Interestingly, the opposite trend for the $J_{sc}$ was found. With decreasing ZOPTAN-TPA concentration, the $J_{sc}$ increases up to a peak value of 3.87 mA/cm² at a PCBM:ZOPTAN-TPA mass ratio of 2:1. The FF is relatively modest for all investigated devices, and its maximum of 32 % was recorded for a mass ratio of 1:1.

Figure 2.4. The relative change in (a) the short-circuit current density and (b) the power conversion efficiency as a function of annealing time at 70 °C (red squares, solid lines) and at 90 °C (blue diamonds, dotted lines). 3×3 µm² AFM micrographs of (c) a pristine and (d) a thermally annealed PCBM:ZOPTAN-TPA (mass ratio = 2:1) blend film. The thermal annealing was executed for 5 min under inert atmosphere.
Table 2.2. Performance metrics of PCBM:ZOPTAN-TPA films as a function of composition.

<table>
<thead>
<tr>
<th>Ratio</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:2</td>
<td>0.99 (±0.03)</td>
<td>1.12 (±0.32)</td>
<td>23 (±0.5)</td>
<td>0.26 (±0.08)</td>
</tr>
<tr>
<td>1:1</td>
<td>1.01 (±0.01)</td>
<td>2.94 (±0.15)</td>
<td>32 (±0.6)</td>
<td>0.94 (±0.07)</td>
</tr>
<tr>
<td>2:1</td>
<td>0.92 (±0.02)</td>
<td>3.87 (±0.54)</td>
<td>30 (±0.5)</td>
<td>1.07 (±0.11)</td>
</tr>
<tr>
<td>4:1</td>
<td>0.86 (±0.01)</td>
<td>3.76 (±0.62)</td>
<td>29 (±0.7)</td>
<td>0.92 (±0.13)</td>
</tr>
</tbody>
</table>

In order to investigate whether the poor FF is due to a non-balanced transport of holes and electrons to their respective charge-collecting electrode, the electron and hole mobilities were measured using a field-effect transistor setup. We find that the electron mobility consistently is 3 orders of magnitude larger than the hole mobility in the blend film used as the active material in solar cells. It is therefore probable that an improvement in the hole mobility of ZOPTAN-TPA will result in an improved FF. We note that the hole mobility increases after annealing, but that this improvement is due to ZOPTAN-TPA phase crystallization, as deduced from the XRD and DSC data, which unfortunately has a negative impact on the charge-separation efficiency.

From the IPCE measurements, we find that the three PCBM-rich samples exhibit similar efficiency over the entire visible wavelength range, with the EQE being >30% in the wavelength regime of 450-530 nm, i.e. in the range where the ZOPTAN-TPA molecule exhibits the highest absorption (see Figure 2.3c). This supports the notion that the photons are primarily absorbed on the ZOPTAN-TPA donor on the merit of its higher absorption coefficient in the visible regime, as shown in Figure 2.4. The PCBM-poor device with a PCBM:ZOPTAN-TPA mass ratio of 1:2 features a notably lower EQE value over the entire wavelength range, which implies that a too low PCBM loading is concomitant with a poor charge-separation and/or charge-transport process.
We wish to emphasize that the data in Table 2.2 represent the average values (and standard deviations) derived from characterization of 14 independent devices, and that it is common that the performance of BHJ-OSC can vary significantly between different devices. In Figure 2.5b we have therefore chosen to include data from our “champion” device, being a non-annealed ITO/PEDOT-PSS/PCBM:ZOPTAN-TPA/Al solar cell, with a PCBM:ZOPTAN-TPA mass ratio of 2:1. The champion device featured the following performance parameters: \( J_{sc} = 6.01 \text{ mA/cm}^2 \), \( V_{oc} = 0.98 \text{ V} \), \( FF = 32 \% \), and \( PCE = 1.86 \% \).

Additionally, during the course of the project, we have also synthesized and characterized other D-A-D small-molecule donor compounds with a similar base structure as ZOPTAN-TPA. The second best solar-cell performance was obtained by replacing the thiophene group on the central donor unit with a furan group for the synthesis of 2-(4--2,5-bis-octyloxy-phenyl)-3-[5-(4-diphenylamino-phenyl)-furan-2-yl]-acrylonitrile (ZOPFAN-TPA; for chemical structure, see paper 1 SI). BHJ-OSCs based on an optimized PCBM:ZOPFAN-TPA mass ratio of 3:1 delivered the following average performance: \( J_{sc} = 2.64 \text{ mA/cm}^2 \), \( V_{oc} = 0.66 \text{ V} \), \( FF = 30 \% \), and \( PCE = 0.51 \% \).
2.4 Summary

- A donor-acceptor-donor small molecule denoted ZOPTAN-TPA, with a cyano-arylenevinylene as the electron-withdrawing unit, was designed and synthesized for use as the donor material in organic solar cells.

- The Small molecule exhibited a high open-circuit voltage of 1.0 V due to the low-lying HOMO level.

- The tendency of ZOPTAN-TPA to crystallize with temperature and time hinders the attainment of an optimal phase morphology required for the achievement of a higher efficiency.
3 Investigation of phenothiazine derivatives with different end groups

3.1 Background

Generally, π-conjugated small molecules exhibit a stronger tendency to self-assemble and to form large crystalline aggregates in comparison to conjugate polymers. The small molecule ZOPTAN-TPA presented in chapter 2 is such an example whose aggregate size was much larger than the exciton diffusion length which resulted in poor film morphology and low PCEs. This challenge can be addressed to a certain extent by disrupting π-π stacking through the incorporation of bulky side chains on the conjugated backbone and/or changing the thin film processing conditions. Another viable option can be incorporating a nonplanar moiety in the conjugate backbone which can suppress excessive aggregation behaviour, thereby offering good solubility, favourable domain sizes and optimal mixing with electron acceptors. Certainly, this strategy has to be in conjunction with the judiciously designed conjugated backbone to achieve the desired light absorption, solution processability and film-morphology for obtaining efficient small-molecules for OSCs.

In this study, we employed phenothiazine as a non-planar building block for constructing small molecules whose unusual “butterfly” type of geometry is known to hinder the molecular aggregation and intermolecular excimer formation. End-group engineering of small molecules is deemed as a useful strategy to tune material properties and understand the molecular structure–material property–device performance relationships. The electron withdrawing malononitrile (MN) and 1,3-indandione (IND) dyes were chosen based on previously reported studies to investigate the influence of subtle variations on the absorption of light, red-ox levels, morphology and photovoltaic performance of two small molecules containing the PTZ unit, and find additional design guidelines for high performance organic solar cells.
### 3.2 Design and synthesis

An A-π-D-π-A molecular framework was chosen, with the planar benzodithiophene (BDT) unit as the central building block, connected to terminal acceptors via PTZ linker units. We anticipated that the bent geometry of the small molecules could make the acceptor units spatially accessible for interactions with the fullerene derivatives. The BDT-PTZ core was decorated with alkyl chains to ensure solubility in organic solvents, making them suitable for solution processing. The small molecules with malononitrile and 1,3-indandione end groups are named as SM1 and SM2 respectively, and their structures are shown in Figure 3.1.

![Figure 3.1. Structural formulas of SM1 and SM2.](image)

The synthetic strategy employed for the synthesis of intermediates and target small molecules are shown in Figure 3.2. Phenothiazine was used as starting material, which was alkylated with ethylhexylbromide in the presence of NaH and then formylated via the Vilsmeyer-Haack reaction, to generate intermediate 2. The bromination of 2 with NBS resulted in compound 3. Subsequently, 3 reacted with 4 under palladium-mediated Stille coupling reaction conditions to prepare intermediate compound 5. Finally, Knoevenagel condensation of 5 and malononitrile or 1,3-indandione resulted in the target molecules SM1 and SM2, respectively.
3.3 Material characterization

3.3.1 DFT modelling

The B3LYP/6-31G(d,p) geometry optimizations from various start conformations of SM1 and SM2 resulted in lowest-energy structures of both compounds with the planar BDT group and the expected bent shape of the PTZ groups as shown in Figure 3.3. For both compounds, the HOMO mainly belongs to the PTZ-BDT-PTZ \( \pi \)-electron system, while the LUMO is localized at the \( \pi \)-system of the acceptor groups. For SM1, the DFT HOMO and LUMO energies are \(-5.38\) and \(-2.79\) eV, respectively, while SM2 has the corresponding MO energy values of \(-5.08\) and \(-2.49\) eV. Hence, the DFT
HOMO energy for both SM1 and SM2 appears to be low enough for a high open circuit voltage to be foreseen, as discussed in the photovoltaic properties section below. The TD-DFT calculations resulted in three excitation wavelengths ($\lambda_{\text{exc}}$) above 400 nm with oscillator strength ($f$) above 0.1, for both compounds.

Figure 3.3. B3LYP/6-31G(d,p)-calculated structures of compounds SM1 (a-d) and SM2 (e-f). From upper to lower panels: top and side views, isodensity LUMO and HOMO surfaces.

The difference between ground state dipole moments ($\mu_{gs}$) and the excited state dipole moments ($\mu_{es}$) were found to be small for SM1 (5.3 and 9.2 D) and zero for SM2 due to symmetric nature of the small molecules. The connections between molecular dipole moment and degree of self-association have been treated in many contexts in the chemical literature, including organic dyes for photovoltaic purposes.88, 89, 90 Because of the zero or small values of $\mu_{gs}$, and some variation in $\mu_{gs}$ between the two conformations of lowest energy for SM1 and SM2, analysis of $\mu_g$ for a possible correlation with aggregation was not considered in this study. Another relationship, between the change of dipole moment from the ground state to excited state ($\Delta \mu_{ge}$) and both longer exciton lifetime and slower geminate electron-cation pair recombination, has been suggested in studies of polymer and SM BHJ-SCs.90, 91 Because of the signified electron redistributions in a HOMO-LUMO
excitation in the SM1 and SM2 type of structure (Figure 3.3), two sizeable, but counteracting, components of $\mu_{es}$ can be expected. To obtain an estimate of the magnitude of the counteracting components, $\Delta\mu_{ge}$ was calculated for the asymmetric model compounds M1 and M2 (Figure 3.4) using the B3LYP and PBE0 functionals, with and without a solvent reaction field applied by the PCM method in the Gaussian software. The calculations showed that the use of PBE0 instead of B3LYP, and an increased dielectric constant in PCM (from 0 to 5.6 to 10.4), resulted in decreased $\Delta\mu_{ge}$ values for both compounds. The largest difference $\Delta\mu_{ge}(\text{M1})-\Delta\mu_{ge}(\text{M2})$ was 30.7–25.7 D for B3LYP and in vacuo, while the smallest was 25.5–25.1 D for PBE0 and PCM($\varepsilon=10.4$). Since the larger $\Delta\mu_{ge}$ values were found for M1, it was not in agreement with the better photovoltaic data of SM2 in comparison with SM1, and did not motivate further analyses of $\Delta\mu_{ge}$ in this study.

![Figure 3.4](image)

**Figure 3.4.** Structural formulas and PBE0/6-31G(d,p)-calculated HOMO/LUMO isodensity surfaces of model compounds M1 (a-c) and M2 (d-f). Lower panels show the HOMO plots.
3.3.2 Optical and electrochemical properties

The UV-visible absorption spectra of SM1 and SM2 in dilute chloroform solution and their thin film cast from chloroform are shown in Figure 3.5a. In solution, both small molecules showed two dominant absorption bands, centered at 338 nm and 506 nm for SM1, and at 354 nm and 530 nm for SM2. Similar to that of ZOPTAN-TPA (chapter 2), the band at shorter wavelength was assigned to the π-π* transition of the conjugated backbone while the other was assigned to the ICT between the donor and acceptor units. The observed bathochromic shifting of the ICT band for SM2 compared to that of SM1 may be attributed to the stronger electron withdrawing ability of IND than of MN. Further, the absorption bands in the thin film spectra were significantly red-shifted and broadened along with the appearance of a vibrionic shoulder at longer wavelengths for both SM1 and SM2 indicating intermolecular π-π stacking in the solid state. Hence, the effect is more pronounced with the IND group than the SM2. This notion is supported by the XRD studies (see paper II) where neat films of SM2 exhibit more intense diffraction peaks than neat films of SM1. The observed stronger lamellar peak and lower value of a π-π stacking distance in SM2 may lead to higher hole mobility than in SM1, which is expected to result in higher J_sc and FF in the resulting SM2 OSCs.
The HOMO and LUMO energy levels of the molecules estimated using cyclic voltammetry and optical data are -5.32/-3.16 eV for SM1 and -5.28/-3.24 eV for SM2. The difference in the HOMO energy levels (0.04 eV lower for SM1) is very small which can be expected since the compounds have the same electron-donating backbone. Contrarily, the LUMO level of SM2 is positioned 0.08 eV below that of SM1 suggesting a greater electron accepting ability of the IND end group.

Figure 3.5. (a) Normalized absorption spectra of SM1 and SM2 in dilute chloroform solution and thin films cast from chloroform solvent. Black – SM1 solution, red – SM2 solution, blue – SM1 film, green – SM2 film. (b) Normalized absorption spectra of SM1:PC71BM and SM2:PC71BM blend thin films processed under different conditions.
3.3.3 Photovoltaic properties

BHJ-OSCs were fabricated using SM1 and SM2 as electron donor materials along with PC$_7$BM as electron acceptor with a device structure glass/ITO/PEDOT:PSS/donor:acceptor/PFN/Al. The current-voltage (J-V) characteristics of the OSCs based on the optimized weight ratio (1:2) for SM1:PC$_7$BM and SM2:PC$_7$BM active layers as-cast from chloroform are shown in Figure 3.6, and the photovoltaic parameters are summarized in Table 3.1. Modest PCEs were obtained for both small molecules with 2.18% for SM1 and 2.73% for SM2. As envisioned by DFT calculations quite high $V_{oc}$ was obtained for SM1 and SM2 due to the presence of deep HOMO energy levels. The higher $J_{sc}$ for SM2 was most likely due to the broader absorption characteristics in the visible region and the same was confirmed from the IPCE spectra of the devices.

The poor PCEs found for as-cast small molecules were attributed to un-optimized nano-scale morphologies. Solvent vapour annealing (SVA) was then used to improve the morphology of the active layer.94, 95
After the SVA treatment of the blend films, the resultant OSCs showed significant enhancement in overall PCE, i.e. 6.20 % ($J_{sc} = 11.18 \text{ mA/cm}^2$, $V_{oc} = 0.99 \text{ V}$ and FF = 0.56) and 7.45 % ($J_{sc} = 12.06 \text{ mA/cm}^2$, $V_{oc} = 1.04 \text{ V}$ and FF = 0.60), for SM1 and SM2, respectively. Despite the slight drop in $V_{oc}$, the values of both $J_{sc}$ and FF were significantly increased, leading to the higher PCEs. The enhancement in $J_{sc}$ and FF may be attributed to the fact that during

**Figure 3.6.** (a) J-V characteristics under illumination and (b) IPCE spectra of the devices based on active layer processed with and SVA treatment using SM1 or SM2 as donor and PC$_{71}$BM as acceptor.
SVA, the solvent molecules inside the BHJ film can promote the crystallization and aggregation of donor materials.\textsuperscript{96, 97}

The $J_{sc}$ of the OSCs is mainly related to the absorption property of the active layers and charge transport within the active layers, and therefore, to get further information about the differences of photovoltaic performance for these two small molecules and processing conditions, the absorption and charge transport properties were investigated.

The absorption spectra of blend films cast from chloroform and SVA treated (\textbf{Figure 3.5b}) revealed that the absorption bands of SVA treated films were bathochromically shifted and showed a pronounced shoulder peak in comparison to as-cast films, conforming the obtained high $J_{sc}$ values. The performance of the above devices was also supported by the results of the IPCE measurements (\textbf{Figure 3.6b}).

Further, the hole and electron mobilities of SM1 and SM2 were measured by the space-charge limited current (SCLC) method and are shown in Table 3.1. Enhancement of hole mobility was observed for SVA treated devices as compared to the as-cast devices. However, there is only a slight change in the electron mobility values, measured from dark J-V characteristics of an electron only device.

\textit{Table 3.1. Photovoltaic parameters of the OSCs based on SM1 and SM2 as donors and PC$_{71}$BM processed under different conditions.}

<table>
<thead>
<tr>
<th>Active layer</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>$\mu_h$ (cm$^2$/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SM1:PC$_{71}$BM (CF)</td>
<td>7.24</td>
<td>1.04</td>
<td>0.29</td>
<td>2.18</td>
<td>6.14 x 10$^{-5}$</td>
</tr>
<tr>
<td>SM2:PC$_{71}$BM (CF)</td>
<td>8.16</td>
<td>1.08</td>
<td>0.31</td>
<td>2.73</td>
<td>8.87 x 10$^{-5}$</td>
</tr>
<tr>
<td>SM1:PC$_{71}$BM SVA</td>
<td>11.18</td>
<td>0.99</td>
<td>0.56</td>
<td>6.20</td>
<td>9.89 x 10$^{-5}$</td>
</tr>
<tr>
<td>SM2:PC$_{71}$BM SVA</td>
<td>12.06</td>
<td>1.04</td>
<td>0.60</td>
<td>7.45</td>
<td>1.89 x 10$^{-4}$</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Average of 10 devices
The variation of $V_{oc}$ with illumination intensity ($P_{in}$) was used to illustrate the order of recombination processes in the BHJ active layer (see paper II). Although all the devices (as-cast and SVA treated) showed slopes greater than $kT/q$ indicating the presence of trap-assisted recombination, the smaller values for SVA treated devices suggested that the trap-assisted recombination was reduced after SVA treatment. Similarly, the variation of $J_{sc}$ with $P_{in}$ plots revealed that bimolecular recombination was effectively suppressed with SVA- treatment leading to the higher $J_{sc}$ and FF for the SM1 and SM2 devices.

Further, the $J_{ph}$-$V_{eff}$ plots (see paper II) show that photocurrent significantly improved with SVA treatment for both SM1 and SM2. The as-cast devices layers did not show any clear saturation in the $J_{ph}$ with increasing $V_{eff}$ whereas SVA-treated counterparts showed field independent saturation suggesting that photogenerated excitons are dissociated into free charge carriers and charge carriers are collected at the electrodes very efficiently, with little germinate or bimolecular recombination, resulting in enhanced FF.

The morphologies of as-cast and SVA-treated blend films of SM1 and SM2 were studied by transmission electron microscopy (TEM) and images are shown in Figure 3.7. In the images, the white and dark domains are assigned to SM-rich and PC71BM-rich regions respectively. As can be seen from the TEM images, as-cast films did not show any clear phase difference between the small molecule and PC71BM, which hinders the charge transport and results in low values of both $J_{sc}$ and FF. However, after SVA treatment, both blend films show larger domains (15-20 nm) and a clearer phase-separated interpenetrating network compared to as-cast blend films.
3.4 Summary

- Two A-π-D-π-A configured small molecules SM1 and SM2 with a BDT central donor core and π-conjugated bridge (phenothiazine), and different terminal acceptor units (MN and IND) were synthesized and employed as donors along with PC71BM as an acceptor for solution-processed BHJ OSCs.

- The electron-withdrawing property of the terminal acceptor units has a significant influence on the optical absorption properties, HOMO/LUMO energy levels, molecular ordering, charge carrier mobility and morphology of the resulting active layers.

- Enhancement of PCEs by solvent vapour annealing was attributed to the high hole mobility, and better-sized nanocrystal phases with interpenetrating network morphology.

*Figure 3.7. TEM images of (a) as-cast SM1: PC71BM, (b) SVA-treated SM1: PC71BM, (c) as-cast SM2: PC71BM and (d) SVA-treated SM2: PC71BM films.*
4 Asymmetric small molecules with varying terminal acceptor groups

4.1 Background

In chapter 3, the phenothiazine moiety of our interest has been introduced as a π-linker into an A−π−D−π−A framework for the design and synthesis of donor materials for BHJ-OSCs. The resulting small molecules exhibited desired physicochemical features along with respectable PCEs. Motivated by the results, the idea of using of the PTZ unit as a central building block has been conceived and for that, an asymmetric structural configuration D-D´-A was chosen based on the following considerations.

Asymmetric design frameworks such as D–A, A−D−A’, D−D´−A and D−A−A’ with pronounced dipolarity are interesting alternatives to the widely used symmetrical motifs (eg. A−D−A, D−A−D, etc.). However, these systems are relatively less explored and their photovoltaic performances are lagging behind those of SCs from symmetric SMs. For asymmetric molecules, the molecular dipole moment has been correlated to their orientation and assembly, and to materials morphology associated with photovoltaic parameters. A significant dipole moment might be expected to result in extensive self-assembly and formation of too large aggregates in relation to the exciton diffusion length (ca. 5-15 nm) in normal organic materials. However, it is hypothesized that excessive aggregation can be reduced by introducing appropriate side groups and/or bends in the main SM skeleton. Further, it was reported that the polar molecules can self-assemble in antiparallel structures which reduces the polar character of each dimer in a growing aggregate.

In this study, the asymmetric approach has been combined with the previously explored end-group engineering strategy to design a series small molecules with electron-withdrawing 3-ethylrhodanine (Rh), malononitrile (MN) and 1,3-indandione (IND) terminal groups. The effect of varying end groups of different electron accepting ability and polarity on molecular packing, absorption properties, electronic energy levels, carrier transport properties, and photovoltaic properties are discussed.
4.2 Design and synthesis

The D-D’-A molecular design comprised of a large conjugate donor backbone of triphenylamine (TPA) and PTZ moieties connected to a relatively small terminal electron acceptor for the facilitation of substantial electron redistribution from the donor to the acceptor upon photoexcitation. Further, it was envisaged that the ‘propeller’ structure of TPA and the bent shape of PTZ render a suitable nonplanarity to the SM, and by that probably reduce the risk of excessive aggregation and formation of too large SM domains in the active layer with PC_{71}BM. The choice of the 3-ethylrhodanine, malononitrile and 1,3-indandione groups were based on their known acceptor strength and common use for the same purpose in many other D-A compounds,$^{81,83,85,102}$ which could be beneficial for comparisons with similar OSC studies. The small molecules with Rh, MN and IND end groups are named as M1, M2, and M3 respectively, and their structures are shown in Figure 4.1.

![Figure 4.1. Structural formulas of M1, M2, and M3.](image)

The synthetic strategy employed for the synthesis of intermediates and target small molecules are shown in Figure 4.2. The synthetic details of intermediates 1, 2 and 3 were described in chapter 3. Compound 3 was reacted with 4 under palladium-mediated Suzuki coupling reaction conditions to prepare intermediate compound 5. Subsequently, Knoevenagel
condensation of 5 and 3-ethylrhodanine or malononitrile or 1,3-indandione resulted in M1, M2, and M3 respectively.

\[ \text{Figure 4.2. Synthetic route of M1, M2 and M3 small molecules, (i) ethylhexyl bromide, NaH, DMF, room temperature, (ii) POCl}_3, \text{DMF, DCE, 70°C, (iii) NBS, CHCl}_3, \text{room temperature, (iv) Pd(PPh}_3)_4, 2M K}_2\text{CO}_3, \text{THF/H}_2\text{O, 110°C, and (v) piperidine, CH}_3\text{CN, 85°C.} \]

4.3 Material characterization

4.3.1 DFT modelling

The B3LYP/6-31G(d,p) geometry optimization from various start conformations of M1-M3 exhibited a similar characteristic bent form of the PTZ unit. The nodal plane of the \( \pi \)-systems of the terminal electron-withdrawing groups are nearly coplanar with the adjacent benzenoid ring of the PTZ unit, while there is a dihedral angle of 35° between the other PTZ
benzenoid ring and the phenylene unit of the TPA group. For all three compounds, the HOMO is mainly distributed over the TPA-PTZ conjugated system, while the LUMO is spread over the terminal acceptor units and on the nearby ring atoms of the PTZ unit as shown in Figure 4.3. The TD-DFT calculations resulted in two excitations at wavelengths ($\lambda_{\text{exc}}$) above 400 nm and oscillator strengths ($f$) in the range of 0.14-0.28 for all three SM’s.

The calculated HOMO/LUMO energy levels of $M_1$, $M_2$ and $M_3$ are, in unit eV: $-4.97/-2.42$, $-5.08/-2.63$, and $-4.93/-2.39$, respectively. Although DFT calculations of this type can give results which differ substantially from experimental data, these energy levels did support the idea that the SMs would have both HOMO and LUMO energies suitable for blends with PC71BM.

![Figure 4.3. Top and side views, isodensity HOMO and LUMO surfaces of geometry optimized $M_1$, $M_2$ and $M_3$ small molecules.](image)

The reliable estimation and understanding of the electron-withdrawing strength of the acceptor in an SC perspective prior to the synthesis would be quite advantageous. A way to estimate the electron-withdrawing ability of the acceptor for the specific process of photoexcitation is to apply a method for calculation of the electron distribution in both the ground state and the excited states that are involved in the exciton formation.
In this study, the B3LYP/6-31G(d) Mulliken charges for the ground state and the first excited state (which corresponds to the HOMO-to-LUMO transition and a charge transfer (CT) absorption band) are utilized to get an estimate of the difference in electron-withdrawing strength of the acceptors in M1-M3. For this, the sum of the Mulliken charges for all atoms in the acceptor group, including the methine group that connects the TPA-PTZ unit to the acceptor are taken (Accordingly, the sum of the charges in the TPA-PTZ donor unit is the same as in the acceptor group but with a positive sign). The total charge obtained in this way for the acceptor group in M1, M2 and M3 in the ground state are -0.188, -0.261 and -0.232, respectively. The corresponding values for the vertically excited state are -0.540, -0.669 and -0.673. This resulted in the GS-to-excited-state charge differences of -0.325, -0.408 and -0.441 for the acceptor group in M1, M2 and M3, respectively. The increased electron density is thus 25% from M1 to M2 and 8% from M2 to M3, which suggested that indandione is the strongest electron acceptor in the sense that it accumulates more electron density than the other two upon photoexcitation, for further exciton development to free charge carriers, which may translate to better J_sc and FF.

4.3.2 Optical and electrochemical properties

The normalized optical absorption spectra of the small molecules (M1, M2, and M3) in dilute chloroform solution and thin film cast from the chloroform solution are shown in Figure 4.4a and 4.4b. In solution, all three small molecules showed two absorption bands: one located in the shorter wavelength region (300-400 nm) attributed to a $\pi-\pi^*$ transition, and one in the visible region (450-650 nm) assigned to the ICT from the TPA-PTZ conjugate backbone to the terminal acceptor unit in the SMs. The ICT band of M3 is significantly red-shifted relative to that of M1 and M2. For the thin films, the absorption bands of the compounds are red-shifted and significantly broadened towards the lower energies compared to the solution spectra. Although all three films showed a vibronic shoulder at a longer wavelength, the effect was more pronounced in M3 indicating a more ordered molecular packing and stronger crystalline properties for M3, presumably linked to the planar indandione $\pi$-system. This notion was well supported by the XRD
studies (Figure 4.6) where neat films of M3 exhibit more intense diffraction peaks than neat films of M1 and M2.

Figure 4.4. Normalized optical absorption spectra of M1, M2, and M3 in (a) dilute chloroform solution and (b) thin films cast from the solvent chloroform.

The HOMO and LUMO energy levels of the M1, M2 and M3 estimated using cyclic voltammetry and optical data are -5.21/-3.03 eV, -5.31/-3.16 eV, and -5.28/-3.26 eV respectively. On the whole, the HOMO/LUMO energy levels for these SMs match well with that for PC71BM for efficient exciton dissociation and charge transfer from donor to acceptor, and a high V_{oc} for M2 was expected by virtue of its deeper HOMO levels.

4.3.3 Photovoltaic properties

BHJ solar cells using these small molecules with PC71BM as acceptor were fabricated in chloroform as processing solvent. The J-V characteristics of the devices based on M1:PC71BM, M2:PC71BM and M3:PC71BM active layers without any treatment showed poor PCEs of range 1.90-3.03 % (Table 4.1). The order of PCE followed the trend M3 > M2 > M1, and it was obvious that the best performance of the M3 based device is due to higher values of J_{sc} and FF. As envisioned by DFT calculations, the device based on M2 exhibited high
V_{oc} in comparison with other two SMs owing to the presence of deeper HOMO energy levels.

The modest PCEs of as-cast films were attributed to the poor nanoscale morphologies. A novel two-step annealing process (TSA), i.e., thermal annealing followed by solvent vapour annealing was adopted to optimize the morphology of the active layer as reported in the literature.\textsuperscript{85,103-105} After the TSA, the M\textsubscript{1}, M\textsubscript{2} and M\textsubscript{3} based OSCs showed overall PCEs of 4.79 % \((J_{sc} = 9.88 \text{ mA/cm}^2, V_{oc} = 0.77 \text{ V}, \text{FF} = 0.63)\), 6.18 % \((J_{sc} = 10.68 \text{ mA/cm}^2, V_{oc} = 0.89 \text{ V}, \text{FF} = 0.65)\), and 7.25 % \((J_{sc} = 12.36 \text{ mA/cm}^2, V_{oc} = 0.85 \text{ V}, \text{FF} = 0.69)\), respectively. The J-V characteristics are shown in Figure 4.5a and corresponding PV characteristics are summarised in Table 4.1. Although the \(V_{oc}\) was slightly decreased, the \(J_{sc}\) and \(\text{FF}\) were significantly increased after TSA, which resulted in enhancement of PCEs for all three small molecules.

\begin{table}
\centering
\caption{Photovoltaic parameters of the OSCs based on optimized M\textsubscript{1}:PC\textsubscript{71}BM, M\textsubscript{2}:PC\textsubscript{71}BM and M\textsubscript{3}:PC\textsubscript{71}BM active layers.}
\begin{tabular}{cccc}
\hline
Donor & \(J_{sc}\) (mA/cm\(^2\)) & \(V_{oc}\) (V) & \(\text{FF}\) & PCE (%) \\
\hline
M\textsubscript{1} & 9.88 & 0.77 & 0.63 & 4.79 (4.67)\textsuperscript{a} \\
M\textsubscript{2} & 10.68 & 0.89 & 0.65 & 6.18 (6.07)\textsuperscript{a} \\
M\textsubscript{3} & 12.36 & 0.85 & 0.69 & 7.25 (7.14)\textsuperscript{a} \\
\hline
\end{tabular}
\end{table}

\textsuperscript{a}Average of 12 devices

The performance of the above devices was also supported by the results of the IPCE measurements as shown in Figure 4.5b. The IPCE values for the device based on M\textsubscript{3} are found to be higher through the entire wavelength region than those for the devices based on M\textsubscript{1} and M\textsubscript{2}, which also confirmed the higher values of \(J_{sc}\) for M\textsubscript{3} based devices.
The hole and electron mobility measurements of the three molecules based on the SCLC model demonstrated that both hole and electron mobilities are higher for the M3:PC71BM blend than for the other two, and the change in hole and electron mobilities in the order M1 to M2 to M3 agreed well with the corresponding trends in the variation in Jsc and FF of the OSCs (Table 4.2). Moreover, the ratio of electron to hole mobility was found to be in the order of M3 (2.14) < M2 (3.21) < M1 (5.09). Hence, the relatively high and more balanced charge transport in the OSCs based on M3 resulted in the higher Jsc, FF, and PCE in comparison with that of the other two counterparts.

Table 4.2. Hole and Electron mobilities for the optimized active layers.

<table>
<thead>
<tr>
<th>Active layer</th>
<th>Hole mobility (μh) (cm²/Vs)</th>
<th>Electron mobility (μe) (cm²/Vs)</th>
<th>μe/μh</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1:PC71BM</td>
<td>4.28x10⁻⁶</td>
<td>2.18x10⁻⁴</td>
<td>5.09</td>
</tr>
<tr>
<td>M2:PC71BM</td>
<td>7.16x10⁻⁵</td>
<td>2.29x10⁻⁴</td>
<td>3.21</td>
</tr>
<tr>
<td>M3:PC71BM</td>
<td>1.13x10⁻⁴</td>
<td>2.43x10⁻⁴</td>
<td>2.14</td>
</tr>
</tbody>
</table>

X-ray diffraction measurements were applied to explore the crystallinity and molecular ordering in the optimized active layers (Figure 4.6). All three active layers showed a strong (100) diffraction peak at 2θ = 5.12°
corresponding to the lamellar distance of 1.78 nm and a moderate (010) diffraction peak at $2 \theta = 23.18^\circ$ for $M_1$, 23.62 for $M_2$, and 23.85 for $M_3$, corresponding to the respective $\pi-\pi$ stacking distances of 0.383 nm, 0.376 nm and 0.372 nm, respectively. The observed stronger lamellar peak and lower value of a $\pi-\pi$ stacking distance in the $M_3$:PC71BM film indicated a more ordered structure and a higher degree of crystallinity than of the other two blend films. This also suggested that the indandione group in $M_3$ enables a denser molecular packing, which may induce a better nanoscale phase separation between donor and acceptor in the blend film and result in the higher $J_{sc}$ and FF for the $M_3$ device. In addition to the above mentioned peaks, a weak diffraction peak from the PC71BM was also observed.

![X-ray diffraction patterns](image)

**Figure 4.6.** X-ray diffraction patterns of the optimized $M_1$:PC$_{71}$BM, $M_2$:PC$_{71}$BM and $M_3$:PC$_{71}$BM films.

### 4.3.4 Dipole moments and electron charge distribution from DFT calculations

The dipole moments of SMs in gas phase and solvent reaction field (chloroform) were obtained from the B3LYP/6-31G(d) geometry optimizations to study the influence of dipole moment on the molecular self-assembly and aggregation. In gas phase and solvent reaction field, the
acquired dipole moments for \textbf{M1}, \textbf{M2} and \textbf{M3} are 6.0, 10.2 and 3.7 D and 7.2, 11.7 and 4.5 D, respectively. A linear correlation between the magnitude of the dipole moment and crystallinity was not observed as reported by Huang \textit{et al.} and others.\textsuperscript{98, 106} Nevertheless, dipole moment seemed to have an effect on molecular orientation and self-assembly. From the XRD results it was evident that the quality of the SM:PC\textsubscript{7}BM layer decreased in the order \textbf{M3} > \textbf{M2} > \textbf{M1}, which was rationalized by a more favourable \(\pi\)-\(\pi\)-stacking for \textbf{M3} than for \textbf{M1}. With the inputs from XRD data and optimized geometries, we proposed the \(\pi\)-\(\pi\) stacking model for \textbf{M1-M3} SMs with the antiparallel alignment of the individual molecules as shown in Figure 4.7 (\textbf{M1} and \textbf{M3} are shown for the representation).

\textbf{Figure 4.7.} Proposed \(\pi\)-\(\pi\)-stacking with antiparallel alignment of the individual molecules; (a) \textbf{M1}, where the N-ethyl group inhibits a tight stacking due to steric hindrance. (b) \textbf{M3}, where a steric hindrance such as that of \textbf{M1} does not exist.
The high-performing \textbf{M3} appears to better align in the anti-parallel fashion with tight $\pi$-$\pi$ stacking over the long range due to the larger planar $\pi$-system of its acceptor group, while a similar anti-parallel alignment for \textbf{M1} may be less favoured because of a steric hindrance due to the out-of-plane atoms (CH$_3$) of the N-ethyl group. This hypothesis is in accordance with the observed distinct vibronic shoulder in the absorption spectrum of the film, the strong XRD diffraction peaks, the shorter $\pi$-$\pi$ stacking distance of 3.72 Å and also the better FF values for \textbf{M3} in comparison with \textbf{M1}. We presumed that the close $\pi$-$\pi$ -stacking renders microstructural order and a higher degree of crystallinity to \textbf{M3}, which result in the better charge transporting abilities. In addition to the contributions from local electrostatic forces (dipole-dipole), molecular packing and resulting aggregation of small molecules seem to be influenced by the structural features of terminal acceptor units.

\subsection{4.4 Summary}

- Three asymmetric SMs, \textbf{M1}, \textbf{M2}, and \textbf{M3} based on the same triphenylamine-phenothiazine conjugate backbone end capped with different acceptors (Rh, MN, IND) have been designed, synthesized, and characterized as electron donor materials in BHJ-OSCs.

- Compound \textbf{M3} exhibited high PCE due to the broader absorption, shorter $\pi$-$\pi$ stacking distance, balanced charge-carrier mobilities and better FF.

- The dipole moment of the small molecules was found to increase in the order $\textbf{M3} < \textbf{M1} < \textbf{M2}$ whereas PCEs increased as $\textbf{M1} < \textbf{M2} < \textbf{M3}$. Though there is no obvious correlation with PCE, the dipole moment seems to influence the formation of self-assembled dimers or similar aggregates.

- The electron— withdrawing and packing behaviour of varied end groups affected electronic and photovoltaic characteristics of SMs.
5 Side chain engineering of phenothiazine derivatives

5.1 Background

Solution processability of conjugate semiconductors is vital for the realization of flexible, light-weight and low-cost OSCs. To accomplish desired solubility characteristics in organic solvents, side chains are commonly introduced on to the conjugated backbone of polymers or small molecules. However, beyond this relatively straightforward influence, they have also been found to play a key role for backbone orientation in molecular packing, and for miscibility with the fullerene acceptors, in BHJ blend films. Moreover, recent studies have also demonstrated that type, position, shape (linear or branched) and length of side chains influences material energy levels, charge transport, and active layer morphology, and eventually photovoltaic performance of a solar cell.

The oligo(ethylene glycol) (OEG) chains are well-known for their hydrophilicity due to the presence of many ether groups and have been widely explored in bio-related and optoelectronic applications. The OEG side chains were found to enhance the dielectric constants ($\varepsilon_r$) of the resulting BHJ blends without significantly altering the charge carrier mobilities. The increased $\varepsilon_r$ values could reduce the exciton binding energies of organic semiconductors and may result in efficient charge separation with minimum recombinations. In addition, organic semiconductors with sufficiently high $\varepsilon_r$ may rule out the need for BHJ configuration and also possibly may open up the window for the homojunction devices (single semiconductor solar cell). The higher degree of flexibility of C–O units of OEGs induces a closer $\pi$-$\pi$ stacking along the conjugate backbones in comparison to widely used alkyl chains. Furthermore, red-shifted absorption spectra, smaller bandgap, higher hole mobilities and enhanced PCEs were also observed for the solar cells with polymer:PC$_{71}$BM active layers. However, to the best of our knowledge, there are no reports for the small molecules with OEGs for BHJ-OSCs.

In the current study, the effect of replacing ubiquitous alkyl solubilizing groups with short 2-(methoxyethoxy)-ethyl chains on the basic optoelectronic and dielectric properties of PTZ-based small molecules is discussed along with an evaluation of their photovoltaic results.
5.2 Design and synthesis

The `A-A-D-A-A´ design configuration involved an electron withdrawing 3-ethylrhodanine (A´) connected to a central phenothiazine (PTZ) core through another electron-accepting 2,1,3- benzothiadiazole (A) block. The alkyl or 2-(methoxyethoxy)-ethyl side chains are introduced onto the central PTZ unit. The resulting chemical structures of small molecules are shown in Figure 5.1. For SM1 and SM2, an octyl-substituted thiophene was introduced as π-linker in between the D and A´ units anticipating good solubility in common organic solvents and broad absorption characteristics. However, it was found that SM2 exhibited modest solubility in chloroform and other device processing solvents due to the presence of the polar oligo ether side chain. Consequently, the small molecule SM3 was designed and synthesized to obtain enhanced solubility and extended absorption breadth by a π-linker inserted between D and A. We also envisioned that `A-A-D-A-A´ the molecular framework would possess deep-lying HOMO energy levels due to the presence of two electron withdrawing groups. These good light-harvesting abilities due to the extended π-conjugated backbone were supported by DFT and TD-DFT calculations on structures of the SM1-SM3 type as discussed further below.
Figure 5.1. Chemical structure of SM1, SM2 and SM3.

The synthetic route to intermediates and target SMs are outlined in Figure 5.2. Compound 1 was obtained by the dibromination of starting material phenothiazine using the NBS in DMF. Intermediates 2a and 2b were obtained by the introduction of alkyl (ethylhexyl) or oligo ether (2-(2-methoxyethoxy)ethyl) side chains on to the nitrogen atom of 1 in the presence of NaH in DMF. Treatment of 2a and 2b with bis(pinacolato)diboron under PdCl$_2$(dppf)/KOAc/dioxane led to the corresponding diboronic esters 3a and 3b. Compound 2b was reacted with 4 under palladium-mediated Suzuki coupling reaction conditions to prepare intermediate compound 5. Dibromination of 5 by NBS in DMF afforded 6 which was transformed into the corresponding stannylate via lithiation and subsequent quenching with trimethyltin chloride to generate 7. Vilsmeier-Haack formylation of 10 provided intermediate 11. Knoevenagel condensation of 11 and 3-ethylrhodanine generated 12. Suzuki coupling of precursors 3a, 3b and 7 with intermediate 12 resulted in targets molecules SM1, SM2, and SM3 respectively.
Figure 5.2. Synthetic route of SM1, SM2 and SM3 small molecules, (i) ethylhexyl bromide or 2-(2-methoxyethoxy)ethyl-4-methylbenzenesulfonate, NaH, DMF, rt; (ii) bis(pinacolato)diboron, Pd(dppf)Cl₂, CH₃COOK, dioxane, 85 °C; (iii) Pd(PPh₃)₄, 2M K₂CO₃, THF/H₂O, reflux; (iv) NBS, CHCl₃, rt; (v) n-BuLi, THF, -78 °C, 1h. (b) (CH₃)₃SnCl, THF, -78 °C to rt; (vi) Pd(PPh₃)₄, toluene, reflux; (vii) POCl₃, DMF, DCE, 70 °C; (viii) 3-ethylrhodanine, piperidine, CH₃CN, 85 °C; (ix) Pd(PPh₃)₄, 2M K₂CO₃, THF/H₂O, reflux.

5.3 Material characterization

5.3.1 DFT modelling

DFT and TD-DFT calculations were conducted primarily to get estimates of HOMO and LUMO energy levels and excitation wavelengths in the SM1-SM3 type of compound, but also to collect information on dipole moment and other characteristics of the electronic ground state. After a screening procedure for the lowest energy conformation of SM1 using AM1 and DFT calculations on smaller molecular entities of the SM1 structure, six B3LYP/6-31G(d,p) geometry-optimizations were done on the SM1/SM2 type of structure (for screening and numerical results refer to paper IV SI).

All six geometry-optimized conformers showed the normal bent shape of the PTZ core and differed by the orientation of the other moieties relative to the PTZ group. However, the BT, thiophene and rhodanine ring systems are
coplanar on each side of the PTZ unit in all six structures. Four of the six geometry-optimized structures differed by only 3 kJ mol\(^{-1}\) in total energy (without ZPE correction) and have HOMO energies of \(-5.24 \pm 0.03\) eV and LUMO energies of \(-3.14 \pm 0.04\) eV. The structures of lowest and second lowest energy which are differed by the twist angle (+31° and –31°) between the planes of the BT group and the PTZ benzenoid ring, on each side of the PTZ core virtually have the same energy (difference 0.5 kJ mol\(^{-1}\)) and have the HOMO/LUMO energies \(-5.24/\ -3.14\) eV and \(-5.27/\ -3.16\) eV, respectively.

Similarly, two \(\text{SM3}\) type of structures with the same orientations of the other ring units relative to the PTZ group as in the two \(\text{SM1}\) structures of lowest energy were geometry-optimized with the same B3LYP method. The orientation of the additional thiophene rings was decided from AM1 and PM3 calculations. Two \(\text{SM3}\) structures differ by only 0.1 kJ mol\(^{-1}\) in total energy and have HOMO/LUMO energies of \(-5.08/-3.18\) and \(-5.09/-3.18\) eV. Isodensity MO surfaces for the \(\text{SM1}\) and \(\text{SM3}\) structures are shown in Figure 5.3.

From these results, we concluded that the calculated \(\text{SM1-SM3}\) structures did not contradict our hypothesis of a moderate degree of crystallization in an active layer blend. The calculations also indicated a high \(V_{oc}\) by the SM1-SM3 HOMO energies, while the range of LUMO levels implied that the exciton can be sufficiently energetic for fast electron transfer to PC\(_{71}\)BM, of all structures.

TD-DFT B3LYP/6-31G(d,p) calculations for the two \(\text{SM1}\) and \(\text{SM3}\) structures and TD PBE0/6-31+G(d,p) for \(\text{SM1}\) were performed to get information on light absorption characteristics (TD-DFT can give irregular results for molecular structures where charge-transfer excitations are involved\(^{124,125}\) so to get a better assessment of the absorption properties PBE0 method was used).
For all five calculations, the strongest excitation in the wavelength region 400-800 nm is mainly described by a HOMO-LUMO transition and is consistent with an ICT from the PTZ centre to the other units (Figure 5.3 and paper IV SI). The B3LYP calculations showed that SM1 (both conformations) and SM3 (both conformations) have the ICT excitation close to 700 nm and ca. 750 nm, respectively. The PBE0 method showed the corresponding excitation for SM1 at 644 nm, which seemed consistent with the expectation that the PBE0 functional can give less underestimated excitation energies compared with the B3LYP method. In addition, two or three somewhat weaker excitations are found in the region between ca. 400 and 530 nm for SM1 and between ca. 500 and 600 nm for SM3.

### 5.3.2 Optical and electrochemical properties

The normalized optical absorption spectra of SM1, SM2, and SM3 in chloroform and thin film cast from the chloroform solution are shown in Figure 5.4. In solution, the three SMs showed very similar absorption

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**Figure 5.3.** Isodensity MO surfaces for the SM1 (left column) and SM3 (right column) structures; from upper to lower panels: LUMO+1, LUMO, HOMO, HOMO-1.
spectra with two absorption bands; in the shorter wavelength region centred around 317-325 nm assigned to $\pi-\pi^*$ transitions in accord with TD-DFT results, and in longer wavelength region centred around 523-527 nm for SM1 and SM2 and 543 nm for SM3. These absorptions at longer wavelength are attributed to ICT from the PTZ donor to the other units in the molecular backbone, which also is in agreement with the TD-DFT data. The distinct similarity between the absorption spectra of SM1 and SM2 indicated that the difference in the side chains at the PTZ nitrogen does not affect the electronic structure of the molecular backbone in in solution. The redshift observed in SM3 as compared to SM1 and SM2 is very likely due to the increased conjugation length by the additional thiophene linker between the PTZ core and BT. In addition to the two major bands, the three spectra display an absorption shoulder at ca. 450-460 nm.

In comparison with solution, the absorption spectra of the SMs in the thin film show that $\lambda_{\text{max}}$ of the ICT bands are red-shifted to ca. 549 nm, 565 nm and 557 nm, respectively. This shift may be attributed to the interaction between the conjugated backbones of the SMs in the solid state. The redshift in the absorption peak was more pronounced for SM2 (38 nm) than SM1 (26 nm) indicating closer packing in solid state due to flexible 2-(methoxyethoxy)-ethyl side chain. This observation was consistent with the XRD measurement of neat films of small molecules. Moreover, the absorption band shoulder at ca. 450-460 nm is more prominent in the films of SM1 and SM2 as compared...
to the solution spectra, which may also be caused by increased $\pi$-$\pi$ interactions with resultant transitions.

The HOMO and LUMO energy levels of the $\text{SM}_1$, $\text{SM}_2$ and $\text{SM}_3$ estimated using cyclic voltammetry and optical data are $-5.27/-3.27 \text{ eV}$, $-5.23/-3.21 \text{ eV}$, and $-5.21/-3.25 \text{ eV}$ respectively. The HOMO/LUMO energy levels for these SMs match well with that for PC$_{71}$BM for efficient exciton dissociation and charge transfer from donor to acceptor as well as from acceptor to donor.

### 5.3.3 XRD and dielectric measurements

XRD measurements were conducted to probe the solid-state ordering of the molecular chains in small molecules (Figure 5.5). All small molecules exhibited a strong (100) diffraction peak around $2\theta = 5.10$-5.25° corresponding to the lamellar distance of 1.84 nm. In addition, a moderate diffraction peak (010) related to $\pi$-$\pi$ stacking of molecular backbone was observed at $2\theta = 21.76$ (4.02 Å) for $\text{SM}_1$ and at 22.38 (3.91 Å) for the $\text{SM}_2$ and $\text{SM}_3$. The decreased $d_{\pi-\pi}$ with 2-(methoxyethoxy)-ethyl side chain for $\text{SM}_2$ and $\text{SM}_3$ was due to the greater flexibility than the alkyl chain. The steric hindrance of alkyl side chain prevents the close $\pi$-$\pi$ stacking of conjugated backbone of $\text{SM}_1$ whereas the flexible 2-(methoxyethoxy)-ethyl side chain mitigates the steric hindrance, thus favouring the compact $\pi$-$\pi$ stacking of conjugated backbone of $\text{SM}_2$ and $\text{SM}_3$.

The dielectric constants of these SMs were measured with a device ITO/PEDOT:PSS/SM/Au configuration using impedance spectroscopy. The observed dielectric constants at 1 Mhz are about 3.47, 4.12 and 4.16 for $\text{SM}_1$, $\text{SM}_2$ and $\text{SM}_3$, respectively. The increase in the dielectric constant for $\text{SM}_2$, $\text{SM}_2$ as compared to $\text{SM}_1$, may be attributed to the enhanced $\pi$-$\pi$ stacking and higher flexibility of 2-(methoxyethoxy)-ethyl side chains, which enable a fast change in the direction of the dipoles. The similar values of dielectric constant for $\text{SM}_2$ and $\text{SM}_3$ indicates that the additional thiophene linker does not affect the dielectric constant.
5.3.4 Photovoltaic properties

The BHJ-OSCs were fabricated using SM1, SM2 and SM3 as the donor and PC71BM as the electron acceptor materials with a device structure ITO/PEDOT:PSS SM1-3:PC71BM with different weight ratios/PFN/Al. After the optimization of weight ratio, the active layers with weight ratio 1:1.5 donor to acceptor processed from the chloroform solvent found to exhibit best photovoltaic characteristics (Table 5.1). The devices based on as cast SM1, SM2 and SM3 showed an overall PCEs of 1.69 %, 2.78 % and 3.22 % respectively. Small molecules SM2 and SM3 exhibited higher J_{sc} values compared to that of SM1 demonstrating the beneficial role of 2- (methoxyethoxy)-ethyl side chain (enhanced π–π stacking). The marginally higher J_{sc} for SM3 than of SM2 was due to the extended conjugation (additional thiophene linker).

![X-ray diffraction patterns of pristine SM1, SM2 and SM3 thin films.](image)
Table 5.1. Photovoltaic parameters of the OSCs based on SM1, SM2 and SM3 as donor and PC71BM as acceptor processed under different conditions.

<table>
<thead>
<tr>
<th>Active layer</th>
<th>J&lt;sub&gt;sc&lt;/sub&gt; (mA/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt; (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SM1: PC&lt;sub&gt;71&lt;/sub&gt;BM (as cast)</td>
<td>6.12</td>
<td>0.84</td>
<td>0.33</td>
<td>1.69 (1.54)</td>
</tr>
<tr>
<td>SM2: PC&lt;sub&gt;71&lt;/sub&gt;BM (as cast)</td>
<td>8.06</td>
<td>0.96</td>
<td>0.36</td>
<td>2.78 (2.67)</td>
</tr>
<tr>
<td>SM3: PC&lt;sub&gt;71&lt;/sub&gt;BM (as cast)</td>
<td>8.58</td>
<td>0.96</td>
<td>0.39</td>
<td>3.22 (3.15)</td>
</tr>
<tr>
<td>SM1: PC&lt;sub&gt;71&lt;/sub&gt;BM (SVA)</td>
<td>9.38</td>
<td>0.81</td>
<td>0.52</td>
<td>3.95 (3.82)</td>
</tr>
<tr>
<td>SM2: PC&lt;sub&gt;71&lt;/sub&gt;BM (SVA)</td>
<td>11.94</td>
<td>0.93</td>
<td>0.59</td>
<td>6.55 (6.47)</td>
</tr>
<tr>
<td>SM3: PC&lt;sub&gt;71&lt;/sub&gt;BM (SVA)</td>
<td>12.42</td>
<td>0.93</td>
<td>0.62</td>
<td>7.16 (7.08)</td>
</tr>
</tbody>
</table>

Although all the as-cast devices showed a reasonably high V<sub>oc</sub> owing to the deeper HOMO energy levels, the lower PCEs were mainly due to the low values of J<sub>sc</sub> and FF. To improve the morphology of the active layer, the solvent vapour annealing (SVA) was adopted as reported in the literature. The carbon disulfide was chosen as a solvent for SVA treatment as it has high vapour pressure and desired medium solubility for the donor molecules. The J–V characteristics of the devices based on active layers processed with SVA treatment are shown in Figure 5.6a and the photovoltaic parameters are displayed in Table 5.1. The PCEs have been improved up to 3.95 % (J<sub>sc</sub> = 9.38 mA/cm<sup>2</sup>, V<sub>oc</sub> = 0.81 V and FF=0.52), 6.62 % (J<sub>sc</sub> = 11.94 mA/cm<sup>2</sup>, V<sub>oc</sub> = 0.93 V and FF=0.57) and 7.16 % (J<sub>sc</sub> = 12.42 mA/cm<sup>2</sup>, V<sub>oc</sub> = 0.93 V and FF=0.62) for SM1, SM2 and SM3 based devices, respectively, which was mainly due to the enhancement in the J<sub>sc</sub> and FF values.

The IPCE spectra of the OSCs based on optimized active layers are shown in Figure 5.6b and closely resembled with the absorption spectra of the active layers. The IPCE spectra exhibited two bands and indicate that both small molecules and PC<sub>71</sub>BM contribute to the photocurrent generation. The values of IPCEs for SM2 and SM3 based OSCs is higher than SM1 in the entire wavelength range which is consistent with obtained J<sub>sc</sub> values.
Further, to understand the effect of 2-(methoxyethoxy)-ethyl side chain on charge carrier mobility and to find the origin of the improved PCE achieved for \textbf{SM2} and \textbf{SM3}, hole and electron mobilities were determined from the J-V characteristics of the hole and electron-only devices and fitting them with SCLC model (\textbf{Table 5.2}). Although all SMs displayed similar electron mobilities, the hole mobility for \textbf{SM2} and \textbf{SM3} are higher than that for \textbf{SM1} which can be attributed to the close \(\pi\)-\(\pi\) stacking distance between the backbones. The more balanced charge transport in the \textbf{SM2} and \textbf{SM3} as compared to the \textbf{SM1} resulted in the improved FF, \(J_{\text{sc}}\) and overall PCE. The higher value of hole mobility for \textbf{SM3} than \textbf{SM2} can due to the increased conjugation length.

\textbf{Table 5.2}. Hole and electron mobilities for the optimized active layers.

<table>
<thead>
<tr>
<th>Active layer</th>
<th>Hole mobility (\mu_h) (cm(^2)/Vs)</th>
<th>Electron mobility (\mu_e) (cm(^2)/Vs)</th>
<th>(\mu_e/\mu_h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textbf{SM1:PC(_{71})BM}</td>
<td>7.13x10(^{-5})</td>
<td>2.45x10(^{-4})</td>
<td>3.44</td>
</tr>
<tr>
<td>\textbf{SM2:PC(_{71})BM}</td>
<td>1.23 x10(^{-4})</td>
<td>2.53 x10(^{-4})</td>
<td>2.05</td>
</tr>
<tr>
<td>\textbf{SM3:PC(_{71})BM}</td>
<td>1.38x10(^{-4})</td>
<td>2.59x10(^{-4})</td>
<td>1.87</td>
</tr>
</tbody>
</table>
Further, the $J_{ph}$-$V_{eff}$ plots\textsuperscript{129, 130} (see paper IV) revealed that the as-cast devices layers did not show any clear saturation in the $J_{ph}$ with increasing $V_{eff}$ whereas SVA-treated counterparts showed saturation at 1.14 V, 0.63 V and 0.54 V for SM\textsubscript{1}, SM\textsubscript{2} and SM\textsubscript{3}, respectively. The early onset saturation of the $J_{ph}$ observed for the SM\textsubscript{2} and SM\textsubscript{3} based devices indicated that the internal electric field plays a minor role during the charge extraction and the charges are efficiently extracted by the electrodes. Moreover the ratio of the $J_{ph}$ to the saturation current density ($J_{ph\text{sat}}$) under short circuit condition of the devices based on SM\textsubscript{1}, SM\textsubscript{2} and SM\textsubscript{3} are about 0.89, 0.94 and 0.96, which indicated that the charge extraction efficiency is more for SM\textsubscript{2}/SM\textsubscript{3} than that for SM\textsubscript{1}.

The variation of $J_{sc}$ with $P_{in}$ plots (Paper IV) revealed that bimolecular recombination was effectively suppressed for 2-(methoxyethoxy)-ethyl side chain containing SM\textsubscript{2} and SM\textsubscript{3}, leading to more efficient exciton dissociation into free charge carriers, charge extraction. As a result, SM\textsubscript{2} and SM\textsubscript{3} showed higher $J_{sc}$ and FF than the alkylated SM\textsubscript{1} devices.

The microstructures of the SVA treated SM\textsubscript{1}, SM\textsubscript{2} and SM\textsubscript{3} blend films were characterized by transmission electron microscopy to study the influence of the alkyl and 2-(methoxyethoxy)-ethyl side chains of the SMs on the active layer morphology (Figure 5.7). In comparison with alkylated SM\textsubscript{1}:PC\textsubscript{71}BM blend films, the 2-(methoxyethoxy)-ethyl containing SM\textsubscript{2} and SM\textsubscript{3}:PC\textsubscript{71}BM blends films showed better bicontinuous interpenetrating network which led to the improved $J_{sc}$ and FF.
5.4 Summary

- Three new small molecules with phenothiazine (PTZ) as central donor unit and benzothiadiazole, thiophene and 3-ethylrhodanine ring systems on each side of the PTZ core were synthesized for use as electron donors in organic solar cells.

- Compared with alkylated SM1, 2-(methoxyethoxy)-ethyl side chain containing SM2 and SM3 exhibited redshifted absorption spectra, a smaller stacking distance, higher hole mobility, higher dielectric constant, and enhanced crystallinity and higher photovoltaic properties.

- Improved power conversion efficiencies of the SMs by solvent vapour annealing was attributed to high hole mobility and interpenetrating morphology of blend films.

Figure 5.7. TEM images of optimized SM1:PC_{71}BM, SM2:PC_{71}BM and SM3:PC_{71}BM thin films. The scale bar is 200 nm.
6 Conclusions

The remarkable progress made in the field of BHJ-OSCs has manifested in PCEs of over 10% in single and tandem devices. However, to reach the theoretical limit of 20% and realise the commercialization of the OSCs, significant challenges remain to be addressed for the researchers. From the viewpoint of chemists, the quest for an ideal donor material which combines favourable optoelectronic properties such as low bandgap with broad and strong absorption and suitable energy levels with optimal morphological characteristics still remains elusive.

Literature reports are dominated by the donor materials which are based on the planar building moieties with the notion that planarity results in compact molecular packing and long-range π–π stacks, which improve the charge mobility. However, it is often accompanied by excessive aggregation and higher order crystallinity, leading to reduced solubility in the processing solvents and adversely affecting photovoltaic performance.

The work described in this thesis explores an idea that a non-planar molecular building block, which can introduce judicious conformational twist and lower the coplanarity of the conjugated backbone, may reduce improper aggregation behaviour and improve solubility characteristics. The phenothiazine moiety was chosen as the special building block, whose “butterfly” type of geometry is known to hinder the molecular aggregation and intermolecular excimer formation.

In the first project, a small molecule based on cyano-arylenevinylene building block with deep HOMO level has been prepared. Although a high open-circuit voltage of 1.0 V was achieved, the tendency of the small molecule to crystallize at a higher temperature and with time hindered the attainment of an optimal phase morphology required for the achievement of a higher efficiency.

In project 2 and 3, phenothiazine is used as a π-system bridge and as a core unit to construct small molecules based on symmetric and asymmetric frameworks with varying terminal electron-withdrawing groups. The electron-withdrawing property of the terminal units was found to have a significant influence on the optical absorption properties, electronic energy
levels, molecular ordering, charge carrier mobility and morphology of the resulting active layers. The dipole moments of small molecules of asymmetric configuration seemed to be related to the formation of self-assembled dimers or similar aggregates, although no strong correlation with PCE was observed. The electron withdrawing strength of the acceptors was found to increase in the order 3-ethylrhodanine < malononitrile < 1,3-indandione. The small molecules end-capped with indandione showed higher PCEs (7.45% for symmetric and 7.25% for asymmetric molecules) in comparison to other, owing to broader absorption characteristics and to its planarity which endowed better solid-state ordering.

In project 4, solubilizing alkyl groups and short methoxyethoxy ethyl chains at the central phenothiazine unit in symmetrically configured small molecules were compared to study the effect on the basic optoelectronic and dielectric properties. As anticipated, the oxygen-containing groups resulted in higher dielectric constants owing to the flexible C–O units of those chains. Although absorption spectra were very similar for the alkyl and methoxyethoxy ethyl substituted molecules in solution, a tighter π–π stacking was observed in the solid state for the latter compounds.

Further, in projects 2, 3 and 4, film processing techniques (solvent vapour annealing and two-step annealing) were found to significantly enhance the PCEs of the devices as compared to as-cast films mainly due to the better nanoscale morphological characteristics.

In summary, it is demonstrated that phenothiazine is a promising donor material for OSCs. Its versatility as a π-linker and as a central core unit in symmetric and asymmetric configurations has been explored. The use of nonplanar building blocks such as phenothiazine for the construction of donor materials is an interesting strategy for controlling molecular aggregation and difficult solution processability of small molecules if it is combined with the judiciously designed conjugate backbone.
7 Acknowledgements

Finally, I wish to express my sincere gratitude for everyone who has contributed to this journey. Specifically, I want to acknowledge:

First and foremost, I thank my supervisor, Bertil for the opportunity, guidance and support during all these years. I greatly appreciate the freedom and encouragement provided to pursue my ideas. I benefited immensely from his ability to dissect the research problem into as many different ways as possible and to look at them from different angles - I hope it rubs off on me.

I am certain that, I owe my scientific writing skills to Bertil’s tireless corrections, valuable feedbacks and comments on various drafts of manuscripts and thesis.

I owe a debt of gratitude to our collaborator Ganesh Sharma not only for the collaboration but also for being extremely active with the fabrication of photovoltaic devices and writing manuscripts. Things could have been different without his contributions, thanks a lot!

I am indebted to our previous group member Javed for reintroducing me to the synthetic techniques and for useful discussions during the early stages of my PhD studies and for a great company in the lab and office.

This thesis is a result of close collaboration with some intelligent people. I would like to acknowledge our collaborators Subhayan Biswas from India and Ludvig Edman, Christian Larsen, Jia Wang, Jenny Enevold, Thomas Wågberg, Hamid Reza Barzegar at the physics department in Umeå for the science done.

I would also like to thank Johannes Messenger, Jyri-Pekka Mikkola and Lennart B-Å Johansson for their valuable comments and suggestions during the annual evaluations.

I would like to thank Anurag and Robin Sandström for helping me with CV and TGA measurements.

I am grateful to Artificial Leaf Project for the financial support, Kempe foundation for a research grant and Wallenberg and Åforsk foundations for generous travel grants.
Department of Chemistry has been a great place to work at and I would like to thank all the colleagues of the 3rd and 4th floor where I shared office and lab space. I would like to also mention administrative staff especially Maria Jansson and Sara Filppa for helping with documentation stuff.

Many thanks to Naresh, Pardeep, Deepak, Prasad and Karam for the tricks and tips related to the synthesis and of course with many other things on the personal front.

Although I really enjoyed working in the lab, distractions from my work were highly appreciated. I thank Sandeep, Dharmesh, and Tanumoy for the dinners, drinks, and hangouts, it was fun! My summers in Umeå would have been mundane without cricket and I would like to thank all my cricketing friends for intense yet friendly matches. I thank my Indian friends in Umea for the good times and nice get-togethers.

I would like to express my deepest gratitude to my family for their support and encouragement during this journey. Finally, I would like to thank my wife Sarika for bearing with me during the final stages of PhD and comforting me in stressful times.
8 Appendix

The field of organic solar cells is a multidisciplinary research area which lies at the cross-section of chemistry, material science, physics, and engineering. Starting from the design organic semiconductors to device fabrication it requires the synergistic efforts among chemists, physicists, and engineers. This section briefly deals with the synthetic and characterization tools which are employed to prepare and characterize the $\pi$-conjugated systems.

8.1 Synthesis and purification

Organic synthesis involves the construction of organic compounds via organic reactions. In this thesis standard solution phase synthetic methods are used to prepare the small molecules. Bromination, Vilsmeier–Haack reaction, Knoevenagel Condensation and palladium-mediated Stille and Suzuki coupling are the reactions commonly used in this thesis to synthesize the intermediate and target molecules.

After deciding upon promising synthetic routes with a minimum number of steps and mild reaction conditions, the synthesis of compounds were carried out. Reagents were mixed and allowed to react in the solvent followed by extraction and purifications. The progress of the reactions was monitored by thin-layer chromatography.

The performance parameters of OSCs have been found to be extremely sensitive to the impurity content. Therefore reduction of impurities is a critical issue for the performance and lifetime of OSCS. The techniques used in the work of this thesis are column or flash chromatography and recrystallization. The prepared target compounds generally showed moderate to poor solubilites common organic solvents, as a result purification often turned into a tedious and repetitive process. As these compounds are highly colored, purification by recrystallization offered limited success. Nevertheless, column chromatography and flash chromatograhy were used extensively to purify the compounds. The typical column with different fractions along with solvent extraction process is shown in Figure 8.1
8.2 Characterization methods

Structural characterization

To confirm that the desired product is synthesized, various characterization techniques are used. Nuclear magnetic resonance (NMR) gives the information about the atomic connectivity of the compound, from which the compound structure can be deduced. $^1$H and $^{13}$C NMR were used in this thesis work to confirm the correct products. In addition, mass spectrometry and elemental analysis are used to get the mass and atomic composition of the compounds.

Optical characterization
UV-Vis spectroscopy was performed to investigate the absorption characteristics of small molecules. The extinction coefficient ($\varepsilon$) can be calculated using the well-known Beer-Lambert’s equation,

$$A = \varepsilon c l$$

where $A$ is the absorbance of the molecules, $c$ is the concentration of the species in solution, and $l$ is the path length. All samples were measured in a 10 mm quartz cuvette at room temperature with the concentration of $10^{-5}$ M in chloroform.

**Thermal characterization**

Thermal stability of optoelectronic materials is of paramount importance for the construction of organic solar cells. Therefore, melting points and decomposition temperatures of the target molecules measured by differential scanning calorimetry and thermo-gravimetric analysis under an inert atmosphere with a heating and cooling rate of $10$ K min$^{-1}$.

**Electrochemical characterization**

Cyclic voltammetry experiments were performed on electrochemistry workstation Autolab PGSTAT302, Metrohm. All measurements were carried out at room temperature with a conventional three-electrode configuration employing a glassy carbon electrode as the working electrode, Ag/AgCl electrode as the reference electrode, and a Pt wire as the counter electrode. Tetrabutylammonium tetrafluoroborate ($\text{NBu}_4\text{BF}_4$, 0.1M) in dichloromethane was used as the supporting electrolyte, and the scan rate was 100 mV s$^{-1}$. The redox couple ferrocene/ferrocenium ($\text{Fc/Fc}^+$) vs vacuum was measured to be $-4.51$ eV in this system. The HOMO energy levels of small molecules are estimated from the onsets of oxidation potentials while the LUMO energy levels were calculated according to

$$E_{\text{HOMO}} = (E_{\text{ox}} + 4.51)$$

$$E_{\text{LUMO}} = E_{\text{HOMO}} - E_{\text{g opt}}$$

where $E_{\text{g opt}}$ is the optical band gap.
9 References


