Enhancing the Photo-oxidative Stability of Non-Fullerene Electron Acceptors

Thesis by
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ABSTRACT

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Salman Alsharif

Even though improvements in the efficiency of organic solar cells encouraged the commercialization of this technology in the past two decades, the stability of organic solar cells is still an active area of research. The effect of photo-oxidative degradation on the performance of organic solar cell devices is significant. One way to lower the rate of photo-oxidation degradation is by preventing oxygen molecules from reaching the active layer of organic solar cells. This could be achieved by fabricating the devices in an inert environment in the absence of oxygen. Once the devices are fabricated, they would be encapsulated in a transparent material.\(^1\), \(^2\) Even though this is a viable solution, there are two main issues. First, it was shown that oxygen molecules could diffuse through the encapsulating material and degrade the devices.\(^3\) Second, implementing this solution would increase the fabrication cost of these devices, which would make this solution commercially unfeasible compared to other solar cell technologies.\(^3\) Speller and his colleges reported a possible mechanism of the photo-oxidative degradation and showed a relationship between the rate of degradation and LUMO energy levels of electron acceptor molecule\(^4\). In this thesis, we report the photo-oxidative degradation rate of O-IDTBR and O-IDTBR-(C\(_3\)N\(_2\))\(_2\). The later electron acceptor is analogous to O-IDTBR with deeper LUMO by 0.1 eV. After four hours of constant irradiation from a 1-sun intensity xenon solar simulator, the maximum UV-Vis absorbance of O-IDTBR is reduced by 12% relative
to O-IDTBR-(C₃N₂)₂. Lower absolute degradation rates were observed when 1-sun LED
solar simulator was used compared to xenon solar simulator.
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<th>Description</th>
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<tr>
<td>PT</td>
<td>polythiophenes</td>
</tr>
<tr>
<td>PPV</td>
<td>polyphenylenevinylenes</td>
</tr>
<tr>
<td>P3TH</td>
<td>Poly(3-hexylthiophene-2,5-diyl)</td>
</tr>
<tr>
<td>BCPM</td>
<td>[6,6]-Phenyl C₆₁ butyric acid methyl ester</td>
</tr>
<tr>
<td>PF</td>
<td>polyfluorenes</td>
</tr>
<tr>
<td>PCDTBT</td>
<td>poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4,7-di-2-thienyl-2′,1′,3′-benzothiadiazole]</td>
</tr>
<tr>
<td>PC₇₀BM</td>
<td>[6,6]-Phenyl C₇₁ butyric acid methyl ester</td>
</tr>
<tr>
<td>O-IDTBR</td>
<td>3-ethyl rhodanine-benzothiadiazole-coupled indacenodithiophene</td>
</tr>
<tr>
<td>MDMO-PPV</td>
<td>Poly[2-methoxy-5-(3′,7′-dimethyl-octyloxy)]-1,4-phenylene vinylene</td>
</tr>
<tr>
<td>TQ1</td>
<td>Poly[[2,3-bis(3-octyloxyphenyl)-5,8-quinoxalinediyl]-2,5-thiophenediyl]</td>
</tr>
<tr>
<td>IDT</td>
<td>Indacenodithiophene</td>
</tr>
<tr>
<td>O-IDT</td>
<td>n-octyl Indacenodithiophene</td>
</tr>
<tr>
<td>O-IDTB</td>
<td>n-octyl 3-ethylrhodanine-benzothiadiazole-coupled indacenodithiophene</td>
</tr>
<tr>
<td>O-IDTBR-(C₃N₂)₂</td>
<td>2-(1,1-dicyanomethylene)-3-ethyl rhodanine-benzothiadiazole-coupled indacenodithiophene</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------------------------------------------</td>
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<tr>
<td>O-IDTBR-(C₃N₂)₄</td>
<td>2,4-bis(1,1-dicyanomethylene)-3-ethyl rhodanine-benzothiadiazole-coupled indacenodithiophene</td>
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<tr>
<td>OSC</td>
<td>Organic solar cell</td>
</tr>
<tr>
<td>OVP</td>
<td>Organic photovoltaics</td>
</tr>
<tr>
<td>Bt</td>
<td>2,1,3-Benzothiadiazole</td>
</tr>
<tr>
<td>R</td>
<td>3-ethyl rhodanine</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>PCE</td>
<td>Power conversion efficiency</td>
</tr>
<tr>
<td>Vᵦₜ</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>Iₛₜ</td>
<td>Short circuit current</td>
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Chapter 1. Introduction:

In 2015, fossil fuel (oil, coal, and gas) accounted for about 86% of the primary energy consumption; there was no significant change to this trend for 15 years (2005-2015). The current energy resources are not meeting mankind's current energy demand, threaten our existence, and hinder our future development. According to the United Nations (UN), a tenth of the world population is without access to electricity. Around 40% of the world's populations are using wood, coal, charcoal, or animal waste as a primary source of energy. The General Assembly of the United Nations (UN), in September 2015, approved the 2030 Agenda for Sustainable Development, which consists of 17 Sustainable Development Goals. The 7th is Affordable and Clean Energy.

Even though our current energy sources are failing to meet our demand, they also have severe local and global side effects. According to the UN, 4.3 million people lost their lives due to household air pollution from flammable fuel. Globally, the use of fossil fuel is one of the main contributors to global warming. Fossil fuel is combustible material, and the generated thermal energy is used to evaporate water. The generated steam produces electricity using large steam turbine. The products of the combustion reaction, in addition to heat, are water vapor, carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), and fluorinated gases. The mentioned products, except for water vapor, are greenhouse gases. The increasing concentration of greenhouse gases in the atmosphere is blame for the global warming crisis, according to the International Panel on Climate Change (IPCC). In their Fifth Assessment Report (AR5), they show evidence and correlation between the concentration of greenhouse gases and average global temperature. “Human influence on the climate system is clear, and recent anthropogenic emissions of greenhouse gases are
the highest in history. Recent climate changes have had widespread impacts on human and natural systems.\(^7\)

Dealing with the current primary energy sources is not only a big issue for this generation but also, if not addressed, a hindering problem for the next generation. The human population is expected to reach 8.5 billion people by 2030, base on the medium-variant projection.\(^8\) The increase in population will also increase the demand for energy. BP Energy Outlook predicted a 37% increase in energy consumption globally by 2035.\(^9\) Meeting the increasing demand for energy should not come from the current energy sources. In addition to the previously mentioned issues of the current energy sources, the finite nature of these sources emphasizes the need for renewable and clean sources of energy.

1.1 **Solar Energy:**

Solar energy is the result of converting the energy stored in electromagnetic waves into electrical power by taking advantage of the photovoltaic effect. This discovery (photoelectric effect) enables calculating the energy associated with electromagnetic wave frequency. In 1921, Albert Einstein was awarded the Nobel Prize for the discovery of the photoelectric effect.\(^10\) Solar energy is converted to electricity by solar cell devices that use solar energy to create electrical potential along a junction of two semiconducting materials. This form of energy has been used for millions of years to power the creation of the biodiversity that we observed on earth. Therefore, this source of energy is a prime candidate to replace fossil fuel. It is renewable, clean, scalable, and easily integrated into our power systems.
1.2 Organic solar cells (OSCs):

For the past decades, organic photovoltaics (OPV) efficiency has significantly improved. The 2000 Nobel Prize was awarded to all of Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa for the discovery and development of organic semiconducting polymers, which initiate the field of organic electronics.\textsuperscript{11} A year later, the first single-junction organic solar cell efficiency was certified to be around 3\% by the National Renewable Energy Laboratory (NREL), which is funded and owned by the United States Department of Energy.\textsuperscript{12} Also, the first tandem organic solar cell (OSC) was certified in 2008, with around 4\% efficiency. In addition to certifying solar cells, the NREL track and publish the incremental improvement in the efficiency of all solar cells technology. Figure 1 shows an exponential-like trend in the efficiency of organic solar cells between 2001 and 2020, which show the tremendous effort that was put into improving the efficiency of OSCs. Currently, the highest efficiency of tandem OSC was reported by Lingxian Meng and high coworkers in 2018 with 17.3\% efficiency.\textsuperscript{13} Moreover, Yuanbao Lin and his colleges with 17\% efficiency, which is the fabricated highest efficiency of a single-junction OSC currently.\textsuperscript{14}

OSCs produce power in five-step process. The first step is a photoinduced excitation of an electron occupying highest occupied molecular orbital (HOMO) to lowest an occupied molecular orbital (LUMO), which creates a Frenkel exciton (a bound pair of an electron and a hole). This step could occur to either donor polymer or electron acceptor molecule if the energy of the absorbed photon is equal or greater than the bandgap. The second step is the diffusion of excitons to donor/acceptor interfaces. If the excitons do not reach the
interfaces during their lifetime, the bounded pair would recombine geminally. The next step is a charge-transfer (CT) process between the donor polymer and acceptor molecule, which results in the formation of a CT exciton. This process happens in one of two ways either an electron hopping from LUMO of the donor to LUMO of the acceptor or an electron hopping from HOMO of the donor to HOMO of the acceptor. A CT pair exciton is a coulombically bound electron-hole pair, where the electron is on the acceptor, and the hole is on the donor. The fourth step is the dissociation of CT pairs and the generation of charge carriers. The dissociation is the result of the built-in electric field. The final step is the collection of the generated charge carriers. Free holes drift through donor to the anode, and electrons drift through acceptor to the cathode. Free charges could still recombine non-geminally. A tremendous amount of research has been done on engineering organic solar cell devices’ architecture and optimizing their performance.
A Single-junction OPV device consists of multiple layers that are organized in one of two architectures. The conventional design consists of four layers, figure 2 (a). Photons are absorbed and converted into electrons and holes in the active later, which is a bulk heterojunction of a donor polymer and a small acceptor molecule. The generated charge carriers are then collected at metal electron, which are the top and bottom layers. Electrons drift toward low work-function (WF) metal cathode such as aluminum (Al) and calcium (Ca), and holes drift toward metal anode such as indium-tin oxide. The fourth layer is holes extraction layer (HEL) between the active layer and indium tin oxide. It is used to promote electrode collection of holes such as graphene oxides (GOs), and transition metal oxide (MoO₃, WO₃, NiO₃, and V₂O₅). The inverted structure has the same sandwich structure as a conventional structure, but with five layers, figure 2 (b). The active layer is between the hole extraction layer (such as the materials mentioned above) and the electron extraction layer like transition metal oxide (TMOs) and alkali-metal, which facilitate the mobility of electrons to metal electrodes. The cathodes are a high work-function electrode such as gold (Au), Silver (Ag), and copper (Cu). The anode is ITO.

1.2.1 Donor:

The discovery and development of organic semiconductors are instrumental to OVP technologies. In the late 1980s, semiconducting polymers were the most viable option for the fabrication of solution-processed low cost organic solar cells. Even though early polyacetylene-based polymers were not successful, first-generation polymers, such as polythiophenes (PT) and polyphenylenevinylenes (PPV), achieved low
performing organic photovoltaics devices, 0.1 % power conversion efficiency (PCE), or lower. It was shown that this performance is due to the high exciton bound energy of organic material compares to inorganic materials. Therefore, an internal electric field is required to provide the necessary energy for the dissociation of bounded charges. As a result, blending a polymer with an acceptor molecule in a bulk heterojunction composition improved the PCE, but the efficiency did not excide 1%.\textsuperscript{22-24} The next significant efficiency improvement was the results of polymer side-chain engineering. Sidechains in polymer affect polymer solubility and prevent polymer aggregation. As a result, Shaheen et al. reported the fabrication of a 2.5 % PCE OSC device.\textsuperscript{25} Even though PPV derivative polymers were monumental to the development of OSC, the best devices reached 3% since PPV derivatives are large bandgap polymers and have low charge mobility. Further improvement to the efficiency of OSC meant the development of next-generation donor
polymer. Poly-alkyl-thiophenes derivatives were a great fit. In 2002, the first P3TH/BCPM was reported, which had the highest short circuit current ($I_{sc}=8.7 \text{ mA cm}^{-2}$) and power conversion efficiency of 3.5-4 %. However, this device suffers from low open-circuit voltage ($V_{oc}$) 0.66 ev. Improving $V_{oc}$ required the development of new polymers with higher ionization energy. Two polymers were developed to address this issue. Andersson and his colleges designed polyfluorenes (PF), which had high $V_{oc}$.

When it was used in OPV devices; their efficiency was 6%. Leclerc also developed poly(2,7)carbazoles, which has similar properties and efficiency to PF. Finally, conducting polymers is an active area of research, and The next step is the development of small bandgap polymers with low laying HOMO and LUMO to achieve not only high $V_{oc}$ but also high $I_{sc}$.

1.2.2 Acceptor:

The presence of an electron acceptor molecule in the active layer of an OPV device is vital for excitons dissociation. The difference between the energy levels of the LUMO of the donor and the acceptor is critical for generating an internal electric field to dissociate bound generated charges. The ideal energy difference is 0.3-0.5 eV. Less than the ideal difference would lead to high gamenal recombination, and more than the ideal difference would lead to small $V_{oc}$ and $I_{sc}$. As mentioned above, the first introduction of electron acceptors in OSCs improved the efficiency drastically. It changed the dream of solution-processed OPV into reality.

1.1.1.1 Fullerene electron acceptors:

Fullerene derivatives were the first type of electron acceptors. They were used for their superior advantages. The energy difference between LUMO of first-generation donor
polymers and LUMO of fullerene derivative is within the ideal range for exciton dissolution. Sung and his colleagues fabricated OSCs using bulk heterojunction active layer composed of PCDTBT/PC$_{70}$BM with 6% PCE.\textsuperscript{33} Moreover, fullerene derivatives have high electron mobility, and the three-dimensional spherical shape enabled this type of molecules to have good electron-accepting and transporting properties in three dimensions. Additionally, fullerene acceptors are susceptible to aggregation. This property is both a benefit and a disadvantage. The aggregation of acceptor molecules is significant during the device fabrication process since it would lead to the formation of both pure acceptor and donor domains, and mixed domains. Having both pure and mixed domains are important for OPV devices’ performance. Nonetheless, fullerene derivative molecules suffer from drawbacks. OPV devices, which have a fullerene derivative as an acceptor, experience operational instability over time, burn-in. The power conversion efficiency decreases steadily over time.\textsuperscript{3} Moreover, fullerene molecules do not have a high absorption coefficient; therefore, the short circuit current is limited by the polymer absorption. Furthermore, tuning the energy levels of those acceptors is challenging, which significantly restricts $V_{oc}$ and $I_{sc}$. Additionally, the synthetic cost of fullerene derivative reduces the economic advantage of OSC devices. It is clear now that the development of the next generation of electron acceptor is essential to improve the performance of OPV further.

1.1.1.2 Non-fullerene acceptors:

Non-fullerene electron acceptors have recently developed electron acceptors that overcome fullerene derivative limitations. First, the synthesis of non-fullerene electron acceptors is relatively cheaper, and scalable. This is important for organic solar cells to compete in the market against mature inorganic solar cell technologies. Additionally, non-fullerene
electron acceptors have easily tunable HOMO and LUMO energy levels. Fine-tuning energy levels lead to improved \( V_{oc} \) and PCE. Another advantage of non-fullerene acceptors is absorptivity. They have a higher absorption coefficient, which improves charge generation and \( I_{sc} \). For both of absorptivity and tunability, non-fullerene acceptor devices efficiency exceed fullerene solar cells. The highest PCE of an organic solar cell device is 17 %, which was achieved using a non-fullerene electron acceptor. Moreover, these acceptors are more stable under operational conditions than fullerene electron acceptors. In 2016, Sarah and her colleges designed the first burn-in-free non-fullerene electron acceptor, O-IDTBR. This molecule aggregate only under high annealing temperature, which enables crystallinity during device fabrication and prevents aggregation during operation.

1.3 Stability of Organic Solar Cell:

Even though significant progress has been achieved in improving the efficiency of organic solar cells, the commercialization of this technology requires highly stable OSC than currently available. Operational Stability is one of the major challenges of OSC. Mainly, four environmental factors negatively affect the performance of OSC, water, oxygen, temperature, and irradiation.

1.3.1 Water and Oxygen:

Both water and oxygen molecules chemically react with different layers of OSCs. It is well documented and studied that oxygen and water molecules diffused through OSC layers. Oxygen molecules react with a low work-function electrode and reduce its ability to collect charge carriers. Also, oxygen molecules that reach the active layer undergo photooxidative reaction under irradiation with both donor polymers and acceptor molecules,
which hinder the efficiency of absorbing photons and generating charge carriers.\textsuperscript{41, 42} Water molecules are also reactive toward low work-function electrodes, which reduce the performance of the cell.\textsuperscript{43} Additionally, water molecules create barriers between the active layer and the extraction layers, which limit the mobility of charge carriers.\textsuperscript{44} Moreover, water-induced fullerene acceptor molecules to aggregates which limit charge generation.\textsuperscript{45}

**1.3.2 Temperature:**

The effect of operating temperature on the performance of organic photovoltaic devices is inversely proportional. Heat-induced degradation of the active layer,\textsuperscript{46-48} active layer/electrode interfaces,\textsuperscript{49} and extraction layers.\textsuperscript{50} The morphology of the active layer change when the environment temperature is higher than the glass temperature.\textsuperscript{51} This is due to the mobility of the donor polymer. At this high temperature, both donor polymer and acceptor molecule aggregate. The result of this aggregation is a reduction in the device performance since donor/acceptor interfaces shrink. This behavior has been documented in different examples like MDMO-PPV/PC\textsubscript{61}BM,\textsuperscript{52} P3HT/PC\textsubscript{61}BM,\textsuperscript{53} PCDTBT/PC\textsubscript{71}BM,\textsuperscript{54} TQ1/PC\textsubscript{61}BM.\textsuperscript{55} Moreover, the duration of heat exposure is proportional to the reduction in performance. This is due to crystals formation of acceptor molecule and aggregation of donor polymer. The exposure time correlate with crystal size and number as well as a reduction in performance.\textsuperscript{56}

**1.3.3 Irradiation:**

Even though OSCs rely on solar irradiation to generate power, solar irradiation is a source of instability. A significant reduction in the power conversion efficiency of organic solar cells over a short operational time has been observed\textsuperscript{57, 58}. The reduction in performance is the result of chemical and physical degradation. We will only consider chemical
degradation in this thesis. Chemical degradation in OSCs is the result of photo-oxidative reactions. Different reports showed reductions in performance as a consequence of chemical degradations of different layers of OSCs: active layer, transporting layers, and electrodes' interfaces. The degradation is irreversible chemical reactions of photoexcited molecules and molecular oxygen. The results of these reactions are chemically different molecules that possess different properties. Two of the effects of the chemical transformation are the reduction of charge carriers generation and the increase in charge recombination.

The suggested mechanism of the photo-oxidative degradation of OSCs involves the formation of radical superoxide ion. According to Speller and his colleges, the first step is the photo-excitation of an electron occupying HOMO of the donor polymer followed by an electron transfer to LUMO of the acceptor molecule, figure 3. Depending on the energy difference between the LUMO of an acceptor and the electron affinity of the oxygen molecules, another electron transfer could occur. This would result in the formation of radical superoxide ions, which are reactive species that could react with either the donor or the acceptor. Also, the formation of the superoxide ions could be triggered by the excitation of an electron occupying the acceptor HOMO.

1.3.4 Photo-oxidative stability:

One way to lower the rate of photo-oxidation degradation is by preventing oxygen molecules from reaching the active layer of OSCs. This could be achieved by fabricating the devices in an inert environment in the absence of oxygen. Once the devices are fabricated, they would be encapsulated in a transparent material. Even though this is a
viable solution, there are two main issues. First, it was shown that oxygen molecules could diffuse through the encapsulating material and degrade the devices; also, the oxygen molecules could be trapped in the active layer during the fabrication process even if it was processed in inert conditions. Second, implementing this solution would increase the fabrication cost of these devices, which would make this solution commercially unfeasible compared to other solar cell technologies.

A different way to tackle this issue is with electron acceptors with deeper LUMO. Speller and his colleagues reported a strong correlation between the photo-oxidative degradation rate of an active layer of OSC and the acceptor’s LUMO energy levels. They show that the LUMO energy level of the acceptor influence the electron transfer process to molecular
oxygen. The deeper the LUMO related to the electron affinity of the oxygen molecule, the lower the rate of electron transfer will be, and the more stable the device would be. Moreover, this solution would not only decrease the photo-oxidative degradation rate but also keep the production cost of these devices low and commercially competitive.

1.4 Aims and Objectives:

1.4.1 Aim:
In the past two decades, the efficiency of organic solar cells has significantly improved. Even though these improvements encouraged the commercialization of this technology, the stability of organic solar cells is still an active area of research. It is as important as the efficiency of organic solar cells. This project intends to investigate the hypothesized relationship between LUMO energy levels of electron acceptors and photo-oxidative degradation of the active layer. The research would be conducted by examining the photo-oxidative degradation of O-IDTBR and two of its analogs with deeper LUMO, O-IDTBR-(C₃N₂)₂ and O-IDTBR-(C₃N₂)₄.

1.4.2 Objectives:

1) To synthesize, purify, and characterize all of O-IDTBR, and O-IDTBR-(C₃N₂)₂ and O-IDTBR-(C₃N₂)₄.

2) To conduct spectroscopic experiments on the synthesized molecules to determine their optical properties.

3) To perform photo-aging experiments in the air with periodic UV-VIS spectroscopic scans.

4) To examine and compare the degradation behavior of the synthesized materials.
5) Evaluate the hypothesized photo degradation relationship with the results of synthesized materials.
Chapter 2. Experimental Methods and Materials:

2.1 Materials

The mentioned starting reactants, reagents, and solvents were used as received from a commercial source, except 7-bromo-2,1,3-benzothiadiazole-4-Carboxaldehyde (Bt). Most materials were acquired from Merch, Alfa Aesar, and VWR chemicals. Bt was synthesized in the lab. Before it was used, Bt was purification, and the structure was confirmed.

2.2 Synthetic Procedure of O-IDTBR

O-IDTBR was synthesized in five-step synthesis, applying previously published synthetic procedures, figure 34, 63, 64. This synthetic route is divided into three main stages. Starting with indacenodithiophene (IDT), the first stage is the addition of the side chains by reacting IDT with 1-bromo-octane in basic solution. The second stage is the addition of 2,1,3-Benzothiadiazole (Bt) to the periphery of the stannylated and alkylated IDT, 4. Tetrakis-(triphenylphosphine) palladium was used for the transformation. The third and final stage is the knoevenagel condensation of 3-ethyl rhodanine and 5.

2. 1 (3 g, 10 mmol) was dissolved in anhydrous DMSO (40 mL). Then, sodium tetr-butoxide (6 g, 70 mmol) was added in small portions. The reaction mixture was stirred for an hour at 80 °C. After that, 1-bromo-octane (10 mL, 70 mmol) was added dropwise. The solution was stirred for 5 hours at 90 °C. The reaction mixture was poured into ice-water. The filtrate was washed with water and methanol. 2 was purified by silica flash chromatography using hexane. After condensation, the product is dark yellowish oil (86%, 6.9 g). $^1$H NMR (400 MHz, CDCl₃) δ 7.30 (s, 2H), 7.28 (d, $J$ = 4.8 Hz, 2H), 6.99 (d, $J$ = 4.8 Hz, 2H), 1.99 (s, 0H), 1.88 (s, 1H), 1.12 (s, 15H), 0.84 (s, 5H). $^{13}$C NMR (101 MHz,
Figure 4. General synthetic scheme of O-IDTB

3. 2 (5.3 g, 7.5 mmol) was dissolved in a mixture of DMF (35 mL) and THF (66 mL) followed by the addition of NBS N-Bromosuccinimide (2.9 g, 16 mmol). The reaction mixture was stirred in the dark overnight. The crude product was poured into water and the filtrate was crystalized in acetone. The yield product was fine orange crystals (68%, 4.5 g). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.17 (s, 2H), 6.97 (s, 2H), 1.92 (ddd, $J = 13.2, 11.7, 4.8$ Hz, 4H), 1.81 (ddd, $J = 13.3, 11.6, 4.8$ Hz, 4H), 1.29 – 1.03 (m, 44H), 0.82 (t, $J = 7.0$ Hz, 18H). 13C
NMR (101 MHz, CDCl3) δ 154.19, 152.28, 142.00, 135.63, 125.42, 113.14, 111.89, 55.32, 39.96, 31.95, 30.09, 29.37, 24.68, 22.77, 14.23.

5. A solution of 3 (3.9 g, 4.5 mmol) and anhydrous THF was cool to –78 °C. n-butyllithium (7.8 mL, 15.6 mmol) was then added dropwise to the solution, which was stirred at this temperature for an hour. The reaction mixture was warmed to room temperature and stirred overnight after trimethyltin chloride (15.6 mL, 15.6 mmol) was added dropwise at –78 °C. The crude product was workup and extracted with ethyl acetate. Crude product of 4 was used directly in the following reaction with no purification or characterization. Bt (2.7g, 11.2 mmol) was added to a solution of 4 and toluene. The solution stirred for 45 minutes before the addition of tetrakis-(triphenylphosphine) palladium (216 mg, 0.19 mmol). The solution was heated to 100 °C and stirred overnight. The product was purified by flash column chromatography using CH2Cl2 and petroleum (70:30) and yield dark purple solid (58%, 2.3 g).\[^1\]H NMR (400 MHz, CDCl3) δ 10.70 (s, 2H), 8.26 (s, 2H), 8.23 (d, J = 7.6 Hz, 2H), 8.04 (d, J = 7.6 Hz, 2H), 7.44 (s, 2H), 2.11 (td, J = 13.3, 11.7Hz, 4H), 1.97 (td, J = 13.3, 11.6 Hz, 4H), 1.22 – 1.06 (m, 48H), 1.02 – 0.80 (m, 5H), 0.76 (t, J = 6.8 Hz, 11H).\[^{13}\]C NMR (101 MHz, CDCl3) δ 191.55, 157.86, 154.41, 154.09, 152.38, 147.76, 140.79, 136.55, 134.25, 133.10, 124.96, 122.91, 114.24, 54.55, 39.29, 31.93, 30.12, 29.35, 24.42, 22.73, 14.19.

6. 5 (500 mg, 0.48 mmol), 3-ethylrhodanine (233 mg, 1.4 mmol) and piperidine (2 drops) were dissolved in tert-butanol. The reaction mixture was stirred overnight as 85 °C. The product was purifired by falsh column chromatography on silica using CH2Cl2 follow by precipitation in methanol. The collected pure filterate was fine dark blue solid (60%, 380
mg. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.53 (s, 2H), 8.22 (s, 2H), 8.01 (d, $J = 7.7$ Hz, 2H), 7.73 (d, $J = 7.8$ Hz, 2H), 7.43 (s, 2H), 4.26 (q, $J = 7.2$ Hz, 4H), 2.11 (td, $J = 12.8$, 4.6 Hz, 4H), 1.97 (td, $J = 12.7$, 4.6 Hz, 4H), 1.34 (t, $J = 7.2$ Hz, 6H), 1.12 (s, 10H), 0.78 (t, $J = 6.9$ Hz, 13H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 193.21, 168.60, 157.18, 154.77, 154.34, 151.92, 146.27, 139.44, 136.53, 131.51, 130.70, 127.45, 124.65, 124.41, 124.20, 123.97, 117.40, 53.20, 40.69, 39.31, 31.48, 30.14, 29.45, 29.36, 24.86, 22.74, 14.81, 12.48.

Figure 5. Knoevenagel condensation reaction of O-IDTBR and 3-ethylrhodanine conditions

2.3 Synthetic procedure of O-IDTBR-(C$_3$N$_2$)$_2$

Synthesis of O-IDTBR-(C$_3$N$_2$)$_2$ is similar to the synthesis of O-IDTBR. The only difference is in the last step. A dicyano-vinyl 3-ethyl rhodanine derivative is used instead of 3-ethyl rhodanine. Thioxo moiety is substituted with dicyanon-vinyl group, figure 6.

Figure 6. Knoevenagel condensation reaction of O-IDTBR-(C$_3$N$_2$)$_2$ and dicyanon-vinyl 3-ethylrhodanine derivative conditions
7.5 (500 mg, 0.48 mmol), 3-ethylrhodanine (325 mg, 1684 mmol) and piperidine (2 drops) were dissolved in tert-butanol. The yield solid is dark blue in color (40%, 669 mg). $^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.64 (s, 2H), 8.27 (s, 2H), 8.03 (d, $J = 7.8$ Hz, 2H), 7.83 (d, $J = 7.9$ Hz, 2H), 7.45 (s, 2H), 4.39 (d, $J = 5.0$ Hz, 4H), 2.18 – 2.08 (m, 4H), 1.98 (dq, $J = 13.2$, 4.7 Hz, 4H), 1.54 (s, 8H), 1.46 (t, $J = 5.0$ Hz, 6H), 1.29 – 1.24 (m, 6H), 1.22 – 1.07 (m, 44H), 1.02 – 0.82 (m, 15H), 0.78 (td, $J = 6.9$, 1.8 Hz, 12H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 166.40, 166.10, 157.30, 154.38, 154.18, 151.76, 146.77, 140.91, 136.46, 132.76, 131.69, 131.43, 124.67, 123.61, 123.05, 117.80, 114.09, 113.17, 112.25, 55.87, 54.43, 40.69, 39.14, 31.80, 29.98, 29.30, 29.21, 24.30, 22.60, 14.22, 14.06.

2.4 Attempts synthesis of O-IDTBR-(C$_3$N)$_4$

The used rhodanine derivatives in the synthesis of both O-IDTBR and O-IDTBR-(C$_3$N)$_2$ were commercially available, yet the rhodanine derivative that is needed for the synthesis of O-IDTBR-(C$_3$N)$_4$ was not commercially available. Three different approaches were attempted for the synthesis of bis-(dicyanovinyl)-3-ethyl-rhodanin. The first approach was analogously designed to the synthesis of rhodanine, figure 7. 2-(1-amino-2-chloroethylidene)-propanedinitrile was condensed with carbon disulfide (CS$_2$) and triethylamine (NEt$_3$). After 24 hours, the starting materials were obtained.
The first attempt of the synthesis of O-IDTBR-(C3N2)4: a) the industrial synthetic procedure of rhodamine; b) the attempted synthetic conditions for the synthesis of bis-(dicyanovinyl)-3-ethyl-rhodanine.

The second approach was a direct condensation of dicyanon-vinyl-3-ethyl-rhodanine derivative with malononitrile in acetic anhydride. Since no product was formed, the reaction conditions were repeated with two different organic bases. Yet, the reactions were unsuccessful, figure 8.
The final approach was the conversion of the oxo moiety to thioxo group since it was shown that thioxo group is more susceptible to malononitrile under condensation conditions.\textsuperscript{65} Five different thionation reagents were used. However, none of the reactions was successful, figure 9.

Figure 9. The third attempt of the synthesis of O-IDTBR-(C3N2): a) shows the reported transformation; b) presents all the attempted conditions.
2.5 Characterization Techniques:

2.5.1 Nuclear Magnetic Resonance (NMR):
All synthesized molecules were characterized using either Bruker Advance III 500 MHz equipped with BBFO probe, or Bruker Advance III 400 MHz equipped with BBFO cryoprobe. $^1$H and $^{13}$C spectra were analyzed using TopSpin III. In addition to $^1$D spectra, $^1$H-$^1$H COSY and $^1$H-$^{13}$C HMQC spectra of O-IDTBE-(C$_3$N$_2$)$_2$ were collected.

2.5.2 Mass Spectrometry:
The MALDI FT ICR MS measurement was performed on a SolariX XR 9.4 Tesla instrument at the Analytical Chemistry core Lab, KAUST. The sample was mixed with DCTB matrix of the ratio 1:50 and deposited to the MALDI sample plate. The FT ICR MS instrument was calibrated with red phosphors first. Then the spectrum was acquired with MALDI source with the laser energy of 30%. The data was acquired with the mass range of 154-1600 Da.

2.5.3 Photoelectron Spectroscopy in Air (PESA):
O-IDTBE-(C$_3$N$_2$)$_2$ HOMO energy level was measured using AC-2 PESA. O-IDTBE-(C$_3$N$_2$)$_2$ (12 mg/mL) solution in chloroform was spin-coated on a glass substrate. The substrate was subjected to 2000 revolutions per second for 30 seconds.

2.5.4 UV-VIS-NIR spectroscopy:
UV-VIS Spectra of O-IDTBR and O-IDTBE-(C$_3$N$_2$)$_2$ were collected in solution, drop-cast film, and annealed film using Cary Series UV-VIS-NIR spectrophotometer. The range of the measured spectra is 1200-200 nm. The solution sample was prepared by dissolving both molecules in chloroform and place the solution in 1 cm$^2$ quartz cuvette. Both drop-cast and annealed samples were spin-coated onto 5 cm$^2$ glass substrate. All prepared
substrates were subjected to 2000 revolutions per second for 30 seconds; they were made using 12 mg/mL stock solutions. Annealed substrates were then placed on a hot plate for 10 minutes at 130 °C.

2.5.5 Solar Simulators:

Two Solar simulators were used in aging experiments in air. Asahi Max-303 Xenon light source fitted with AM 1.5 filter and Max UV-NIR mirror module is one of the used solar simulate. The other solar simulator is ReTest light emitting diode (LED) solar simulator. The xenon solar simulator more closely simulates the solar irradiation compare to LED solar simulator. At the same time, the ELD solar simulator only simulates two bandwidths of the solar irradiation with high intensity, 425-475 nm, and 550-650 nm, Figure 10.

Figure 10. comparison of spectral irradiance of solar simulator and solar irradiance
Chapter 3. Results and Discussion:

After O-IDTBR-(C₃N₂)$_2$ were synthesized, its optical properties were obtained. O-IDTBR-(C₃N₂)$_2$ HOMO energy level was measured using photoelectron spectroscopy in air; the bandgap energy was estimated using drop-cast thin-film UV-VIS absorbance spectrum, table 1, and Figure (%). Also, UV-VIS absorption spectra of both O-IDTBR-(C₃N₂)$_2$ and O-IDTBR were collected in chloroform, drop-cast thin film, and annealed film. The UV-VIS maximum absorbance of O-IDTBR-(C₃N₂)$_2$ in chloroform is red shifted by 26 nm compare to O-IDTBR. These measurements show experimentally that LUMO energy levels of both O-IDTBR-(C₃N₂)$_2$ is deepened by 0.1 eV relative to O-IDTBR.

Table 1: Optical properties of both O-IDTBR-(C₃N₂)$_2$ and O-IDTBR

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{\text{max}}$ solution (nm)*</th>
<th>$\lambda_{\text{max}}$ film (nm)</th>
<th>$\lambda_{\text{max}}$ ann. (nm)</th>
<th>$E_g$ opt. (eV)</th>
<th>EA (eV)</th>
<th>IP (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-IDTBR-(C₃N₂)$_2$</td>
<td>676</td>
<td>710</td>
<td>719</td>
<td>1.5</td>
<td>4.00</td>
<td>5.55</td>
</tr>
<tr>
<td>O-IDTBR</td>
<td>650</td>
<td>687</td>
<td>725</td>
<td>1.63</td>
<td>3.88</td>
<td>5.51</td>
</tr>
</tbody>
</table>

*Chloroform

Substituting thioxo moiety with bis(dicyano-vinyl) group on rhodanine deepened O-IDTBR, which is an example of calamitic non-fullerene electron acceptors. This class of NFA consists of three joint units with different properties. For O-IDTBR, at the center of the molecule is an electron-donating group, IDT. On the peripheries are two electron-withdrawing groups, Bt and R. One of the features of this class of electron acceptors is the exclusive distribution of HOMO on the electron-donating unit and LUMO on the electron-
withdrawing units. Therefore, changing the electron deficiency of the electron-
withdrawing groups would exclusively change the energy level of LUMO. The same effect
occurs with an electron-donating group. LUMO of O-IDTBR in located on bt and R units
and HOMO on IDT. Therefore, substituting thioxo moiety with bis(dicyano-vinyl) group
deepened the LUMO since bis(dicyano-vinyl) group is a more electron deficient than
thioxox. Furthermore, bis(dicyano-vinyl) group has been used to deepen the LUMO of
other NFAs.66-69

![Graphs showing spectroscopic spectra of O-IDTBR-(C3N2)2 and O-IDTBR.]

Figure 11. Spectroscopic spectra of O-IDTBR-(C3N2)2 and O-IDTBR. a) Uv-vis absorbance
spectra of O-IDTBR-(C3N2)2 in solution (chloroform), thim film, and annealed thin film at 130 °C;
b) Uv-vis absorbance spectra of O-IDTBR in solution (chloroform), thim film, and thin film
annealed at 130 °C; Photoelectron spectroscopy in air (PESA) of O-IDTBR-(C3N2)2

3.1 Bathochromic Shifts:

Both O-IDTBR-(C3N2)2 and O-IDTBR have similar bathochromic behavior. The drop-cast
thin film UV-VIS maximum absorbance of both molecules is red shifted around the same
magnitude (34 and 37 nm, respectively) relative to the maximum absorbance of the solution samples. However, upon annealing, O-IDTBR is redshifted more than O-IDTBR-(C3N2), 38 nm and 9 nm, respectively. These observations led us to hypothesize that the degree of crystallinity of O-IDTBR-(C3N2) and O-IDTBR are similar in drop-cast film; simultaneously, O-IDTBR is more crystalline in an annealed film than O-IDTBR-(C3N2).

Sarah and her colleagues have shown the degree of crystallinity of O-IDTBR and red shift are correlated.57

3.2 Photo-oxidative degradation:

Both molecules were subjected to aging experiments under 1 sun intensity in air. O-IDTBR-(C3N2)2 is shown to be more stable than O-IDTBR. After four hours of constant irradiation from 1-sun intensity xenon solar simulator, the maximum absorbance of O-IDTBR is reduced by 12% relative to O-IDTBR-(C3N2)2, figure 12 a, b, and c. Moreover, the same pattern is observed with an LED Solar Simulator. After 19 hours of exposure, the maximum absorbance of O-IDTBR is reduced by 14% compare to O-IDTBR-(C3N2)2, figure 13 a,b and c. This significant difference in the degradation rate is a result of deepening the LUMO of O-IDTBR-(C3N2)2 relative to O-IDTBR. These results confirm the hypothesized relationship between the LUMO energy level of electron acceptor and photo-oxidative stability, which was reported by Speller and his colleagues.59

Even though the difference in a relative reduction in absorbance between O-IDTBR-(C3N2)2 and O-IDTBR is similar using both xenon and LED solar simulator, the absolute degree of degradation is different. The xenon solar simulator caused 41% reduction in maximum absorbance of O-IDTBR and 29% of O-IDTBR-(C3N2)2, figure 12. On the other hand, the LED solar simulator caused only 25% reduction in maximum absorbance of O-
IDTBR and 11% of O-IDTBR-(C₃N₂)₂, figure 13. Even though both solar simulators are calibrated to 1-sun intensity, they have different spectral irradiance. Xenon solar simulator is more analogous to solar irradiance than LED. Also, it emits high energy photons between 400-350 nm. Alternatively, LED solar simulator to emit high-intensity photons in only two areas of visible spectrum between 700-500 nm and 475-425 nm. It does not emit photons with a shorter wavelength than 400 nm. A possible explanation for the difference in the degradation rate is the absorption of high energy photos emitted by xenon solar simulator. Figure 12 c shows moderate absorption at 420 nm for both O-DTBR-(C₃N₂)₂ and O-IDTBR. This peak persists in solution, drop-cast thin film, and annealed film.
Figure 13. LED solar simulator aging experiment in air of both of O-IDTBR-(C$_3$N$_2$)$_2$ and O-IDTBR; a and b) Spectra of degraded thin film sample of O-IDTBR-(C$_3$N$_2$)$_2$ and O-IDTBE respectively over four hours; c) the degradation rate of maximum absorbance over four hours; b) comparison between molecular absorption spectra of both molecules and spectral irradiance of the solar simulator.
Chapter 4. Conclusion and Future Outlook:

4.1 Conclusion

The reposted finding in this thesis confirms the effect of the LUMO energy level of an electron acceptor molecule on the active layer's photo-oxidative stability. This observation should be taken into consideration when designing new materials. Deepening the LUMO of acceptor would also entail designing a new electron acceptor with deeper HOMO and LUMO. At the same time, it would involve the design of new donor polymer with matching energy levels to the new acceptor molecule to achieve high stability and performance.

4.2 Future work:

This thesis has been focused on investigating the effect of LUMO energy level of acceptor molecules on photo-oxidative degradation rate. While doing the research, we have identified interesting ideas that are worth investigating. Fabricating organic solar cell devices of both O-IDTBR and O-IDTBR-(C$_3$N$_2$)$_2$ and studying power conversion efficiency over time would yield a complete picture. Even though both electron acceptors have similar chemical structures, they show different red-shift after thin-film annealing. Studying morphology of O-IDTBR-(C$_3$N$_2$)$_2$ by transition electron microscope (TEM), using x-ray diffraction (XRD), and differential scanning calorimetry (DSC) would provide us with the solution. Moreover, continuing the effort to synthesizing second O-IDTBR analogs is important to further confirm the trend. It was shown in this thesis that oxo moiety is unreactive in rhodanine. A different strategy would be substituting thioxo moiety with an electron-donating group that would raise the LUMO energy level of O-IDTB.
Appendix:

2. O-IDT:
3. O-IDT-Br:
5. O-IDTB:
6. O-IDTBR:
7. O-IDTBR-\((C_3N_2)_2\)
References:


derivative as an interfacial layer for inverted polymer solar cells with high efficiency.


