Molecular design for improved self-organization of conjugated molecules for optoelectronics applications

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NANYANG
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**MOLECULAR DESIGN FOR IMPROVED
SELF-ORGANIZATION OF
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OPTOELECTRONICS APPLICATIONS**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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List of Abbreviations

2-D	Two dimensional
AFM	Atomic force microscopy
Au	Gold
BHJ	Bulk heterojunction
C ₆₀	Buckminsterfullerene
CdTe	Cadmium Telluride
CDCl ₃	Deuterated chloroform
CELIV	Carrier extraction by linearly increasing voltage
CHCl ₃	Chloroform
CIGS	Copper Indium Gallium Selenide
¹³ C NMR	Carbon nuclear magnetic resonance
COOH	Carboxylic acid
D-A	Donor-acceptor
DI water	Deionized water
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
DPP	Diketopyrrolopyrrole
DSC	Differential scanning calorimetry
DSSC	Dye-sensitized solar cell
EQE	External quantum efficiency
FF	Fill factor
FTIR	Fourier transform infrared spectroscopy
GADDS	General Area Detector Diffraction System
HBC	Hexa-peri-hexabenzocoronene
HCl	Hydrogen chloride
HMDS	Hexamethyldisilazane
¹ H NMR	Proton nuclear magnetic resonance
HRMS	High-resolution mass spectrometry
HOMO	Highest occupied molecular orbital
ICBA	Indene-C ₆₀ bisadduct
IP	Ionization potential
isoQT-DA	Isomeric structural to QT-DA
ITO	Indium tin oxide
KOH	Potassium hydroxide
LUMO	Lowest unoccupied molecular orbital
MEH:PPV	Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene]
MoO ₃	Molybdenum trioxide
<i>M_w</i>	Molecular weight
Na ₂ CO ₃	Sodium carbonate
NBS	N-Bromosuccinimide
NDI	Naphthalenediimide
NDT	Naphthodithiophene
NMR	Nuclear magnetic resonance
OPV	Organic photovoltaic
OTFT	Organic thin film transistor
OTS	<i>n</i> -octadecyltrichlorosilane
P3AT	Poly(3-alkylthiophene)

P3CAT	Poly[3-(carboxyalkyl)thiophene-2,5-diyl]
P3HT	Poly(3-hexylthiophene)
PC ₆₁ BM	Phenyl-C61-butyric acid methyl ester
PC ₇₁ BM	Phenyl-C71-butyric acid methyl ester
PCE	Power conversion efficiency
PDI	Perylenediimide
PDMS	Polydimethylsiloxane
Pd(PPh ₃) ₄	Tetrakis(triphenylphosphine)palladium (0)
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)
PESA	Photoelectron spectroscopy in air
PL	Photoluminescence
PPV	Poly(p-phenylene vinylene)
QT-DA	Dicarboxylic acid functionalized quarterthiophene small molecule
QT-ES	Diester functionalized quarterthiophene small molecule
r.m.s	Root mean square
SAMFETs	Self-assembled field effect transistors
SCLC	Space charge limited current
STM	Scanning tunnelling microscope
TGA	Thermogravimetric analysis
TOF	Time of flight
THF	Tetrahydrofuran
UV-vis	UV-visible
XRD	X-ray diffraction

List of Symbols

2θ	2 theta angle
λ	Wavelength of light
$\lambda_{\max}$	Wavelength at maximum absorption
π – π	pi-pi
α	Alpha
ω	Omega
μ	Charge mobility
μ_h	Hole mobility
ϵ_0	Permittivity of free space
ϵ_r	Relative permittivity
ΔH_{fus}	Enthalpy of fusion
C	speed of light
E_g^{opt}	Optical band-gap
eV	Electronvolt
h	Planck's constant
J	Current density
J_{MP}	Current density at maximum power
J_{sc}	Short circuit current density
J - V	Current density-voltage
m/z	Mass-to-charge ratio
P_{in}	Incident power
q	Elementary charge
R_s	Series resistance
R_{sh}	Shunt resistance
$SR(\lambda)$	Spectral response in A/W
t	Thickness of active layer
T_C	Crystallization temperature
T_d	Decomposition temperature
T_M	Melting temperature
V_{eff}	Effective voltage
V_{MP}	Voltage at maximum power
V_{oc}	Open circuit voltage
V_{th}	Threshold voltage

Abstract

Organic solar cells offer interesting benefits like flexibility, solution processability and good power conversion efficiency in low lighting conditions. Among these desirable qualities, solution processability is of particular interest for many applications as it provides the possibility of low cost and large scale fabrication. In general, solution processable organic solar cells are often categorized according to the nature of the donors in the active blend - polymeric or small molecule solar cells. In polymer solar cells, the active ink will mostly be comprised of a polymeric donor and a small molecule acceptor. Although all-polymer solar cells have been reported, they tend to have relatively lower efficiency. While polymers offer good film-forming properties, generally good solubility and high charge carrier mobility, there are disadvantages like polydispersity, poor batch to batch reproducibility and difficulty in purification. On the other hand, in solution processable small molecule solar cells both the donor and acceptor are small molecules and these molecules offer the advantages of monodispersity, ease of purification and good batch to batch reproducibility. However, in order to impart solubility, alkyl chains are usually substituted onto the conjugated core. These solubilising chains often disrupt the π - π stacking and crystallinity of the molecules thereby resulting in lower charge carrier mobility in solution processed small molecule devices. In order to circumvent this problem, hydrogen-bonding is proposed as a viable approach where hydrogen-bond induced π - π interaction is postulated to enhance both the intermolecular connectivity and crystallinity in solution processed small molecule films. Hence small molecule functionalised with two carboxylic acids and alkoxy solubilising groups, abbreviated as QT-DA, was

synthesized and its thermal, optical and structural properties were investigated and the impact of some of these properties on the device performance were also explored to understand the influence of molecular design. A diester analogue, abbreviated as QT-ES, was also synthesized and used as a comparison to study the effects of hydrogen-bonding on device performances. Increase in mobility for both the in-plane and out-of-plane direction was observed for the acid-functionalised molecule as compared to the diester analogue. Organic solar cells were fabricated with QT-DA/ QT-ES as the donor molecules and PC₆₁BM as the acceptor. A two-fold increase in power conversion efficiency was observed for the QT-DA blend as compared to QT-ES. The main contributing factor was found to be due to an increase in the short circuit current density of the QT-DA:PC₆₁BM device. This was attributed to an enhanced crystallinity in the as-cast QT-DA blend films and thus a higher hole mobility in the films. Formation of nano-fibers in QT-DA was observed in the as-cast blend films which were due to the presence of hydrogen-bond induced π - π stacking in the molecule. The effect of the position of the functional groups on the molecular orientation and device performance was also investigated. A positional isomer of QT-DA, abbreviated as isoQT-DA, was synthesized and compared with respect to QT-DA. It was found that the crystallinity and device performance was lower in isoQT-DA as compared to QT-DA. Despite so, enhanced crystallinity was obtained in the as-cast blend film of isoQT-DA as compared to QT-ES which correlates well with the proposed concept. Furthermore, an increase in solubility was observed for isoQT-DA indicating that solubilising chains substituted at the α - and ω -position of a molecule maybe a possible design strategy for synthesis of molecules with high solubility.

Chapter 1

Introduction

1.1 Background and Motivation

Organic photovoltaic (OPV) or organic solar cells together with dye-sensitized solar cells (DSSC) have been viewed as an alternative technology to the conventional solar cells such as silicon (crystalline and amorphous), CdTe and CIGS based systems for the harvesting of solar energy. OPV provides several benefits like (a) potential low production cost since printing techniques can be used (b) flexibility when used with plastic substrates and (c) good performance in low/indoor lighting conditions.^{1, 2} However, OPV is unlikely to take over the inorganic solar industry but rather go into areas not reachable by conventional solar cells. Some niche areas that are being proposed are on textile for wearable electronics, mobile devices and energy harvesting windows. A forecast by IDTechEx shown in Fig 1.1 predicts that the market value of OPV will hit US\$300,000 in 2015 and rise to US\$87 million by 2023.²

In general, OPV can be categorized as polymeric and small molecule solar cells which differ in the types of donor used. In polymeric solar cells, semiconducting polymers are used as the donor while usually a fullerene derivative (most commonly phenyl-C61-butyric acid methyl ester, PC₆₁BM or phenyl-C71-butyric acid methyl ester, PC₇₁BM) acts as the acceptor molecule. All-polymer solar cells have been demonstrated; however they suffer from relatively lower efficiency. Some advantages of polymeric semiconductors are their good film-forming properties, solution processability and high carrier mobility due to their extended conjugated backbones.³⁻⁶ However, they are plagued by problems such as batch to batch reproducibility and difficulty in purification which can present issues for large scale production of polymeric semiconductors. On the other hand, a conjugated small molecule provides the

advantage of ease in purification, being monodisperse in molecular weight with good batch to batch reproducibility as compared to its polymeric counterparts. However, the film forming property, inter-molecular connectivity and crystallinity in solution deposited films of these small molecules are relatively poorer as compared to polymers.⁷⁻⁹ This in turn will result in lower charge carrier mobilities in these films. These problems can be attributed to the alkyl chains that are substituted onto aromatic groups to impart solubility in small molecules. These alkyl chains are electrically inert and hinder the π - π stacking of the molecules.¹⁰ Poor charge transport will mean that the charge collection efficiency will be adversely affected, resulting in poor power conversion efficiency when the films are used for solar energy harvesting. Such a problem is less severe in polymeric semiconductors as a large number of aromatic groups are covalently bonded, giving rise to a long conjugated backbone, thereby providing efficient charge transportation and enhanced π - π interaction.

Highly crystalline, solution processed small molecule films have been reported but due to their high crystallinity, they are often less soluble and require solvent additives to improve their solubility for device fabrication.¹¹ The addition of solvent additives will result in an increase in the time required for process optimization as the amount and type of additive may be different for different molecules. Thermal annealing is another common method that has also been used to improve the crystallinity of spin-coated small molecule films.^{12, 13} This technique has been widely employed in polymeric solar cells and has been proven to be effective but may not be ideal for large scale production. Therefore, in order to address the problems faced by small molecules it would be important to improve the connectivity and crystallinity of

the solution processed small molecules while maintaining its solubility. Hence, it is postulated that with the use of hydrogen-bonding in combination with solubilizing chains, the abovementioned problems relating to small molecules can be overcome. Furthermore it is predicted that the use of solvent additives and thermal annealing can be avoided since the presence of hydrogen-bonding will induce closer interaction between the molecules and hence better π - π interaction of the molecules.

1.2 Objectives and Scope

The main objectives and scope of this thesis are:

- (a) To demonstrate the possibility of using hydrogen-bonding to enhance inter-molecular connectivity and hence induced an increase in the π - π interaction and crystallinity in solution processed small molecule films. Small molecules bearing two carboxylic acid functional groups that provide hydrogen-bond interactions will be synthesized and characterized. An ester analogue, which cannot form any hydrogen bond, will also be synthesized and used as a comparison.
- (b) To understand the effects of the functional groups have on the film morphology and hence the charge mobility in thin films and performance of organic solar cell. The dicarboxylic acid and diester functionalized molecules will be used as donor molecules together with PC₆₁BM as the acceptor molecule for the organic solar cell devices. The device performance, film morphology and crystallinity of the spin-coated films will be some of the key properties that will

be characterized and the effects of the functional groups will be investigated. In-plane and out-of-plane mobility will also be measured to understand the effects of functional group have on the carrier mobility.

- (c) Investigate the effect of isomerism on molecular packing and device performance of small molecule solar cell. Small molecules present an additional advantage of versatility in the position of the substitution of functional groups. The functional groups can be placed perpendicular or parallel to the conjugated backbone of the molecule. For better molecular design, it is important to understand how the positional isomerism will affect the molecular orientation and device performance.

1.3 Thesis Organization

This thesis consists of 7 chapters with the first chapter giving a brief introduction for organic solar cells, the motivation of the work and the objectives of this thesis. Chapter 2 presents the literature review for the state of the art organic solar cells including both polymeric and small molecule based devices. A review on works of self-assembly and hydrogen-bonding in organic electronics will also be covered in Chapter 2.

In Chapter 3, synthesis and characterization of material properties of the small molecules bearing two carboxylic acid functional groups (abbreviated as QT-DA) and its diester analogue (abbreviated as QT-ES) will be reported. Key properties which are important for device performance like thermal transition temperatures, absorption profile and energy levels will be highlighted.

Chapter 4 details the fabrication and characterization of thin film

transistors and hole-only diodes for the in-plane and out-of plane mobility measurements respectively. As hole mobility plays an important role in the performance of solar cell devices, hence it is crucial to understand how it can be affected by the presence of functional groups. Furthermore, thin film transistor is an active area for organic semiconductors in terms of academic research and industrial application. In the transistor fabrication, it was found that the presence of –COOH groups provide for simultaneous passivation of dielectric layers and formation of crystalline active channels.

Fabrication and characterization of the organic solar cells with the synthesized small molecules as the donor while PC₆₁BM as the acceptor is described in Chapter 5. Device optimization of the small molecule solar cells will first be reported followed by comparison of the diacid and diester functionalized molecules. Besides the device characteristics, thin film morphology and crystallinity are also reported and correlated to the device performance. Effects of the functional groups in solar cell device performance will be discussed and molecular orientation for QT-DA and QT-ES will also be proposed from the X-ray diffraction measurements.

Chapter 6 reports the synthesis and material properties for the isomer of QT-DA, isoQT-DA. Out-of-plane mobility results followed by solar cell device characteristics will be shown. Effects of the functional group positioning on inter-molecular connectivity, crystallinity, morphology, hole mobility and solar cell device performance will be discussed.

Lastly, in Chapter 7 a summary of the work reported in the various chapters of this thesis are presented. Besides that, some possible future directions stemming from this thesis are also suggested and discussed.

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Chapter 2

Literature Review

2.1 Working Principles and Device Characteristics of Organic Solar Cells

The field of organic solar cell can be dated back to 1986 when the first device with an efficiency of 1 % was presented by C. W. Tang.¹ The device was a bilayer device fabricated with copper phthalocyanine and a perylene tetracarboxylic derivative via vacuum deposition. It was later realised that in order to achieve efficient dissociation of excitons a inter-penetrating structure between the donor and acceptor would be more ideal. Polymer-small molecule blends became the research focus with poly-3-hexylthiophene and phenyl-C61-butyric acid methyl ester as the most widely investigated blends.^{2, 3} Subsequent improvement in the device performance was achieved by the synthesis of low band-gap polymers. This provided a wider absorption of the solar spectrum thereby providing a higher short circuit density. After close to 30 years of developments in this field, we now begin to see a growing interest in soluble small molecules being used as both the donor and acceptor of the inter-penetrating network device structure.

Organic solar cells can be broadly divided into polymeric and small molecule solar cells. In both types of solar cells, the most widely studied device architecture is the bulk heterojunction (BHJ) solar cell where the donor and acceptors are intimately mixed after the spin-coating of the active layer. Such device architecture provides large interfacial area for the splitting of the excitons created upon light absorption.^{4, 5} Besides the presence of interfacial contact between the donor and acceptor phase, an offset in the energy level of at least 0.3 eV has been found to be required for charge transfer to occur⁵. Fig 2.1 depicts the processes in the active layer of organic solar cells upon absorption of light.

Fig 2.1 Schematic of the process in the active layer upon absorption of light (a)

Generation of excitons upon absorption of light, where filled circle represents electron while empty circle represents hole (b) Diffusion of excitons to interface leading to charge transfer followed by charge transportation in donor and acceptor phases to respective electrodes (c) Charge collection at electrodes (d) Current generation for the powering of load

Excitons are generated upon light absorption which will be separated into electrons and holes upon diffusing to the donor acceptor interface. After the charge separation process, the charges will have to travel through the donor and acceptor phases. Charge extraction occurs when the electrons and holes reaches the electrodes thereby producing current. Some of the loss process that may take place within the lifetime of generated excitons can include recombination of the excitons before reaching the interface, recombination of separated charges before or during charge transportation, recombination near the electrodes, limited charge mobility and energetic barrier for charge collection at

the electrodes.⁴ An exciton diffusion length of 10~20 nm have been measured for most organic semiconductors.^{4, 5} This length scale defines the optimal phase separation of the donor and acceptors to achieve exciton splitting prior to recombination.

Fig 2.2 Current density-voltage (J - V) graph of organic solar cell. Shaded area represents maximum power, detail explanation provided in text.

Fig 2.2 shows a typical current density-voltage (J - V) graph of an organic solar cell upon illumination. Some of the key parameters that are of interest will be the short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and power conversion efficiency (PCE). The J_{sc} is given as the measured current output at zero applied bias divided by the area of the working device. The V_{oc} is the voltage whereby no net current flows in or out of the device and can be seen as the maximum voltage that can be obtained. The fill factor is a ratio of the actual maximum output power to the theoretical maximum output power that can be achieved with the measured J_{sc} and V_{oc} . Lastly, PCE is the ratio of the maximum output power from the device to the incident light intensity and the common light intensity used is 100 mW/cm². Besides the J - V

graph, another important characteristic of organic solar cell is the external quantum efficiency (EQE). This is a measure of how efficient the device is at converting photons to electrons for the various wavelengths and is related to the spectral response of the test cell by the following equation:

$$EQE(\lambda) = \frac{hc}{q\lambda} SR(\lambda)$$

where h = Planck's constant

c = speed of light

q = elementary charge

λ = wavelength

$SR(\lambda)$ = spectral response in A/W

2.2 Polymer Solar Cells

In polymeric solar cells, the most common combination will be a donor polymer with an acceptor small molecule. Poly(3-hexylthiophene) (P3HT) is one of the most studied polymeric donor in organic solar cells. Efficiencies of up to 6.5% have been reported for blends of P3HT with indene-C₆₀ bisadduct (ICBA).⁶ Due to the relatively large band-gap of P3HT (~1.9 eV) it has a limited absorption range, therefore a large amount of research effort have been invested into the synthesis of low band-gap polymers. One of the most common strategies involves the coupling of electron-rich (donor) and electron-deficient (acceptor) aromatic groups into polymeric chains.⁷⁻¹⁰ The molecular orbital mixing of the donor and acceptor groups will lead to intramolecular charge transfer and lowering of the band-gap. Another method in achieving low band-gap polymers involves the stabilization of the quinodal structure in the polymer.^{11, 12} Some of the widely reported low band-gap polymers are based on

diketopyrrolopyrrole (DPP)^{8, 10, 13}, benzothiadiazole^{7, 9}, thieno-[3,4-*b*]thiophene^{14, 15} and benzodithiophene^{12, 16, 17}. A PCE of up to 7.4 % have been reported for a polymer-small molecule solar cell based on PTB7 as the polymeric donor and PC₇₁BM as the acceptor.¹² Further enhancement in solar cell efficiency was observed when moving from single layer solar cells to tandem structure where complimentary light absorption can be achieved in different layers via the use of different polymers. You *et. al.* have demonstrated a polymeric tandem solar cell based on P3HT:ICBA and PDTP-DFBT:PC₆₁BM with a certified efficiency of 10.6 %.¹³ Some of the polymeric structures mentioned above are shown in Fig 2.3.

Fig 2.3 Examples of polymeric donors mentioned in text

Besides donors, polymeric structures are also being designed to work as acceptors too. An all-polymer solar cell have been demonstrated which offers advantages of enhance absorption due to presence of 2 polymers (as polymers have a higher absorption coefficient as compared to small molecules) and convenient tuning of the solution viscosity for large scale solution processing.¹⁸ Most of the acceptor polymers have a low band-gap and contain strong electron-withdrawing groups within the conjugated backbone to lower the lowest unoccupied molecular orbital (LUMO) level. The electron-deficient aromatic groups that are commonly utilized include benzothiadiazole¹⁹⁻²¹, cyano-PPV²²⁻²⁴, perylenediimide (PDI)^{25, 26} and naphthalenediimide (NDI)^{27, 28}. Some of the acceptor polymers are shown in Fig 2.4.

Fig 2.4 Examples of polymeric acceptors mentioned in text

The efficiencies of these all-polymer solar cells are typically below that of 3 % which is much lower as compared to the polymer-small molecule ones

mentioned above.¹⁸ Low or unbalanced electron-hole mobility of the acceptor polymers were found not to be the reason for the poor performing devices as field effect electron mobility of $4 \times 10^3 \text{ cm}^2/\text{Vs}$ was demonstrated.^{18, 26} It was realised that all-polymer solar cells suffer from morphological issues brought about by phase separation of polymers. Loi *et. al.* investigated a polymer blend based on P3HT as the donor and an acceptor polymer based on PDI and found a vertical phase separation to occur upon solvent evaporation leaving behind a bilayer-like structure.²⁷ Due to the small interfacial area between the donor and acceptor phases in a bi-layer architecture, exciton recombination within the donor and acceptor phases takes place thereby resulting in a low J_{sc} of $0.34\sim 0.40 \text{ mA}/\text{cm}^2$ and a low PCE of $\sim 0.16 \%$. On the other hand, work by Kietzke *et. al.* demonstrated the possibility of leveraging on the difference in solubility of MEH:PPV and CN-ether-PPV in fabricating efficient all-polymer solar cells.²³ The limited solubility of MEH:PPV in chlorobenzene resulted in its precipitation during drying of the solvent thereby creating a vertically graded bilayer structure. This provided an increase in interfacial area for charge generation and presence of pure phases for efficient charge transport at the same time. This yielded a high PCE of 1.7% for the PPV based all-polymer solar cells. Further improvement in all-polymer solar cells is expected from a more ideal phase separation in the blend morphology with new material developments. This was demonstrated by a blend of NDI-based polymer acceptor and a proprietary donor polymer ActivInk PV1013 from Polyera which gives a PCE of 4.2% .¹⁸

2.3 Small Molecule Solar Cells

Small molecule solar cells have previously only been fabricated using vacuum processing due to its lack of solubility. Recent developments in the area have looked into substituting solubilising groups onto the conjugated core thereby imparting solubility to small molecules. Walker *et. al.* demonstrated one of the first solution processed small molecule solar cell to reach a PCE of ~4 % which was close to the performance of its polymeric counterparts.²⁹ The work was based on a benzofuran substituted DPP small molecule as the donor molecule and PC₇₁BM as the acceptor whereby the latter aided in part of the absorption. The as-cast film gave a relatively low performance of 0.2 % however, upon thermal annealing increase of more than 20 times in the PCE was observed mainly coming from an increase in the J_{sc} . Following that, small molecule donors based on oligothiophenes³⁰, squaraine dyes³¹, dithieno(3,2-b;2',3'-d)silole³² and benzodithiophene^{33, 34} units were reported to give efficiencies exceeding 4 %. Sun *et. al.* reported a molecule based on acceptor-donor-acceptor core structure which gave an efficiency of 6.7 %.³² It was discovered that an addition of 0.25 % v/v of 1,8-diiodooctane resulted in smaller domain sizes and improved efficiency of the devices. This could be related to improved solubility of the small molecule with the presence of solvent additives. A more recent publication from Zhou *et. al.* demonstrated a 8.12 % small molecule solar cell based on benzodithiophene core with 3-ethylrhodanine as the end group and a similar acceptor-donor-acceptor molecular design concept was employed.³⁴ Additive was also found to be beneficial in improving the device performance of the benzodithiophene based small molecule solar cell. However, in this case polydimethylsiloxane (PDMS)

was used as other additives like 1,8-diiodooctane and 1-chloronaphthalene did not show any improvements. Fig 2.5 shows some of the small molecule donors that are mentioned above.

Fig 2.5 Examples of small molecule donors mentioned in text

Although fullerene derivatives are the most widely used n-type small molecule in organic solar cell, huge research efforts are seen in the development of new non-fullerene n-type small molecules.³⁵⁻³⁸ Oligothiophenes substituted with cyano electron-withdrawing groups to lower its LUMO level was synthesized and widely reported.^{11, 39, 40} Uhrich *et. al.* demonstrated a vacuum deposited small molecule solar cell with cyano end-capped oligothiophene as the acceptor and a quarterphenyl derivative as the donor that showed a PCE of 1.63 %.⁴¹ Besides thiophene based molecules, Sellinger *et. al.* have developed a non-fullerene acceptor based on alkylvinazene as the end-capping aromatic group.⁴²⁻⁴⁴ A PCE of up to 0.75 % was reported for a polycarbazole donor coupled with a Vinazene derivative, EV-BT, where a high open circuit voltage of 1.3 V was observed for solution processed devices. Due to the electron

deficient nature of the DPP aromatic unit, besides being used in p-type molecules and polymers, it was also being used as a building block for n-type small molecules. Sonar *et. al.* demonstrated a solution processed bulk heterojunction solar cell with P3HT as the donor polymer and an acceptor based on DPP core with fluorocarbons as the end-capping group that achieved a PCE of 1.0 %.⁴⁵ Some other aromatic structures that have been used for non-fullerene acceptors are fluoranthene-fused imides⁴⁶, perylene^{38, 47} and 9-9'-bifluorenylidene⁴⁸. Some of these small molecule acceptors are shown in Fig 2.6.

Fig 2.6 Examples of n-type small molecule mentioned above

2.4 Self-Assembly of π -Conjugated Systems

It is widely believed that strong π - π interaction and high crystallinity are crucial to improving the charge mobility and device performance of organic electronics, hence self-assembly has been a natural choice for achieving the goal.^{49, 50} Various self-assembly techniques have been applied to both polymeric and small molecule conjugated systems.

In π -conjugated polymers, the self-assembly is strongly affected by the planarity of the polymeric backbone, number of and type of substituent and regioregularity of the polymers.⁵¹⁻⁵⁴ Fig 2.7 depicts graphically, the concept of self-assembly in polymeric chains. In Fig 2.7a, the polymers are in a random fashion and charge movements are via hopping between the chains. However in Fig 2.7b, organization can be observed for both intra- and inter-polymeric chains. These organizations results in crystalline regions thereby providing a closer lattice spacing for charge movement. Poly(3-alkylthiophene)s (P3AT)s were one of the most widely studied polymers in this area. It was realised that an increase in regioregularity will aid in enhancing the planarity and therefore π - π interaction of P3ATs.⁵¹ Other method in effecting crystallization and self-assembly of P3ATs involved the use of solvent mixtures and elevated temperatures.⁵⁵⁻⁵⁸ The concept behind utilizing solvent mixtures is to create an environment of limited solubility for the polymers. At elevated temperatures, the polymers will dissolve in the solvent mixture but upon cooling π - π stacking occurs resulting in the formation of nano-fibers.

Fig 2.7 (a) Polymeric chains in random fashion (b) Polymeric chains exhibiting organization (regions boxed in red)

Some other interesting assembly techniques for conjugated polymers will be the complexation of cations with polymers and the use of block copolymers.⁵⁹⁻⁶¹ In the former, conjugated polymers with side chains containing

crown ether and acid groups have shown attractive forces with cations. Upon complexation, chain aggregation occurs due to hydrophobic interaction or due to π - π stacking.⁶⁰ In the block copolymer approach, conjugated oligomers are covalently linked to insulating segments like polystyrene, poly(methyl methacrylate) and polydimethylsilane.⁶¹ Due to the low entropy of mixing in block copolymers, spontaneous phase separation occurs for the blocks thereby achieving π - π interaction. Using the concept of phase separation in block copolymers, Qiu *et. al.* have shown that by spin-coating P3HT/polystyrene blends from a marginal solvent, interconnected nano-fibers can be obtained.⁶² This resulted in transistors with good field effect mobility of $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, low threshold voltage and enhanced environmental stability due to encapsulation provided by the polystyrene.

Beside conjugated polymers, self-assembly of conjugated small molecules are widely reported too. Discotic molecules like triphenylene and hexabenzocoronenes are found to self-assemble into columnar structures.⁶³⁻⁶⁵ A schematic diagram for the packing of hexabenzocoronenes is presented in Fig 2.8. Transient time-of-flight measurements for triphenylene derivatives showed mobilities of up to $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.⁶³ Mullen *et. al* pioneered work on the extension of the aryl cores of triphenylenes to give hexabenzocoronenes which showed high charge carrier mobility of up to $0.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.⁶⁵ This increase in mobility as compared to triphenylenes was attributed to the extension in π - π stacking of hexabenzocoronenes.

Fig 2.8 Schematic diagram for the packing of hexabenzocoronenes due to its discotic nature

Hydrogen-bonding is another extensively explored tool for the self-assembly of π -conjugated systems. Functional groups that bear similarity to the hydrogen-bonding in DNA molecules are employed to provide directionality in the bonding.⁶⁶⁻⁷¹ These groups are namely diaminotriazine, ureidotriazine and 2-ureido-4[1H]-pyrimidinone. Helical wires and tubes were demonstrated from triazine functionalized oligo(p-phenylenevinylene)s dissolved in water and in apolar solvents.⁶⁷ Another interesting concept based on hydrogen-bonding in small molecules is its application in the formation of donor acceptor dyads for the fundamental study of the energy and electron transfer processes.^{69, 72} Oligo(p-phenylenevinylene) and PC₆₁BM derivatives bearing quadruple hydrogen-bonding groups were shown to form helical aggregates of approximately 7 nm in width and several micrometers long.⁶⁹ It was found that the close proximity brought about by hydrogen-bonding between the donor and acceptor molecules ensures the occurrence of charge transfer within a few picoseconds. However, recombination rate was also enhanced concurrently due to the bonding between the molecules. Another elegant design of molecules in achieving donor acceptor assembly was reported by Yamaguchi *et. al.* where

formation of nanotubes with high aspect ratio was observed from a carboxylic acid functionalised zinc porphyrin with C₆₀ molecules.⁷³ It was found that the cooperative action of hydrogen-bonding from porphyrin and the π -interaction between C₆₀ and porphyrin molecules was crucial in the formation of nanotubes. Such supramolecular assembly of donor acceptor molecules is envisioned to provide potential application in photoelectronic devices.

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Chapter 3

Synthesis of Small Molecule Donors QT-ES and QT-DA

3.1 Introduction

Alkyl chains are often present on semiconducting polymers and small molecules to aid in their solubilization. However, these solubilizing alkyl groups are non-conducting and at times they can hinder the packing and crystallization of the active materials.^{1, 2} Branched and bulky alkyl chains have been reported to impart good solubility but result in disruption of long-range molecular ordering. While linear ones do not hinder π -stacking, they are generally less effective in improving the solubility compared to branched chains. Hence, in this work in order to improve the crystallization of small molecules with solubilising chains, functional groups with the potential to form hydrogen-bonds are present by design in the molecules. Using this approach, it is envisioned that despite the use of branched alkyl chains, facile crystallization can still be achieved.

Long range self-assembly of monomeric units, molecules and oligomers using hydrogen-bonding has been widely investigated for use in organic electronics.¹⁻⁷ Some of this work discussed the use of end-functionalized units that provide quadruple and triple hydrogen-bonding (e.g. diaminotriazine, ureidotriazine, 2-ureido-4[1H]-pyrimidinone and etc.).^{3, 6, 8-10} These nature-inspired multiple hydrogen-bond interactions can provide directionality and strong non-covalent attractive forces between the molecules. The fibrillar structures formed was usually columnar or helical in nature, depending on the backbone structure and the functional group used. However, these molecules were mostly used for fluorescence and crystal structure studies. Solar cell devices were not fabricated using these molecules largely because their optical absorption range is fairly narrow as the molecules were mostly based on

oligo(p-phenylenevinylene)s and they also have poor solubility. Hydrogen-bonding was also used to enable the supramolecular assembly of donor-acceptor molecules.¹¹⁻¹⁴ This was achieved through the mono- or di-functionalised donor and acceptor molecules thereby attracting both moieties together to form an extended network. These dyad assemblies were then investigated for presence of energy transfer due to the close proximity of the molecules brought about by the presence of hydrogen-bonding.

Fig 3.1 Hydrogen-bonding derived from amide functional groups

Amides derived from secondary amines and carboxylic acids or acyl chlorides have also been employed for their hydrogen-bonding properties. The electron lone pairs from the oxygen atom act as hydrogen-bond acceptor while the proton attached to the nitrogen atom serves as the hydrogen-bond donor (Fig. 3.1).^{1, 15} A conductive gel was obtained from this interaction but due to the presence of a hypsochromic shift in the absorption/ fluorescence spectrum of this film, it is unsuitable to be used for the fabrication of solar cell. The hypsochromic shift observed was an indication of the formation of H-aggregates in the nano-fibers.¹⁶ The substitution of amides at the α - and ω -

position has a strong tendency to promote the formation of H-aggregates due to the π - π stacking interaction and directionality of the intermolecular hydrogen-bonding.¹⁵ A similar concept was seen for an alcohol end-functionalized phenylenevinylene whereby a conductive organogel was also formed due to the synergistic effect of hydrogen-bonding and π - π stacking.⁷

As discussed so far, it can be seen that hydrogen-bonding is a viable approach in increasing crystallinity of thin organic films. However, improved solubility of the films and prevention of H-aggregate formation are required for the design to be suitable for use in organic solar cells. Carboxylic acid has long been known for its hydrogen-bond forming ability and di- or tri-carboxylic acid functionalised molecules can exist as dimers, trimers or oligomers, both in solution and in solid state form. The formation of oligomers can be confirmed using Fourier transform infrared spectroscopy (FTIR) studies^{17, 18} and the monolayer films can be imaged with scanning tunnelling microscopy (STM).¹⁹⁻²² The presence of carboxylic acids at the two ends of the molecule coupled with the π - π interaction from the quaterthiophene conjugated core should result in spontaneous self-assembly of the molecules. These crystalline structures will be beneficial for efficient charge transportation, and hence may result in improvement of device performance.

Another advantage of carboxylic acids is their ease of synthesis. Some of the common methods employed to do so for conjugated electronic molecules are hydrolysis^{23, 24}, carboxylation of Grignard reagents^{25, 26}, oxidation of aldehydes^{27, 28} and alcohols.^{29, 30} In this study, we have chosen to perform a hydrolysis of the diester functionalized molecule due to the convenience and

ease of purification. A diester molecule bearing a similar chemical structure, abbreviated as QT-ES, served as a direct comparison of material properties and device performances with the diacid molecule, abbreviated as QT-DA. This allowed us to compare the effects of the diacid functional groups with the same conjugated core on the thin film properties and device performances (both transistors and solar cells). The synthetic route employed for QT-DA and QT-ES and the characterization of the material properties such as thermal transitions, optical absorptions and energy levels will be presented next.

3.2 Experimental Techniques

All solvents were purchased as anhydrous grade from Sigma Aldrich. Tetrakis(triphenylphosphine)palladium (0) ($\text{Pd(PPh}_3)_4$) was purchased from Strem Chemicals. All other chemicals were purchased and used without further purification.

Synthesis of 3-(2-butyloctyloxy)thiophene and 2-bromo-3-(2-butyloctyloxy)thiophene was according a modified method of the synthetic procedure in ref 31. ^1H NMR and ^{13}C NMR spectra were performed on a Bruker DPX 400MHz spectrometer. Chemical shifts are given in ppm downfield with respect to tetramethylsilane. UV-Vis spectra were recorded on a Shimadzu model 2501-PC. Fourier transform infrared spectroscopy (FTIR) was performed on KBr discs using a Perkin Elmer Spectrum GX. Matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) measurements were conducted on a Shimadzu Biotech AXIMA Performance with Ditrinol as the matrix.

Thermogravimetric analysis (TGA) was conducted with TA instruments HI-Res TGA 2950 with a heating rate of $10\text{ }^{\circ}\text{Cmin}^{-1}$. Differential scanning calorimetry (DSC) was carried out under nitrogen environment in a TA Instrument DSC Q100 equipment with a heating rate of $10\text{ }^{\circ}\text{Cmin}^{-1}$. Highest occupied molecular orbital (HOMO) levels for the molecules were measured with photoelectron spectroscopy in air (PESA) using a Riken Keiki AC-2 spectrometer. In PESA, the sample is first spin-coated onto a glass slide and subjected to UV irradiation. This results in the emission of electrons from the surface of the organic sample due to photoelectric effect. As the experiment is performed in air, the electrons will then result in the ionization of oxygen molecules which are then attracted and accelerated onto a counter. The point of inflexion between the background count and the signal picked up will be known as the photo-emission threshold which will be the HOMO level. This onset is determined by the software upon selecting the background counts and the signal counts

Synthesis of 3-(2-butyloctyloxy)thiophene³¹: 3-methoxythiophene (5.0 g, 43.8 mmol), 2-butyloctan-1-ol (14.7 g, 78.8 mmol, 1.8eq.) and anhydrous sodium hydrogen sulfate (0.263 g, 2.19 mmol, 0.05eq.) were charged into a round bottom flask. Toluene (50 mL) was then added, purged with argon for 30 min and the mixture was heated to $130\text{ }^{\circ}\text{C}$ for 15 hr under argon protection. After

cooling to room temperature, Deionized (DI) water was added and extraction with ethyl acetate was done. The organic layer was dried over anhydrous MgSO_4 , filtered and concentrated for purification via column chromatography (silica gel, hexane/ CH_2Cl_2 , 3:1, v/v) (yield: 10.00 g, 85%). ^1H NMR (400 MHz, CDCl_3) δ ppm 7.17 (d, $J = 8$ Hz, 1H), 6.75 (d, $J = 8$ Hz, 1H), 6.21 (s, 1H), 3.82 (d, $J = 6$ Hz, 2H), 1.77 (sextet, $J = 6$ Hz, 1H), 1.44 (quintet, $J = 6$ Hz, 4H), 1.32-1.28 (m, 12H), 0.92 (t, $J = 5.6$ Hz, 6H).

Synthesis of 2-bromo-3-(2-butyloctyloxy)thiophene³¹: 3-(2-butyloctyloxy)thiophene (3.0 g, 11.18 mmol) was dissolved in 10 mL of anhydrous CHCl_3 and the solution was cooled down to $0 \sim 4^\circ\text{C}$ using an ice bath. N-Bromosuccinimide (NBS) (1.89 g, 10.62 mmol, 0.95eq.) was then dissolved in anhydrous DMF (10 mL) and added into the solution drop wise via a dropping funnel. The mixture was then stirred for 1 hr with exclusion from light, removed from the ice bath and allowed to warm up to room temperature. It was then stirred overnight with protection from light. DI water was added and extraction with CHCl_3 was done. The organic layer was dried over anhydrous MgSO_4 , filtered and concentrated for purification via column chromatography (silica gel, hexane) (yield: 3.16 g, 81.3%). ^1H NMR (400 MHz, CDCl_3) δ ppm 7.18 (d, $J = 6$ Hz, 1H), 6.75 (d, $J = 6$ Hz, 1H), 3.91 (d, $J = 5.6$ Hz, 2H), 1.76

(sextet, $J = 5.6$ Hz, 1H), 1.47 (quintet, $J = 6$ Hz, 4H), 1.33-1.29 (m, 12H), 0.93 (t, $J = 6$ Hz, 6H).

Synthesis of ethyl 4-(3-(2-butyloctyloxy)thiophene-2-yl)benzoate: 2-bromo-3-(2-butyloctyloxy)thiophene (3.05 g, 8.78 mmol) and 4-(ethoxycarbonyl)phenylboronic acid (2.04 g, 10.54 mmol, 1.2 eq.) was charged into a round bottom flask, 75 mL of toluene and 5 mL of ethanol was added. Na_2CO_3 (1.86 g, 17.56 mmol, 2eq.) was dissolved in 8mL of DI water and added into the solution which was purged with argon for 30 min. $\text{Pd(PPh}_3)_4$ (0.3 g, 0.263 mmol, 0.03 eq.) was added and the solution was heated at 85 °C for 48 hr. After cooling down to room temperature, DI water was added and extraction with ethyl acetate was done. The organic layer was dried over anhydrous MgSO_4 , filtered and concentrated for purification via column chromatography (silica gel, hexane/ CH_2Cl_2 , 1:1, v/v) (yield: 3.00g, 82%). ^1H NMR (400 MHz, CDCl_3) δ ppm 8.03 (d, $J = 8.4$ Hz, 2H), 7.85 (d, $J = 8.4$ Hz, 2H), 7.22 (d, $J = 5.6$ Hz, 1H), 6.93 (d, $J = 5.6$ Hz, 1H), 4.41 (quartet, $J = 7.2$, 2H), 4.00 (d, $J = 5.6$ Hz, 2H), 1.82 (sextet, $J = 5.6$ Hz, 1H), 1.50 (quintet, $J = 6$ Hz, 3H), 1.43 (quartet, $J = 7.2$, 4H), 1.33-1.27 (m, 12H), 0.91 (t, $J = 6$ Hz, 6H).

Synthesis of ethyl 4-(5-bromo-3-(2-butyloctyloxy)thiophene-2-yl)benzoate:

4-(3-(2-butyloctyloxy)thiophene-2-yl)benzoate (3.00 g, 7.19 mmol) was dissolved in 10 mL anhydrous CHCl_3 separately. The solution was protected from light and a solution of (NBS) (1.21 g, 6.83 mmol, 0.95eq.) in anhydrous DMF (10 mL) was added in dropwise via a dropping funnel. The mixture was then allowed to stirred for overnight with protection from light. DI water was added and extraction with CHCl_3 was done. The organic layer was dried over anhydrous MgSO_4 , filtered and concentrated for purification via column chromatography (silica gel, hexane/ CH_2Cl_2 , 1:1, v/v) (yield: 2.50 g, 70%). ^1H NMR (400 MHz, CDCl_3) δ ppm 8.01 (d, $J = 8.4$ Hz, 2H), 7.73 (d, $J = 8.4$ Hz, 2H), 6.92 (s, 1H), 4.40 (quartet, $J = 3.6$, 2H), 3.95 (d, $J = 5.6$ Hz, 2H), 1.80 (sextet, $J = 5.6$ Hz, 1H), 1.45-1.38 (m, 7H), 1.33-1.27 (m, 12H), 0.91 (t, $J = 6$ Hz, 6H).

Synthesis of QT-ES: 2,2'-bithiophene-5,5'-diboronic acid bis(pinacol) ester (0.96g, 2.3 mmol) and ethyl 4-(5-bromo-3-(2-butyloctyloxy)thiophene-2-yl)benzoate (2.51 g, 5.06 mmol, 2.2 eq.) was charged into a round bottom flask,

50 mL of toluene and 5 mL of ethanol was added. Na_2CO_3 (0.79 g, 7.45 mmol, 3.2eq.) was dissolved in 3 mL of DI water and added into the solution and purged with argon for 30 min. $\text{Pd}(\text{PPh}_3)_4$ (80 mg, 0.069 mmol, 0.03 eq.) was added into the solution and at 85 °C for 48 hr. After cooling down to room temperature, DI water was added and extraction with ethyl acetate was done. The organic layer was dried over anhydrous MgSO_4 , filtered and concentrated for purification via column chromatography (silica gel, hexane/ CH_2Cl_2 , 1:3, v/v) and recrystallized from CH_2Cl_2 /hexane to afford an orange solid (yield: 1.49 g, 65%). ^1H NMR (400 MHz, CDCl_3) δ ppm 8.03 (d, J = 7.6 Hz, 2H), 7.84 (d, J = 7.6 Hz, 2H), 7.15 (d, J = 3.6, 1H), 7.12 (d, J = 3.6, 1H), 7.00 (s, 1H), 4.41 (quartet, J = 7.2, 2H), 4.05 (d, J = 5.6 Hz, 2H), 1.85 (sextet, J = 5.6 Hz, 1H), 1.53-1.39 (m, 7H), 1.34-1.26 (m, 12H), 0.93 (t, J = 6 Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ ppm 166.84, 155.28, 138.20, 136.72, 136.58, 134.55, 130.19, 127.93, 126.25, 124.88, 124.77, 118.48, 114.42, 75.04, 61.22, 38.68, 32.27, 31.83, 31.52, 30.09, 29.50, 27.27, 23.45, 23.11, 14.77, 14.52, 14.50. HRMS: found m/z , 995.4467 (M^+), calcd for $\text{C}_{58}\text{H}_{75}\text{O}_6\text{S}_4$ 995.4441.

Synthesis of QT-DA: QT-ES (520 mg, 0.522 mmol) was dissolved in 100 mL of THF while anhydrous KOH (1.758 g, 31.34 mmol, 60 eq.) was dissolved in 10 mL of DI water separately. The aq. KOH was added into the organic solution and the mixture was purged for 30 min with argon after which was heated at 70 °C for 48 hr. After the reaction was cooled to room temperature, 2M HCl was

added in for the protonation of the potassium salt. The solvent was then removed on a rotary evaporator and the solid residue was rinsed with water till the washings became neutral (pH 7). The compound was then purified via column chromatography (silica gel, hexane/THF, 3:1, v/v) and recrystallized from THF/hexane to afford a reddish solid (yield: 220 mg, 45%). ^1H NMR (400 MHz, $\text{C}_4\text{D}_8\text{O}$) δ ppm 8.01 (d, $J = 8.4$ Hz, 2H), 7.88 (d, $J = 8.4$ Hz, 2H), 7.28 (d, $J = 4$ Hz, 1H), 7.26 (s, 1H), 7.23 (d, $J = 3.6$, 1H), 4.14 (d, $J = 5.6$ Hz, 2H), 1.86 (sextet, $J = 5.6$ Hz, 1H), 1.56-1.40 (m, 7H), 1.37-1.29 (m, 12H), 0.93 (t, $J = 6$ Hz, 6H). Solubility of QT-DA was too low for ^{13}C NMR. HRMS: found m/z , 939.3854 (M^+), calcd for $\text{C}_{54}\text{H}_{67}\text{O}_6\text{S}_4$ 939.3815.

3.3 Synthesis of QT-ES & QT-DA

Fig. 3.2 shows the molecular design of the quaterthiophene bearing the dicarboxylic acid functional groups abbreviated as QT-DA. Quaterthiophene was chosen as the semiconducting core because of its good hole mobility and ease of synthesis.³²⁻³⁵ Branched solubilising alkoxy chains were used as branched chains provide much better solubility than straight alkyl chains and ether bonds are highly flexible which contributes to enhanced solubility of the small molecule.³⁶⁻³⁸ An added advantage from the use of alkoxy side chains is that it is electron donating in nature. Hence, it is expected that there will be a certain degree of intra-molecular donor-acceptor (D-A) interaction between the side chains and the electron-withdrawing carboxylic end groups. Furthermore, since the solubilising chains were placed at the 3-position of two of the thiophene rings within the core and carboxylic acid groups at the ends, this allows QT-DA to form a pseudo-polymer without any obstructions to the

organization of the neighbouring molecules relative to each other. This design essentially combines the advantage of small molecules (ease of synthesis and purification) and polymers (good inter-molecular connectivity).

Fig 3.2 Molecular structure of quarterthiophene with dicarboxylic acid end groups (QT-DA)

Scheme 3.1 Synthetic Route for QT-ES and QT-DA

Scheme 3.1 depicts the synthetic route adopted for the synthesis of QT-ES and QT-DA. Firstly, nucleophilic substitution of 3-methoxythiophene with 2-butyl-octanol catalysed by sodium hydrogen sulphate was carried out. This resulted in 3-(2-butyl-octyloxy)thiophene with a yield of 85 %. Bromination of 3-(2-butyl-octyloxy)thiophene at the α position was then carried out at 0°C with N-Bromosuccinimide (NBS). Selective bromination via electrophilic substitution at the α -position was favoured as the C2 carbon had a relatively

higher electron density with respect to the C5 carbon due to the presence of the alkoxy side chain. Bromination was carried out at low temperature to prevent di-bromo products due to the high reactivity of alkoxy thiophenes. Suzuki coupling of the 2-bromo-3-(2-butyloctyloxy)thiophene with 4-(ethoxycarbonyl)phenylboronic acid was performed to obtain 4-(3-(2-butyloctyloxy)thiophene-2-yl)benzoate with a yield of 82 %. Bromination of this compound by NBS at room temperature afforded 4-(5-bromo-3-(2-butyloctyloxy)thiophene-2-yl)benzoate which was then used in a second Suzuki coupling with 2,2'-bithiophene-5,5'-diboronic acid bis(pinacol) ester to give QT-ES with a yield of 65 %. Hydrolysis of QT-ES with aqueous potassium hydroxide at 70 °C in THF followed by column chromatography and recrystallization from THF/ Hexane afforded pure QT-DA with a yield of ~45 %.

Fig 3.3 Attempted synthesis of alkoxy quarterthiophene

An alternative synthetic route for QT-DA was attempted and shown in Fig 3.3 where 2-bromo-3-(2-butyloctyloxy)thiophene was coupled directly with 2,2'-bithiophene-5,5'-diboronic acid bis(pinacol) ester. However, this did not

afford the target compound but resulted in dimers, trimers and oligomers of the alkoxy thiophene instead. This was postulated to be related to the possibility of halogen-boron exchange in 2-bromo-3-(2-butyloctyloxy)thiophene resulting in homo-coupling of the alkoxy thiophenes.

3.4 Results and Discussions

The molecular structure for the QT molecules was studied using Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR) spectroscopy and high-resolution mass spectrometry (HRMS). The key properties that are important for solar cell application such as thermal transitions, optical absorbance and energetic levels for both molecules are also investigated and compared. The results are presented here.

3.4.1 Molecular Structure of QT-ES & QT-DA

The FTIR spectrums of QT-ES and QT-DA for the region 1000 cm^{-1} to 4000 cm^{-1} are shown in Fig 3.4. There is a shift in the carbonyl (C=O) peak from 1702 cm^{-1} to 1680 cm^{-1} which is an indication that carboxylate ester (COOR) has been successfully converted to carboxylic acid (COOH) group.^{17, 39} The shift was attributed to a change in the stabilization of the resonance structures and the presence of hydrogen-bonding between the COOH groups. The presence of a peak at 3450 cm^{-1} belonging to $-\text{OH}$ vibrations was another indication of the successful hydrolysis of the COOR to COOH . The $-\text{OH}$ peak was centred at 3450 cm^{-1} , as opposed to $3600 - 3700\text{ cm}^{-1}$ for free $-\text{OH}$ groups, indicated an oligomeric nature due to hydrogen-bonding between the COOH

groups.¹⁸ This oligomeric form was expected to give QT-DA a pseudo-polymer characteristic and thereby improving the connectivity and electronic transportation between the molecules.

Fig 3.4 FTIR spectrum of QT-ES (in black) and QT-DA (in red) for 1000 – 2000 cm⁻¹ (left) and 2500 – 4000 cm⁻¹ (right)

The FTIR studies confirmed the presence of ester and acid functional groups in QT-ES and QT-DA respectively. In order to verify the molecular structure of QT-ES and QT-DA, HRMS was used. The m/z value obtained from the HRMS measurements of 995.4467 and 939.3854 was equivalent to the calculated value for the structure of QT-ES (995.4441) and QT-DA (939.3815) respectively (spectra shown in Appendix). This provided further proof for the structure of both molecules.

Fig 3.5 NMR spectrum of aromatic region for (a) QT-ES and (b) QT-DA where peak **a** represents the quartet protons, peak **b** the α protons in the alkoxy side chain and peak **c** the proton signal for the acid group.

^1H -NMR spectra of the molecules were also collected and the absence of the quartet protons at 4.39 ppm for QT-DA as compared to QT-ES (index as peak **a** in Fig. 3.5a for QT-ES) was observed which was due to the loss of the ethyl groups after QT-ES have undergone hydrolysis. Furthermore, the proton signal (in Fig 3.5b for QT-DA) recorded at close to 11 ppm corresponds to the

OH in QT-DA. All this information provided evidence for the successful synthesis of QT-ES and QT-DA. Once the molecular structure was confirmed, the thermal, optical properties and energy levels, which are important characteristics for device performances, were studied.

3.4.2 Thermal Analysis

Table 3.1 Summary of thermal properties of QT-ES and QT-DA.

Sample	T_d (°C)	T_M (°C)	T_C (°C)	ΔH_{fus} (J/g) ^a
QT-ES	389	132.28	74.70	53.25
QT-DA	362	333.02	319.80	95.35

^aEnthalpy of fusion from DSC measurements

A summary of the thermal properties for QT-ES and QT-DA are presented in Table 3.1. The decomposition temperature (T_d) was measured using the thermogravimetric analyser (TGA) and it is defined as the temperature at 5 % weight loss. The T_d for both molecules lies above 350 °C which signifies good temperature stability useful for both device fabrication and operation. The melting (T_M) and crystallization (T_C) temperatures were then measured using differential scanning calorimetry (DSC). As QT-ES and QT-DA are small molecules, they are not expected to have glass transition temperature. Both T_M and T_C can be detected for both molecules and these transition temperatures were more than 200 °C higher for QT-DA as compared to QT-ES. This remarkable increase in the melting and crystallization temperature was attributed to the presence of hydrogen-bond induced π – π interactions in QT-

DA. Both T_M and T_C can be observed for QT-ES and is attributed to the presence of crystalline regions as a result of π - π interaction between the conjugated thiophene cores. Besides the π - π interaction mentioned in QT-ES, in QT-DA system there are also hydrogen-bonds present. It has been reported previously by Sautter *et. al.* that the presence of hydrogen-bonds in cyclic hydrocarbon structures can result in the aggregation of these structures even in dilute solutions.⁴⁰ This hydrogen-bond driven π - π interaction will result in increased inter-molecular interaction and result in longer range ordering of the molecules thereby increasing the thermal transition temperatures and enthalpy of fusion as seen from in Table 3.1. Hence, this study provided an initial evidence to the fact that the carboxylic acid groups improve the crystallinity in thin films of solution processed small molecules.

3.4.3 Optical Analysis

The optical properties of the small molecules are important for its application in solar cells. Next, UV-vis absorption and photoluminescence (PL) measurements were performed for QT-ES in (CHCl_3) and QT-DA (in THF) respectively. Solutions of low concentration (10^{-5} M) were used to ensure minimal aggregation of the molecules as this will lower the PL intensity.

Fig 3.6 (a) UV-Vis absorption and PL measurements of QT-ES and QT-DA with a concentration of 10^{-5} M (b) Normalized thin film absorption of QT-ES and QT-DA.

It is seen from Fig 3.6a that the absorption profile and absorbance of QT-ES and QT-DA in solution were very similar; however QT-DA has a lower PL intensity as compared to QT-ES. This phenomenon could be due to the presence of non-radiative decay like triplet states or quenching due to hydrogen-bonding.⁴¹⁻⁴⁵ It has been shown that PL quenching can be due to inter-molecular hydrogen-bonding or hydrogen-bonding between molecules and solvent.⁴¹⁻⁴³ In this case, it is proposed that the quenching is most likely to have

been due to inter-molecular hydrogen bonding as THF had a lower tendency for hydrogen-bond formation as compared to between two -COOH groups. Hence it is possible that even at 10^{-5} M, there were dimers or trimers of QT-DA present which result in self-quenching and therefore a lower PL intensity. This was further confirmed by the increase in PL intensity upon decreasing the concentration of QT-DA to 10^{-6} M (PL plot provided in Appendix). The graph in Fig 3.6b shows the thin film absorption for both compounds and the bandgap shown in Table 3.2 was calculated from the onset of absorption. There is a red-shift in the absorption spectrum in the thin films of both molecules (Fig 3.6b) as compared to the solution. This red-shift observed for the thin film samples is attributed to the formation of J-aggregates in the molecules and an increase in the mixing of the molecular orbitals.¹⁶ However, an interesting point to note was that the extent of red-shift in the absorption for the QT-DA thin films (50 nm) was more as compared to QT-ES (23 nm). Since QT-ES and QT-DA in solution have very similar absorption profile, this red-shift in the absorption profile for the thin films cannot be related to a push-pull effect due to the presence of -COOH group in QT-DA. Therefore the larger extent in red-shift for the absorption onset in QT-DA films is attributed to an increase in the inter-molecular orbital mixing brought about by the hydrogen-bond induced π - π interaction.

3.4.4 Energy levels of QT-ES & QT-DA

In order to use the QT molecules in solar cell devices, it is important to determine the energy levels of the molecule so as to select a compatible acceptor. Photo-electron spectroscopy in air (PESA) can be used for the estimation of the highest occupied molecular orbital (HOMO) level for QT-ES and QT-DA (shown in Fig 3.7) and a subtraction of the HOMO level by the optical bandgap will give an estimation of the lowest unoccupied molecular orbital (LUMO). The PESA was done on thin film samples to get a close representation of the actual device structure. As the PESA works by exciting the sample with a UV source and detecting the escaped electrons, it is actually measuring the ionisation potential (IP) of the film, however in most cases the IP is very close to the HOMO level and can be assumed to be similar.⁴⁶⁻⁴⁸ Table 3.2 summarizes the optical properties and energy levels of QT-ES and QT-DA. The LUMO offset of more than 0.3 eV between QT-ES or QT-DA with PC₆₁BM shown in Fig. 3.8 indicates that both donor molecules will match well with PC₆₁BM as the acceptor molecule in a photovoltaic cell.

Fig 3.7 Graph of PESA measurement for thin films of QT-ES and QT-DA

Table 3.2 Summary of optical properties and energy levels of QT-ES and QT-DA

Sample	λ_{max} (nm)		HOMO (eV)	LUMO (eV)	$E_{\text{g}}^{\text{opt}}$ (eV) (film)
	solution ^a	film			
QT-ES	457	480	-5.50	-3.31	2.19
QT-DA	456	506	-5.18	-3.11	2.07

^aSolution UV-Vis absorption for QT-ES and QT-DA are done in Chloroform and THF respectively.

Fig 3.8 Energy diagram for QT-ES, QT-DA and PC₆₁BM

3.5 Conclusion

In summary, quaterthiophene molecules bearing carboxylic acid groups were successfully synthesized from the hydrolysis of the ester derivatives. Characterization of QT-ES and QT-DA with FTIR, MALDI-TOF and NMR was done to confirm the structure of the molecules. Molecular structure, thermal and optoelectronic properties were studied to evaluate its suitability in device applications. TGA showed that the decomposition temperature of the both QT-ES and QT-DA were sufficiently high and hence it would be compatible with

the fabrication process and its use in photovoltaic devices. Much higher transition temperatures (T_M and T_c) were observed for QT-DA as compared to QT-ES due to the presence of the dicarboxylic acid groups providing hydrogen-bonding and increased π - π interaction between the cores of the molecules. Interestingly, the solution phase absorption of both QT-ES and QT-DA are very similar however a larger degree of red-shifting in the thin film sample was observed for QT-DA. This was attributed to an increase in the inter-molecular orbital mixing due to the presence of hydrogen-bond induced π - π interaction. The HOMO level was measured from PESA while the LUMO was derived from the subtraction of the bandgap. The values obtained indicate that both molecules will couple well with PC₆₁BM as the acceptor in the BHJ photovoltaic devices.

3.6 References

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Chapter 4

**Improvement in Carrier Mobility from Acid-Functionalised
Molecule**

4.1 Introduction

Some of the common device configurations that can be used for the measurement of the charge mobility in organic semiconductors are thin film transistor (TFT), space charge limited current (SCLC), time of flight measurements (TOF), carrier extraction by linearly increasing voltage (CELIV) and photogenerated charges in CELIV (photo-CELIV).¹ However, organic thin film transistor (OTFT) based measurements are currently the most widely used testing platform for mobility measurements because its device architecture is very similar to integrated circuits.²⁻⁴ One of the most commonly used device architecture is the bottom gate top contact configuration due to the ease of fabrication and results that are easily comparable with literature when a SiO₂/Si substrate is used. However, the SiO₂ dielectric layer contains surface hydroxyl (-OH) groups and surface defects that will act as charge trapping sites.^{5, 6} Therefore, silane treatments are usually used to passivate the dielectric surface prior to the active layer deposition. However due to the low surface energy from the alkyl chains after silane treatments, wetting issues may arise and result in poor film coating. During the fabrication of OTFTs with the QT molecules, poor wetting was observed on octadecyltrichlorosilane treated surface which resulted in non-repeatable results.

Surface passivation of oxide surfaces have previously been reported with the use of alkanephosphonic acids.⁷ It was shown that the use of anthryl terminated phosphonic acid molecules for the passivation can result in enhanced crystallinity of pentacene active layer due to favourable interaction between the molecule and anthracene-terminated substrate surface.

Furthermore, a similar device concept has previously been demonstrated in self-assembled field effect transistors (SAMFETs).⁷⁻¹⁰ Monolayer deposition of the active material was achieved by immersing the substrates in dry solutions of the mono-functionalized molecules. Mobility for such devices can be as high as $0.04 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for a channel length of $40 \text{ }\mu\text{m}$.⁸ Besides immersion, Hutchins *et. al.* have also shown that SAMFETs can be deposited through spin-coating of mono-phosphonic acid functionalized small molecule.¹⁰ Hence it is postulated that the $-\text{COOH}$ group in QT-DA will be able to passivate the SiO_2 dielectric layer during spin-coating and form the semiconducting channel concurrently. This will eliminate the need for surface treatments when di-acid functionalised molecules are used as the active material.

Besides using OTFTs, the space charge limited current (SCLC) method is another way to determine the mobility of organic semiconductors where the Mott-Gurney equation has been used in the calculation of the charge carrier mobility. While in OTFT configuration, the mobility measured is parallel to the substrate (in-plane mobility); the SCLC method determines the mobility perpendicular to the substrate (out-of-plane mobility). The SCLC have been commonly seen in the current-voltage characteristics of organic light emitting diodes and now has also been used for determining the mobility of materials used for solar cells due to the similarity in device architecture.¹¹⁻¹³ A unipolar (hole-only or electron-only) device can be constructed when contacts that provide low injection barrier for one charge carrier while blocking the injection of the other charge carrier. SCLC regime can be observed from the unipolar device in the current-voltage characteristics where the mobility can be

determined. However, a drawback for the SCLC measurements is the strong dependence of the mobility, μ , calculations on the layer thickness, t , ($\mu \propto t^3$). This may result in inaccurate mobility values due to non-uniformity in layer thickness or inaccurate layer thickness estimation due to metal penetration during thermal evaporation. Nevertheless, the SCLC measurement is still widely used and gives reasonable mobility values. Blom *et. al.* have successfully used the method to determine the hole and electron mobility of blends of poly(p-phenylene vinylene)s (PPV) and 6,6-phenyl C61-butyric acid methyl ester (PC₆₁BM).^{14, 15} McGehee *et. al.* have also reported a molecular weight dependence in mobility of poly(3-hexyl-thiophene) (P3HT) diodes where an increase in an order of magnitude was observed when moving from a low molecular weight to a high molecular weight P3HT.¹³ Measurement of the SCLC is one of the most direct methods to evaluate the mobility in the out-of-plane direction using a diode configuration.

In this chapter, effects of packing on these mobilities obtained using OTFTs and hole-only diodes will be discussed. It was observed that a higher hole mobility was achieved by the QT-DA molecules in both the in-plane and out-of-plane direction. The presence of carboxylic acid groups in the active material opens up new possibilities for future design of molecular structures in solution processable OTFTs.

4.2 Experimental Techniques

Heavily doped p-type silicon wafers with about 200 nm thick thermally evaporated SiO₂ were used as substrates for the top contact OTFTs. The substrates were cleaned by ultrasonicing in acetone for 10 min followed by in isopropanol for another 10 min. After which the substrates were rinsed with DI water and blown dry with N₂ gas and treated with UV-ozone heated to 100 °C for 20 min prior to spin coating. For the silanization of the surface, the substrates were immersed in 0.1 M *n*-octadecyltrichlorosilane (OTS) in toluene at 60°C for 20 min. The Si/SiO₂ substrates were rinsed using toluene and blown dry using N₂ gas. The QT molecules were prepared at a concentration of 4 mg/mL and spin-coated on the substrates at speed of 1200 rpm for 60 s. The source and drain electrode made of 80 nm gold were deposited by thermal evaporation through a shadow mask. OTFT testing was performed on a calibrated testing system consisting of a probe station equipped with microscope and Keithley 4200 parameter analyzer.

Hole-only devices for SCLC measurements were fabricated with the configuration of ITO/ PEDOT/ Active layer/ MoO₃/ Al. The ITO/glass substrates were cleaned in Hellmanex solution (10 min), distilled water twice (10 min each), acetone (15 min) and isopropanol (15 min) and subsequently blow dry with N₂ gas. The dried substrates were then subjected to UV-Ozone cleaning for 10 min prior to the spin coating of a 40 nm thick PEDOT:PSS hole transporting layer (CLEVIOS P VP Al 4083, HC Stark). Annealing of the PEDOT:PSS layers were done in a N₂ gas glove box at 140°C for 10 min. QT solutions of 10 mg/mL were then prepared and spin coated onto PEDOT:PSS at

1200 rpm for 60s. Deposition of MoO₃ and aluminium were done via thermal evaporation through a shadow mask with a thickness of 10 nm and 50 nm respectively. Hole mobility was determined by fitting the dark current curve with the field-dependent mobility equation:

$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu_h \frac{V_{eff}^2}{L^3}$$

where J is the current density, μ_h is the hole mobility, ϵ_0 the permittivity of free space, ϵ_r the relative permittivity of the materials (assumed to be 3 which is typical of organic semiconducting materials), L is the film thickness and V_{eff} is the effective voltage. The effective voltage is obtained by subtracting the applied voltage with the built-in voltage and the voltage drop from the series resistance in the device. Built-in voltage was obtained from the turn-on voltage of illuminated J - V curve. While the voltage drop across the device was measured from a device without the active layer (i.e. ITO/PEDOT:PSS/MoO₃/Al).

Film thickness was measured using a step profiler KLA Tencor P-10 while Atomic force microscopy (AFM) images were obtained with a Digital Instruments Nanoscope IIIa in tapping mode. Molecular modelling was carried out with ChemBio Office ChemBio 3D Ultra, v. 11.0 (CambridgeSoft, Cambridge, MA) using the energy minimization with molecular mechanics (MM2). X-ray diffraction (XRD) patterns were collected using the Bruker General Area Detector Diffraction System (GADDs) with a Cu K α radiation and a 2D detector. Scans were collected for a 2θ range of 2° - 30° with scan duration of 10 min.

4.3 Results and Discussion

4.3.1 In-plane Mobility of QT-ES & QT-DA

The bottom-gated device architecture was used for the OTFT measurements (refer to Fig 4.1). Heavily p-doped silicon substrate acts as the gate electrode while a thermally grown SiO_2 layer ($\sim 200\text{nm}$) functioned as the dielectric layer. The active layer was spin-coated directly onto the dielectric surface. Gold contacts were thermally evaporated through a shadow mask and these serve as the source and drain electrodes. The work function of Au is between -5.1 eV and -5.5 eV making it suitable for hole conduction due to the small energy offset with the HOMO level of QT-ES (-5.5 eV) and QT-DA (-5.18 eV).

Fig 4.1 Schematic drawing of a bottom gate top contact OTFTs

As the SiO_2 dielectric layer usually contains charge trapping sites due to the presence of hydroxyl groups ($-\text{OH}$) and surface defects, this will result in high threshold voltage and the lowering of charge carrier mobility measured.^{2,4} Hence, silane treatment is usually used to passivate the surface prior to the deposition of the active layer. The silanes that are commonly used are

hexamethyldisilazane (HMDS)^{16, 17} and octadecyltrichlorosilane (OTS).¹⁸⁻²⁰ A monolayer of silane is deposited through either solution or vapour phase treatment. It was observed that besides being able to passivate the surface, the interaction between the silane and the organic molecules can promote long-range ordering in the latter thereby improving device characteristics.²¹ Although surface passivation provides the abovementioned benefits, however due to the long alkyl chain length of the silane molecules the surface becomes highly hydrophobic and the surface energy becomes very low. This may lead to problems with the wettability of the substrates and thereby resulting in poor film quality. Non-reproducible results may occur due to varying film thickness and poor surface coverage. However as QT-DA bears two carboxylic acid functional group, it was predicted that it can function as both the surface passivation layer and the active channel at the same time. QT-ES and QT-DA devices with and without OTS treatment on SiO₂ layer were fabricated. However QT-ES and QT-DA solutions were unable to wet the treated surface resulting in poor film coverage and non-repeatable data, therefore only results for bare SiO₂ are presented.

Chapter 4: Improvement in Carrier Mobility from Acid-functionalised Molecule

Fig 4.2 Output characteristics of (a) QT-ES and (b) QT-DA. Transfer curves of (c) QT-ES and (d) QT-DA

The output characteristics and transfer curves of QT-ES and QT-DA are shown in Fig. 4.2. Both molecules displayed the typical p-channel behaviour. Due to the low mobility of QT-ES, the output characteristics are fairly noisy. The hole mobility (μ_h) was calculated from the slope of $I_D^{1/2}$ vs V_G curve at the saturation region with an applied drain voltage of -70 V. It was observed that QT-DA displayed at least an order of magnitude increase in hole mobility as compared to QT-ES. The average mobility values for QT-DA and QT-ES was $2.7 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (highest mobility: $1.3 \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) and $2.6 \times 10^{-5} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (highest mobility: $3.2 \times 10^{-5} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) respectively. These values are relatively on the lower end as compared to some of the state of the art small molecule transistors reported recently.²²⁻²⁶ Some of the recent hole mobility of

vacuum deposited small molecules can go up to $8 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ while solution processed generally falls within 1 to $2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at maximum.^{22, 25, 26} Vacuum deposited devices tend to have a much higher mobility due to a more crystalline film since the substrate was heated up during deposition. However, this loses one of the main advantages of organic molecules - solution processibility. The QT molecules were lower than the recently reported solution processed small molecule transistors mainly due to differences in the core chemical structures. Generally the high mobility small molecules consist of fused aromatic rings restricting the degree of rotation thereby increasing the crystallinity. Despite so, it was shown that the presence of the $-\text{COOH}$ groups improved the hole mobility of the device performance as compared to its ester analogue. Besides an increase in μ_h , the current on-off ratio was 2 orders of magnitude higher for QT-DA (10^4) as compared to QT-ES (10^2). Most interestingly is that there is a 9-fold decrease in threshold voltage (V_{th}) of QT-DA as compared to QT-ES. The V_{th} for QT-DA was estimated to be -3 V while that of QT-ES was -28 V. This decrease in V_{th} was a strong indication that the dielectric oxide layer is successfully passivated by QT-DA. Attachment of carboxylic acid groups onto metal oxide surfaces²⁷⁻²⁹ have been widely reported especially in the case of dye-sensitized solar cells³⁰⁻³² and similar interaction was expected to occur on SiO_2 surfaces. Upon spin-coating of the QT-DA solution on SiO_2 surface, spontaneous attachment of the $-\text{COOH}$ groups onto the oxide surface occurred which had a similar effect compared to the silane treatment commonly employed. On the hand, unlike QT-DA, the SiO_2 surfaces are essentially not passivated by the deposition of QT-ES. As previously mentioned, it is worth noting that the fabrication of transistors for both QT-DA and QT-ES from silane

treated SiO₂/Si substrates were attempted but due to wetting issues it was unsuccessful. Further proof of the attachment of QT-DA onto SiO₂ and its molecular arrangement will be discussed in the following sections.

4.3.2 Characterization of Molecular Orientation

The crystallinity and molecular orientation of the QT films on SiO₂/Si substrates was investigated by X-ray diffraction (XRD). From the out-of-plane XRD measurements as shown in Fig. 4.3, strong diffraction peaks were observed at $2\theta = 4.16^\circ$ and 3.46° for QT-ES and QT-DA respectively. These angles correspond to a d -spacing of 22 Å for QT-ES and 25 Å for QT-DA. The difference in the d -spacing can be attributed to a difference in the molecule orientation on the substrate whereby QT-ES adopted an edge-on configuration while QT-DA had a vertical alignment due to the preferential interaction between the carboxylic acid end groups and the substrate. Molecular dimensions were calculated using MM2 energy minimization³³⁻³⁵ and the dimensions are shown in the inset of Fig. 4.3. The calculated height of 23.6 Å matches fairly well to an edge-on stacking with d -spacing of 22 Å for the QT-ES films. The slightly smaller dimension could be related to presence of interdigitation of solubilising alkyl chains. For QT-DA films, the characteristic dimension of 25 Å may be related to the QT-DA molecule orientating lengthwise at a tilt angle of 64° to the substrate surface.

Fig 4.3 Out-of-plane XRD of QT-DA (red) and QT-ES (black) on SiO₂/Si substrates (graphs are offset for clarity). Inset shows schematic drawing with dimensions of QT-DA and QT-ES

Fig 4.4 Contact angle measurements for spin-coated films of QT-DA (left) and QT-ES (right) on SiO₂/Si substrates. Inset shows schematic drawings for the arrangement of the molecules on the substrates

To confirm the organization of QT-DA and QT-ES on SiO₂/Si surfaces, contact angle of both the QT-ES and QT-DA thin films were measured. From Fig. 4.4 we observed a small contact angle of 29 ° for QT-DA which clearly indicated that it possesses a hydrophilic surface. On the hand, for QT-ES the comparatively larger contact angle of 79 ° showed that it was hydrophobic. This is a good indication that QT-DA maybe aligned vertically lengthwise and the surface of the film would be rich in –COOH groups which are hydrophilic in nature while QT-ES will give a hydrophobic surface due to its alkyl chains (shown in schematic diagram in the inset of Fig. 4.4). To further prove that a spontaneous attachment of QT-DA molecules can occur on SiO₂ surfaces during spin coating, an adsorption test was performed. 10 mg of silica particles were immersed in solutions of QT-DA or QT-ES (0.2 mg/ mL concentration) for 1 min. Centrifuge and washing cycles with solvents was then performed till the supernatant was colourless. The photographs of the silica particles after repeated washing are presented in Fig. 4.5 and it can be seen that the attachment of QT-DA onto SiO₂ surfaces occurred spontaneously with a robust interaction that resists redissolution in THF even after 7 cycles of washing. On the other hand, QT-ES which is washed off after 2 cycles means that it lacks interaction with the SiO₂ particles. The interaction present between QT-DA and the SiO₂ is similar to that reported in dye-sensitized solar cells where the main bonding is via a monodentate ester linkage.^{28, 30} Similar interaction and surface passivation have been reported previously in self-assembled field effect transistor (SAMFETs) where the immersion of silicon substrates into dilute solution of monoacid functionalized semiconducting molecules was performed.⁷⁻¹⁰

Fig 4.5 Photographs of silica particles for absorption test

4.3.3 Film Morphology of OTFT Devices

Annealing treatment was performed in an attempt to improve the crystallinity and hence the mobility values of the transistors made with the QT molecules. The annealing temperatures were chosen to be between the crystallization and the melting temperatures (75 ° for QT-ES and 100 ° for QT-DA). Annealing seems to have very little impact on the mobility. The reason for this lack of improvement is attributed to the formation of grain boundaries and film discontinuity that occurred concurrently with crystallization. The voids and grain boundaries will result in charge scattering and negate the improvements brought about by the ordering of the structures. Such a phenomenon has previously been reported for vacuum deposited small molecule transistors.³⁶ In

order to study the effect of annealing on the morphology of films, the topography of QT-DA and QT-ES films was collected using AFM and these images are shown in Fig. 4.6. It was observed that upon annealing besides the formation of prominent grains and nano-fibers in QT-ES and QT-DA respectively, voids arise simultaneously.

Fig 4.6 AFM images of non-annealed (a) QT-ES, (c) QT-DA films and annealed (b) QT-ES, (d) QT-DA films

4.3.4 Out-of-plane Mobility of QT-ES & QT-DA

In the last section, in-plane mobility for QT-ES and QT-DA was investigated using the TFT configuration. These measurements are very sensitive to the local organization of the molecules, especially near to the contacts and the charge transport direction is parallel to the substrate. In order to better evaluate the suitability of a material for the solar cell device, diodes were fabricated so that out-of-plane mobility can be determined. Hole-only devices were fabricated and the mobilities were calculated from the SCLC regime. A schematic diagram for the device is shown in Fig. 4.7. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and molybdenum trioxide (MoO_3) were used as the hole-transporting layers due to the matching energy levels (5.2 eV and 5.3 eV respectively) with the HOMO level of both molecules thereby providing an ohmic contact. MoO_3 was favoured over Au due to its lower temperature (900 °C vs 1132 °C) required for evaporation and larger molecular size which will reduce diffusion into the organic layers.^{37, 38} This will ensure that the device will not be shorted and that the thickness estimation will be much more accurate.

Fig 4.7 Schematic diagram of hole-only device for SCLC mobility measurements

An active layer of 70 nm in thickness was spin-coated onto PEDOT:PSS followed by the evaporation of MoO₃ and aluminium as the top contact. Voltage was then applied across the device and at a sufficiently high voltage the J - V curve can be described by the following relationship -

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_h \frac{V_{eff}^2}{L^3}$$

where J is the current density, μ_h is the hole mobility, ε_0 the permittivity of free space, ε_r the relative permittivity of the materials (assumed to be 3 which is typical of organic semiconducting materials), L is the film thickness and V_{eff} is the effective voltage. The effective voltage is obtained by subtracting the applied voltage with the built-in voltage and the voltage drop from the series resistance in the device.

Fig 4.8 Graph of $J^{0.5}$ vs V_{eff} for hole-only devices of QT-DA (red) & QT-ES (black)

Fig. 4.8 shows a plot of $J^{0.5}$ vs V_{eff} . The hole mobility of the molecules can be calculated from the gradient of the plot and was found to be 2.83×10^{-5}

$\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ and $6.91 \times 10^{-6} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for QT-DA and QT-ES respectively. The trend for the enhanced hole mobility for QT-DA compared to QT-ES was similar to that found from TFT measurements. The discrepancy in the mobility between the TFT and the diode devices is believed to be a result of the strong dependence of mobility on charge carrier density whereby the carrier density is increased by the gate voltage in TFTs.³⁹ The increase in carrier density aids in the filling of charge trapping states and therefore leading to higher mobility.

4.3.5 Microstructure of Hole-only Devices

AFM images for the QT-DA and QT-ES layers from the SCLC devices are shown in Fig. 4.9. These are similar to those observed for OTFTs as shown in Fig 4.6. The particles are more prominent for the QT-DA film as compared to QT-ES and are likely to be attributed to the hydrogen-bond induced π - π interaction. The surface roughness for both films was measured to be approximately 4.2 nm which is relatively smooth thereby eliminating uncertainties in the mobility calculations coming from uneven film thickness. The crystallinity of the films was then investigated by XRD with the diffraction patterns being shown in Fig. 4.10. A similar diffraction peak was observed for the SCLC devices ($2\theta_{\text{QT-ES}} = 3.90^\circ$ and $2\theta_{\text{QT-DA}} = 3.32^\circ$) as compared to TFTs ($2\theta_{\text{QT-ES}} = 4.16^\circ$ and $2\theta_{\text{QT-DA}} = 3.46^\circ$) indicating that QT-DA and QT-ES adopts a similar molecular orientation. Upon closer observation, a weak 2nd order diffraction peak can be seen for the QT-DA neat film (shown in inset of Fig. 4.10, right). This 2nd order peak was absent for the QT-ES neat film. This is related to the longer range order in the QT-DA films as compared to QT-ES

films due to the presence of hydrogen bonding. The enhanced out-of-plane hole mobility of QT-DA as compared to QT-ES is believed to be due to 2 reasons: 1) a more crystalline film in QT-DA which provides better charge transport properties;⁴⁰⁻⁴² 2) the vertical alignment of QT-DA which allows charge transportation along the backbone of the molecules as compared to charge hopping across the alkyl chains for QT-ES.^{43, 44}

Fig 4.9 AFM image of hole-only device for (a) QT-DA and (b) QT-ES

Fig 4.10 Out-of-plane XRD of QT-ES (left) and QT-DA (right) for hole-only devices.

Inset in QT-DA graph shows the enlarge portion of the 2nd order peak

4.4 Conclusion

In conclusion, the in-plane and out-of-plane mobility for the QT molecules were characterized by using TFT and diode configurations respectively. In the TFTs with unsilanized substrates, in-plane mobility for QT-DA was at least an order of magnitude higher than QT-ES. For OTS treated substrates, wettability issues were present and hence repeatable results could not be obtained. It was also interesting to note that QT-DA displayed mobilities that are comparable to both the thiophene based polymers and small molecules reported in literature.⁴⁵⁻⁴⁷ Typical values for P3HT are $\sim 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ but values as high as $0.24 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ have been reported.⁴⁷ The higher values arise from treatment of both the substrate and the electrodes. However, due to the presence of $-\text{COOH}$ groups in QT-DA, surface treatments was not required to achieve crystalline films and optimal hole mobility. This provides an additional design strategy for future organic small molecular transistors. More importantly, was the out-of-plane mobility as it has the same sandwich structure as solar cell devices. Likewise, it was found that QT-DA displayed one order of magnitude enhancement in mobility from the SCLC calculations. This was primarily due to an enhanced crystallinity and vertical alignment which improves the charge transportation.

4.5 References

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Chapter 5

**Understanding the Effect of Functional Group on Solar Cell
Device Performance**

5.1 Introduction

Interest in small molecule solar cells have been revived recently as a few research groups has demonstrated solar cells with comparable performance to polymeric cells.¹⁻⁶ Research on small molecule solar cells can be broadly categorized according to deposition methods: (a) evaporation^{3, 7-9} and (b) solution processed.^{1, 2, 4-6, 10} Both methods have been able to produce device efficiencies exceeding 6%^{3, 5}, however solution processable small molecules have the appeal of being suitable for low cost and large scale fabrication processes such as printing. Solution processable small molecules also have the advantage of ease in purification, mono-disperse in molecular weight and good batch to batch reproducibility which are lacking in its polymeric counterpart. However, one of the major disadvantages for solution processed small molecules is the lack of inter-molecular connectivity which is the result of steric hindrance from solubilising chains and lack of strong attractive forces between molecules.^{10, 11} This lack of interconnectivity can result in poor charge transport properties which will lead to low device efficiency. It was previously shown in polymeric solar cells that high molecular weight (M_w) is crucial in obtaining good cell performance.¹²⁻¹⁶ This was attributed to both an improved inter-chain connectivity between high M_w polymers and higher charge mobility within the polymer chains due to a longer conjugated backbone. When the M_w was increased, the hole mobilities for poly(3-hexyl-thiophene) can increase by up to 3 orders of magnitude.^{12, 16} On the other hand, when the M_w of a polyfluorene derivative is increased a different underlying reason for the improved solar cell performance was found.¹³ The hole mobilities calculated from space-charge limited current was virtually unaffected moving from low M_w of $\sim 5.1 \times 10^3$

g/mol to a high M_w of $\sim 1.9 \times 10^5$ g/mol. It was found that an optimal phase separation in the blend film was the key factor to achieve an increase in the short circuit current density and fill factor with the higher M_w polymers. Low M_w polymers lack the ability to phase separate into donor and acceptor phase thereby resulting in charges being trapped in isolated domains. Hence, it can be deduced that inter-molecular connectivity may also affect the phase separation in the blend films of small molecule solar cells. Recently, Fréchet *et. al.* have reported on the use of pyrene for self-assembly and to increase the inter-molecular connectivity and crystallinity of small molecules.¹¹ Pyrene was being used as end-groups for a diketopyrrolopyrrole (DPP) core due to its tendency for aggregation. An improvement in device efficiency (mainly from an increase in short circuit current density) was observed due to the π - π interaction of pyrene molecules which results in enhanced inter-molecular connectivity. An interesting point to note was that in the abovementioned study, the pyrene substitution site was crucial and self-assembly property was seen only for C2 substitution (shown in Fig 5.1).

Fig 5.1 Structures reported in reference 11 where self-assembly only observed in **1** for the C2 substitution. R represents alkyl chains for solubility.¹¹

Therefore, it can be observed that the lack of inter-molecular connectivity is a potential problem in solution processed small molecule solar

cells. Hence, the use of carboxylic acid functional groups as a structural directing agent for the initiation of self-assembly is proposed. Furthermore, the hydrogen-bond induced π - π interaction is also postulated to enhance the interconnectivity and crystallinity of the molecules. Previously, Müllen *et. al.* have reported on the functionalization of hexa-peri-hexabenzocoronene (HBC) with mono- and dicarboxylic acids resulting in supramolecular ordering of the molecules.¹⁷ They have observed that the alkyl spacer between the aromatic core and the carboxylic acid functional group plays a vital role in achieving the supramolecular assembly where a short alkyl chain of 3 carbon atoms was more effective as compared to 10 carbon atoms. However, the focus of the paper was on the effect of hydrogen bonding on the distinct columnar packing of HBCs and its application in organic solar cell was not reported.

In both chapters 3 and 4, it was shown that there was an enhancement in the inter-molecular connectivity and crystallinity in QT-DA as compared to QT-ES due to the presence of hydrogen bonding from -COOH groups. The presence of hydrogen-bonding resulted in the formation of a pseudo-polymer in QT-DA upon spin-coating. Most significantly, improvement in hole mobility in the sandwich device configuration was observed. In this chapter, application of the QT molecules (donor) with PC₆₁BM (acceptor) in solution processable small molecule solar cells was explored and the effect of -COOH group will be discussed. It was observed that a two-fold increase in device efficiency was achieved for the QT-DA blends as compared to QT-ES. The main contribution to the improvement was attributed to an increase in short circuit current density which was brought about by an enhanced crystallinity and mobility. For the blend films, improved inter-molecular connectivity and crystallinity with the

presence of hydrogen-bonding induced π - π interaction was more pronounced as compared to neat QT films. Observation of nano-fibers from as-cast blend films of QT-DA was an indication of the pseudo-polymer nature of the molecule. The presence of nano-fibers has been reported to aid in charge transportation and thereby improving the short circuit current density of devices.¹⁸⁻²²

5.2 Experimental Techniques

Solar cells were fabricated using indium tin oxide (ITO) coated glass from Kintec Co. with an average sheet resistance of $14 \Omega/\square$ as the substrate. The ITO/glass substrates were ultrasonicated in Hellmanex solution (10 min), distilled water twice (10 min each), acetone (15 min) and isopropanol (15 min) and subsequently blow dry using nitrogen gas. The dried substrates were then subjected to UV-Ozone cleaning for 10 min at 100 °C prior to the spin-coating of a 40 nm thick poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) hole transporting layer (CLEVIOS P VP Al 4083, HC Stark). Annealing of the PEDOT:PSS layers were done in a nitrogen gas glove box at 140 °C for 10 min. Subsequently, blends of the active material were spin-coated on top of the PEDOT:PSS layer in the glove box. Aluminium cathodes (~80 nm thick) were evaporated through a shadow mask under a pressure of less than 6×10^{-6} torr to obtain devices with an active area of 9 mm². No interfacial hole blocking/ electron transporting layer was used in the device. The blend solutions were prepared by dissolving QT-ES and PC₆₁BM simultaneously in chloroform or chlorobenzene. The solutions were heated at 50 °C and stirred for 14 hr. For the blend solutions containing QT-DA, the molecules were first dissolved in THF and DMF (at 1:1 volume ratio) and stirred at 50 °C for 2 hr while the PC₆₁BM were dissolve separately in *o*-dichlorobenzene at 50 °C for 2 hr. After which the PC₆₁BM solution was added into the donor solution and stirred overnight at 50 °C. The total solid content was kept constant at 20 mg/mL while the amount of donor to acceptor was varied to achieve different weight ratios. Spin-coating speed was varied to achieve varying active layer thickness while the total solid content was kept constant at 20 mg/mL.

The external quantum efficiency (EQE) was measured with a mechanically chopped (213 Hz) monochromatic light from a 300 W Xe lamp. A Stanford Research System 830 lock-in amplifier was used to detect the spectrally resolved photocurrent via a voltage signal by passing the current through a 50 Ω resistor. Current density-voltage (J - V) characteristics were measured with a Keithley SMU 2400 sourcemeter. Illuminated J - V characteristics were obtained with a solar simulator calibrated to a power intensity 100 mWcm⁻² under standard AM1.5G and corrected for spectral mismatch with a NREL calibrated silicon photodiode fitted with a KG5 color filter.^{23, 24} The calculated J_{sc} from the integration of EQE spectra showed that the measured J_{sc} did not differ from it by more than 10 %. This cross check prevented overestimation of device efficiency in the fabricated solar cells. All measurements were conducted in a glove box under nitrogen environment with at least 6 devices being fabricated and tested for each condition.

5.3 Results and Discussion

5.3.1 Energy Level and Optical Properties of QT-ES & QT-DA

In Section 3.4.3, it was shown that the peak absorption for thin film samples of QT-DA is red-shifted by ~20 nm with respect to QT-ES (Fig 3.6b). The absorption coefficient (α) calculated for the peak absorption of both QT-ES and QT-DA was $\sim 4.3 \times 10^4$ cm⁻¹. This value is similar to that reported previously by Nicolas DiCésare *et. al.* for quaterthiophene molecules.²⁵ The relatively lower α of the QT molecules as compared to polythiophenes ($\sim 10^5$ cm⁻¹) is attributed to the limited aromatic units in the conjugated backbone of

small molecules as compared to their polymeric counterparts.^{26, 27} Therefore, a thicker active layer is needed to achieve the same amount of absorption for the QT molecules as compared to polymeric semiconductors, which could potentially indicate that a thicker active is required to produce an equivalent amount of current. Fig 5.2a shows the solution phase and thin film optical absorption for both QT molecules while the energy level diagram for QT-ES, QT-DA and PC₆₁BM is depicted in Fig 5.2b. It has been reported that an energy offset of at least 0.3 eV is required for charge transfer to occur, therefore the LUMO offset of at least 0.6 eV makes them compatible as donor and acceptor

components in a bulk heterojunction solar cells.^{28, 29}

Fig 5.2 (a) Normalized absorption for solution phase and thin film samples of QT-ES and QT-DA (b) Schematic drawing of energy diagram for QT-ES, QT-DA and PC₆₁BM

5.3.2 Device Architecture & Fabrication

The organic photovoltaic (OPV) devices were fabricated with a normal device architecture of ITO/PEDOT:PSS/active blend/Al. Fig. 5.3 shows a schematic diagram of the OPV devices prepared for this study.

Fig 5.3 Schematic drawing of the organic photovoltaic device architecture

Optimization of the donor to acceptor weight ratio was first carried out. Due to a difference in polarity between QT-ES and QT-DA, different solvents were used for the processing of both blends. QT-ES was soluble in the usual chlorinated solvents and hence it was dissolved together with PC₆₁BM. Chloroform was used as the processing solvent in the weight ratio and thickness variation study. For QT-DA, a solvent mixture of THF:DMF in 1:1 ratio by volume was used as the processing solvent. This was because the solubility of QT-DA in THF was too low and would be difficult to achieve a reasonable thickness using this solution via spin coating. On the other hand, the high boiling point and low vapour pressure of DMF will result in films with pin-holes and short circuiting when it is used as the processing solvent. Therefore, a solvent combination of THF and DMF was employed and both good solubility and processability was achieved. Upon optimizing of the weight ratio, the active layer thickness was varied by changing the spin speed while keeping the net concentration of the blend to be 20 mg/mL.

5.3.3 Optimization of Weight Ratio

The device performance of a range of donor to acceptor ratio of 2:1 (2.0), 1:1 (1.0) and 1:2 (0.5) were studied and the plots of power conversion efficiency (PCE), open circuit voltage (V_{oc}), short circuit current density (J_{sc}) and fill factor (FF) with varying weight ratio are shown in Fig 5.4. The J_{sc} and fill factor (FF) was found to be the most affected parameters when the weight ratios were varied. A decrease of up to 78 % in J_{sc} and 46 % in the FF was observed from the study.

Fig 5.4 Graphs of power conversion efficiency (PCE), open circuit voltage (V_{oc}), short circuit current density (J_{sc}) and fill factor (FF) vs weight ratio. Weight ratio is recorded as QT:PC₆₁BM and with active layer thickness of ~70 nm.

Both QT molecules showed the worst performing device for a donor to acceptor ratio of 1:2. On top of J_{sc} and FF a decrease in the open circuit voltage (V_{oc}) was observed. At such a high acceptor loading ratio, unbalanced charge transportation can occur resulting in the build up of charges in the active layer. It has been reported that the electron mobility of PC₆₁BM is $2 \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (measured via SCLC)³⁰, which is 3 orders of magnitude higher as compared to the hole mobility of QT molecules presented in Section 4.3.4. This difference is believed to result in unbalanced charge transport thereby leading to a reduction in the built-in potential of the device and lowering of the V_{oc} . Furthermore, presence of excess charges in the active layer can lead to the increase in the probability of recombination of charges causing a drop in the V_{oc} and affecting the FF drastically.^{31, 32} The optimum donor to acceptor weight ratio for both QT molecules was found to be 1:1.

5.3.4 Optimization of Active Layer Thickness

Variation of active layer thickness was studied as ideally a thicker layer can provide a higher optical density and hence result in improved absorbance of the device. The enhanced absorbance can result in an increase in the J_{sc} and therefore higher PCE values. Fig. 5.5 shows the J - V graph for films with thickness of about 80 nm and 135 nm for both QT molecules. Device data for layer thickness below 70 nm were not presented as the films were too thin and contained large pin-holes which resulted in leaky or short circuiting of devices. From Table 5.1, it was found that the J_{sc} and FF of the devices decreased upon increasing the active layer thickness. This resulted in the deterioration in the PCE of the devices. This is attributed to the relatively low hole mobility in both

QT molecules as seen from the SCLC measurements (Chapter 4, Fig 4.8). A hole mobility of $2.83 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $6.91 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for QT-DA and QT-ES was obtained respectively. As the active layer gets thicker, effective charge transportation becomes more difficult. In thick active layers, the low mobility can result in poor charge transportation and the lowering of J_{sc} .³³ This was in line with the substantial increase in series resistance (R_s) when the active layer thickness was increased from $\sim 80 \text{ nm}$ to $\sim 130 \text{ nm}$ (from Table 5.1). Therefore, the optimum active layer thickness was found to be in the range of $80 \pm 10 \text{ nm}$.

Fig 5.5 *J-V* graph of varying active layer thickness for QT-ES:PC₆₁BM (black) and QT-DA:PC₆₁BM (red) devices with D:A ratio of 1:1

Table 5.1 Photovoltaic characteristics for varying thickness of QT-ES:PC₆₁BM and QT-DA:PC₆₁BM

sample		V_{oc} (V)	J_{sc} (mA/ cm ²)	FF (%)	PCE (%)	R_s (Ω cm ²)	R_{sh} (Ω cm ²)
QT-ES:PC ₆₁ BM	80 nm	0.78	1.44	34	0.39 (± 0.04)	244	909
	135 nm	0.80	0.98	29	0.22 (± 0.02)	667	1428
QT-DA:PC ₆₁ BM	80 nm	0.71	2.86	45	0.91 (± 0.04)	79	1250
	135 nm	0.65	2.37	35	0.56 (± 0.04)	156	808

R_{sh} and R_s are calculated from the inverse slope of illuminated curves at short circuit and open circuit conditions

5.3.5 Effect of Functional Group on Device Performance

Upon optimization of the fabrication parameters for QT-ES and QT-DA blends, investigation on the effect of the functional group on the device properties was carried out. The device characteristics of the as-cast and annealed QT:PC₆₁BM cells for 1:1 donor to acceptor weight ratio with active layer thickness of 80 ± 10 nm are shown in Fig 5.6. It was observed that for QT-ES devices, annealing at 70 °C (temperature chosen to be near T_C of QT-ES; Table 3.1) for 10 min was required to achieve optimized device performance while a longer duration resulted in degradation of device efficiencies. Heat treatment is a common method used to increase the crystallization in polymeric³⁴⁻³⁶ and small molecule solar cells³⁷⁻³⁹ by providing energy for molecular rearrangement. The donor and acceptor phases were intimately mixed in the as-cast films which resulted in poor charge transportation

channels. Upon thermal annealing, the crystallization of molecules leads to the formation of donor and acceptor phases which improves the charge transportation. Besides chloroform, high boiling point solvents like chlorobenzene and *o*-dichlorobenzene were used to delay the drying process and provide additional time for the crystallization of molecules and formation of donor and acceptor rich domains. An increase in the device performance of QT-ES:PC₆₁BM cells fabricated from chlorobenzene was observed where the J_{sc} and V_{oc} was doubled as compared to chloroform processed devices (from Table 5.2). However, it was realized that annealing was still necessary to achieve the optimum device performance. This was believed to be due to the low crystallization ability of QT-ES (shown from XRD in Section 5.3.6), hence even when a high boiling point solvent was used, the extent of crystallization was still too low to form donor and acceptor rich domains for effective charge transportation. It was observed that after annealing, the PCE of the QT-ES devices increased by at least 7-fold.

Fig 5.6 J - V graph (left) & EQE spectra (right) for QT-ES:PC₆₁BM and QT-DA:PC₆₁BM devices with D:A ratio of 1:1 and active layer thickness ~70 nm

Table 5.2 Photovoltaic characteristics of QT molecules as donor with PC₆₁BM as the acceptor (1:1 weight ratio). Device structure: ITO/PEDOT:PSS (40 nm)/active layer (70 nm)/ Al(80 nm).

sample		V_{oc} (V)	J_{sc} (mA/ cm ²)	FF (%)	PCE (%)	R_s (Ω cm ²)	R_{sh} (Ω cm ²)
QT-ES:PC ₆₁ BM ^a	Non-annealed	0.36	0.22	27	0.02 (± 0.01)	1428	2000
	Annealed	0.78	1.44	34	0.39 (± 0.04)	244	909
QT-ES:PC ₆₁ BM ^b	Non-annealed	0.53	0.45	26	0.06 (± 0.01)	1111	1429
	Annealed	0.74	1.98	29	0.42 (± 0.02)	250	455
QT-DA:PC ₆₁ BM ^c	Non-annealed	0.71	2.86	45	0.91 (± 0.04)	79	1250
	Annealed	0.63	1.35	35	0.30 (± 0.03)	244	1000

^aDevice fabricated from chloroform

^bDevice fabricated from chlorobenzene

^cDevice fabricated from THF/DMF

R_{sh} and R_s are calculated from the inverse slope of illuminated curves at short circuit and open circuit conditions

It is interesting to note that despite both chloroform and chlorobenzene annealed QT-ES:PC₆₁BM devices giving similar PCE of ~0.40 %, the J - V characteristics were different. It can be seen from Table 5.2 that annealed devices from chlorobenzene displayed a higher J_{sc} and a lower V_{oc} as compared to the chloroform ones. This is believed to be related to the film morphology and was observed from the atomic force microscopy (AFM) images in Fig 5.7. It can be seen that the film processed from chlorobenzene shows a smaller domain size (Fig 5.7a) as compared to that from chloroform (Fig 5.7b). This was further evident from the root-mean-square (RMS) roughness values of 3.07 nm and 3.58 nm for chlorobenzene and chloroform processed films respectively. The origin for smaller domain sizes obtained from the chlorobenzene processed films could be attributed to a higher solubility of QT-ES in the solvent. The smaller domains gave rise to an increase in the surface area between the donor and acceptor phases which would increase the exciton

splitting efficiency and charge generation rate. Therefore this gave rise to an increase in J_{sc} for the chlorobenzene processed blends. However, the increased surface area could increase the probability of recombination between electron-hole pairs during transportation. The shunt resistance (R_{sh}) has been related to recombination of charge carriers near the donor acceptor interfaces or near the electrode interfaces.⁴⁰⁻⁴² From table 5.2, the lower R_{sh} of 455 Ωcm^2 (for chlorobenzene) as compared to 909 Ωcm^2 (for chloroform) indicates an increase in recombination in the former. This will therefore lead to an increase in the V_{oc} of the devices from 0.74 V (chlorobenzene) to 0.78 V (chloroform).³¹

For QT-DA:PC₆₁BM devices, it was found that annealing was detrimental to its performance. A decrease of ~60% in the PCE was observed for the annealed QT-DA blends. The V_{oc} , J_{sc} and FF were all adversely affected by the heat treatment with the J_{sc} being the most affected parameter whereby a deterioration of 50 % was observed. Upon examination of the AFM images in Fig 5.7c and Fig 5.7d, it can be observed that more pronounced fibers were seen after thermal annealing accompanied by an increase in the RMS roughness of the film (from 14.42 nm for as-cast film to 16.84 nm) which was ascribed to aggregation of the QT-DA molecules. This increased roughness can result in a poor contact between the active layer and the cathode resulting in increased electrical resistance which was in line with the increase in R_s observed in Table 5.2. Furthermore, the aggregated QT-DA molecules (which can lead to aggregation of PC₆₁BM molecules concurrently) may lead to a decrease in the donor/acceptor interfacial area thereby lowering the exciton separation yield and charge generation.^{43, 44} Annealing temperatures ranging from 100 to 120 °C were used; however all the temperatures resulted in poorer device performance.

A point to note was that annealing temperatures below 100 °C had no effect on the performance of QT-DA:PC₆₁BM devices. This indicated that the morphology was relatively stable and would not change during device operation. Therefore an ideal phase separation between the donor and acceptor was achieved from the as-cast QT-DA:PC₆₁BM films.

More importantly, it was observed that QT-DA:PC₆₁BM devices had a 2-fold increase in PCE as compared to QT-ES:PC₆₁BM cells (0.91 % vs 0.41 %) whereby the improvement mainly came from an increase in J_{sc} . The EQE measurements showed a similar profile as the thin film absorption (shown in Fig 5.2) where QT-DA devices were red-shifted with respect to QT-ES. A higher FF of 45 % was also seen from the QT-DA devices as compared to 34 % from QT-ES. This was attributed to a more balanced electron and hole transport in the QT-DA:PC₆₁BM devices which was also brought about by the higher mobility of QT-DA (shown in Fig 4.8).^{31, 37} The higher V_{oc} obtained from the QT-ES based devices was attributed to the deeper HOMO level of QT-ES (-5.5 eV) with respect to QT-DA (-5.2 eV). An important difference between the QT-DA and QT-ES molecules was that annealing was not required to attain the optimum device performance for QT-DA blends. This will can be translated to time and cost savings which will be beneficial for large-scale production. Morphological differences for the blends from both QT molecules and X-ray studies will be presented and discussed in the following section.

5.3.6 Microstructure of Blend Films

To further elucidate the effect of $-\text{COOH}$ groups on the solar cell device performance; AFM images were first collected to understand the morphology of the active layer. Fig. 5.7 shows the AFM images for non-annealed and annealed blend films of both QT molecules.

Fig 5.7 Height images from AFM tapping mode for annealed QT-ES:PC₆₁BM films from (a) chlorobenzene, (b) chloroform and QT-DA:PC₆₁BM films (c) non-annealed, (d) annealed. The scale bars in (a)/ (b) are 30 nm while (c)/ (d) are 120 nm with scan size of 20 x 20 μm for all

A remarkable difference in morphology was observed between the QT blends. In Fig. 5.7c and 5.7d, nano-fibers can be seen from the QT-DA:PC₆₁BM active layers which was attributed to the high propensity to crystallize for QT-

DA. A schematic diagram for the packing of QT-DA molecules from hydrogen-bonding induced π - π interaction is shown in Fig 5.8. Similar nano-fibers (with a smaller length scale) were previously imaged from the neat films of transistor devices (Fig 4.6). The presence of these fibers can provide pathways for efficient hole transportation which will increase J_{sc} of the devices. This was indeed the case as seen from Table 5.2 whereby the enhanced PCE for QT-DA based devices came mainly from an increase in the J_{sc} and FF. An increase of up to 2 times in the J_{sc} of QT-DA devices (2.86 mA/cm²) as compared to QT-ES (1.44 mA/cm²) was observed. The increase in J_{sc} of organic solar cells for blend microstructures containing nano-fibers had been widely reported by others^{18, 19, 21} and our group.^{20, 22} These previous reports were mostly based on preformed nano-fibers by anti-solvent crystallization and were mixed with fullerenes to form the active blend solution. However in this study, molecular engineering of the small molecules was employed whereby hydrogen-bonding induced π - π interaction lead to an in-situ formation of the nano-fibers. Besides an active layer with enhanced crystallinity, the higher hole mobility of QT-DA as seen from the SCLC measurements from Section 4.3.4 is another contributing factor for the better performing device. The higher hole mobility can provide for a more balance electron and hole transport thereby improving FF of the devices.

Fig 5.8 Schematic drawing of the packing of QT-DA molecules

X-ray diffraction (XRD) measurements were performed to prove the enhanced crystallinity of QT-DA blend films as compared to QT-ES. Fig 5.9a shows the graph for annealed QT-ES:PC₆₁BM while the inset is for the as-cast film. It can be seen that prior to annealing, a very weak signal is observed which upon annealing can be accurately indexed as $2\theta = 3.8^\circ$. This is calculated to be a d-spacing of 23.3 Å which corresponded well with the height of the molecule (23.6 Å). This showed that QT-ES adopted an edge-on configuration similar to that seen in the transistor film in the previous chapter. The weak diffraction peak for the as-cast film indicated a low crystallinity film which provided further evidence for the explanation of the poor device performance mentioned previously. On the contrary, diffraction peaks in Fig 5.9b were clearly visible for QT-DA blend films even prior to thermal annealing. Furthermore besides the 1st order peak, a weak signal coming from the 2nd order peak can be observed. The appearance of 1st and 2nd order peak gave strong evidence that QT-DA blend films were more crystalline as compared to QT-ES. This is ascribed to the presence of hydrogen-bonding induced π - π interaction which enhances the inter-molecular connectivity and

crystallinity. The 2 θ peak for QT-DA blend films corresponded to a d-spacing of 26.7 Å which was close to the length of the molecule (inset of Fig 5.9b). Likewise, similar observation was made from the XRD scans of the QT-DA transistor films. Therefore it is believed that QT-DA adopted a vertical orientation in the blend film which can be beneficial in solar cell device architecture. In the vertical orientation, charge transportation in the diode configuration occurs mostly along the conjugated backbone which is more efficient as compared to hopping between the conjugated chains in the edge-on configuration.

Fig 5.9 Integrated XRD patterns for annealed (a) QT-ES:PC₆₁BM and as-cast (b) QT-DA:PC₆₁BM. Inset in (a) shows the XRD pattern for non-annealed QT-ES:PC₆₁BM while in (b) are the molecular dimensions of QT-DA where a similar height was found for QT-ES due to the same alkyl chain length.

Hence, from the AFM and XRD experiments it can be observed that the introduction of –COOH end-functional groups in QT-DA small molecules lead to an increase in the crystallinity of the blend films and formation of nano-fibers. These properties afforded higher PCE values as compared to the ester derivative which was lacking in the hydrogen-bonding. Furthermore, ideal

blend morphology was achieved in the as-cast film of QT-DA:PC₆₁BM eliminating the need for an annealing step which will be beneficial for large scale fabrication.

5.4 Conclusion

In conclusion, it was demonstrated that carboxylic acids can be a useful end-functional group in the molecular design of solution processable small molecule solar cells. The introduction of the –COOH groups increases the molecules' propensity for crystallization by enhancing the inter-molecular connectivity. The increase in crystallization ability was seen from the formation of nano-fibers and crystalline peaks in AFM and XRD respectively. Upon annealing, the crystallization of QT-DA occurs and a higher density of nanofibres can be observed from the AFM images. However, no improvement in device performance was observed. This was attributed to a non-ideal phase separation between QT-DA and PCBM. A decrease in the donor/acceptor interface area could have occurred thereby leading to a lowering of the exciton generation and charge generation. The aggregation of PCBM is expected to take place concurrently with the crystallization of QT-DA. This is due to the forcing out of PCBM molecules from the QT-DA phases during its crystallization process. However, this could not be proved as PCBM peaks (13.9°, 16.7°, 25.3° and 29.3°) was not detected from the XRD scans.

An interesting point was that –COOH functionalized molecules adopted a vertical alignment which should provide better charge transportation as compared to edge-on configuration in the solar cell device architecture. The QT-DA blends resulted in devices with higher PCE as compared to the diester

functionalized molecules which lacks the hydrogen-bonding induced π - π interaction. The main contribution to the increase in PCE came from an increase in the J_{sc} and FF of the devices which was attributed to a higher hole mobility in QT-DA and a more balanced charge transport in the devices. It is believed that the use of this interaction will be particularly useful in the enhancement of structural order in molecules with low crystallization ability and at the same time improve crystallinity of solution processed small molecule films.

5.5 References

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Chapter 6

**Impact of –COOH Position on Packing of Molecules and Device
Characteristics**

6.1 Introduction

In polymeric semiconductors, the attachment of solubilizing chains and other functional groups are generally restricted to directions perpendicular to the conjugated backbone. Studies on chain-end functionalization of poly(3-alkylthiophenes) (P3ATs) have been reported with emphasis on their application in hybrid solar cells.¹⁻⁵ Polar groups such as amines, carboxylic acids and phosphonates have been employed as anchoring groups to improve the interaction between polymers and inorganic crystals. Another similar example of chain-end functionalization of P3ATs is the grafting on of C60 molecules to act as compatibilizers for P3HT and PC₆₁BM bulk heterojunction solar cells.⁶ Generally in chain-end functionalization, the density of the functional groups will be limited and its effect might be diluted by the much longer polymeric backbone.

Small molecules have the versatility of enabling the functional groups to be attached both perpendicular and parallel to the conjugated backbone without suffering these limitations and/or dilution of properties. In the previous chapter it was shown that functionalization of small molecules at the α - and ω -positions can increase the inter-molecular connectivity and crystallinity. It would be of value for future molecular design to understand how the position of the –COOH functional group can affect the packing of the molecules, i.e. the effect of positional isomerism. The investigation of structural isomerism has been reported for both small molecule and polymers where the effect was mainly seen in the symmetry and planarity of the molecules/ monomers which translates into the degree of curvature in polymers.⁷⁻¹² Takimiya *et. al.* investigated a series of naphthodithiophenes and demonstrated how the

structural isomerism affects the symmetry of molecules.⁹ It was shown that the molecules NDT3 and NDT4 bearing an angular shape displayed a deeper HOMO level and larger bandgaps as compared to their linear counterparts, NDT1 and NDT2 (shown in Fig 6.1). However, when it comes to field effect mobility of the vacuum deposited NDT molecules, NDT2 showed the lowest mobility presumably due to its having axial symmetry rather than centrosymmetry with respect to the thiophene moieties as in the other 3 molecules. These effects of symmetry was also translated onto polymers when they were included into the conjugated backbones.⁸

Fig 6.1 Molecular structures of naphthodithiophene isomers⁹

A recent example of structural isomerism in polymers has been shown by Facchetti *et. al.* for 3,6-dithiophen-2-yl-diketopyrrolo[3,2-*b*]pyrrole (a positional isomer of DPP) as an acceptor building block.¹² The DPP isomer building block showed a deeper HOMO level and larger bandgap due to longer bond lengths and lowered conjugative interaction between the thiophene rings and the electron-deficient isoDPP core as compared to DPP. Hence, positional isomerism can have a huge impact on the properties of the thin films. Chapter 6 explore the effects of small molecule functional group positioning have on the material properties and device performance of bulk-heterojunction (BHJ) solar

Fig. 6.2 Molecular structure of isoQT-DA (left) and QT-DA (right)

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P3CATs. For instance, in the presence of small ions like NH_4^+ the polymer can undergo hydrophobic self-assembly generating aggregates with red-shifted absorption. However, with large counterions like NBu_4^+ the polymers remain dispersed due to the steric effects of the substituent. This can serve as metal ion sensor through changes in colour upon complexation of the –COO^- groups with cations.

Simulation studies from Casanovas *et. al.* have shown that attractive forces are present between the oxygen atom of the C=O group and the hydrogen atom from neighbouring thiophene ring when –COOH groups are directly attached onto the 3-position of thiophene.¹⁶ This can therefore lead to a more rigid and planar molecule. Furthermore, based on their theoretical calculations, the –COOH substitution at the 3-position should result in the lowering of both the HOMO and LUMO level of the molecule with a stronger effect on the former. Hence, the HOMO level of –COOH substituted thiophenes bears a deeper HOMO level as compared to unsubstituted ones giving them better ambient stability.

In isoQT-DA, similar to results of the abovementioned simulations, a deeper HOMO level with respect to QT-DA was observed (-5.45 eV vs -5.18 eV). Hydrogen-bonding was also found to be present but the inter-molecular connectivity was weaker as compared to QT-DA. This decrease in interconnectivity was deduced from a smaller degree of red-shifting in the onset of thin film absorption.^{17, 18} Solar cell devices were fabricated with isoQT-DA and PC_{61}BM as the donor and acceptor. Device efficiency was found to be lower for isoQT-DA as compared to QT-DA partly due to a narrower spectral

absorption for the former. The hole mobility obtained from the space-charge limited current (SCLC) reveals a lower charge mobility in isoQT-DA. Atomic force microscopy (AFM) images and X-ray diffraction (XRD) scans for isoQT-DA neat and blend films showed presence of crystallinity even in the as-cast films. This confirms the enhancement in crystallinity of –COOH bearing small molecules via hydrogen-bond induced π – π interaction even upon switching of the acid position as compared to the diester functionalized molecules, QT-ES. However, the crystallinity in isoQT-DA was found to be lower as compared to QT-DA which was probably due to presence of steric hindrance from the alkoxy groups. On the other hand, it was realised that the solubility of isoQT-DA is three times higher as compared to QT-DA. Therefore from this study, it is believed that the number of aromatic units in isoQT-DA can be increased without running into solubility issues which is beneficial as the aromatic units can be added as side chains creating a 2-D conjugated small molecule.

6.2 Experimental Techniques

Synthesis of Ethyl 2-bromothiophene-3-carboxylate: 2-bromothiophene-3-carboxylic acid (4.0 g, 19.32 mmol), anhydrous sodium hydrogen sulfate (2.562 g, 21.25 mmol, 1.1eq.) and ethanol (200 mL) were charged into a round bottom flask. The contents were purged with argon for 30 min and the mixture was refluxed overnight under argon. After cooling to room temperature, DI water was added and extraction with ethyl acetate was done. The organic layer was dried over anhydrous MgSO_4 , filtered and concentrated for purification via column chromatography (silica gel, hexane/ CH_2Cl_2 , 2:1, v/v) (yield: 3.27 g, 72%). ^1H NMR (400 MHz, CDCl_3) δ ppm 7.36 (d, $J = 5.8$ Hz, 1H), 7.21 (d, $J = 5.8$ Hz, 1H), 4.35 (q, $J = 7.1$ Hz, 2H), 1.38 (t, $J = 7.1$ Hz, 3H)

Synthesis of 1-bromo-4-(2-butyloctyloxy)benzene: 4-bromophenol (3.0 g, 17.34 mmol), 5-(bromomethyl)undecane (5.186 g, 20.8 mmol, 1.2 eq.), anhydrous potassium hydroxide (3.83 g, 27.71 mmol) and DMF (40 mL) was charged into a round bottom flask. The mixture was then stirred overnight at room temperature. DI water was added and extraction with CHCl_3 was done. The organic layer was dried over anhydrous MgSO_4 , filtered and concentrated for purification via column chromatography (silica gel, hexane) (yield: 4.14 g, 70 %). ^1H NMR (400 MHz, CDCl_3) δ ppm 7.35 (d, $J = 8.9$ Hz, 2H), 6.77 (d, $J =$

8.9 Hz, 2H), 3.79 (d, $J = 5.7$ Hz, 2H), 1.75 (dd, $J = 11.8, 5.9$ Hz, 1H), 1.42 – 1.24 (m, 13H), 0.88 (td, $J = 6.8, 2.5$ Hz, 9H).

Synthesis of 2-(4-(2-butyl-octyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 1: 1-bromo-4-(2-butyl-octyloxy)benzene (4.5 g, 13.18 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (4.18 g, 16.48 mmol, 1.2 eq.), potassium acetate (1.94 g, 19.78 mmol), Pd(dba)₂ (227 mg, 0.40 mmol) and tri-o-tolylphosphine (289 mg, 0.95 mmol) were charged into a round bottom flask followed by 3 cycles of evacuating and refilling with argon. 15 mL of dioxane was then added and heated at 85 °C for 15 hr. After cooling down to room temperature, DI water was added and extraction with ethyl acetate was done. The organic layer was dried over anhydrous MgSO₄, filtered and concentrated for purification via column chromatography (silica gel, hexane/CH₂Cl₂, 3:1, v/v) (yield: 2.71 g, 53 %). ¹H NMR (400 MHz, CDCl₃) δ ppm 7.73 (d, $J = 8.5$ Hz, 2H), 6.88 (d, $J = 8.5$ Hz, 2H), 3.85 (d, $J = 5.7$ Hz, 2H), 1.76 (dt, $J = 11.9, 5.8$ Hz, 1H), 1.47 – 1.23 (m, 25H), 0.94 – 0.82 (m, 9H).

Synthesis of ethyl 2-(4-(2-butyloctyloxy)phenyl)thiophene-3-carboxylate:

Ethyl 2-bromothiophene-3-carboxylate (1.73 g, 7.36 mmol) and **1** (2.6 g, 6.69 mmol) was charged into a round bottom flask, 80 mL of toluene and 2 drops of Aliquat 336 was added. Na_2CO_3 (1.34 g, 13.39 mmol, 2eq.) was dissolved in 6 mL of DI water and added into the solution which was then purged with argon for 30 min. $\text{Pd}(\text{PPh}_3)_4$ (220 mg, 0.19 mmol, 0.03 eq.) was added into the solution and heated up to 85 °C for 48 hr. After cooling down to room temperature, DI water was added and extraction with ethyl acetate was done. The organic layer was dried over anhydrous MgSO_4 , filtered and concentrated for purification via column chromatography (silica gel, hexane/ CH_2Cl_2 , 1:2, v/v) (yield: 1.81 g, 65%). ^1H NMR (400 MHz, CDCl_3) δ ppm 7.48 (d, J = 5.4 Hz, 1H), 7.42 (d, J = 8.6 Hz, 2H), 7.17 (d, J = 5.4 Hz, 1H), 6.91 (d, J = 8.6 Hz, 2H), 4.21 (q, J = 7.1 Hz, 2H), 3.87 (d, J = 5.6, 2H), 1.78 (dt, J = 12.0, 5.8 Hz, 1H), 1.48 – 1.26 (m, 13H), 1.22 (t, J = 7.1, 3H), 0.9 (q, J = 6.9 Hz, 9H)

Synthesis of Ethyl 5-bromo-2-(4-(2-butyloctyloxy)phenyl)thiophene-3-carboxylate, **2:** 2-(4-(2-butyloctyloxy)phenyl)thiophene-3-carboxylate (1.14 g, 2.73 mmol) was dissolved in anhydrous CHCl_3 and N-Bromosuccinimide (NBS) (0.48 g, 2.73 mmol) was dissolved in anhydrous DMF separately. The solution was protected from light and NBS solution was added in drop wise via a dropping funnel. The mixture was then stirred overnight with protection from light. DI water was added and extraction with CHCl_3 was done. The organic layer was dried over anhydrous MgSO_4 , filtered and concentrated for purification via column chromatography (silica gel, hexane/ CH_2Cl_2 , 1:1, v/v) (yield: 1.08 g, 80%). ^1H NMR (400 MHz, CDCl_3) δ 7.44 (s, 1H), 7.38 (d, $J = 8.6$ Hz, 2H), 6.90 (d, $J = 8.7$ Hz, 2H), 4.19 (q, $J = 7.1$ Hz, 2H), 3.86 (d, $J = 5.6$ Hz, 3H), 1.78 (dd, $J = 11.8, 5.9$ Hz, 1H), 1.47 – 1.25 (m, 13H), 1.22 (t, $J = 7.1$ Hz, 3H), 0.89 (q, $J = 6.8$ Hz, 9H).

Synthesis of isoQT-ES: 2,2'-bithiophene-5,5'-diboronic acid bis(pinacol) ester (0.72 g, 1.72 mmol) and **2** (1.88 g, 3.78 mmol, 2.2 eq.) was charged into a

round bottom flask, 50 mL of toluene and 2 drops of Aliquat 336 was added. Na_2CO_3 (0.64 g, 6.04 mmol) was dissolved in 3 mL of DI water and added into the solution which was then purged with argon for 30 min. $\text{Pd}(\text{PPh}_3)_4$ (60 mg, 0.052 mmol, 0.03 eq.) was added into the solution and heated up to 85 °C for 48 hr. After cooling down to room temperature, DI water was added and extraction with ethyl acetate was done. The organic layer was dried over anhydrous MgSO_4 , filtered and concentrated for purification via column chromatography (silica gel, hexane/ CH_2Cl_2 , 1:3, v/v) to afford a yellowish orange viscous liquid (yield: 1.16 g, 68%). ^1H NMR (400 MHz, CDCl_3) δ 7.54 (s, 1H), 7.46 (d, J = 8.6 Hz, 2H), 7.10 (s, 2H), 6.92 (d, J = 8.6 Hz, 2H), 4.24 (q, J = 7.1 Hz, 2H), 3.87 (d, J = 5.6 Hz, 2H), 1.79 (dd, J = 11.4, 5.6 Hz, 1H), 1.47 – 1.21 (m, 22H), 0.89 (t, J = 7.5 Hz, 3H).

Synthesis of isoQT-DA: isoQT-ES (400mg, 0.40 mmol) was dissolved in 100 mL of THF while anhydrous KOH (1.35 g, 24.60 mmol, 60 eq.) was dissolved in 12 mL of DI water separately. The aq. KOH was added into the solution which was purged for 30 min with argon after which it was heated at 70 °C for 48 hr. After the reaction was cooled to room temperature, 2M HCl was added in for the protonation of the potassium salt. The solvent was rotavap off and the solids rinsed with copious amount of water till pH 7 was reached. The compound was then purified via column chromatography (silica gel, hexane/THF, 3:1, v/v) and recrystallized from THF/hexane to afford a

yellowish solid (yield: 169 mg, 45%). ^1H NMR (400 MHz, THF) δ 7.90 (s, 0.25H), 7.61 (s, 1H), 7.52 (d, $J = 8.7$ Hz, 2H), 7.22 (s, 2H), 6.93 (d, $J = 8.6$ Hz, 2H), 3.93 (d, $J = 5.4$ Hz, 2H), 1.58 – 1.30 (m, 14H), 0.97 – 0.87 (m, 9H). HRMS: m/z , 939.3851 (M^+), calcd for $\text{C}_{54}\text{H}_{67}\text{O}_6\text{S}_4$ 939.3815.

6.3 Synthesis and Material Characterization of isoQT-DA

A positional isomer of QT-DA, isoQT-DA (molecular structure shown in Fig 6.2) was synthesized and characterized. The motivation was to investigate how the molecular properties and structural orientation will be affected by the positioning of the hydrogen-bonding. Hydrogen-bonding of the molecules are expected to be perpendicular to the conjugated backbone in isoQT-DA. The effectiveness in enhancement of the inter-molecular connectivity for isoQT-DA will be explored and compared with respect to QT-DA.

6.3.1 Synthesis of isoQT-DA

Scheme 6.1 Synthetic Route for isoQT-DA

Scheme 6.1 depicts the synthetic route employed for the synthesis of isoQT-DA. The 1-bromo-4-(2-butyl-2-octyloxy)benzene was prepared via a Williamson ether synthesis, followed by replacing the bromine with a boronic ester using bis(pinacolato)diboron to afford **1**. Esterification of 2-bromothiophene-3-carboxylic acid with ethanol gave ethyl 2-bromothiophene-3-carboxylate which was further used for Suzuki coupling with 2-(4-(2-butyl-2-octyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane to afford ethyl 2-(4-(2-butyl-2-octyloxy)phenyl)thiophene-3-carboxylate which was purified via

column chromatography in a yield of 75 %. Bromination of the product with N-Bromosuccinimide (NBS) at room temperature at the exclusion of light gave ethyl 5-bromo-2-(4-(2-butyloctyloxy)phenyl)thiophene-3-carboxylate, **2**, in 85 % yield. A second Suzuki coupling between **2** and 2,2'-bithiophene-5,5'-diboronic acid bis(pinacol) ester gave isoQT-ES, a yellow viscous liquid. Finally, hydrolysis of isoQT-ES with aqueous potassium hydroxide at 70 °C in THF followed by column chromatography and recrystallization from THF/Hexane afforded pure isoQT-DA as a yellow-orange solid with a yield of ~48 %.

An interesting point to note was the difference in physical state of isoQT-ES and QT-ES where the former is a viscous liquid while the latter is a solid. This indicates that isoQT-ES has a weaker π - π interaction probably due to presence of steric hindrance from the branched alkyl chains at the α - and ω -positions. A further comparison of the acid molecules of isoQT-DA and QT-DA showed that the solubility of the former (30 mg/mL in THF) was three times higher than the latter (10 mg/mL in THF). This enhanced solubility could likewise be related to a weaker π - π interaction in isoQT-DA as seen for the ester analogues.

6.3.2 Structure Confirmation of isoQT-DA

The structure of isoQT-DA was confirmed using HRMS (shown in Appendix) and NMR spectroscopy. A peak corresponding to m/z value of 939.3851 was obtained from HRMS which matched the calculated value of 939.3815 for the structure of isoQT-DA. Further confirmation of the molecular structure was seen from the NMR spectra in Fig. 6.3 where the loss of the quartet proton signal from the ethyl groups at around 4.50 ppm is accompanied by the appearance of acid proton at 7.91 ppm.

Fig 6.3 NMR spectrum of aromatic region for isoQT-ES (left) and isoQT-DA (right) where peak **a** represents the quartet protons, peak **b** the α protons in the alkoxy side chain and peak **c** the proton signal for the acid group

FTIR peaks of isoQT-DA in the range from 1000 to 2000 cm^{-1} showed a similar acid carbonyl peak as that of QT-DA at the position of 1684 cm^{-1} (Fig 6.4).^{19, 20} However, there was an absence of the -OH peak between 3000 to 4000 cm^{-1} range for isoQT-DA and the reason is unclear but is believed to be likely related to a weak OH resonance absorption in isoQT-DA.

Fig 6.4 FTIR spectrum of isoQT-DA (in black) and QT-DA (in red) for 1000 – 2000 cm^{-1} (left) and 2500 – 4000 cm^{-1} (right)

6.3.3 Thermal Analysis

Decomposition temperature (T_d) were measured using the thermogravimetric analysis (TGA) while melting (T_M) and crystallization (T_C) temperatures were measured using a differential scanning calorimetry (DSC). Fig. 6.5a shows the change in weight loss when heated from 30 °C to 450 °C at 10 °Cmin⁻¹. A stepwise decomposition was observed for isoQT-DA where an initial loss of ~10.0 wt% was observed at 303 °C follow by further decomposition at 350 °C. The initial 10.0 wt% loss can be attributed to the decarboxylation of isoQT-DA or the loss of 4 carbon atoms from the branch alkoxy groups where the theoretical weight loss was 9.4 wt% and 11.9 wt% respectively. The experimental value is closer to that for decarboxylation and a similar observation was also previously reported by Krebs *et. al.* for polythiophenes bearing tertiary ester solubilising groups.^{21, 22} Therefore it is believed that the initial weight loss was due to the decarboxylation of isoQT-DA.

Fig 6.5 Graph of (a) TGA and (b) DSC isoQT-DA. Melting and crystallization temperature are marked as T_M and T_C .

This observation was very different from the TGA profile of QT-DA where a single decomposition temperature at 362 °C was seen (from Table 3.1 and Fig 6.5). This is believed to be related to the high T_M of 333 °C in QT-DA which prevented decarboxylation prior to decomposing of the main conjugated backbone. The thermal transitions for isoQT-DA as recorded by DSC showed a single T_M and T_C of 235 °C and 216 °C respectively (Fig. 6.5b) which is approximately 100 °C lower as compared to the values for QT-DA of 333 °C for T_M and 319 °C for T_C (from Table 3.1 and Fig 6.5b). The lower T_M and T_C for isoQT-DA compared to QT-DA correlates well with the weaker inter-molecular connectivity in the former. This weak inter-molecular interaction relates to the decarboxylation of isoQT-DA due to the melting of the structure at a temperature below that of decarboxylation. It was observed from TGA that the decarboxylation of isoQT-DA occurred at 303 °C while the melting of the molecule was at 235 °C. The melting of isoQT-DA lead to the breaking of the

polymeric structure resulting in non-hydrogen-bonded carboxylic acid groups which was susceptible to decarboxylation.

6.3.4 Optical Analysis

UV-vis absorption and photoluminescence (PL) of isoQT-DA solution were recorded for a dilute solution of 10^{-5} M in THF to avoid the aggregation of the molecules. The solution phase absorption/photoluminescence and thin film absorption are presented in Fig 6.6.

Fig 6.6 (a) UV-Vis absorption and PL measurements of isoQT-DA and QT-DA with a concentration of 10^{-5} M (b) Normalized thin film absorption of isoQT-DA and QT-DA

It can be observed from Fig 6.6a that the absorption of isoQT-DA in solution was blue-shifted as compared to QT-DA. This could be attributed to a weaker conjugative interaction at the 3-position of thiophenes as shown from simulation studies by Kao *et. al.* and Notario *et. al.*^{23, 24} Another possible reason for the blue-shift in the absorption is due to a lower degree of planarity in isoQT-DA. A dihedral angle of 55° between the quaterthiophenes and the phenyl ring was observed for isoQT-DA whereas in QT-DA the angle was 34°

(calculated from MM2 energy minimization; shown in Appendix). This twisting could be related to the presence of steric hindrance between the carbonyl oxygen and the hydrogen from the neighbouring phenyl ring. Hence, this will result in a decrease of the effective conjugation length within isoQT-DA resulting in the blue-shift of absorption.^{16, 24}

It has been reported that a torsion angle of 40° and above can result in an increase in the energy gap of about 0.25 to 0.4 eV.²⁵⁻²⁷ This coincides with the 0.23 eV larger bandgap of isoQT-DA as compared to QT-DA (refer to Table 6.1).

Likewise, the PL of isoQT-DA showed a blue-shift with respect to QT-DA with an increase in intensity. The difference in PL intensity was postulated to be due to presence of dimers and trimers which resulted in self-quenching of QT-DA PL as mentioned previously in Chapter 3.²⁸⁻³⁰ This indicates that the hydrogen bond interaction in isoQT-DA is weaker as compared to QT-DA. The onset of absorption for isoQT-DA matches fairly well with the peak absorption (λ_{max}) of the PL which was calculated to give a bandgap (E_g^{opt}) of ~2.6 eV. Fig 6.6b shows the thin film absorption of isoQT-DA where a red-shift in the onset of absorption and λ_{max} can be seen as compared to the solution phase absorption. The E_g^{opt} for the thin film sample was estimated to be 2.3 eV which was 0.3 eV higher as compared to QT-DA. Similarly, the wider bandgap in thin film samples of isoQT-DA was believed to be related to the reasons mentioned in the solution phase absorption.

6.3.5 Energy Levels of isoQT-DA

The highest occupied molecular orbital (HOMO) level for isoQT-DA was measured using photoelectron spectroscopy and estimated to be 5.45 eV (Fig 6.7). The attachment of –COOH electron-withdrawing groups at the 3-position reduces the energy of both the HOMO and LUMO with a greater stabilization in energy for the former.¹⁶ Hence, a deeper HOMO level was observed for isoQT-DA as compared to QT-DA. As it has been reported that in organic bulkheterojunction solar cells the V_{oc} is equivalent to the difference in the LUMO of the acceptor and HOMO of the donor, therefore the deeper HOMO in isoQT-DA should ideally provide an enhanced V_{oc} .³¹ Furthermore, the deeper HOMO can give rise to a better stability in the solar cell devices due to increased energetic barrier to oxidation.^{32, 33} A summary of the optical properties and energy levels of isoQT-DA and QT-DA is given in Table 6.1.

Fig 6.7 Graph of PESA measurement for thin films of isoQT-DA and QT-DA

Table 6.1 Summary of optical properties and energy levels of QT-diacid molecules.

Sample	$\lambda_{\max}$ (nm)		HOMO (eV)	LUMO (eV)	E_g^{opt} (eV) (film)
	solution	film			
isoQT-DA	415	438	-5.45	-3.15	2.30
QT-DA	456	506	-5.18	-3.11	2.07

6.4 Results and Discussions

6.4.1 Out-of-plane Mobility of isoQT-DA

The out-of-plane hole mobility of neat isoQT-DA was estimated using the space charge limited current (SCLC) in the diode configuration. The out-of-plane mobility was measured as it provides a direct correlation to the performance of the film in a solar cell configuration. Fig 6.8 shows the $J^{0.5}$ vs V plot for isoQT-DA films and QT-DA films with a device architecture of ITO/PEDOT:PSS/isoQT-DA/MoO₃/Al.

Fig 6.8 Graph of $J^{0.5}$ vs V_{eff} for hole-only devices of QT-DA (red) and isoQT-DA (black)

As discussed earlier in Section 4.4, the mobility measurements can be derived by fitting the data to the equation of $J = \frac{9}{8} \epsilon_o \epsilon_r \mu_h \frac{V^2}{L^3}$. It can be observed that the black solid line for isoQT-DA fits well from 3 V onwards giving a mobility of $7.13 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (four times lower as compared to QT-DA – $2.83 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). The presence of a non-linear region below 3 V is an indication that isoQT-DA exhibits field-dependent mobility owing to the presence of charge trapping sites such as grain boundaries and amorphous regions in the film.^{34, 35} The possibility of injection problems in isoQT-DA hole-only devices was ruled out as the ionization energy of MoO₃ and PEDOT:PSS has been reported to be 5.2 ~ 5.4 eV³⁶⁻³⁸, hence both materials will be able to form ohmic contacts with isoQT-DA.

Fig 6.9 AFM image of hole-only device for (a) QT-DA and (b) isoQT-DA. The scale bars are 30 nm for QT-DA and 10 nm for isoQT-DA with scan size of 5 x 5 μm for both.

The AFM images for the hole-only devices of both QT-diacid films are shown in Fig 6.9. A similar fibrous morphology is observed for both films however, the roughness based on r.m.s values revealed that isoQT-DA bears a smoother film as compared to QT-DA (1.13 nm and 4.23 nm respectively).

Furthermore, the nano-fibers in QT-DA neat films are more prominent as compared to isoQT-DA. This is attributed to a more crystalline film in the former as compared to isoQT-DA. The difference in crystallinity was further seen from XRD as shown in the later section (Fig 6.12a). The AFM images correlates well with the findings from the SCLC mobility measurements where a more fibrous film provides efficient charge transport channels thereby resulting in an enhanced hole mobility in QT-DA as compared to isoQT-DA.

6.4.2 OPV Characterization of isoQT-DA

An optimized donor to acceptor weight ratio of 1:1 for isoQT-DA and PC₆₁BM was used for solar cell device fabrication. Due to similar solubility of both QT-diacid molecules, the processing solvent employed for the isoQT-DA devices was THF:DMF 1:1 by volume. Fig. 6.10 shows the current density-voltage (*J-V*) and external quantum efficiency (EQE) characteristics of isoQT-DA and QT-DA devices.

Fig 6.10 *J-V* graph (left) & EQE spectra (right) for isoQT-DA:PC₆₁BM & QT-DA:PC₆₁BM devices with D:A ratio of 1:1, active layer thickness ~70 nm

Table 6.2 Photovoltaic characteristics of QT-diacid molecules as donor with PC₆₁BM as the acceptor (1:1 weight ratio). Device structure: ITO/PEDOT:PSS (40 nm)/active layer (70 nm)/Al(80 nm).

sample		V_{oc} (V)	J_{sc} (mA/ cm ²)	FF (%)	PCE (%)	R_s (Ω cm ²)	R_{sh} (Ω cm ²)
isoQT-	Non-annealed	0.79	0.89	35	0.24	454	2000
DA:PC ₆₁ BM	Annealed	0.83	0.70	33	0.19	714	2100
QT-DA:PC ₆₁ BM	Non-annealed	0.71	2.86	45	0.91	79	1250
	Annealed	0.63	1.35	35	0.30	244	1000

It was observed that isoQT-DA displayed a much lower device performance with respect to QT-DA with a three times decrease in the power conversion efficiency (PCE) (Table 6.2). The as-cast device for isoQT-DA had a PCE of 0.24 %, short circuit current density (J_{sc}) of -0.88 mA/cm² and open circuit voltage (V_{oc}) of 0.79 V. The increase in V_{oc} for isoQT-DA with respect to QT-DA can be rationalised by the deeper HOMO level of the molecule (Table 6.2). The main drawback with the isoQT-DA devices was with its low J_{sc} . This was in part due to the narrow absorption of the molecule which limited the EQE range to 540 nm resulting in a lost of a large portion of the solar spectrum. Secondly, the low hole mobility of isoQT-DA also contributed to the low J_{sc} of the devices. Furthermore, the rougher surface of isoQT-DA seen from AFM images in the following section can result in poor cathode contact resulting in increased resistivity. From Table 6.2, it was found that the series resistance (R_s) of isoQT-DA was almost six times higher (454 Ω cm² vs 79 Ω cm²) as compared to that of QT-DA.

For both QT-diacid molecules, annealing treatment was detrimental to the device performances. Temperatures from 90 °C to 120 °C were tried but no improvement was observed. Similar to QT-DA, temperatures below 90 °C did not result in any changes to the device performance for isoQT-DA. Hence, it is believed that an optimal phase separation was also obtained for the as-cast isoQT-DA:PC₆₁BM blend films. Despite the fact that isoQT-DA displayed a lower PCE as compared to QT-DA, the former showed an increased in solubility. Therefore, more aromatic units can be included into isoQT-DA's structure which will help increase the π - π interaction strength and its crystallinity, without resulting in a loss of solubility. Hence, the substitution of solubilising groups at the α - and ω -position of the molecule is a possible design strategy for producing high solubility conjugated small molecules.

6.4.3 Blend Morphology and Molecular Orientation of isoQT-DA

The morphology of the active layer blends was studied using AFM. Fig 6.11 shows the as-cast and annealed films of QT-DA and isoQT-DA blends where a very different surface morphology was observed. Fiber formation was also seen in the as-cast isoQT-DA blend films (Fig 6.11a) but they are shorter and thicker in width as compared to that of QT-DA (Fig 6.11c). The root mean square (r.m.s) roughness of isoQT-DA films was slightly higher as compared to that of QT-DA for both as-cast and annealed films which could be related to the thicker fibers observed (isoQT-DA - 15.94 nm (as-cast)/ 17.51 nm (annealed) and QT-DA - 14.42 nm (as-cast)/ 16.84 nm). These shorter fibers observed from isoQT-DA:PC₆₁BM active layers correlates well with the low J_{sc} observed

in the devices as charges will have to hop through multiple grain boundaries or could be trapped at discontinuous paths. Upon annealing, an increase in the density of fibers can be observed in the isoQT-DA blend films (Fig 6.11b) which was attributed to the aggregation of the isoQT-DA molecules. Despite observing an increase in the number of fibers from AFM, no improvement in device performance was obtained. From Table 6.2, it can be observed that there is an increase in the R_s upon thermal annealing. Hence, it is believed that the rougher surface upon annealing resulted in poor electrical contact between the active layer and the cathode therefore an increase in the R_s was observed together with a decrease in the J_{sc} of the devices. The increase in V_{oc} observed in Table 6.2 for the annealed isoQT-DA devices as compared to the as-cast sample is attributed to the burning of shunts in the films during thermal annealing.^{39, 40}

Fig 6.11 Height images from AFM tapping mode for isoQT-DA:PC₆₁BM (a) as-cast and (b) annealed films and QT-DA:PC₆₁BM (c) as-cast and (d) annealed films. The scale bars are 120 nm with scan size of 20 x 20 μm for all. Annealing was performed at 100 °C.

Fig 6.12 (a) Integrated XRD

patterns for isoQT-DA:PC₆₁BM (black) QT-DA:PC₆₁BM (red) and (b) contact angle measurements for neat films of isoQT-DA

To further elucidate the packing structure and crystallinity in QT-DA:PC₆₁BM active layers, X-ray diffraction (XRD) measurements were conducted. Fig 6.12a shows the integrated XRD patterns for the as-cast blend films of both isoQT-DA and QT-DA for comparison. The intensity of the crystalline peak in isoQT-DA was lower as compared to that of QT-DA which indicated a less crystalline film in the former. This correlates well with the AFM images observed in Fig 6.9 and Fig 6.11. Furthermore, the decrease in hole mobility of isoQT-DA as compared to QT-DA (shown in Section 6.4.1) can be attributed to the lower crystallinity.⁴¹⁻⁴³ Besides a lower intensity, the peak position for isoQT-DA was also found to be shifted to a higher angle with respect to QT-DA. The 2θ angle of 4.06° for isoQT-DA blend films corresponded to a d-spacing of $21.7 \text{ \AA}$. Similar XRD pattern was observed for the neat films of isoQT-DA (shown in Appendix). In order to understand the structural configuration of isoQT-DA with respect to the substrate, contact angle measurements were performed for neat films and shown in Fig 6.12b. The relatively large contact angle of 78° obtained for isoQT-DA shows a

hydrophobic film surface which is postulated to be related to exposed alkyl chains. This value is similar to that seen for QT-ES films which had alkyl chains on its surface. Therefore it is believed that isoQT-DA adopted a standing configuration similar to that of QT-DA. As the d-spacing of 21.7 Å is much smaller as compared to the length of a fully extended structure of isoQT-DA (32.3 Å calculated from ChemBio 3D programme), twisting of the alkyl chains about the flexible ether linkage was deduced. A proposed schematic diagram for the packing of isoQT-DA with respect to the substrate surface is shown in Fig 6.13.

Fig 6.13 Proposed packing of isoQT-DA molecules; alkyl chains are represented by R for clarity

6.5 Conclusion

The isomer of QT-DA, isoQT-DA was synthesized and characterized for both its material properties and device characteristics. It was shown that the positioning of the –COOH can have a huge effect on both the optical absorption and the crystallinity of the molecule. A blue-shifting in the absorption of isoQT-DA as compared to QT-DA was observed and attributed to a weaker conjugative interaction of the –COOH functional group at the 3-position and the presence of twisting in the conjugated core.

The device performance of isoQT-DA:PC₆₁BM was found to be lower as compared to QT-DA mainly due to a low mobility and crystallinity of the molecule. It was however interesting to note that similar to QT-DA, isoQT-DA displayed a crystalline film for the as-cast blend films which was not observed for QT-ES. This indicates that the hydrogen-bonding can greatly improve the inter-molecular connectivity and π – π interaction between the conjugated backbones effecting crystallization in solution processed films. Furthermore, it was realised that the attachment of branch solubilising group at the α - and ω -positions of the molecule, as in the case of isoQT-DA, resulted in a more soluble molecule as compared to QT-DA. Hence, the number of aromatic units can be increased in isoQT-DA without running into solubility issues. The additional aromatic groups can be substituted as side chains thereby creating a 2-D conjugated small molecule while -COOH groups can be added to further enhance the crystallinity through hydrogen-bonding induced π – π interaction. Further details will be discussed as future work in the following chapter.

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Chapter 7

Summary and Future Work

7.1 Summary of Work

In conclusion, it has been shown that the introduction of carboxylic acid as end-functional groups can enhanced the inter-molecular connectivity and crystallinity of solution processed small molecule films. This is due to the hydrogen-bond induced π - π interaction induced by the -COOH groups. As a proof of concept, quaterthiophene bearing dicarboxylic acid end groups (abbreviated as QT-DA) and a diester analogue (abbreviated as QT-ES) was synthesized and compared. QT-DA showed an increase in its thermal transition temperatures as compared to QT-ES. The melting and crystallization temperature was found to be at least 200 °C higher for QT-DA. Interestingly, the solution absorption profile for both QT-DA and QT-ES was found to be similar however, a larger extent of red-shift in the absorption of thin film samples was observed for QT-DA (50 nm in QT-DA as compared to 23 nm in QT-ES). This increase in the degree of red-shift in absorption indicated an enhanced inter-molecular connectivity and π - π stacking in QT-DA as compared to QT-ES.

Besides the red-shifting in absorption, the increased connectivity and crystallinity provided QT-DA with a higher hole mobility both in the in-plane and out-of-plane direction. In the transistor fabrication for in-plane mobility measurements, QT-DA displayed both passivation of dielectric layer and formation of crystalline active channel simultaneously. This was made possible by the attachment of one end of the -COOH onto the oxide surface while the other end forms hydrogen-bonding with subsequent QT-DA molecules. A threshold voltage observed for QT-DA and QT-ES on bare SiO₂ was -3 V and -28V respectively. The high threshold voltage (V_{th}) in QT-ES was attributed to

the presence of charge trapping sites in unpassivated SiO₂ surfaces.^{1, 2} On the other, passivation was achieved by QT-DA giving it a 9-fold decrease in the V_{th} . Hence prior surface passivation of the dielectric oxide layers can be omitted thereby avoiding additional preparation time and wetting issues related to low surface energy of alkylsilane treated surfaces.

The application of –COOH functionalized molecules in bulk heterojunction solar cell devices was then explored whereby QT-DA and QT-ES acted as the donor molecule while PC₆₁BM as the acceptor. It was found that QT-DA:PC₆₁BM devices had a two-fold improvement in power conversion efficiency as compared to QT-ES:PC₆₁BM. This improvement was mainly coming from an increase in the short circuit current density of QT-DA devices which was attributed to an enhanced crystallinity and hole mobility. Furthermore, it was shown that QT-DA: PC₆₁BM blend films had an optimal phase separation for the as-cast film and hence no thermal treatment was required to improve the device efficiency. This is beneficial for large scale production as time and cost can be saved. Interestingly, QT-DA adopted a similar molecular orientation in the organic solar cell blend as with the transistor neat film – vertical alignment. This will be beneficial for devices with diode configuration as charge transport is more effective along the conjugated backbone of the molecules.

Upon establishing the effectiveness of –COOH end-functionalized small molecule in solution processed organic solar cells, the effect of the positioning of –COOH group was investigated. As mentioned, small molecules possess molecular flexibility in substituting functional groups parallel and perpendicular to the conjugated backbone. Hence, it would be beneficial for

future molecular design to explore the effects of the positioning of the –COOH groups in molecular packing and device performance. QT-DA-2, which bears the exact same functional groups as QT-DA but with a switch in the substitution position of alkoxy solubilising chains and –COOH structural directing groups, was synthesized and compared with QT-DA. The ester analogue of QT-DA-2, QT-ES-2, was found to be a viscous yellow liquid while QT-ES was a orange solid. This indicated that π – π stacking was hindered upon placing the solubilizing chains at the α - and ω -position. However upon hydrolysis of QT-ES-2, QT-DA-2 was obtained as a yellow solid which was attributed to the presence of hydrogen-bonding induced π – π interaction. The melting and crystallization temperature of QT-D-2 was ~ 100 °C lower as compared to QT-DA. Furthermore, a decarboxylation was observed at ~ 300 °C for QT-DA-2 from TGA measurements. These observations were believed to be related to a weaker inter-molecular connectivity and lower crystallinity in QT-DA-2 as compared to QT-DA.

Despite so, QT-DA-2 also displayed enhanced crystallinity in as-cast films and shows relatively higher thermal transition temperatures as compared to QT-ES. However, due to the narrow absorption range and low hole mobility of QT-DA-2, the solar cell device performances of QT-DA-2:PC₆₁BM was much lower as compared to QT-DA:PC₆₁BM. The reason for the blue-shifting in optical absorption of QT-DA-2 was due to the weaker orbital coupling at the 3,4- positions of thiophenes as compared to the 2,5- positions, hence the donor-acceptor interaction between the conjugated core and –COOH groups was less pronounced. Although poor device performance was observed from QT-DA-2 relative to QT-DA, a higher solubility was observed in the former (30mg/mL vs

10mg/mL). This may provide insight to future small molecule design which will be further discussed in the following section.

7.2 Future Work

As mentioned in the introduction of Chapter 6, poly[3-(carboxyalkyl)thiophene-2,5-diyl] (P3CAT) was studied by different groups employing different solvents.^{3, 4} DMSO and pyridine were being used as the processing solvent for the transistor and solar cell study respectively. Although both studies were done for different types of devices, however there was indication that pyridine appears to produce a more crystalline film as compared to DMSO. Hence, it would be of importance to investigate the effect of different processing solvent. In this work THF/DMF was used as the processing solvent, hence there is room for further exploration with pure pyridine, solvent mixtures of THF/pyridine and DMF/pyridine. As the substitution of –COOH groups in small molecules for solution processed organic solar cells is a relatively new direction, optimization of the processing solvent maybe required as seen in the case of poly(3-hexylthiophene). Furthermore, pertaining to the configuration of QT-DA molecules on the SiO₂ surfaces, variable angle XPS or Near Edge X-Ray Absorption Fine Structure (NEXAFS) can be performed to further strengthen the claim of the vertical alignment.

Another possible future work will be the application of –COOH groups in low band-gap small molecules. In the current study, quaterthiophene was used as the conjugated core however it was observed that the band-gap of QT-DA was ~2 eV. A lower band-gap small molecule in the range of 1.8 ~ 1.6 eV will enable the absorption of a larger portion of the solar spectrum. The enhanced absorption may lead to an increase in the short circuit current density

of the solar cell devices thereby improving the device efficiency.

An interesting future direction will be the exploration of 2-D conjugation in electroactive small molecules which can be achieved by side chain substitution of -COOH functionalized aromatic groups. Such conjugated side chain engineering have previously been employed in polymeric semiconductors to increase the absorption range, tunability of energy levels and enhanced hole mobility.⁵⁻⁷

Fig 7.1 Proposed structure for 2-D conjugation of small molecule

Fig. 7.1 shows the proposed schematic structure of the 2-D conjugated small molecule. As observed in Chapter 6, the placement of solubilizing groups at the α - and ω -position of the molecule results in improved solubility which is therefore the choice for the proposed structure. Side chain bearing 1 ~ 2 aromatic units can be used to improve the absorption range and π - π interaction of the molecule while the presence of -COOH groups can enhanced the inter-molecular connectivity.

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List of Publications

Kwan Hang Lam, Thelese Ru Bao Foong, Zien Ooi, Jie Zhang, Andrew Clive Grimsdale, Yeng Ming Lam, “Enhancing the Performance of Solution-Processed Bulk-Heterojunction Solar Cells Using Hydrogen-Bonding-Induced Self-Organization of Small Molecules”, *ACS Appl. Mater. Interfaces*, 2013, 5 (24), 13265-13274

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Oral Presentation

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Poster Presentation

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Appendix

Fig S1 High-resolution mass spectroscopy of QT-ES

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Fig S3 High-resolution mass spectroscopy of isoQT-DA

Fig S4 Graph of TGA for QT-ES (black) and QT-DA (red)

Fig S5 Graph of DSC for QT-ES (left) and QT-DA (right), T_M and T_C represents melting and crystallization temperature respectively.

Fig S6. Graph of PL for different concentration of QT-ES (in CHCl_3 ; left) and QT-DA (in THF; right)

Fig. S7. AFM topography and step height of 26 Å for monolayer of QT-DA

Fig S8 Integrated XRD patterns for neat films of isoQT-DA (black) and QTDA (red)

Fig S9 *J-V* graph of isoQT-DA:PC₆₁BM (2:1 weight ratio). For isoQT-DA:PC₆₁BM 1:2 weight ratio all devices displayed short circuit characteristics.

Table S1 Photovoltaic characteristics of isoQT-DA:PC₆₁BM with varying weight ratio. Device structure: ITO/PEDOT:PSS (40 nm)/active layer (70 nm)/ Al(80 nm).

isoQT-DA:PC ₆₁ BM ^a		V_{oc} (V)	J_{sc} (mA/ cm ²)	FF (%)	PCE (%)
2:1	Non-annealed	0.65	0.16	23	2.38×10^{-2}
	Annealed	0.70	0.065	14	6.4×10^{-3}
1:1	Non-annealed	0.79	0.89	35	0.24
	Annealed	0.83	0.70	33	0.19

^aNote that short circuit devices was observed for 1:2 weight ratio of isoQT-DA:PC₆₁BM.

Fig S10 Molecular model of QT-DA simulated with MM2 energy minimization. A Dihedral angle of 34 ° between the thiophene and phenyl ring is shown.

Fig S11 Molecular model of isoQT-DA simulated with MM2 energy minimization. A Dihedral angle of 55 ° between the thiophene and phenyl ring is shown.