Mixed Alloy Compositions, Cascade Device Structures, and Lifetime Studies, of Boron Subphthalocyanine and its Derivatives in Organic Photovoltaic Devices

by

Richard Kyle Garner

A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
Department of Chemical Engineering and Applied Chemistry
University of Toronto

© Copyright by Richard Kyle Garner 2017
Mixed Alloy Compositions, Cascade Device Structures, and Lifetime Studies, of Boron Subphthalocyanine and its Derivatives in Organic Photovoltaic Devices

Richard Kyle Garner

Master of Applied Science
Department of Chemical Engineering and Applied Chemistry
University of Toronto
2017

Abstract

This thesis encompasses my work to advance the field of organic photovoltaics, as well as my efforts to enable others to make further steps. It first details my investigation of the novel \( \mu \)-oxo-(BsubPc)\(_2\) compound, including usage of codeposition to achieve a mixed alloy composition, and several device engineering strategies employed to increase performance. Secondly, it describes my work to establish structure-property relationships with regard to molecular degradation in boron subphthalocyanine-containing organic photovoltaic devices. Next, it presents my analysis of the effects of various mixed alloy compositions of the chloro-(chloro)\(_n\)-boron subnaphthalocyanine molecule on device performance. Finally, it illustrates my work in designing and building automated data collection and artificial solar aging systems to facilitate further exploration of degradation properties. These efforts serve to identify useful molecular and device design strategies to optimize both the performance and lifetime of organic photovoltaic devices containing derivatives of the boron subphthalocyanine molecule.
Acknowledgments

I wish to acknowledge David Josey, who was responsible for my original training, for the reliable functionality of the fabrication and analysis equipment on which I have depended, and finally for an unending bounty of generously given and sound advice. I also wish to acknowledge my supervisor, Professor Tim Bender, whose astute guidance has ensured that my efforts have never strayed from fruitful ground. Both have my sincere thanks.
Table of Contents

Acknowledgments........................................................................................................................................... iii
Table of Contents............................................................................................................................................. iv
List of Tables .................................................................................................................................................. vii
List of Figures ................................................................................................................................................ v
List of Appendices ........................................................................................................................................ x
List of Abbreviations .................................................................................................................................. xi

Chapter 1 Introduction ..................................................................................................................................1
  1.1 Organic Photovoltaic Devices.............................................................................................................1
  1.2 Chloro Boron Subphthalocyanine and its Derivatives........................................................................3
  1.3 Structure-Property Relationships......................................................................................................4

Chapter 2 Characterization of μ-oxo-(BsubPc)₂ in Multiple Architectures of Organic Photovoltaic Devices: Comparing Against and Combining with Cl-BsubPc.................................7
  2.1 Introduction..........................................................................................................................................8
  2.2 Results..................................................................................................................................................11
    2.2.1 Opto-electronic Characterization of the Solid Film.................................................................11
    2.2.2 Testing the Application of μ-oxo-(BsubPc)₂ as an Electron Donor and/or an Electron Acceptor.........................................................................................................................13
    2.2.3 Application With Other Electron Acceptors in Photovoltaic Devices..............................17
    2.2.4 Application as a Bi-Functional Interlayer Material in Cascade Architectures .........20
    2.2.5 Application in Subphthalocyanine Mixture Donor Layers.................................................23
  2.3 Conclusions........................................................................................................................................25

Chapter 3 Boron Subphthalocyanines as Electron Donors in Outdoor Lifetime Monitored Organic Photovoltaic Cells ..................................................................................................................27
  3.1 Introduction........................................................................................................................................28
  3.2 Results and Discussion.......................................................................................................................29
3.3 Conclusions

Chapter 4 The mixed and alloyed chemical composition of chloro-(chloro)$_n$-boron subnaphthalocyanines dictates their physical properties and performance in organic photovoltaics

4.1 Introduction

4.2 Results

4.2.1 Planar Heterojunction Devices

4.2.2 Bulk Heterojunction Devices

4.3 Discussion

4.3.1 Open-Circuit Voltage

4.3.2 Short-Circuit Current

4.3.3 Fill Factor

4.4 Conclusion

Chapter 5 Design and Operation of Automated OPV Monitoring and Data Collection Systems

5.1 Introduction

5.2 Constant Potentiometric Monitoring

5.3 Automated J-V Curve Acquisition

5.4 Artificial Solar Aging Apparatus Design

5.4.1 Chamber Structure

5.4.2 OPV Substrate Mounting

5.4.3 Light Source

5.4.4 Safety Considerations

5.5 Initial Full-System Results

Chapter 6 Conclusions and Future Work

References

Appendices
7.1 Appendix A: Materials and Methods Sections ................................................................. 79

7.1.1 Experimental Section for Chapter 2: Characterization of μ-oxo-(BsubPc)2 in Multiple Architectures of Organic Photovoltaic Devices: Comparing Against and Combining with Cl-BsubPc ................................................................. 79

7.1.2 Materials and Methods Section for Chapter 3: Boron Subphthalocyanines as Electron Donors in Outdoor Lifetime Monitored Organic Photovoltaic Cells ..... 81

7.1.3 Materials and Methods Section for Chapter 4: The mixed and alloyed chemical composition of chloro-(chloro)n-boron subnaphthalocyanines dictates their physical properties and performance in organic photovoltaics .... 82

7.2 Appendix B: Supplemental Information Sections ................................................................ 84

7.2.1 Supplemental Information for Chapter 2: Characterization of μ-oxo-(BsubPc)2 in Multiple Architectures of Organic Photovoltaic Devices: Comparing Against and Combining with Cl-BsubPc .................................................. 84

7.2.2 Supplemental Information for Chapter 3: Boron Subphthalocyanines as Electron Donors in Outdoor Lifetime Monitored Organic Photovoltaic Cells ..... 98

7.2.3 Supplemental Information for Chapter 4: The mixed and alloyed chemical composition of chloro-(chloro)n-boron subnaphthalocyanines dictates their physical properties and performance in organic photovoltaics .................... 103

Copyright Acknowledgements .................................................................................................. 106
List of Tables

Table 2.1. Mean device parameter comparison of Cl-BsubPc to μ-oxo-(BsubPc)₂ employed as an electron donor or electron acceptor.ᵃ ................................................................. 16

Table 2.2. Mean device parameter comparison of Cl-BsubPc to μ-oxo-(BsubPc)₂ employed as an electron donor with fullerene acceptor materials.ᵃ ................................................................. 18

Table 2.3. Mean device parameter comparison of μ-oxo-(BsubPc)₂ energy cascade and charge cascade devices, with bilayer devices included for reference.ᵃ ......................................................... 22

Table 2.4. Mean device parameter comparison of μ-oxo-(BsubPc)₂:Cl-BsubPc mixture devices, with bilayer devices included for reference.ᵃ ................................................................. 24

Table 3.1. Mean device parameter comparison of various BsubPcs as electron donating materials when paired with C₆₀ electron acceptors. ................................................................. 30

Table 4.1. Material Properties from Various Synthetic Routes.ᵃ ................................................................. 40

Table 4.2. PHJ J-V metrics for the various Cl-ClnBsubNcs ................................................................. 44

Table 4.3. BHJ J-V metrics for the various Cl-ClnBsubNcs. ................................................................. 47
List of Figures

Figure 1.1. Basic functionality of an organic photovoltaic device................................................. 2

Figure 1.2. A basic PHJ OPV structure. .......................................................................................... 3

Figure 1.3. Structure of Cl-BsubPc Molecule................................................................................. 4

Figure 2.1. Chemical structures of relevant compounds used within this study ....................... 9

Figure 2.2. (a) The chemical structure of μ-oxo-(BsubPc)_2. (b) A depiction of the solid state arrangement of μ-oxo-(BsubPc)_2 taken from a crystal obtained by sublimation. (c) Absorbance spectrum of μ-oxo-(BsubPc)_2 in solution (purple) and in a solid film (blue). ......................... 11

Figure 2.3. Schematic of energy levels for various acceptor and donor layer materials. .......... 13

Figure 2.4. Schematic of the device structure for testing μ-oxo-(BsubPc)_2 as an electron donor, acceptor, or bi-functional layer, in basic, cascade, or mixed donor PHJ devices............... 14

Figure 2.5. (a) J-V curves comparing Cl-BsubPc containing devices to μ-oxo-(BsubPc)_2 containing devices. (b) Solid state film absorbances for Cl-BsubPc (magenta), μ-oxo-(BsubPc)_2 (blue), α6T (orange), and C_{60} (dark grey) and external quantum efficiency spectra................. 17

Figure 2.6. (a) J-V curves comparing acceptors for pairing with μ-oxo-(BsubPc)_2, with Cl-BsubPc included for reference. (b) Solid state film absorbances for Cl-BsubPc (magenta), μ-oxo-(BsubPc)_2 (blue), C_{60} (dark grey), C_{70} (black) and external quantum efficiency spectra .......... 19

Figure 2.7. (a) J-V curves comparing μ-oxo-(BsubPc)_2/C_{70} cascade devices, with Cl-BsubPc/C_{70} and μ-oxo-(BsubPc)_2/C_{70} devices for comparison. (b) External quantum efficiency spectra. ..... 23

Figure 2.8 (a) J-V curves comparing μ-oxo-(BsubPc)_2/Cl-BsubPc mixture devices, with Cl-BsubPc/C_{70} and μ-oxo-(BsubPc)_2/C_{70} devices for comparison. (b) External quantum efficiency spectra. ......................................................................................................................... 25

Figure 3.1. The full device layer stack is shown at left. Molecular structures of compounds (used independently) in active layers are shown at right................................................................. 29
Figure 3.2. Temperature and solar irradiation data is shown in the uppermost plot of a), with device power flux during the corresponding time period displayed below. Part b) shows temperature, solar irradiation and power flux for α6T/C60 devices

Figure 3.3. Device efficiencies were measured using simulated AM1.5G light after each day of irradiation

Figure 3.4. J-V curves taken at significant time points in degradation process

Figure 4.1. Structures of the PC$_{70}$BM and C$_{70}$ molecules, as well as the Cl-Cl$_n$BsubNc molecule, where n ranges from 0 to 2 bay chlorines for each of the three isoindoline subgroups

Figure 4.2. Device structures of a) PHJ and b) BHJ devices. Diagrams not to scale

Figure 4.3. a) PHJ J-V curves showing two separate fabrication runs of devices for each Cl-Cl$_n$BsubNc source. b) Upper plot shows EQEs of each set. c) Lower plot rescales each plot so as to have the same integrated current, for comparison of relative material contributions

Figure 4.4. a) J-V and b) EQE plots of Cl-Cl$_n$BsubNc:PC70BM BHJ OPVs

Figure 4.5. Changes to topology after successive film additions (2 μm x 2 μm scan area)

Figure 5.1. Breadboard permitting load resistor installation

Figure 5.2. Circuit diagram of automated testing system

Figure 5.3. Structure of chamber with substrate holders in place, before wiring or incorporation of electrical systems

Figure 5.4. Schema/renders of substrate holder and cover plate

Figure 5.5. Plot of drop in efficiency over time. Break at 70 hour point corresponds to a one month pause from illumination

Figure 5.6. Comparison of solar and metal halide bulb spectra. Solar Spectra from National Renewable Energy Laboratory
List of Appendices

Appendix A: Materials and Methods Sections ................................................................. 79

Appendix B: Supplemental Information Sections ......................................................... 84
List of Abbreviations

α6T – alpha-sexithiophene

AFM – atomic force microscopy

Ag – silver

B – boron

BCP – bathocuproine

BHJ – bulk heterojunction

BsubNc – boron subnaphthalocyanine

BsubPc – boron subphthalocyanine

Cl – chlorine

Cl-BsubPc – chloro boron subphthalocyanine

Cl-Cl_{n}BsubNc – chloro-(chloro)_{n}-boron subphthalocyanine

C_{60} or C_{70} – C_{60} fullerene or C_{70} fullerene

ETL – electron transporting layer

FF – fill factor

HOMO – highest occupied molecular orbital

ITO – indium tin oxide

J-V – current-voltage

J_{SC} – short-circuit current

LUMO – lowest unoccupied molecular orbital
MoOx – molybdenum(VI) oxide

μ-oxo-BsubPc – mu-oxo boron subphthalocyanine

NMR – nuclear magnetic resonance spectroscopy

OPV – organic photovoltaic device

OSC – organic solar cell

PC70BM – [6,6]-phenyl-C-71-butyric acid methyl ester

PCE – power conversion efficiency

PEDOT:PSS – poly(3,4-ethylenedioxythiophene) polystyrene sulfonate

Ph-BusbPc – phenyl boron subphthalocyanine

PHJ – planar heterojunction

PhO-BsubPc – phenoxy boron subphthalocyanine

QCM – quartz crystal microbalance

SD – standard deviation

TPBi – 2,2′,2″-(1,3,5-Benzenetriyl)-tris(1-phenyl-1-H-benzimidazole)

USB – universal serial bus

UPS – ultraviolet photoelectron spectroscopy

Voc – open-circuit voltage

XPS – x-ray photoelectron spectroscopy

XRD – x-ray diffraction

ZnPc – zinc phthalocyanine
1.1 Organic Photovoltaic Devices

Organic photovoltaic devices (OPVs) use organic molecules to convert light into electricity, rather than the silicon used by traditional photovoltaic cells. OPVs are considered to be promising due to their predicted ease of manufacturing and relatively inexpensive photo- and electro-active materials, in comparison to silicon photovoltaics. Due to the versatility of organic chemistry, there are effectively infinite possibilities for highly-performing candidate materials, as well as infinite dead-ends. The field of organic photovoltaics is therefore a diverse area of research, with many types of OPV structures and material families are under active research. Many factors can affect the performance of an OPV, so it is not a simple matter to develop and test a new candidate material, nor device structure, without a full understanding of the system. Substance purity, interfacial effects, optical interferences, and encapsulation methodology are all examples of phenomena which can complicate investigative efforts. It is therefore beneficial to have a research stream that integrates chemical synthesis and device engineering, which is the approach taken by the Bender Laboratory. To do otherwise risks drawing conclusions from an incomplete dataset, potentially leading valuable research efforts away from the most viable materials.

Figure 1.1 demonstrates the fundamental working principle of an OPV. When light is absorbed by the active layers, an electron is excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The electron becomes electrostatically bound to the now-empty orbital it left behind, referred to as a hole. These electron-hole pairs are referred to as excitons, which must be dissociated for the charges to be collected. The exciton will diffuse through its material layer until it either recombines or reaches the interface with the other material. A well-performing organic electronic material will make it difficult for the exciton to relax before it can reach the interface. This other material has different HOMO and/or LUMO levels than the original material, and so an opportunity is presented for either the electron or the hole to jump to the other material. If the material which generated the exciton has higher
energy levels, the electron will hop to the other material, so we refer to the former as an electron donor and the latter as an electron acceptor. If the exciton is generated on the lower-energy material, it will be the hole which jumps to the other side, which in reality is an electron from the electron donor’s HOMO level relaxing to the HOMO level of the electron acceptor. In either case, the charges become separated, and are free to diffuse to their respective electrodes. At its most basic level, the current produced is a function of the number of electrons collected, and the voltage produced is a function of the difference between the molecular energy levels.

**Figure 1.1. Basic functionality of an organic photovoltaic device.**

**Figure 1.2** shows a cross-sectional diagram of a basic OPV, called a planar heterojunction (PHJ) due to its flat material layers. Light enters the device through the bottom and is absorbed in the organic layers, which ideally have high extinction coefficients in their region of optical absorption. The substrate can be any transparent and smooth surface that provides mechanical strength to the device. This includes flexible plastic substrates, which enable cost-saving roll-to-roll manufacturing methods. The next layer up is a transparent conducting cathode, of which indium tin oxide (ITO) is the most common variety. The next layer is a hole transport layer, which permits the diffusion of holes in the HOMO band to the ITO electrode but discourages the diffusion of electrons in the LUMO band. The next two layers up are the electron donating layer and electron accepting layer respectively. The subsequent layer is an electron transport layer, which provides a similar gatekeeping functionality for the final layer, the metal anode.
Figure 1.2. A basic PHJ OPV structure.

1.2 Chloro Boron Subphthalocyanine and its Derivatives

The family of functional organic electronic materials known as boron subphthalocyanines (BsubPcs), headed by the prototypical chloro boron subphthalocyanine (Cl-BsubPc) \(^3\)-\(^5\), are undergoing active research due to their relatively high power conversion efficiencies (PCEs), ease of synthesis and processing, and physical tunability.\(^6\)-\(^8\) In PHJ OPVs, Cl-BsubPc has been shown as functioning in electron donating\(^9\)-\(^10\) and electron accepting\(^10\)-\(^12\) capacities, including as a bi-functional interlayer.\(^13\) Its structure is shown in Figure 1.3. When used as an electron donor material in PHJ OPVs, BsubPcs are most frequently paired with a C\(_{60}\) electron acceptor\(^8,\,12,\,14\)-\(^17\) or the analogous C\(_{70}\).\(^18\) A record 8.4% PHJ OPV power conversion efficiency was recently achieved by Cnops et al.,\(^19\) with a device containing Cl-BsubPc and chloro boron subnaphthalocyanine (Cl-BsubNc) as an electron acceptor and bifunctional layer respectively. Cl-BsubNc is a closely related material to Cl-BsubPc – still a boron-chelating macrocycle with three subunits, but derived from naphthal reactants containing an additional carbon ring each.
Figure 1.3. Structure of Cl-BsubPc Molecule

BsubPcs and their analogues have the useful chemical property that their axial and peripheral positions can be functionalized with a variety of substituents and molecular fragments. Instead of the prototypical axial chlorine atom, other halogens or organic fragments can be easily substituted in place. This allows for the adjustment of the molecule’s properties, including the solid state arrangement and distribution of its energy levels. The benefits of the latter are twofold: First, energy levels can be tuned to provide efficient exciton dissociation with acceptors in bilayer PHJ structures or with other layers in cascade architectures. Second, the absorption spectra can be shifted to different wavelengths, such that a device incorporating multiple BsubPcs could absorb a wider fraction of the solar spectrum. This incorporation can be accomplished via the use of cascade architectures or co-deposited layers, some of which have shown signs of organic alloying effects. The versatility of BsubPcs in both chemical synthesis and device engineering make them a continually attractive candidate for future OPV research.

1.3 Structure-Property Relationships

Much of the work in this thesis focuses on the identification of molecular structure-property relationships and the development of device engineering techniques. This means establishing the precise effects that a modification made to a component molecule or device design will have on its properties. These relationships are discovered by fabricating OPVs of various designs and comparing their performance by a number of different metrics, including current-voltage (J-V) sweeps in light or dark conditions, external quantum efficiency scans in simulated solar spectra, or device lifetime tests. In these studies, it is important for all significant variables to be
controlled, and for uncontrolled variables to at least be characterized and understood, in order to draw meaningful conclusions.

An important aspect of these research efforts is the establishment of “baseline” devices. These devices have a fixed structure, and are fabricated periodically to ensure that no changes have occurred regarding the deposition systems, material purity, testing conditions, etc. They also establish a global point of comparison between various experiments, turning disparate efforts into a single cross-comparable dataset. Even in cases where the performance of baseline devices has shifted over time (for example, due to changes between commercially supplied material lots), the other devices in an experiment can be compared to the baseline devices made alongside them. Subsequently, the difference between the baseline devices made in the current experiment and baselines fabricated some time prior can be examined in order to establish a relative comparison to the devices made in other experiments. The work of Chapters 2, 3 and 5 directly utilize baseline devices to help establish structure-property relationships, and a baseline device was made prior to the devices in Chapter 4 to ensure the continued functionality of the fabrication system.

This thesis addresses several structure-property relationships in particular, helping to investigate novel and relatively unexplored spaces within the field of OPV research. The first set of relationships, detailed in Chapter 2, explore the properties of the μ-oxo-(BsubPc)₂ dimer in comparison to Cl-BsubPc. The work goes on to examine the effects on device performance of blending the dimer with Cl-BsubPc in a device’s active layers, or using the dimer as an interlayer in two other OPV architectures. Chapter 3 directly identifies the relationship between the axial substituents of various, otherwise identical, BsubPc compounds, and the lifetime of OPV devices that incorporate them as the electron donor. It also investigates BsubPc-free devices in order to help determine the primary mechanisms of degradation. Lifetime information is of particular value to a synthetic chemist, since a material with superior initial performance may not lead to a commercially viable product if it degrades rapidly in an OPV. Such efforts help keep research on course, by ensuring that robust material families are not overlooked in favour of higher “Day Zero” efficiency values. Chapter 4 confirms the structure-property relationships between different mixed alloy compositions of BsubNcs, using various material synthesis pathways and device structures in order to characterize the differences between the various mixtures. Finally,
Chapter 5 details the design of an automated lifetime testing system, intended to make the identification of further relationships more efficient.
Chapter 2
Characterization of $\mu$-oxo-(BsubPc)$_2$ in Multiple Architectures of Organic Photovoltaic Devices: Comparing Against and Combining with Cl-BsubPc

This work was co-authored with Dr. Jeffrey S. Castrucci, whose specific contributions to the paper’s language and content are noted. Unannotated sections contain work undertaken and subsequently described solely by Richard Garner, though both co-authors extensively reviewed all sections of the text prior to submission.

Other than the preceding notes and the following details, this work is shown as-published by the journal ACS Applied Materials & Interfaces: the experimental section has been moved to Appendix A, and initial contextual details in the Introduction are omitted, as they are redundant with Chapter 1 of this work.

The full author list of the paper is as follows:
Jeffrey S. Castrucci,†‡¶ Richard K. Garner,†‡¶ Jeremy D. Dang,‡ Emmanuel Thibau,‡ Zheng-Hong Lu,‡ and Timothy P. Bender*,†‡¶§

†Department of Chemical Engineering & Applied Chemistry, University of Toronto, Toronto, Ontario M5S 3E5, Canada
‡Department of Materials Science and Engineering, University of Toronto, 184 College Street, Toronto, Ontario M5S 3E4, Canada
§Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 3H6, Canada

We demonstrate the first application of a unique boron subphthalocyanine (BsubPc) derivative, the oxygen bridged dimer $\mu$-oxo-(BsubPc)$_2$, as a multi-functional material within planar
heterojunction organic photovoltaic (OPV) devices. We first explored the pairing of \( \mu \text{-oxo-(BsubPc)}_2 \) with well-known electron accepting and electron donating materials to explore its basic functionality. These preliminary device structures and metrics indicated that \( \mu \text{-oxo-(BsubPc)}_2 \) is best applied as an electron donating material when used in simple bilayer structures, as it yielded comparable OPV device efficiencies to that of the more well-established and highly optimized chloro-boron subphthalocyanine (Cl-BsubPc) OPV device structures. Thereafter we established that the HOMO/LUMO energy levels of \( \mu \text{-oxo-(BsubPc)}_2 \) are well-placed to apply it as a bi-functional donor/acceptor interlayer material in both energy and charge cascade OPV device architectures. Within this context, we found that \( \mu \text{-oxo-(BsubPc)}_2 \) was particularly effective in a charge cascade device as an interlayer between Cl-BsubPc and C70. We finally found evidence of an alloying-like effect for devices with mixed electron donor layers of (Cl-BsubPc) and \( \mu \text{-oxo-(BsubPc)}_2 \), achieved through co-deposition. The overarching conclusion is therefore that \( \mu \text{-oxo-(BsubPc)}_2 \) has the ability to improve the performance of Cl-BsubPc OPV devices and is a multifunctional material worthy of further study.

2.1 Introduction

*This section primarily authored and researched by Dr. Castrucci.*

The oxygen-bridged dimer of BsubPc, \( \mu \text{-oxo-(BsubPc)}_2 \) (Figure 2(a)), was serendipitously discovered approximately 20 years ago when Cl-BsubPc was treated with NaOH in the presence of a phase transfer catalyst while attempting to synthesize HO-BsubPc.\(^{22}\) It was immediately shown that this dimeric molecule had unique spectroscopic properties. For example, its solution optical absorption spectrum shows a significant hypsochromic/blue shift (i.e. shift to higher energy) in the Q band compared to typical BsubPcs.\(^{22}\) Moreover the Q and B bands are similar in intensity, whereas normal BsubPcs have Q bands that are more intensive than the corresponding B band. To further illustrate its unusual spectroscopic behavior, the \(^1\text{H} \) NMR spectrum of \( \mu \text{-oxo-(BsubPc)}_2 \) shows an up-field shift in the resonance signals for both terminal (2,3-position) and bay (1,4-position) hydrogens, where the effect is more pronounced on the latter. This effect is attributed to the close proximity of these hydrogen atoms to the \( \pi \)-electron cloud of the second BsubPc macrocycle.\(^{22}\)
Figure 2.1. Chemical structures of relevant compounds used within this study.

Although μ-oxo-(BsubPc)$_2$ and its basic properties have been known for a considerable amount of time, its physical properties have been largely unexplored until the recent contributions made by our group towards synthetic processes.\textsuperscript{7, 23} We attribute the lack of study to the low yielding synthetic processes that preceded our work. We initially focused our efforts on the preparation of μ-oxo-(BsubPc)$_2$ with a reasonable yield and with sufficiently high purity such that it would be suitable for detailed physical characterization and incorporation into organic electronic devices.\textsuperscript{7, 23} We found that reacting equimolar amounts of HO-BsubPc with Br-BsubPc in the presence of tripotassium phosphate (K$_3$PO$_4$) base in 1,2-dichlorobenzene at 180 °C for 1 hour followed by the sequential purification steps of a Soxhlet extraction, Kaufmann column chromatography, and two rounds of train sublimation was the best process that afforded highly pure μ-oxo-(BsubPc)$_2$ in a 27-30% yield.\textsuperscript{7} Single crystals of non-solvated μ-oxo-(BsubPc)$_2$, acquired by sublimation, exhibited a solid state arrangement with high symmetry, close intermolecular π-π interactions, and high chromophore density (Figure 2 (b)). These features were also present in hydrated and 1,2-dichlorobenzene-solvated crystals of μ-oxo-(BsubPc)$_2$.\textsuperscript{23} The optical absorption spectrum ($\lambda_{\text{max}} = 532$ nm) was considerably blue-shifted by comparison to typical BsubPcs ($\lambda_{\text{max}} > 560$ nm), consistent with the earlier findings (Figure 2 (c)).\textsuperscript{22} Evidence of solvatochromism (i.e. solvent-dependent absorption) was also found.\textsuperscript{7} Cyclic voltammetry measurements (in degassed dichloromethane solution relative to Ag/AgCl) showed a single oxidation (+0.95 V) and reduction (-1.03 V) with potentials that are relatively in line with Cl-BsubPc (+1.04 and -1.05 V).\textsuperscript{7, 24} Despite its high molar mass, we have also previously shown that it can be easily sublimed under vacuum deposition conditions.\textsuperscript{25} The resulting film had a solid absorption profile\textsuperscript{25} with a peak at $\lambda_{\text{max}} = 578$ nm and a shoulder at $\lambda = 555$ nm. In contrast, the dilute solution in
dichloromethane shows a shoulder at $\lambda = 545$ nm and a peak at $\lambda_{\text{max}} = 532$ nm, thus indicating a reversal in band intensity ratio (Figure 2c).

Considering that Cl-BsubPc has already been well-established as an active material in organic photovoltaics (OPVs)$^6,9,13,18,19,26$ and the fact that $\mu$-oxo-(BsubPc)$_2$ shares similar electrochemical behavior with Cl-BsubPc,$^7$ we were motivated to characterize $\mu$-oxo-(BsubPc)$_2$'s performance in OPV devices. Furthermore as mentioned above, $\mu$-oxo-(BsubPc)$_2$ possesses some unique traits within the family of BsubPcs that could potentially serve as enhancing features in this application. These include its solid state arrangement$^{23}$ and its hypsochromic-shifted absorption spectrum,$^7,22$ which helps extend the range of wavelengths that can be harnessed by BsubPc-based devices. For example, multiple bathochromic-shifted BsubPcs have been demonstrated previously,$^{20}$ which would benefit from pairing with a more hypsochromic BsubPc. An overlay of the absorbance spectrum of $\mu$-oxo-(BsubPc)$_2$ with the solar spectrum can be found in the Supporting Information, Figure S1.

In this paper we begin to explore the application of $\mu$-oxo-(BsubPc)$_2$ and report its frontier orbital energy levels and thereby suggest promising OPV material pairings. Second, we demonstrate the performance of $\mu$-oxo-(BsubPc)$_2$ as an electron donor material and as an electron acceptor material in planar heterojunction OPVs. Finding higher efficiency with a donor configuration, we then explore pairings with other acceptor materials. We demonstrate that $\mu$-oxo-(BsubPc)$_2$, as a donor, produces devices of comparable efficiency to the widely explored Cl-BsubPc. Noting that the energy levels of $\mu$-oxo-(BsubPc)$_2$ are more suited for use as an electron acceptor with an additional boron subphthalocyanine donor than with $\alpha$6T, we then found that it performed well as a bi-functional inter-layer in cascade structures between a fullerene acceptor and Cl-BsubPc donor. Lastly, exploring donor layer mixtures of $\mu$-oxo-(BsubPc)$_2$ and Cl-BsubPc showed evidence of beneficial alloying-like effects, potentially revealing yet another route for the development of well-optimized BsubPc based OPVs. Thus, we open a new class of BsubPc derived materials for future study and application in organic photovoltaic devices.
**Figure 2.** (a) The chemical structure of $\mu$-oxo-(BsubPc)$_2$. (b) A depiction of the solid state arrangement of $\mu$-oxo-(BsubPc)$_2$ taken from a crystal obtained by sublimation. (c) Absorbance spectrum of $\mu$-oxo-(BsubPc)$_2$ in solution (purple) and in a solid film (blue). Figure 2 (b) is reproduced with permission of the International Union of Crystallography, and can be found online at http://journals.iucr.org.

**Results**

2.2.1 Opto-electronic Characterization of the Solid Film

*This section is jointly authored, with experimental work undertaken by Dr. Castrucci.*

We have previously described the synthesis and basic physical characterization of $\mu$-oxo-(BsubPc)$_2$, the details of which are outlined in the introduction of this paper. Building on our previous studies, we began by using ultraviolet photoelectron spectroscopy (UPS) to determine the highest occupied molecular orbital (HOMO) energy and the Fermi energy of $\mu$-oxo-(BsubPc)$_2$, the results of which are shown in Figure S2 (a) and (b). The HOMO of $\mu$-oxo-(BsubPc)$_2$ was measured to be 5.9 eV and the Fermi level to be 4.5 eV, respectively, with both
values reported relative to a free electron in vacuum. This compares well with the measured oxidation potential of +0.95 V which by using the Thompson-Forrest equation\textsuperscript{27} yields 5.9 eV.

Using the solid state absorption of a vacuum deposited films of $\mu$-oxo-(BsubPc)$_2$\textsuperscript{25} (Figure 2 (c)) and the corresponding onset of absorption the optical band gap was calculated. The lowest unoccupied molecular orbital (LUMO) energy was then calculated using the HOMO energy less the optical band gap and therefore set to be 4.0 eV. The optical gap of 1.9 eV is similar to the electrochemical gap of 1.98 V.

Having determined the frontier orbital energy levels and their positions relative to the Fermi energy, we then constructed band diagrams under the assumption of vacuum energy alignment for $\mu$-oxo-(BsubPc)$_2$ when paired with electron acceptors and donors of interest (Figure 3, the materials shown are all used in this work in various device architectures and material pairings). In all the pairings identified, the HOMO and LUMO energies of the electron accepting materials exceed those of the electron donating materials, forming a difference in HOMO energies ($\Delta_{\text{HOMO}}$) and a difference in LUMO energies ($\Delta_{\text{LUMO}}$), an obvious prerequisite for driving exciton dissociation at the donor/acceptor interface. Additionally, if one considers a charge cascade device architecture, such as those demonstrated by Cnops \textit{et al.},\textsuperscript{13} the bi-functional center layer provides a dissociating interface to both the electron donating material and the electron accepting material, acting as an acceptor and donor to each respectively. In an energy cascade device architecture, ideally the HOMO energies of two donor layers/materials are identical, yielding a non-dissociating exciton energy transfer interface such as that shown by Ichikawa \textit{et al.}.\textsuperscript{28} When positioned as a donor, the interfacial gap of $\mu$-oxo-(BsubPc)$_2$ ($I_{\text{gap}} = \text{HOMO}_D - \text{LUMO}_A$) is larger than that of Cl-BsubPc due to the higher HOMO energy (5.9 eV vs. 5.6 eV). The $I_{\text{gap}}$ is generally positively correlated with open circuit voltage in organic photovoltaics.\textsuperscript{29} All the energy levels are shown in numeric detail in the Supporting Information, Table S1, while the compound structures relevant to this discussion are illustrated in Figure 1 and Figure 2 (a).
Figure 2.3. Schematic of energy levels for various acceptor and donor layer materials. HOMO energies other than $\mu$-oxo-(BsubPc)$_2$’s are from References.\textsuperscript{30-33} All LUMO energies are calculated by offsetting the HOMO energy with our measurements of the optical gaps of the solid films. See Supporting Information Table S1 for more information on energy levels.

2.2.2 Testing the Application of $\mu$-oxo-(BsubPc)$_2$ as an Electron Donor and/or an Electron Acceptor

\textit{This section is jointly authored, with experimental work primarily undertaken by Dr. Castrucci.}

To test the application of $\mu$-oxo-(BsubPc)$_2$ first as an electron donating material, OPV devices of the structure ITO/PEDOT:PSS/MoO$_x$(5 nm)/Donor/C$_{60}$/TPBi(3 nm)/Ag(80 nm), where the donor was Cl-BsubPc or $\mu$-oxo-(BsubPc)$_2$, were fabricated (Figure 4, left). The reference to the Cl-BsubPc/C$_{60}$ baseline device configuration is based upon its literature history\textsuperscript{9-10, 30} and our replication of it here serves as a baseline point of comparison between the existing literature and our laboratory's process and fabrication system. However, we did make two modifications to devices present within the literature. TPBi was selected as an electron injection layer after a brief property survey comparing TPBi and BCP (Table S2 and Figure S3). A relatively poor fill factor (FF) was present in initial devices, so a hole extraction layer was introduced by way of a 5 nm
molybdenum oxide (MoO₃) layer. This had been previously seen as having a positive contribution to device metrics; mainly an improved FF and open circuit voltage (V_OC) for devices with Cl-BsubPc and related phthalocyanines as electron donor layers.¹⁵-¹⁷, ³⁴

Figure 2.4. Schematic of the device structure for testing μ-oxo-(BsubPc)₂ as an electron donor, acceptor, or bi-functional layer, in basic, cascade, or mixed donor PHJ devices.

By comparing μ-oxo-(BsubPc)₂ to Cl-BsubPc when both were paired with C₆₀, we found the μ-oxo-(BsubPc)₂ devices have a V_OC of 0.90 (0.898–0.902, 95% confidence interval) V, a J_SC of -3.9 (-4.0–3.8) mA cm⁻², and a FF of 0.59 (0.58–0.60) for a total power conversion efficiency (η_P) of 2.1 (2.0–2.1) % (Table 1 and Figure 5 (a)). While we did expect an increase in V_OC for μ-oxo-(BsubPc)₂, the V_OC, J_SC, and η_P were found to be less than the baseline Cl-BsubPc containing device (p = 8 × 10⁻¹⁵, p = 0.003, p = 9 × 10⁻⁵, respectively; p-values are explained in the experimental section). However, the FF exceeded that of the baseline device (p = 5 × 10⁻⁴).

Some of these differences likely arise from differing device dimensions, but the V_OC in particular is a result of the interface energy band alignment and changed insignificantly during an initial layer dimension property survey (Tables S3 and S4 and Figures S4 and S5). The drop in V_OC despite the increase in I_gap potentially suggests a different surface dipole is formed between μ-oxo-(BsubPc)₂ and C₆₀ compared to that formed between Cl-BsubPc and C₆₀.

The solid state absorption of μ-oxo-(BsubPc)₂ has a peak near 570 nm and C₆₀ has a peak near 350 nm. The corresponding peaks in the external quantum efficiency spectrum for this device indicate excitons are successfully harvested from both the donor and acceptor layers, which each contribute to the total J_SC, in a manner comparable to the baseline device (Figure 5 (b)).

To then test the performance of μ-oxo-(BsubPc)₂ as an electron acceptor, devices of the structure ITO/PEDOT:PSS/α6T/Acceptor/TPBi(3 nm)/Ag(80 nm), where the acceptor was Cl-BsubPc or
μ-oxo-(BsubPc)₂, were also fabricated (Figure 4). We selected an α6T/Cl-BsubPc baseline due to its previous use in the BsubPc OPV literature¹⁹ and a desire to avoid the singlet fission triplet harvesting processes associated with pentacene.⁶,¹²,³²

When using μ-oxo-(BsubPc)₂ as an electron acceptor in place of Cl-BsubPc, substitution resulted in approximately an 80% reduction in J_SC (p = 2 × 10⁻¹⁷), and a moderate reduction in V_OC and FF (p = 1 × 10⁻⁴, p = 4 × 10⁻⁹, respectively), yielding a final device efficiency of less than 0.5%. This is dramatically less than the Cl-BsubPc containing device efficiency of 3.2 (3.0–3.4)% (Figure 5 (a), Table 1), and we judged it unlikely that optimization of layer thicknesses would bridge such a gap. When considering the EQE spectrum for the μ-oxo-(BsubPc)₂ in comparison to the Cl-BsubPc we note that the peaks near 350 nm and 600 nm, corresponding to BsubPc adsorption, are only one third to one quarter as intense. Even more dramatic is the complete absence of a peak near 450 nm, indicating there are no excitons generated in the donor layer that are extracted as current (Figure 5 (b)). Exciton extraction only from the acceptor layer would suggest a poor LUMO_D to LUMO_A alignment preventing the transfer of donor generated electron carriers to the acceptor, but a reasonable ΔHOMO facilitating the extraction of acceptor generated holes to the donor layer. Given that the estimated ΔLUMO should be sufficient, it is possible that some favourable molecular arrangement for electron transfer possessed by the α6T/Cl-BsubPc interface no longer occurs in an α6T/μ-oxo-(BsubPc)₂ interface. The “bent” structure of μ-oxo-(BsubPc)₂ suggests a greater degree of difficulty in forming a regular interface with the linear α6T.

From this initial assessment we concluded that μ-oxo-(BsubPc)₂ clearly showed more promise as an electron donating material than as an electron accepting material, when paired with standard and well defined acceptor and donor materials. This conclusion is consistent with our previous cyclic voltammetry observation of a reversible oxidation process but an irreversible reduction process.⁷ The baseline results for both donor and acceptor screening, as well as relevant solid film absorbances and EQE spectra, are compiled in Table 1 and Figure 5.
Table 2.1. Mean device parameter comparison of Cl-BsubPc to μ-oxo-(BsubPc)₂ employed as an electron donor or electron acceptor.\(^a\)

<table>
<thead>
<tr>
<th>Donor/d(d_D) nm</th>
<th>Acceptor/d(d_A) nm</th>
<th>(J_{SC} (SD)/\text{mA cm}^{-2})</th>
<th>(V_{OC} (SD)/\text{V})</th>
<th>FF (SD)</th>
<th>(\eta_p (SD)/%)</th>
<th>No. of cells tested</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl-BsubPc/10</td>
<td>(C_60/30)</td>
<td>-4.4 (0.47)</td>
<td>1.06 (0.01)</td>
<td>0.52 (0.05)</td>
<td>2.4 (0.21)</td>
<td>12</td>
</tr>
<tr>
<td>(\mu)-oxo-</td>
<td>(C_60/45)</td>
<td>-3.9 (0.13)</td>
<td>0.90 (0.01)</td>
<td>0.59 (0.01)</td>
<td>2.1 (0.07)</td>
<td>7</td>
</tr>
<tr>
<td>((\text{BsubPc})_2/8)</td>
<td>(\alpha 6T/55)</td>
<td>-5.5 (0.54)</td>
<td>1.08 (0.03)</td>
<td>0.55 (0.06)</td>
<td>3.2 (0.44)</td>
<td>17</td>
</tr>
<tr>
<td>(\alpha 6T/30)</td>
<td>(\mu)-oxo-</td>
<td>-1.0 (0.08)</td>
<td>0.96 (0.06)</td>
<td>0.38 (0.04)</td>
<td>0.37 (0.04)</td>
<td>9</td>
</tr>
<tr>
<td>((\text{BsubPc})_2/5)</td>
<td>(\alpha 6T/30)</td>
<td>-1.0 (0.08)</td>
<td>0.96 (0.06)</td>
<td>0.38 (0.04)</td>
<td>0.37 (0.04)</td>
<td>9</td>
</tr>
</tbody>
</table>

\(^a\) The standard deviation (SD) of each value is shown in parentheses. Device structure is ITO/PEDOT:PSS/Donor/Acceptor/TPBi(3 nm)/Ag(80 nm).
Figure 2.5. (a) J-V curves comparing Cl-BsubPc containing devices to \( \mu \)-oxo-(BsubPc)\(_2\) containing devices. Magenta lines denote \( \alpha \)6T/Cl-BsubPc devices, olive lines denote \( \alpha \)6T/\( \mu \)-oxo-(BsubPc)\(_2\) devices, teal lines denote Cl-BsubPc/C\(_{60}\) devices, and blue lines denote \( \mu \)-oxo-(BsubPc)\(_2\)/C\(_{60}\) devices. (b) Solid state film absorbances for Cl-BsubPc (magenta), \( \mu \)-oxo-(BsubPc)\(_2\) (blue), \( \alpha \)6T (orange), and C\(_{60}\) (dark grey) and external quantum efficiency spectra using the key from (a). Shaded regions show the 95% confidence interval.

2.2.3 Application With Other Electron Acceptors in Photovoltaic Devices

This section is jointly authored, containing experimental work by both co-authors.

Moving away from \( \mu \)-oxo-(BsubPc)\(_2\)’s poor performance as an electron acceptor, we then focused on its use as an electron donor, next testing its pairing with C\(_{70}\). Consistent with previously reported photovoltaic devices containing Cl-BsubPc as a donor, the substitution of C\(_{70}\) for C\(_{60}\) as the acceptor\(^\text{18}\) also improved the performance of a \( \mu \)-oxo-(BsubPc)\(_2\) based OPV. The \( J_{SC} \) was increased (\( p = 4 \times 10^{-8} \)) by nearly 50 % to -5.9 (-5.6--6.2) mA cm\(^{-2}\), while \( V_{OC} \) remained similar at 0.89 (0.886--0.894) V and FF fell slightly (\( p = 2 \times 10^{-9} \)) to 0.50 (0.49--0.51)
(Figure 6 (a), Table 2). This resulted in an overall increase in $\eta_P$ ($p = 2 \times 10^{-5}$) to 2.7 (2.5–2.9) %. Based upon the external quantum efficiency spectra (Figure 6 (b)), the increase in current density is attributed primarily to increased quantum efficiency between 450 nm and 550 nm, and between 600 nm and 700 nm, both areas of the spectrum where C$_{70}$ absorbs strongly but $\mu$-oxo-(BsubPc)$_2$ and C$_{60}$ do not (Figure 6 (b)). We can conclude that when pairing $\mu$-oxo-(BsubPc)$_2$ as a donor with C$_{70}$ as an acceptor, the same trends in device performance were observed as when C$_{70}$ is paired with Cl-BsubPc: substitution of C$_{70}$ for C$_{60}$ results in increased $J_{SC}$ and $\eta_P$. The $J_{SC}$ increase for $\mu$-oxo-(BsubPc)$_2$ devices was particularly significant, and thus, our subsequent work was carried out with C$_{70}$.

Table 2.2. Mean device parameter comparison of Cl-BsubPc to $\mu$-oxo-(BsubPc)$_2$ employed as an electron donor with fullerene acceptor materials.$^a$

<table>
<thead>
<tr>
<th>Donor/d$_{D}$ nm</th>
<th>Acceptor/d$_{A}$ nm</th>
<th>$J_{SC}$ (SD)/mA cm$^{-2}$</th>
<th>$V_{OC}$ (SD)/V</th>
<th>FF (SD)</th>
<th>$\eta_P$ (SD)/%</th>
<th>No. of cells tested</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl-BsubPc/10 C$_{60}$/30</td>
<td>-4.4 (0.47)</td>
<td>1.06 (0.01)</td>
<td>0.52 (0.05)</td>
<td>2.4 (0.21)</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>Cl-BsubPc/10 C$_{70}$/30</td>
<td>4.62 (0.11)</td>
<td>1.08 (0.01)</td>
<td>0.52 (0.01)</td>
<td>2.6 (0.09)</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>$\mu$-oxo-(BsubPc)$<em>2$/8 C$</em>{60}$/45</td>
<td>-3.9 (0.13)</td>
<td>0.90 (0.01)</td>
<td>0.59 (0.01)</td>
<td>2.1 (0.07)</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>$\mu$-oxo-(BsubPc)$<em>2$/8 C$</em>{70}$/45</td>
<td>-5.9 (0.62)</td>
<td>0.89 (0.01)</td>
<td>0.50 (0.02)</td>
<td>2.7 (0.34)</td>
<td>12</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ The standard deviation (SD) of each value is shown in parentheses. Device structure is ITO/PEDOT:PSS/MoO$_X$(5 nm)/Donor/Acceptor/TPBi(3 nm)/Ag(80 nm).
In order to develop a standard architecture for our further experimentation with \( \mu \)-oxo-(BsubPc)$_2$/C$_{70}$ devices, an optimization process was carried out. The acceptor layer thickness was varied first, leading to the identification of the ideal optical location of the dissociating interface in relation to the reflective silver electrode. The donor layer thickness was then adjusted to find a balance between optical and excitonic factors. Similarly to its historical Cl-BsubPc/C$_{60}$ analogue, the optimization identified a 10 nm donor and 30 nm acceptor architecture as the highest \( \eta_p \). Details can be found in Table S5 and Figure S6.

![Figure 2.6](image)

**Figure 2.6.** (a) J-V curves comparing acceptors for pairing with \( \mu \)-oxo-(BsubPc)$_2$, with Cl-BsubPc included for reference. Teal lines denote Cl-BsubPc/C$_{60}$ devices, blue lines denote \( \mu \)-oxo-(BsubPc)$_2$/C$_{60}$ devices, black lines denote \( \mu \)-oxo-(BsubPc)$_2$/C$_{70}$, and orange lines denote Cl-BsubPc/C$_{70}$ devices. (b) Solid state film absorbances for Cl-BsubPc (magenta), \( \mu \)-oxo-(BsubPc)$_2$ (blue), C$_{60}$ (dark grey), C$_{70}$ (black) and external quantum efficiency spectra using the key from (a). Shaded regions show the 95% confidence intervals.
2.2.4 Application as a Bi-Functional Interlayer Material in Cascade Architectures

Charge cascade architectures contain multiple dissociating interfaces, with the center bi-functional interlayer working as both an electron donor and acceptor.\(^{13}\) Such architectures provide an efficient exciton dissociation segment within the device, as a result of the average distance to a dissociating interface being reduced following the introduction of a second interface. Charge cascade devices are also a method to enable the incorporation of a third photoactive material into a device. A third material represents a third segment of the solar spectrum which can be targeted for absorption.

An additional cascade architecture demonstrated by Ichikawa et al., is referred to as an energy cascade. In this case, instead, exciton energy must be transferred between respective layers to reach a sole dissociating interface.\(^ {28}\) Given a limited exciton diffusion length, this device type can reduce the number of excitons which reach a dissociating interface. It does, however, permit a third material to be incorporated in a manner which allows the location of charge generation to be tightly controlled – if, for example, electrons experience difficulty travelling from the donor/bi-functional layer interface to the anode in a charge cascade architecture, an otherwise equivalent energy cascade architecture could be used to ensure that all excitons are dissociated closer to the anode.

2.2.4.1 Charge Cascade Architecture

While the performance of \(\mu\)-oxo-(BsubPc)\(_2\) as an acceptor is uninspiring when paired with \(\alpha\)6T, its energy levels (Figure 3) suggest a much more favorable pairing can be made with Cl-BsubPc. The \(I_{\text{gap}}\) of the interface between \(\alpha\)6T/\(\mu\)-oxo-(BsubPc)\(_2\) is only 0.9 eV, whereas for Cl-BsubPc/\(\mu\)-oxo-(BsubPc)\(_2\) it is a much greater, 1.6 eV. A larger \(I_{\text{gap}}\) is associated with higher \(V_{\text{OC}}\).\(^ {29}\) The \(\Delta_{\text{HOMO}}\) between the two compounds is 0.3 eV, with the \(\Delta_{\text{LUMO}}\) a slightly larger 0.5 eV. Given these considerations and the good performance of \(\mu\)-oxo-(BsubPc)\(_2\) as an electron donor paired with C\(_{70}\), we then considered a Cl-BsubPc/\(\mu\)-oxo-(BsubPc)\(_2\)/C\(_{70}\) charge cascade device structure (\(\mu\)-oxo-(BsubPc)\(_2\), interlayer).

Due to the similar optical and electronic properties of the two BsubPc compounds, we elected to simply subtract from the \(\mu\)-oxo-(BsubPc)\(_2\) layer thickness of the above outlined \(\mu\)-oxo-
(BsubPc)₂/C₇₀ cells in order to introduce the Cl-BsubPc layer. We kept the total Cl-BsubPc/μ-oxo-(BsubPc)₂ thickness at the 10 nm, identified by the preceding optimization, enabling direct performance comparison with minimally altered optical effects. We investigated 2.5 nm/7.5 nm, 5nm/5 nm and 7.5 nm/2.5 nm thicknesses, with properties and J-V/EQE figures detailed in Table S6 and Figure S7 respectively. All three charge cascade devices showed greater performance than the Cl-BsubPc/C₇₀ or μ-oxo-(BsubPc)₂/C₇₀ devices, with substantial gains made to the fill factor. V_OC’s were held to roughly the same value of 0.91 V, with the high J_SC of the μ-oxo-(BsubPc)₂/C₇₀ device being mirrored in the cascade devices by a trend of increasing J_SC with increasing μ-oxo-(BsubPc)₂ layer thickness. The 2.5 nm/7.5 nm and 5 nm/5 nm Cl-BsubPc/μ-oxo-(BsubPc)₂ devices proved to be the most efficient of the set at 3.3 (3.21–3.39)% and 3.2 (3.13–3.27)% respectively, having the highest J_SC’s of the charge cascade devices and the highest fill factors in this study at 0.64 (0.63–0.65) and 0.63 (0.62–0.64) respectively. This was a marked improvement over the 2.7 (2.6–2.8)% efficient μ-oxo-(BsubPc)₂/C₇₀ device, indicating that the enhanced exciton dissociation of the charge cascade architecture provides substantial benefits to the μ-oxo-(BsubPc)₂ cascade system. Furthermore, it indicates that μ-oxo-(BsubPc)₂ is a good candidate material for use in future charge cascade studies. Relevant devices and parameters are detailed in Table 3 and Figure 7.

2.2.4.2 Energy Cascade Architecture

Moving then to an energy cascade architecture,²⁸ we paired Cl-Cl₆BsubPc with μ-oxo-(BsubPc)₂. The peripheral chlorination of Cl-Cl₆BsubPc drops its HOMO energy relative to Cl-BsubPc by 0.3 eV, while its optical gap remains the same. Thus, the ΔHOMO between Cl-Cl₆BsubPc and μ-oxo-(BsubPc)₂ is zero and the interface is therefore considered non-dissociating.

In comparison to the analogous 5 nm/5 nm/30 nm Cl-BsubPc/μ-oxo-(BsubPc)₂/C₇₀ charge cascade device (Table 3), the Cl-Cl₆BsubPc device demonstrated small to moderate losses in J_SC, V_OC and FF. Its properties are also listed in Table 3. In Figure 7(a), the slope of the J-V curve indicates high series resistance, which suggests inferior conductivity through the Cl-Cl₆BsubPc layer. The EQE curves shown in Figure 7(b) indicate a reduced contribution from BsubPc materials, demonstrating that the loss of a dissociating interface has reduced the quantum efficiency of exciton dissociation. Thus, there seem to be no benefits from using this type of
cascade architecture. Exciton diffusion appears to be more of a limiting factor than charge transport, a conclusion supported by the comparatively good performance of the charge cascade device.

Table 2.3. Mean device parameter comparison of \(\mu\)-oxo-(BsubPc)\(_2\) energy cascade and charge cascade devices, with bilayer devices included for reference.\(^a\)

<table>
<thead>
<tr>
<th>Donor/d(_0) nm</th>
<th>Device Type</th>
<th>(J_{SC}) (SD)/mA cm(^{-2})</th>
<th>(V_{OC}) (SD)/V</th>
<th>FF (SD)</th>
<th>(\eta_P) (SD)/%</th>
<th>No. of cells tested</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl-BsubPc(10nm)</td>
<td>Bilayer</td>
<td>4.6(0.11)</td>
<td>1.08(0.01)</td>
<td>0.52(0.01)</td>
<td>2.6(0.09)</td>
<td>12</td>
</tr>
<tr>
<td>Cl-Cl(_6)BsubPc(5nm)/(\mu)-oxo-(BsubPc)(_2)(5nm)</td>
<td>Energy Cascade</td>
<td>5.0(0.08)</td>
<td>0.84(0.01)</td>
<td>0.50(0.02)</td>
<td>2.1(0.10)</td>
<td>9</td>
</tr>
<tr>
<td>Cl-BsubPc(5nm)/(\mu)-oxo-(BsubPc)(_2)(5nm)</td>
<td>Charge Cascade</td>
<td>5.7(0.09)</td>
<td>0.89(0.01)</td>
<td>0.63(0.02)</td>
<td>3.2(0.14)</td>
<td>17</td>
</tr>
<tr>
<td>Cl-BsubPc(2.5nm (\mu)-oxo-(BsubPc)(_2)(7.5nm)</td>
<td>Charge Cascade</td>
<td>5.9(0.17)</td>
<td>0.87(0.02)</td>
<td>0.64(0.02)</td>
<td>3.3(0.17)</td>
<td>14</td>
</tr>
<tr>
<td>(\mu)-oxo-(BsubPc)(_2)(10nm)</td>
<td>Bilayer</td>
<td>6.3(0.14)</td>
<td>0.91(0.01)</td>
<td>0.48(0.02)</td>
<td>2.7(0.15)</td>
<td>15</td>
</tr>
</tbody>
</table>

\(^a\) The standard deviation (SD) of each value is shown in parentheses. Device structure is ITO/PEDOT:PSS/MoO\(_3\)(5 nm)/Donor/C\(_{70}\)(30nm)/TPBi(3 nm)/Ag(80 nm).
Figure 2.7. (a) J-V curves comparing μ-oxo-(BsubPc)$_2$/C$_{70}$ cascade devices, with Cl-BsubPc/C$_{70}$ and μ-oxo-(BsubPc)$_2$/C$_{70}$ devices for comparison. (b) External quantum efficiency spectra. Legends specify the donor layer composition; all devices are paired with 30nm C$_{70}$ as an acceptor. Black lines denote Cl-BsubPc/C$_{70}$ devices, pink lines denote Cl-BsubPc (2.5nm)/μ-oxo-(BsubPc)$_2$ (7.5nm)/C$_{70}$ devices, green lines denote μ-oxo-(BsubPc)$_2$/C$_{70}$ devices, blue lines denote Cl-BsubPc (5nm)/μ-oxo-(BsubPc)$_2$ (5nm)/C$_{70}$ devices, green lines denote μ-oxo-(BsubPc)$_2$/C$_{70}$ devices, and orange lines denote Cl-Cl$_6$BsubPc/μ-oxo-(BsubPc)$_2$/C$_{70}$ devices. Shaded regions indicate 95% confidence intervals.

2.2.5 Application in Subphthalocyanine Mixture Donor Layers

To preface this discussion, a simple comparison of the performances of pure Cl-BsubPc and μ-oxo-(BsubPc)$_2$ donor layers paired with C$_{70}$ acceptors, outlined above, reveals that the μ-oxo-(BsubPc)$_2$ device yields a lower $V_{OC}$. With the principle of organic alloying demonstrated by Street et al.,$^{35}$ we hypothesized that it is possible to increase the $V_{OC}$ of a μ-oxo-(BsubPc)$_2$ donor layer through blending with a material that provides a higher $V_{OC}$ when paired with the same acceptor. If alloying is achieved, the incorporated material contributes to the energy bands in the material to a degree representative of its percent composition in the film, rather than simply forming a trap state. We speculated that the structural similarities between Cl-BsubPc and μ-oxo-(BsubPc)$_2$ would permit the molecular ordering necessary to obtain one group of delocalized energy bands without an additional trap band.
The results of this effort are shown in Table 4 and Figure 8. Varying the concentrations of μ-oxo-(BsubPc)$_2$ and Cl-BsubPc in the donor layer, via co-deposition, successfully shifted the $V_{OC}$ of the devices between the “endpoints” represented by the pure devices, with no deviations from the trend observed. The 3:1 Cl-BsubPc:μ-oxo-(BsubPc)$_2$ mixture, in particular, shows a $V_{OC}$ of 0.99 V, midway between the 1.08V and 0.91V of the Cl-BsubPc and μ-oxo-(BsubPc)$_2$ devices, which was the highest of any of the mixed devices. The 1:1 mixture yielded the greatest efficiency at 3.1%, benefitting proportionally from the high $J_{SC}$ of the μ-oxo-(BsubPc)$_2$ and the higher $V_{OC}$ of the Cl-BsubPc. Notably, the fill factor of any of the mixture devices was higher than those found in either of the pure devices. Fill factor is understood to arise from a complex assortment of electronic considerations which are beyond the scope of this work, including, for example, the degree of matching between charge carrier mobilities.\textsuperscript{36}

### Table 2.4. Mean device parameter comparison of μ-oxo-(BsubPc)$_2$:Cl-BsubPc mixture devices, with bilayer devices included for reference.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Donor</th>
<th>$J_{SC}$ (SD)/mA cm\textsuperscript{-2}</th>
<th>$V_{OC}$ (SD)/V</th>
<th>FF (SD)</th>
<th>η\textsubscript{P} (SD)/%</th>
<th>No. of cells tested</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl-BsubPc</td>
<td>4.6(0.11)</td>
<td>1.08(0.01)</td>
<td>0.52(0.01)</td>
<td>2.6(0.09)</td>
<td>12</td>
</tr>
<tr>
<td>3:1 Cl-BsubPc:μ-oxo-(BsubPc)$_2$</td>
<td>5.1(0.05)</td>
<td>0.99(0.01)</td>
<td>0.56(0.01)</td>
<td>2.8(0.06)</td>
<td>13</td>
</tr>
<tr>
<td>1:1 Cl-BsubPc:μ-oxo-(BsubPc)$_2$</td>
<td>5.7(0.07)</td>
<td>0.94(0.01)</td>
<td>0.58(0.01)</td>
<td>3.1(0.06)</td>
<td>7</td>
</tr>
<tr>
<td>1:3 Cl-BsubPc:μ-oxo-(BsubPc)$_2$</td>
<td>5.5(0.07)</td>
<td>0.93(0.01)</td>
<td>0.58(0.01)</td>
<td>2.9(0.04)</td>
<td>11</td>
</tr>
<tr>
<td>μ-oxo-(BsubPc)$_2$</td>
<td>6.3(0.14)</td>
<td>0.91(0.01)</td>
<td>0.48(0.02)</td>
<td>2.7(0.15)</td>
<td>15</td>
</tr>
</tbody>
</table>

\textsuperscript{a}The standard deviation (SD) of each value is shown in parentheses. Device structure is ITO/PEDOT:PSS/MoO$_x$(5 nm)/Donor Mixture(10nm)/C$_{70}$(30 nm)/TPBi(3 nm)/Ag(80 nm).
2.3 Conclusions

In summary, we have explored the function of the unique BsubPc derivative \( \mu\text{-oxo-}(\text{BsubPc})_2 \) in a variety of device architectures with a variety of material pairings. We tested its performance with standard fullerene acceptor and \( \alpha_6T \) donor materials, finding that it functioned best as a donor in bilayer cells. As with Cl-BsubPc devices, a molybdenum oxide hole transport layer and a C\textsubscript{70} acceptor both improved device efficiency, suggesting that improvements made on Cl-BsubPc containing devices might also be applicable to \( \mu\text{-oxo-}(\text{BsubPc})_2 \) devices.

The HOMO/LUMO energy levels of \( \mu\text{-oxo-}(\text{BsubPc})_2 \) enabled us to then explore its further application in cascade devices with BsubPc and fullerenes as a bi-functional interlayer material. The introduction of the second dissociating interface in the charge cascade architecture significantly improved device performance over equivalent bilayer Cl-BsubPc/C\textsubscript{70} devices. We found that \( \mu\text{-oxo-}(\text{BsubPc})_2 \) bilayer devices had greater efficiency than equivalent Cl-BsubPc devices, due to large gains in \( J_{SC} \) that compensated for minor losses to fill factor and \( V_{OC} \); an effect which was absent in the energy cascade devices of Cl-Cl\textsubscript{6}BsubPc/C\textsubscript{70}. This suggests \( \mu\text{-oxo-}(\text{BsubPc})_2 \) exhibits superior photo conversion.

Figure 2.8 (a) J-V curves comparing \( \mu\text{-oxo-}(\text{BsubPc})_2/\text{Cl-BsubPc} \) mixture devices, with Cl-BsubPc/C\textsubscript{70} and \( \mu\text{-oxo-}(\text{BsubPc})_2/C\textsubscript{70} \) devices for comparison. (b) External quantum efficiency spectra. Legends specify the donor layer composition, which is always 10 nm thick. All devices are paired with 30 nm C\textsubscript{70} as an acceptor.
Given this, we then proceeded to explore mixed donor layers, achieved through codeposition of \( \mu \)-oxo\-(BsubPc)\(_2\) and Cl-BsubPc. The result was devices with promising characteristics, such as a higher \( V_{OC} \) - approaching that of Cl-BsubPc devices - and a significantly higher fill factor. The results suggest an alloying-like behavior could be leveraged to yield devices with more balanced properties than either analogous homogenous-donor device.

Finally, we note that all \( \mu \)-oxo\-(BsubPc)\(_2\)-containing devices, excepting only the energy cascade device, were significantly superior to the analogous Cl-BsubPc devices. The uniqueness of \( \mu \)-oxo\-(BsubPc)\(_2\) and its proven performance enhancement in more advanced device architectures is leading us to further investigate its application in additional OPV device architectures.
Chapter 3
Boron Subphthalocyanines as Electron Donors in Outdoor Lifetime Monitored Organic Photovoltaic Cells

This work is under revision with the journal of Solar Energy Materials and Solar Cells. The Materials and Methods section has been moved to Appendix A. Initial contextual details in the Introduction are omitted, as they are redundant with Chapter 1 of this work.

The full author list of the paper is as follows:
Richard K. Garner,† David S. Josey,† Stephanie R. Nyikos,† Aleksa Dovijarski,† Jon M. Wang,† Greg J. Evans,† Timothy P. Bender†‡§*

†Department of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College Street, Toronto, Ontario, M5S 3E5, Canada

‡Department of Materials Science Engineering, University of Toronto, 180 College Street, Toronto, Ontario, M5S 3E4, Canada

§Department of Chemistry, University of Toronto, 200 College Street, Toronto, Ontario, M5S 3E5, Canada

Structural variants of boron subphthalocyanines were tested as light absorbing and electron donating materials paired with C60 in organic photovoltaic cells, in a rooftop ambient environment according to ISOS-O3 protocols. Constant current monitoring and daily current-voltage sweeps, reinforced by irradiance and temperature tracking, reveal differing degradation rates depending on the chemical structure of the boron subphthalocyanine. Results suggest that the observed initial burn-in efficiency loss observed in all devices is due to C60, but that the longer term degradation trend is attributable to the chemical breakdown of the subphthalocyanine donors through hydrolysis. These findings demonstrate that the molecular structure of boron subphthalocyanines is a significant handle on device longevity, and that a structure-property relationship can be established for stability. The results also highlight the need for alternative electron accepting materials to C60 for pairing with boron subphthalocyanines in planar heterojunction solar cells, as well as the necessity of a more robust encapsulation methodology.
3.1 Introduction

While BsubPcs and other materials are being harnessed to provide ever increasing PCEs, there is as yet insufficient clarity regarding their long term stability. Even where lifetime studies have taken place, the variety of degradation mechanisms and test conditions used have rendered direct comparisons difficult.\textsuperscript{37} Efforts such as ISOS, the International Summit on OPV Stability, have recognized that further emphasis is required in order to identify which molecular lineages are likely to yield an industrially useful result. ISOS has produced consensus standards for OPV stability testing which establish various testing protocols. These protocols allow results to be compared more easily between laboratories, and we have therefore used them in this study.\textsuperscript{38}

Various photo-stability parameters of BsubPcs have been explored in films. González-Rodríguez et. al measured the thermal stability of several BsubPc compounds,\textsuperscript{39} and Yamasaki and Mori measured the thermal and photostability of many BsubPc molecules including the three explored here.\textsuperscript{40} Both found more rigid BsubPc axial bonds to be more stable, with Yamasaki and Mori finding a stability trend of Ph-BsubPc > Cl-BsubPc > PhO-BsubPc. Our own group found that the photostability of BsubPcs was not significantly impacted by substituting a phenoxy axial ligand for the typical halide, in an analysis of BsubPcs incorporating peripheral solubilizing groups and doped into thin polystyrene films.\textsuperscript{41} As we show below, these film-based trends were not predictive of molecular longevity in encapsulated OPV devices.

More or equally relevant to this study, previously explored degradation mechanisms for BsubPcs/C\textsubscript{60} OSCs are discussed in detail by Wang et al.\textsuperscript{42} and Tong et al.\textsuperscript{14} They both indicate the formation of trap states in C\textsubscript{60} as the dominant contributor to burn-in degradation, with similar effects observed in analogous phthalocyanines/C\textsubscript{60} devices.\textsuperscript{43} Burn-in refers to the sharp loss in efficiency measured after the first day of irradiation. To explore these mechanisms, we tested an α-sexithiophene/C\textsubscript{60} (α-6T) PHJ OPV device set, which was used as a point of comparison to help understand the initial burn-in degradation behaviour of the OSCs.

This paper presents our investigation of the stability of several BsubPc compounds under outdoor solar irradiation in a PHJ OPV electron donor arrangement with a C\textsubscript{60} acceptor (Figure 1). Our testing was performed at the ISOS-O3 level, the most rigorous grade of outdoor lifetime monitoring, with further details and minor exceptions reported in the Supporting Information (SI). The primary goal was to identify whether a structure-property relationship exists between
the choice of axial substituents of various BsubPc molecules and the stability of those molecules in devices. The first compound is the prototypical Cl-BsubPc, followed by our previously reported phenoxy-BsubPc \(^4\) (PhO-BsubPc) and phenyl-BsubPc \(^44\) (Ph-BsubPc). Each of these compounds differ only by the axial substituent, which is sufficient to cause devices to vary slightly in their post-fabrication metrics.

In conjunction with this study, our lab has also undertaken a similar stability investigation of the same set of three BsubPcs as electron acceptors.\(^45\) This effort found no evidence of a burn-in effect, which is attributable to the lack of fullerene/C\(_{60}\) in the devices. The degradation trends identified for each material matched those determined by this study, indicating a true structure-property relationship between molecular design and stability under solar irradiance.

Figure 3.1. The full device layer stack is shown at left. Molecular structures of compounds (used independently) in active layers are shown at right.

### 3.2 Results and Discussion

The BsubPc molecular variants used in this study were chosen to investigate the susceptibility of various axial substituents to degradation with an OPV device. The Cl-BsubPc, in addition to being the prototypical BsubPc compound, was selected to test the vulnerability of a halide substituent. The Ph-BsubPc, previously examined for its alternative BsubPc crystal packings,\(^44\) was another interesting candidate due to the rigid boron-carbon bond yielding a perpendicular phenyl molecular fragment. The PhO-BsubPc, which has demonstrated much greater solubilities
The current monitoring results for each BsubPc-based OPV cell were converted to power flux using the load resistance and cell area, and are shown in Figure 2a along with solar irradiance and temperature data. The six power flux plots show the power produced by each of the device sets, with irradiance and temperature aligned above. The chronologically later α6T/C60 data is plotted alongside its own irradiance and temperature data in Figure 2b. Data is plotted according to true time, such that cloudy days (each having its own unique waveform) are aligned vertically. A cloudless day is recognizable through its characteristic “n”-shape. In order for cloudy days to have clearly represented irradiance, data points were plotted with transparency indexed to the rate of change in irradiance per minute. Thus, darker coloured regions indicate stability and the vertically “smeared” regions indicate the presence of intermittent clouds.
Figure 3.2. Temperature and solar irradiation data is shown in the uppermost plot of a), with device power flux during the corresponding time period displayed below. Part b) shows temperature, solar irradiation and power flux for α6T/C60 devices, which were tested at a different time.

As devices were tested over time, Figure 2 shows that their ability to produce power decreased. This is apparent through the slow fall in peak mid-day power fluxes. Devices were tested until reaching their stabilized 80% or 50% efficiency points depending on the set, which correspond to a 20% or 50% loss of efficiency from that measured after the burn-in period. Since burn-in occurs to a different degree for each device, it is often more useful to refer to degradation as a percentage of the stabilized, post burn-in value. Thus, in the ISOS standards, the time point
corresponding to when the device has 80% of its stabilized efficiency (meaning the efficiency measured after the day of burn-in) is designated as “ts80.”

Figure 3 plots the efficiencies recorded by the J-V curves after each day of testing, and is normalized such that the stabilized efficiency is treated as 100%. By normalizing to this “ts0” point, the longer-term degradation trends can be effectively compared. Testing of Ph-BsubPc and PhO-BsubPc based devices proceeded until ts50, whereas testing of Cl-BsubPc and α-6T based devices proceeded to approximately ts80 and ts90 respectively due to time constraints. Each pair of device sets showed the same long-term degradation trends, with the exception of the Ph-BsubPc devices, where Set 2 appears to undergo two days of “burn-in”-like effects. The relative rates of degradation identified here are in agreement with those found when testing these three BsubPcs as electron accepting materials: the Cl-BsubPc devices possess the greatest longevity, followed by the PhO-BsubPc devices, with the Ph-BsubPc devices degrading substantially in a relatively short period of time.

The α-6T/C60 OSC experienced a rapid burn-in effect of a similar nature to that of the BsubPc/C60 device sets, which supports C60-related degradation mechanisms such as dimerization being responsible for the phenomenon. This result is in accordance with literature results for device stability tests on OSCs containing C60 acceptors. The effect appears less substantial, but the α-6T devices experienced more illumination in their first test, which could slightly obscure the burn-in slope. Additionally, the absorption spectra of α-6T and C60 overlap significantly. This could have let the stable α-6T function as a photon shield, reducing the rate at which photons reached the C60 layer. While these devices experienced a reduced degradation rate, their accumulated power shown in Figure 3 demonstrates their poor overall performance. Notably, the α-6T devices experienced the least of the “steady” degradation over time. This indicates that while C60 may have been responsible for the burn-in, hydrolysis of the BsubPcs likely played a larger role in the subsequent degradation.

The hydrolysis of BsubPcs occurs in the presence of water, and so the later “steady” degradation component is likely a result of water within the device. Whether this water was trapped in the initially water-dispersed PEDOT:PSS layer from fabrication, or permeated into the device after encapsulation, should be the subject of further study. Evidence of PEDOT:PSS contributing to device degradation is present in the literature. The different rates of performance loss in the
BsubPcs tested correspond to the susceptibility of their various molecular structures to hydrolysis, as was also observed by Josey et al.\textsuperscript{45} Specifically, the chloro-boron bond should be much harder to hydrolyse than the phenyl- or phenoxy-boron bonds. While an oxidative photobleaching reaction is possible,\textsuperscript{42} we can conclude it is not the dominant effect here: the various BsubPcs would show much more similar degradation were this the case, since such a reaction would take place on the identical chromophores. These findings are supported by the $t_0$ and $ts_{50}/ts_{80}$ EQEs, found in Figure S3 of the SI, which show that the \textasciitilde600nm BsubPc peak was not harmed as substantially in the Cl-BsubPc devices as it was in either of the other BsubPcs’ devices.

![Figure 3.3](image-url)

*Figure 3.3.* Device efficiencies were measured using simulated AM1.5G light after each day of irradiation. Values were normalized to those measured after the first day to decouple the burn-in effect from subsequent degradation trends. Shaded regions indicate 95% confidence intervals on the efficiency.
The J-V curves taken at significant time points are plotted in Figure 4. Comparing the t0 and ts0 curves shows the effect of the first day’s burn-in, with subsequent curves illustrating the longer-term degradation effects. Degradation impacts the J\text{SC} and FF most significantly, with V\text{OC} holding mostly constant. These effects are attributable to the loss of active material via hydrolysis of the BsubPcs, and the formation of trap states in the C\text{60} by dimerization. The extremely poor performance of the α-6T/C\text{60} OSCs is self-evident, likely due to poor energy level alignment damaging the V\text{OC} and the aforementioned overlapping absorption spectra harming the J\text{SC}. Recalling the initial performance metrics in Table 1, PhO-BsubPc would have been identified as the superior material for use in OSCs without this stability analysis. Moving forward, its efficacy versus that of Cl-BsubPc may strongly depend on the ability of encapsulation to prevent hydrolysis.
Figure 3.4. J-V curves taken at significant time points in degradation process. t0 and ts0 are the J-V curves measured after fabrication and after stabilization (one day of burn-in) respectively. ts80 and ts50 refer respectively to the time points at which efficiency was 80 or 50 percent of the ts0 amount. Shaded regions show 95% confidence intervals on the current flux.

3.3 Conclusions

In this study, we have demonstrated that the longevity of BsubPc donor OSCs under solar illumination is strongly affected by the axial substituent. We have also confirmed that the
degradation trends of BsubPc/C60 OPV devices identified in the literature are also evident in outdoor testing. A burn-in effect was most likely driven by C60, and a slower degradation trend was more strongly directed by the vulnerability of each BsubPc variant to hydrolysis. Finally, this study demonstrates the ease with which outdoor testing can be implemented using a relatively inexpensive setup.

Our results suggest that the longevity of OSCs which use the robust and modifiable BsubPc platform as a donor material can be enhanced through structural modification, improvements to encapsulation, and replacing the ubiquitous C60 with more stable materials. The lifetime of OSCs is a critical factor in their commercial viability, and it must be enhanced in order to provide a more competitive alternative energy source than traditional silicon-based photovoltaic devices.
Chapter 4
The mixed and alloyed chemical composition of chloro-(chloro)\textsubscript{n}-boron subnaphthalocyanines dictates their physical properties and performance in organic photovoltaics

A portion of this chapter was authored primarily by Dr. Minh Dang, and is noted below. A paper based on this chapter is ready for submission.

Experimental Methods section moved to Appendix A. Initial contextual details in the Introduction are omitted, as they are redundant with Chapter 1 of this work.

Chloro-(chloro)\textsubscript{n}-boron subnaphthalocyanine (Cl-Cl\textsubscript{n}BsubNc) from a commercial source and two synthetic routes, wherein each sample exhibited varying degrees of bay position chlorination, were tested as electron donating hole-transporting materials in planar as well as bulk heterojunction (PHJ and BHJ) organic photovoltaic (OPV) devices. We have determined that increasing bay chlorination has a beneficial effect on the fill factor of PHJs. Comparison between these device sets, and our past device set utilizing the same set of Cl-Cl\textsubscript{n}BsubNcs as electron acceptors and transports, reveals that the variation and enhancing of fill factor and performance is likely due to enhanced exciton transport. While we identify two possible mechanisms for this, further studies will be required to determine whether the phenomenon is driven by decreased radiative relaxation or due to enhanced thermal hopping from a narrower density of states. In either case, we recommend the usage of Cl-Cl\textsubscript{n}BsubNc with higher levels of bay position chlorination achieved through the “nitrobenzene process” to achieve higher-performance OPVs.
4.1 Introduction

Surprisingly, the true chemical composition and molecular structure of Cl-BsubNc was not fully understood until quite recently. Kahn et al. found evidence that commercial Cl-BsubNc samples contained higher levels of chlorine than pure Cl-BsubNc would have, and that the Cl energy level was different than that of a B-Cl moiety.\textsuperscript{49} Concurrently, the work of Dang et al. in our laboratory determined that several synthetic procedures for Cl-BsubNc production yielded alloyed mixtures of Cl-Cl\textsubscript{n}BsubNc which have at least one, and often more, chlorine atoms substituted in the bay position of the Cl-BsubNc chromophore,\textsuperscript{50} as shown in Figure 1. Positioning of the chlorine atoms was confirmed by x-ray crystallography. Dang et al. therefore proposed that the synthesized mixtures instead be referred to as chloro-(chloro)\textsubscript{n}-boron subnaphthalocyanine (Cl-Cl\textsubscript{n}BsubNc). Each molecular mixture could not be separated according to the number of bay chlorines, yet functioned as a mixed alloy composition in OPV devices. This alloying is what permitted the phenomenon to escape detection.

Our group found the degree of chlorination was dependent on the specific synthetic process and reaction conditions used to synthesize Cl-Cl\textsubscript{n}BsubNc. Using x-ray photoelectron spectroscopy (XPS), our laboratory also quantified the level of bay position chlorination. Our results were in line with the results of Kahn et al., who determined a value of \~1.5 bay chlorines per molecule in commercially purchased Cl-BsubNc.\textsuperscript{49} We also quantified other variants: the “literature route” refers to the synthetic procedure of Torres et al,\textsuperscript{51} “commercial supplier” refers to material purchased from Lumtec, and “nitrobenzene route” refers to our synthetic route variant taking place in nitrobenzene solvent. It was found that the amount of chlorination of literature-Cl-Cl\textsubscript{n}BsubNc was similar to that of the commercial-Cl-Cl\textsubscript{n}BsubNc sample, whereas the nitrobenzene-Cl-Cl\textsubscript{n}BsubNc sample(s) had significantly higher levels of chlorination.
Figure 4.1. Structures of the PC70BM and C70 molecules, as well as the Cl-Cl$_n$BsubNc molecule, where $n$ ranges from 0 to 2 bay chlorines for each of the three isoindoline subgroups.

Through UPS measurements, the level of chlorination was also shown to alter the electronic energy levels of Cl-Cl$_n$BsubNcs (Table 1). Optical absorption and photoluminescence was also shown to vary for Cl-Cl$_n$BsubNcs. As a result of chlorination’s impact on these parameters, the performance of the various Cl-Cl$_n$BsubNc mixed alloy compositions within OPVs also differed. Our laboratory used OPVs with a Cl-Cl$_n$BsubNc electron acceptor layer and an $\alpha$-sexithiophene ($\alpha$-6T) electron donor layer to illustrate this.$^{50}$ The resulting devices showed a trend wherein the $V_{OC}$ decreased with increasing chlorination, while the FF increased with increasing chlorination. The nitrobenzene-Cl-Cl$_n$BsubNc devices achieved the highest PCE with 4.32 ± 0.11 %, despite exhibiting the lowest $V_{OC}$ of the study due to changes to their highest occupied molecular orbital (HOMO) energy level. They measured at 0.930 ± 0.002 V, rather than the 0.972 ± 0.018 V or 0.976 ± 0.005 V measured on literature- and commercial-Cl-Cl$_n$BsubNc OPV. This was due to a substantially higher fill factor: 0.53 ± 0.01, rather than 0.45 ± 0.01 or 0.46 ± 0.01 for literature- and commercial-Cl-Cl$_n$BsubNc. Thus, the effect of increasing bay chlorination on device properties was substantial.
This type of observation is not unique to Cl-Cl\textsubscript{n}BsubNc. Fleetham et al. found that using different synthetic procedures to produce zinc phthalocyanines (ZnPcs) could lead to peripheral chlorination of the phthalocyanine ligand, which benefitted the open circuit voltage of ZnPc/C\textsubscript{60} devices.\textsuperscript{52-53}

Table 4.1. Material Properties from Various Synthetic Routes.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Cl-Cl\textsubscript{n}BsubNc Source</th>
<th>Bay Chlorines via XPS [Kahn et al]\textsuperscript{50}</th>
<th>Peak Absorption, UV-Vis (nm)</th>
<th>Ionization Energy via UPS (eV)</th>
<th>Stokes Shift in Solid Films (nm)</th>
<th>Φ\textsubscript{PL} (Photoluminescent quantum yield, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>literature route</td>
<td>1.21</td>
<td>656</td>
<td>5.32</td>
<td>58</td>
<td>27</td>
</tr>
<tr>
<td>commercial supplier</td>
<td>1.61 [1.5]</td>
<td>656</td>
<td>5.31</td>
<td>47</td>
<td>24</td>
</tr>
<tr>
<td>nitrobenzene route</td>
<td>4.17</td>
<td>664</td>
<td>5.42</td>
<td>52</td>
<td>21</td>
</tr>
</tbody>
</table>

\textsuperscript{a) All data in Table 1 from our laboratory’s prior work by Dang et al. except in square brackets.}

In this follow-up study, we explore the various Cl-Cl\textsubscript{n}BsubNcs as electron donors/hole-transporting materials. They are paired with C\textsubscript{70} as an electron acceptor/transporter in a planar heterojunction OPV device, and with PC\textsubscript{70}BM in a bulk heterojunction (BHJ) OPV configuration. Three Cl-Cl\textsubscript{n}BsubNc variants were used; from the literature synthetic route, the nitrobenzene synthetic route, and from a commercial supplier. Each were integrated into otherwise equivalent devices, in both the PHJ and BHJ configuration. All OPVs fabricated in this work follow the design shown in Figure 2, with a structure consisting of a glass substrate; an indium tin oxide (ITO) cathode; a PEDOT:PSS hole transport layer; light-absorbing layers
comprising Cl-ClₐBsubNc/C₇₀ in PHJs and ClₐBsubNc:PC₇₀BM in BHJs; a bathocuproine (BCP) electron transport layer; and a silver anode. For PHJs, the absorbing layers consisted of a Cl-ClₐBsubNc donor layer and a C₇₀ acceptor layer; in BHJs the absorbing layer was a Cl-ClₐBsubNc:PC₇₀BM BHJ bulk heterojunction.

Figure 4.2. Device structures of a) PHJ and b) BHJ devices. Diagrams not to scale.
4.2 Results

4.2.1 Planar Heterojunction Devices

Literature, commercial and nitrobenzene Cl-Cl$_n$BsubNc were first tested as electron donating/hole-transporting layers in PHJ devices with the following configuration: ITO/PEDOT:PSS/Cl-Cl$_n$BsubNcs (7 nm)/C$_{70}$ (30 nm)/BCP (7 nm)/Ag. This structure was arrived at after a precursory optimization process detailed in Figure S2 of the supplementary information. Figure 3a shows current-voltage (J-V) curves of each set of devices, with shaded regions indicating 95% confidence intervals about the current flux.
Figure 4.3. a) PHJ J-V curves showing two separate fabrication runs of devices for each Cl-Cl\textsubscript{a}BsubNc source. Shaded regions indicate 95% confidence intervals about the current flux. b) Upper plot shows EQEs of each set. c) Lower plot rescales each plot so as to have the same integrated current, for comparison of relative material contributions.

Immediately apparent is the clear separation of open-circuit voltages (V\textsubscript{oc}) with variations in the Cl-Cl\textsubscript{a}BsubNc mixed alloyed composition. The nitrobenzene-Cl-Cl\textsubscript{a}BsubNc devices achieve the highest V\textsubscript{oc}, followed by the commercial- and literature- devices. This ordering, and furthermore the magnitude of V\textsubscript{oc} differences between synthesis routes, directly follows the trend in degree of bay chlorination we previously identified, which is shown in Table 2.
Table 4.2. PHJ J-V metrics for the various Cl-Cl_nBsubNcs. VOC: open circuit voltage, JSC: short circuit current flux, FF: fill factor, PCE: power conversion efficiency. Bracketed values in device metric columns display standard deviations.

<table>
<thead>
<tr>
<th>Device Type</th>
<th>Bay Chlorines via XPS</th>
<th>V_OC (V)</th>
<th>J_SC (mA/cm^2)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>literature route</td>
<td>1.21</td>
<td>0.81 (0.01)</td>
<td>-5.98 (0.14)</td>
<td>0.41 (0.05)</td>
<td>1.99 (0.22)</td>
</tr>
<tr>
<td>commercial supplier</td>
<td>1.61 [1.5]</td>
<td>0.83 (0.01)</td>
<td>-5.99 (0.34)</td>
<td>0.43 (0.02)</td>
<td>2.13 (0.21)</td>
</tr>
<tr>
<td>nitrobenzene route</td>
<td>4.17</td>
<td>0.88 (0.01)</td>
<td>-5.39 (0.24)</td>
<td>0.48 (0.02)</td>
<td>2.28 (0.13)</td>
</tr>
</tbody>
</table>

a) All data in Table 1 from our laboratory’s prior work by Dang et al. except in square brackets.

Another trend is apparent in the fill factor (FF). FF appears to rise with increasing levels of chlorination of Cl-Cl_nBsubNc, though the FF of the PHJ OPVs based on literature- Cl-Cl_nBsubNc devices (0.41 ± 0.05) has too high a standard deviation to conclusively declare it lower than that of the commercial- devices (0.43 ± 0.02). Overall the best PCE was obtained from the PHJ using nitrobenzene-Cl-Cl_nBsubNc, which was a result of increased V_OC and FF.

Variation of J_SC was found between device sets that may indicate a source of run-to-run variation; discussed below. This variation was also observed in the external quantum efficiency (EQE) plots. Figure 3b displays the standard EQE plots and Figure 3c displays EQE data which has been rescaled to normalize each device by its J_SC, in order to more clearly see relevant current contributions from each of the light-absorbing materials. The clearly definable peaks of both Cl-Cl_nBsubNc and C_{70}, and a wide range of absorption, indicate that both active layer
materials are contributed to photogeneration. Generally speaking, the even nature of the EQEs indicated an optically balanced device. Due to the wide area of the solar energy spectrum which is accessed by an absorption range of 330-730nm, further optimization and configuration considerations could yield very well-performing PHJ OPVs.

4.2.2 Bulk Heterojunction Devices

This section was authored primarily by Dr. Minh Dang

Yang et al has previously reported a bulk heterojunction (BHJ) OPV device configuration based on Cl-ClₙBsubNc and [6,6]-phenyl-C-71-butyric acid methyl ester (PC₇₀BM), using the same Cl-ClₙBsubNc supplier as us. They obtained a PCE of 2.3 ± 0.2 % when using the same device architecture as was employed in our efforts.

In an effort to replicate the results of Yang et al., BHJ OPVs were prepared by pairing PC₇₀BM with each Cl-ClₙBsubNc, using the procedures outlined in the Experimental Methods section. The J–V characteristics and EQE spectra of BHJ OPVs under AM1.5G illumination are displayed in Figure 4. Devices incorporating commercial-Cl-ClₙBsubNc yielded an efficiency of 1.71%. The nitrobenzene-Cl-ClₙBsubNc device, which was the best performing, showed a Jₜₜ of 7.07 ± 0.16 mA/cm², a Vₒc of 862 ± 32 V, a FF of 0.347 ± 0.010 and a PCE of 2.12 ± 0.17 %. These values are likely lower than Yang et al.’s because we did not carry out an active-layer thickness optimization, which likely impacted FF and Jₜₜ. The pronounced peaks in the EQE at 462 nm and 690 nm indicate that both active layer compounds are contributing to photogeneration. These results illustrate that Cl-ClₙBsubNcs can act as electron donors in BHJ OPV devices.
Figure 4.4. a) J-V and b) EQE plots of Cl-Cl₈BsubNc:PC70BM BHJ OPVs. Shaded regions show 95% confidence intervals about the y-axes.

All the BHJ devices showed similar current density, resulting in roughly equivalent EQE’s, regardless of the synthetic route used. While lower overall, the $V_{oc}$ followed the same increasing trend in the BHJ device sets as in the PHJ sets. More interestingly, the trend in fill factor, which was observed in the PHJ Cl-Cl₈BsubNc donors above and the PHJ Cl-Cl₈BsubNc acceptors that we produced previously, is also no longer distinguishable in these BHJ devices. The implications of this are discussed in the following section.
Table 4.3. BHJ J-V metrics for the various Cl-Cl\textsubscript{n}BsubNcs. VOC: open circuit voltage, JSC: short circuit current flux, FF: fill factor, PCE: power conversion efficiency.

Bracketed values in device metric columns display standard deviations.$^a$

<table>
<thead>
<tr>
<th>Device Type</th>
<th>Bay Chlorines via XPS [Kahn et al]$^{50}$</th>
<th>VOC (V)</th>
<th>J\textsubscript{SC} (mA/cm\textsuperscript{2})</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>literature route</td>
<td>1.21</td>
<td>0.77 (0.02)</td>
<td>-7.05 (0.52)</td>
<td>0.35 (0.01)</td>
<td>1.93 (0.18)</td>
</tr>
<tr>
<td>commercial supplier</td>
<td>1.61 [1.5]</td>
<td>0.74 (0.02)</td>
<td>-6.93 (0.05)</td>
<td>0.33 (0.01)</td>
<td>1.71 (0.17)</td>
</tr>
<tr>
<td>nitrobenzene route</td>
<td>4.17</td>
<td>0.86 (0.03)</td>
<td>-7.07 (0.16)</td>
<td>0.35 (0.01)</td>
<td>2.12 (0.17)</td>
</tr>
</tbody>
</table>

$a$) All data in Table 1 from our laboratory’s prior work by Dang et al. except in square brackets.

4.3 Discussion

The results above enable comparison of the various Cl-Cl\textsubscript{n}BsubNc mixed alloy compositions, tested as donors in PHJ and BHJ devices in this work, and tested as acceptors in PHJ devices in our prior study. A revealing comparison can be made through these multiple lenses regarding the electronic nature of Cl-Cl\textsubscript{n}BsubNc molecules and mixed alloyed compositions. We have organized the following discussion by relevant device parameter for clarity.

4.3.1 Open-Circuit Voltage

When the various Cl-Cl\textsubscript{n}BsubNc compounds were applied as electron acceptors, increasing chlorination led to a drop in VOC,$^{50}$ yet when applied as a donor the reverse was true for both PHJ and BHJ devices. In PHJ devices, VOCs were $0.81 \pm 0.01$ V, $0.83 \pm 0.01$ V, and $0.88 \pm 0.01$ V, and in BHJ devices, VOCs were $0.77 \pm 0.02$ V, $0.74 \pm 0.02$ V, and $0.86 \pm 0.03$, for literature-,
commercial- and nitrobenzene- Cl-$\text{Cl}_n$BsubNc devices respectively. This effect is likely due to the shift in energy levels, wherein the highest occupied molecular orbital (HOMO) is pushed farther from the vacuum energy level with increasing chlorination. This is evident in the ultraviolet photoelectron spectroscopy measurements shown in Table 1. For Cl-$\text{Cl}_n$BsubNc acceptor devices, this reduced the electronic energy gap between the lowest unoccupied molecular orbital of the acceptor and the HOMO of the donor, which in turn lowered the $V_{\text{OC}}$. In Cl-$\text{Cl}_n$BsubNc donor devices, the same change increased the electronic energy gap and raised the $V_{\text{OC}}$. This is to be expected given that the $V_{\text{OC}}$ is largely determined by the electronic gap between a donor and an acceptor molecule.$^9,55$

The difference in energy levels between PC$_{70}$BM and C$_{70}$ does not explain the degree of $V_{\text{OC}}$ shift between the PHJ and BHJ donor devices, since PC$_{70}$BM has a shallower LUMO level and should therefore provide a greater electronic gap. An example of the expected behaviour, where greater electronic gap correlates with higher $V_{\text{OC}}$s, can be observed in the work of Gasparini et al., who compared C$_{70}$ and PC$_{70}$BM BHJs and found superior $V_{\text{OC}}$s from the PC$_{70}$BM devices.$^{56}$ We attribute our unexpected result to molecular orientation, which has been shown to cause $V_{\text{OC}}$ shifts when molecules such as poly(3-hexylthiophene) and $\alpha$-sexithiophene are used as donors with fullerene acceptors.$^{57-58}$ It is possible that a similar effect is responsible for the lower BHJ $V_{\text{OC}}$s measured here, where the nature of a BHJ device would disrupt Cl-$\text{Cl}_n$BsubNc’s otherwise continuous crystal structure.

### 4.3.2 Short-Circuit Current

A potential cause for the variation in $J_{\text{SC}}$ between sets of vacuum-deposited PHJ Cl-$\text{Cl}_n$BsubNc/C$_{70}$ devices was roughness of the underlying PEDOT:PSS layer. Given that the Cl-$\text{Cl}_n$BsubNc layers were only 7nm thick, the morphology could be strongly affected by a rough
PEDOT:PSS surface. This could cause a number of interfering factors to arise, such as increased interfacial area versus a smooth layer interface, shorter possible carrier paths, or any other of the other standard elements which differentiate planar heterojunctions from those with more complex topologies. If these possibilities had significant effect, then minor variations in the PEDOT:PSS spin coating could exacerbate problematic parameters. Atomic Force Microscopy (AFM) measurements were taken of ITO/glass, spin-coated PEDOT:PSS/ITO/glass, and vapour-deposited commercial-ClnBsubNc/PEDOT:PSS/ITO/glass, in order to characterize these surficial properties, with the results displayed in Figure 5.

![AFM measurements of ITO/glass, spin-coated PEDOT:PSS/ITO/glass, and vapour-deposited commercial-ClnBsubNc/PEDOT:PSS/ITO/glass](image)

**Figure 4.5.** Changes to topology after successive film additions (2 μm x 2 μm scan area). Film thicknesses determined via profilometry.

The bare ITO is initially quite rough, with a morphology of sharp peaks. Spin-coating PEDOT:PSS smooths the substrate, decreasing the number and sharpness of the peaks which
could otherwise penetrate the BsubNc layer and cause shorting. While a root-mean-squared roughness of 0.7nm is not smooth in the context of an underlayer for a 7nm film, and some peak-to-trough features occur with a 6nm height, these variations occur over length scales that are more than an order of magnitude greater than the thickness of the film. Therefore, while it is unlikely that incidence of disruptive individual features caused differences between sets of devices, it remains possible that differences in roughness are responsible for changes in interfacial area. It bears noting that thin planar heterojunctions are only as planar as the substrate beneath them, and vapour-depositing a Cl-Cl$_n$BsubNc layer atop the PEDOT:PSS layer only increased the roughness further. This is likely due to island-type layer growth during the physical vapour deposition (PVD) process; a hypothesis supported by the absence of a similar increase in roughness for the solution-cast Cl-Cl$_n$BsubNc layer. Regardless of the cause, fill factor and $V_{OC}$ measurements proved to be much more consistent between device sets, and as such make up the bulk of this work’s analysis.

The differences in current flux experienced by the PHJ devices were less evident in the BHJ devices, which is apparent in Table 3. This is possibly due to the substantial interface differences which result from using a solution-deposited BHJ rather than a vapour-deposited PHJ, and is potentially a result of solvent restructuring the PEDOT:PSS surface as it is wetted by the BHJ solution. We have demonstrated in Figure S1 that solvent has an effect on layer morphologies through preparation of solution-deposited PHJ devices, wherein the use of chlorobenzene or dichlorobenzene as the solvent led to an 18.5% shift in $J_{SC}$. Finally, there is a notable difference between the EQE’s of the BHJ devices and those of the PHJ devices, which is a small peak at roughly 345nm. This is due to a peak in the absorption spectra of PC$_{70}$BM that is not present in that of C$_{70}$.59
4.3.3 Fill Factor

The fill factor of the PHJ donor devices increased with additional bay chlorination, in addition to the \(V_{OC}\) increase, with values of 0.41 ± 0.05, 0.43 ± 0.02, and 0.48 ± 0.02 for the literature-, commercial- and nitrobenzene-Cl-Cl\(_{B_{subNc}}\) sources respectively. This is despite the expectation that increasing the electronic gap in the device would typically decrease the energy potential associated with dissociation of the exciton, rendering it less thermodynamically favourable. This same trend of increasing FF was apparent when these Cl-Cl\(_{B_{subNc}}\) compounds were employed as acceptors.\(^{50}\) While the field’s wisdom in the past has been that all impurities form trap states,\(^60\)-\(^61\) work carried out by Street et al. on fullerene derivatives,\(^{35, 62}\) our own study on mixed alloy compositions of \(\mu\)-oxo-(B\(_{subPc}\))\(_2\) dimers and Cl-B\(_{subPc}\),\(^{21}\) results from Fleetham et al. on zinc phthalocyanines,\(^{52, 53}\) and indeed our prior efforts by Dang et al.,\(^{50}\) are contributing to a consensus that mixed alloy compositions can have beneficial effects as long as the molecules can co-crystallize. Chlorination of Cl-Cl\(_{B_{subNc}}\) molecules impacts the electronic properties, but appears not to alter molecular shape enough to impact crystalline ordering.\(^{50}\)

Revealingly, the fill factor trend was not present in the BHJ devices, whose mean values fell in the range of 0.33-0.35. We can infer meaning from this by comparing the fundamental properties of BHJ and PHJ devices. Speaking generally, in a PHJ device, excitons and dissociated charges must both travel similar distances – the excitons must reach the interface to dissociate, and the separated charges must travel from the interface to the electrodes. In a BHJ device, excitons are formed much closer to dissociating interfaces, while dissociated charges follow a tortuous path to escape the active region. Seeing an improving trend with chlorination in a device type with longer exciton diffusion pathways and shorter charge transport pathways, and no such trend in a
device type with short exciton and long charge transport paths, implies that exciton transport has been affected. Identifying the cause of this requires a deeper analysis of the differences between the materials.

According to the Smoluchowski-Einstein theory of random walks, the diffusion length of an exciton in a solid is equal to:

\[
L_D = \sqrt{\tau f D} = \frac{1}{d^2 \sqrt{6}} \sqrt{\frac{9 \Phi_{PL} \kappa^2 \tau_f J}{128 \pi^5 n^4}} \quad \Phi_{PL} = \frac{k_r}{k_r + k_{nr}}
\]

where \( \Phi_{PL} \) is the photoluminescent quantum yield, \( \kappa \) is the orientation factor, \( n \) is the spectrally weighted refractive index, \( \tau_f/\tau_0 \) is the lifetime ratio and \( J \) is the spectral overlap. Orientation factor and refractive index are not expected to have changed due to the negligible effect of chlorination on crystal structure. The spectral overlap \( J \) is also unlikely to be responsible, as the degrees of Stokes shifts shown in Table 1 do not correlate with results. The trend of increasing \( \Phi_{PL} \), which is the fraction of radiative exciton relaxation over all forms of exciton relaxation, runs directly opposite to the FF trend in this study, as well as that of our prior work by Dang et al. An increasing \( \Phi_{PL} \) suggests that the rate of radiative relaxation is decreased, or that the rate of nonradiative relaxation is increased. Given our positive results, the former is likely dominant. Thus, a possible explanation is that a decreased rate of fluorescent emission from more-chlorinated Cl-Cl\(_n\)BsubNc compounds is responsible for the FF trend, leading to an increase in exciton lifetime. A gap in support for this hypothesis is that \( \Phi_{PL} \) only describes the ratio of fluorescent to nonradiative relaxation, rather than the actual rate, so further studies such as transient absorption spectroscopy would be required to verify it and compare to exciton lifetimes. A more probable explanation extends from the assumption that the degree of difference in energy levels between variously chlorinated Cl-Cl\(_n\)BsubNc molecules is less substantial at high levels of
chlorination than it is at lower levels, or phrased differently, that the first bay chlorine added to a Cl-Cl\textsubscript{n}BsubNc molecule has more of an impact on its energy level than any subsequent chlorines added. While no study has been directly conducted on this to our knowledge, a comparison can be drawn between other studies on phthalocyanines compounds. Fleetham et al. demonstrate a 0.20 V increase in the $V_{OC}$ of zinc phthalocyanines (ZnPc)-containing OPVs when switching from unchlorinated ZnPcs to mixtures with zero, one or two chlorines per molecule.\textsuperscript{52} Cnops et al. demonstrate $V_{OC}$ shifts of 0.07 V, 0.10 V, 0.08 V and 0.21 V, depending on the choice of donor, when switching from a Cl-Cl\textsubscript{n}BsubPc to a Cl-Cl\textsubscript{6}BsubPc acceptor layer.\textsuperscript{64} Together, these results suggest that each subsequent chlorine added to a phthalocyanines-type material has a diminishing effect on its energy level. In the context of this work, this implies that a more chlorinated mixture like the nitrobenzene-Cl-Cl\textsubscript{n}BsubNc would have a narrower density of states, since the various molecular energy levels present would be more similar. A narrower density of states can be associated with superior exciton transport, since more states are accessible to the exciton as it follows a thermally-induced hopping transport mode. This theory is supported by our prior work, where we found that commercial- and literature-Cl-Cl\textsubscript{n}BsubNc mixed alloyed compositions both contained a fraction of Cl-Cl\textsubscript{n}BsubNc compounds with no bay chlorines (i.e. n=0), while nitrobenzene-Cl-Cl\textsubscript{n}BsubNc compositions contained only Cl-Cl\textsubscript{n}BsubNc compounds with one or more bay chlorines (i.e. n>0).\textsuperscript{50}

Notably, Gommans et al. determined the diffusion length of an exciton in Cl-BsubPc films to be 28nm and the time to fluorescent relaxation to be 0.3ns.\textsuperscript{65} If Cl-Cl\textsubscript{n}BsubNc has similar properties, it would be unlikely that exciton transport efficiency is to blame with our 7nm thick films. However, during the PHJ device structure optimization undertaken for this work, a variety of substantial tweaks to device structure were made in order to improve a low FF. Addition or removal of a hole transport layer, changing C\textsubscript{70} layer thickness, and altering electron transport
layer thickness all failed to improve the FF, but reducing the Cl-Cl\textsubscript{a}BsubNc layer thickness from 10nm to 7nm improved FF from 0.32 to 0.44 with no sacrifices to other device parameters. These results, accessible in Figure S2, suggests a short exciton diffusion length, which is then mitigated by increasing levels of chlorination. A full space charge limiting current study could be undertaken to investigate this further. Another possibility is that the increase in fill factor is simply due to an energy level alignment between donor and acceptor that is more thermodynamically favourable for exciton dissociation; were this the case, however, it would be highly unintuitive to see a simultaneous increase in \( V_{OC} \), which our data shows. Lastly, imbalanced carrier mobility in a device can impact FF\textsuperscript{66}, but if such a phenomenon was responsible for the PHJ FF shift seen here, we would expect the BHJs to be more affected than the PHJs due to the tortuous path that their dissociated charges must take.

### 4.4 Conclusion

In this work, we have demonstrated the usage of various Cl-Cl\textsubscript{a}BsubNc compounds as electron donating materials in PHJ and BHJ device structures. We have confirmed that the \( V_{OC} \) of the PHJ OPVs is largely dependent on electronic gap between donor and acceptor, by comparing their device properties after being employed as donors in this work or as acceptors in our prior efforts. The BHJ devices follow a similar trend albeit in a lower range, which is possibly due to differences in interfacial molecular orientation between BHJ and PHJ devices. We find variability in the \( J_{SC} \) of PHJ devices, potentially due to underlying PEDOT:PSS surface morphology, but note that this did not significantly affect the ability to examine trends in \( V_{OC} \) and FF.

Through comparison of the device structures presented here, and our work on Cl-Cl\textsubscript{a}BsubNc acceptor devices carried out previously, we have surmised that the degree of chlorination of
these organic electronic molecules exerts a substantial influence on exciton diffusion length, which in turn improves device fill factor. We propose two potential causes: first, that decreased photoluminescence is reducing radiative relaxation of excitons before dissociation, or second, that a narrower density of states provided by the mixed alloy compositions is more amenable to exciton transport via thermal hopping. If the latter is the cause, it suggests that mixed alloyed compositions of more energetically similar molecules will improve exciton transport. If the former is correct, it suggests that bay chlorination of subnaphthalocyanine molecules can suppress radiative relaxation. Further investigation is needed to elucidate the precise nature of this beneficial phenomenon. In either case, we recommend that similar effects be sought for in other small-molecule OPVs. Specific to the use of Cl-Cl_BsubNcs, we advise that, in bilayer structures, these versatile molecules be applied as electron donors/transporting materials, so that the improvements to V_OC and fill factor can be enjoyed simultaneously. In more complex structures such as the 8.4% efficient cell developed by Cnops et al., fill factor and therefore performance could be enhanced through use of a more chlorinated Cl-Cl_BsubNc interlayer.
Chapter 5
Design and Operation of Automated OPV Monitoring and Data Collection Systems

5.1 Introduction

In order to understand the degradation mechanisms of BsubPcs and other organic molecules in OPVs, it is critical to establish a system of measurement so that the changes in device properties can be measured over time. Without insight into the longevity of various organic electronic compounds, it is impossible to determine what device designs represent the most economical choice. This is because device lifetime directly impacts the time-to-replacement, and therefore upkeep cost, of any commercial power-producing system. I previously demonstrated that the best-performing device directly after fabrication is not necessarily the best choice once these concerns are taken into account. This can be found in the study outlined by Chapter 3 of this thesis. To restate some of the relevant conclusions briefly, forgoing a longevity analysis when fabricating experimental new device designs and organic electronic materials risks guiding one’s research efforts down an ultimately nonviable path.

With the need for running several device types simultaneously to establish points of comparison, and for analyzing multiple samples per device type for statistical rigour, testing systems need to be high-capacity to conduct meaningful and reliable studies. This introduces a second requirement, which is for substantial automation. Without it, the process of taking even daily current-voltage measurements on large experiments is laborious, and higher-resolution data collection is prohibitively time consuming.

This chapter details the design, operation, and initial results of an automated OPV monitoring system, introducing subsystems in order of increasing complexity. Employed with an artificial light aging chamber, the fully integrated system provides an equal intensity of roughly sun-like light to a collection of organic photovoltaic devices, which have their output potential logged in a real-time manner, and have current-voltage tests performed on them at rates up to sixteen tests per minute. Using the sun as a light source in our rooftop testing operations, the system retains all the same monitoring capabilities, and permits measurement through radio-shielded cabling so
that expensive electronics can be kept indoors. The system also permits for additional measurement devices such as light flux sensors and thermocouples to be integrated, with results delivered alongside the OPV performance information.

5.2 Constant Potentiometric Monitoring

Before developing an artificial solar aging chamber, our lab was first engaged in rooftop solar testing. The apparatus used was designed by Josey et al.,\textsuperscript{45} and used three commercial 4-channel USB current monitors to record the current produced by the solar cells in real time. Outdoor monitoring requires knowledge of the sun’s intensity in order to fully understand the power conversion efficiency of the tested devices, since the intensity of sunlight at ground level is not constant, and so this data was paired with environmental data collected by the Southern Ontario Centre for Atmospheric Aerosol Research (SOCAAR), conveniently collected several feet away from our apparatus. Unfortunately, synchronizing the two data sets required a great deal of data processing work, and in order to meet ISOS-O3 level outdoor testing standards, solar intensity data needed to be collected even closer to our apparatus. Temperature data, as well, needed to be collected by a separate USB-enabled thermocouple. The load resistors paired with each cell were soldered directly into the connecting wires, making the process of switching the apparatus to a new experiment rather laborious. Due to short wires, our laptop and current monitors needed to be placed beside the testing apparatus, placing them under risk of being rained on in a rapid-onset weather event. The data collected in Chapter 3, with the exception of the $\alpha$-sexithiophene/C60 device, was also collected on this system.

Despite the limitations above, the data produced by the roof testing system offered a great deal of insight into the degradation mechanisms of the BsubPc materials. As a result, I designed a higher-capacity system, using a commercial 32-channel potentiometric (rather than amperimetric) NI-9205 monitoring device sold by National Instruments. Since our solar cells were being run against load resistors, Ohm’s Law could be used for conversion to amperes, and the potentiometric method proved to be roughly an order of magnitude less expensive per usable device channel. Most digital sensors convey their data via voltage, which meant the potentiometer could also track the output of a pyranometer of our own, in order to measure the solar light flux falling on the cells. The system could have its temperature data collection integrated in the same manner, though this information was less difficult to process than the light
flux, and has not been implemented to date due to time constraints. Regardless, the light flux
data integration greatly simplified the collection and processing of our information, since all
information could be logged per-time-point in the same file.

In addition to the above improvements, I designed the system to have the load resistors for each
OPV easily plugged into a labelled breadboard indoors, shown in Figure 5.1, with the tested
devices connected via a 50-foot radio-shielded cable. This allowed us to keep our expensive
electronics inside, and permitted easy switching of load resistors during experiment changeovers.
The potentiometric monitor simply had to measure the voltage drop across the installed resistors.
Negative channels from each device were shorted together and grounded to establish a common
zero-volt value, while positive channels each had an individual wire to the relevant port on the
NI-9205 potentiometer.

![Breadboard permitting load resistor installation.](image)

**Figure 5.1. Breadboard permitting load resistor installation.**

I created the code and digital interface to run this system in Labview. The data produced by this
system better met the ISOS-O3 testing standard, and was furthermore much easier to operate,
permitting a scale-up of our testing. The system could also be easily implemented with the
artificial solar aging chamber, which was being designed at the time.

### 5.3 Automated J-V Curve Acquisition

While the real-time potentiometric monitoring system reduced the difficulty of operating the
system, and allowed for more samples to be monitored at a time, it did not fundamentally expand
our capabilities in terms of the type of data we could gather. The most notable of these limitations was that, lacking an ability to measure J-V curves in-situ, we needed to bring our OPVs down to the lab at the end of each day, in order to carry out the J-V tests before remounting the following morning. A time-resolution of one data point per day did not offer sufficient insight into the nature of rapid degradation, such as the burn-in effect discussed in Chapter 3 which we attributed to C_{60}, or some of the more rapidly-degrading compounds like phenoxy boron subphthalocyanine. Therefore, I needed to design our monitoring system to incorporate one of our Keithley SourceMeters in a manner which permitted automatic and frequent J-V sweeps. Now that the electronic systems were set up indoors, it would be possible to integrate one of these more expensive pieces of equipment into the rooftop testing setup, as well as into the future artificial aging apparatus.

The major barrier to incorporating this system was isolating the potentiometric monitor, and all the other solar cells being tested, from the circuit including the Keithley device and the cell to be tested. Otherwise, the Keithley device would force the whole circuit through its voltage sweep, collecting meaningless data and potentially damaging the potentiometer. A digitally controlled switchboard was required, which would switch the output of an OPV away from its load resistor and the potentiometer, and transfer it to a separate circuit containing the Keithley device and no other OPVs. I selected 32-channel USB relays produced by Numato Labs to handle this task, using mechanical relays to ensure total separation of the circuits.

The wiring diagram is shown in Figure 5.2. By triggering both relay boards simultaneously, both the positive and negative leads of an OPV can be transferred to the Keithley Sourcemeter to take a J-V measurement, along the blue/orange circuit. Otherwise, OPV output is sent to its individual load resistor on the breadboard, which is in turn monitored by the NI 9205 potentiometer.
Figure 5.2. Circuit diagram of automated testing system.

Building on my program for running the potentiometric monitoring, and our lab’s existing code for taking J-V measurements using a Keithley SourceMeter, Chang Woo, an undergraduate student I led and supervised, integrated the two functions in a program which also controlled the operation of the mechanical relays. Using his work, a set of devices could be constantly monitored, with J-V sweeps performed on each connected device, one by one, at a frequency set
by the user. The limiting factor to testing rates were simply the length of time necessary to perform one test, and the number of devices to be tested. This system was fully implemented in the artificial solar aging chamber, and can easily be employed in the rooftop testing system when desired. While light flux on the roof is not constant like in an artificially lit chamber, the system could easily be set to conduct J-V tests whenever the luminous intensity falls within a certain range, rather than at certain times. This is possible because the pyranometer’s solar intensity data is collected in the same program as the rest of the data collection, and would ensure that J-V tests are taken under roughly equivalent conditions.

5.4 Artificial Solar Aging Apparatus Design

With monitoring systems which could handle constant 24-hour-per-day testing, our research stood to gain substantially with the development of an artificial aging chamber. With our rooftop OPVs usually spending six hours per day outside, four days per week, an artificially lit chamber could degrade the solar cells roughly seven times faster using similar light intensities in a constantly operating mode. To accomplish this, the chamber primarily needed to provide an equal intensity of sun-like light to any samples mounted within it, keep the cells within a temperature range roughly approximating what they would encounter on the roof, and have built-in safety systems which would disable the chamber’s operation in the event of an unsupervised failure. Lastly, the chamber needed to be “light-tight” to adhere to U of T radiation safety guidelines, due to the brightness of the source. I designed the chamber in full, with the work of machining aluminum and plastic components done by the Department of Chemistry machine shop.

5.4.1 Chamber Structure

I selected an octagonal prism design for the chamber, with sets of four OPV substrates mounted in the center of each of four of the eight faces, in order to ensure that each would receive approximately equal amounts of light from a centrally mounted radial bulb. This yielded an initial capacity of 32-channel monitoring on 16 substrates, which was in line with our common practice of measuring two OPV devices per substrate. It also left four panels free for the mounting of other sensors, or subsequent expansion of the chamber’s capacity. I designed the bulb to be mounted from below the chamber, and a fan to be mounted above the chamber, in order to blow cool air in. I had holes drilled in the base of the chamber for air outflow. The base
plate of the chamber, the legs which held it off the benchtop to permit air outflow, and the vertical rods which held the walls in place were all made of aluminum for its machinability. I layered the aluminum with adhesive tape to prevent electrical contact between the relay boards and the system’s base plate.

The side panels were made of black-dyed polycarbonate, selected for its rigidity, low cost, and ability to block light. Channels were cut in the aluminum posts such that the panels could be easily slid into place. Holes were cut in four of the side walls for substrate mounting, described below. The lid of the chamber was made of black acetal resin, selected for machinability, moderate flexibility to permit a tight fit when closing the chamber lid, and ability to block light. Holes were cut in the lid for each aluminum post to grip it, and a large central hole was cut to permit attachment of an air duct. Several feet away to prevent electrical interference, a 350-cubic-feet-per-minute duct fan forced air into the chamber.

**Figure 5.3. Structure of chamber with substrate holders in place, before wiring or incorporation of electrical systems.**
5.4.2 OPV Substrate Mounting

Figure 5.4. Schema/renders of substrate holder and cover plate.

The substrate holders were roughly based on the design of David Josey,\textsuperscript{45} modified to hold four substrates per holder rather than one. These were also fabricated from black acetal resin for machinability. Gold-plated push-pins, mounted in holes drilled through the resin, were used to make electrical contact with the electrodes on the substrates, which sat in each of the four wells. The pins were positioned to make contact with up to five different device positions on the substrates, though only two channels were assigned to each substrate. On the back of the holder, small screws allowed wires to be clamped into electrical contact, with the screws contacting springs which in turn formed a connection with the back of the gold-plated push-pins. This system formed robust electrical contact, while enabling easy reassignment of channels between different substrate device positions. The total resistance of this contact assembly was less than ten ohms. To hold the substrates firmly against the gold pins, which used pressure to ensure good contact, I designed metal cover slips to grip each substrate by its edge, while still permitting light exposure. These were made of anodized aluminum, in order to prevent electrical shorting between substrates. For easy access to substrates, these substrate holders can be easily detached from the side panels they are mounted into with the removal of four accessible screws.
5.4.3 Light Source

Since aging apparatuses by nature spend a significant amount of time in operation, the light source selected for the chamber had the requirements of being both powerful and economical. While xenon arc bulbs typically provide the closest to solar illumination, they can be quite expensive to continuously replace. I identified metal halide lightbulbs as providing a cost-effective alternative. A subset of these bulbs have been designed to mimic the solar spectrum as closely as possible, for use in indoor horticulture. Unsurprisingly, plants do well in sun-like spectra, and so high-end horticulture bulbs provide a reasonable analog through the visible spectrum. A 400 Watt metal halide bulb provided a light intensity of 1.3 suns at the chamber’s bulb-to-substrate distance. If desired, metal halide bulbs can be dimmed, but the increased testing speed was considered an asset.

5.4.4 Safety Considerations

The system has three primary safety considerations which needed to be addressed. First, the University of Toronto sets radiation safety guidelines which forbid powerful point sources of light from being visible to the naked eye. This meant that the chamber had to be “light-tight,” which was accomplished by designing components to be well-fitting, using opaque materials, and placing the air outflow underneath the chamber. The only light which escapes the chamber does so beneath it, falling onto the matte black countertop below.

The second concern, as with any custom-built electrical equipment, is electrical safety. The metal halide bulb draws 400 Watts, and uses a capacitative ballast to provide pulses of energy to the bulb. I ensured that no bare wires were exposed and placed a plastic guard around the ballast core to prevent accidental contact. The ballast casing and the chamber itself were both grounded. As a final step, I included a 10 ampere fuse in the ballast’s power supply, with the ballast nominally drawing 3.3 amperes. If a short is ever induced, the fuse will break the circuit. As a failsafe, these components are also plugged into a power bar with an automatic shutoff in the event of a short.

The final concern is thermal. In the event that the duct fan fails, temperature in the chamber would begin to climb. While the ignition temperature of the plastics used is high enough that the bulb would fail before a fire started, high temperatures could cause melting of the acetal resin
components. To mitigate this, I installed a thermal fuse into the power wire for the lamp’s ballast, and ran the wire through the chamber. If the temperature reaches 91°C, or if the chamber sustains temperatures of 67°C or more for extended periods of time, the fuse will break the circuit and the bulb will shut off.

5.5 Initial Full-System Results

The first study conducted by this system was an experiment designed to improve the veracity of our substrate preparation standard operating procedures. Our standard method for preparing an OPV includes spin-coating a water-solvated PEDOT:PSS layer atop our indium tin oxide electrode. This water must be removed, since water has an adverse impact on the lifetime of organic electronic devices. Good encapsulation methodology is useful, but it cannot protect a device from water trapped inside during the fabrication process.

Our existing procedure used a ten-minute drying period on a 110 °C hotplate in atmosphere, followed by transfer into a glovebox. We wanted to compare the lifetime of devices prepared in the standard manner with devices which had their PEDOT:PSS layers dried in a glovebox overnight, with the goal of yielding insight on the presence of trapped water.

David Josey prepared four substrates each of our two “baseline” device structures, one of which uses Cl-BsubPc as an acceptor with an α-sexithiophene donor, and the other of which uses Cl-BsubPc as a donor with a C_{60} acceptor. The former, henceforth referred to as “acceptors,” had a structure of ITO/PEDOT:PSS/α-sexithiophene/Cl-BsubPc/BCP/Ag, and the other, henceforth “donors,” had a structure of ITO/PEDOT:PSS/molybdenum (VI) oxide/Cl-BsubPc/C_{60}/BCP/Ag.

Within each set of four acceptors or donors, two substrates had been prepared with our usual “dry” PEDOT:PSS and two were prepared with the “extra-dry” overnight procedure. While the PEDOT:PSS layers had been prepared differently, OPVs of equivalent structure were fabricated atop the PEDOT:PSS layers in the same batch to ensure rigorous comparison. Each substrate had four devices fabricated on it, providing a sufficiently high number of samples. This yielded four sets of devices: Extra-dry acceptors, dry acceptors, Extra-dry donors, and dry donors, with each set containing two substrates/eight devices.
Devices were tested immediately upon fabrication, revealing no significant differences between “dry” or “extra-dry” sets. Substrates were loaded into opposite wall panels in the solar aging chamber, with one substrate per set loaded into each of the four substrate sockets on the holders. Load resistors were selected to run each device at its maximum power point, which were then loaded into the breadboard. Potentiometric monitoring was initiated and J-V scans were set for one hour intervals. While the chamber was capable of 24-hour operation, I decided to run it in an 8-hour-per-day mode, as it was still unproven equipment. After 9 days of testing, I then left the substrates in the dark for a month to gather “shelf life” longevity data, finally running the system for three more days to assess what had changed over the one month gap.

After processing the data, which is presented in Figure 5, there appeared to be no major differences between dry and extra dry device sets in the first 70 hours of testing. During the one-month shelf-life test, the acceptor device sets degraded much more significantly than the donor sets. The high standard deviations shown by the extra dry acceptor set are a result of inconsistent performance by one included device, compounded by a low sample size that was due to electrical connectivity issues. The results may indicate that the extra-dry acceptor set had slightly better shelf life than the dry acceptors, though a second trial is recommended to attain better data, using silver paint on electrodes to ensure connectivity. PEDOT:PSS drying made no discernible difference to donor devices. This allowed us to conclude that for experiments with no lifetime study component, our existing drying procedures are adequate, but that there is a potential effect in long-term testing which merits further study.
Figure 5.5. Plot of drop in efficiency over time. Break at 70 hour point corresponds to a one month pause from illumination.

Much more surprising was the lack of a burn-in effect on either set of donor devices. As described in Chapter 3 of this work, C$_{60}$-containing devices suffer a rapid drop in efficiency over their first several hours to a day of sun exposure, often 20% or more. This did not occur in the artificial aging chamber. With every other detail of the device fabrication and encapsulation processes being identical to the procedures used to fabricate OPVs for rooftop studies, atmospheric differences being insufficient to explain such a change, and temperatures remaining within a reasonable range, the only discernable difference was the light source. While the metal halide bulb replicates the sun’s spectra throughout the visible range, the lack of short-wave ultraviolet light shown in Figure 5.6 was evidently shielding the OPVs from burn-in, or at least drawing the UV-related degradation out over a much longer period of time.
These results gave strong evidence that the burn-in experienced by C$_{60}$-containing cells is due largely to their exposure to ultraviolet wavelengths of light. Therefore, if a means could be found to filter UV light from reaching the OPV, such as by using a polymer substrate, the performance of fullerene-containing OPVs could be significantly enhanced by negating the day-one burn-in effect. A trade-off can be identified between the fraction of desirable light blocked by such a filter, thereby reducing an OPV’s produced power, and the fraction of ultraviolet light blocked, extending its lifetime. That being said, the ideal solution to strive for will be a molecule which can harvest all incoming light without degradation.

An important point made by these results is that OPVs used to power small devices wirelessly in an indoor setting could see better performance and lifetime than OPVs used to generate solar power, due to the lack of UV emission from commercial light sources. In terms of the study at hand, a follow-up investigation would be advisable to ensure that ultraviolet light exposure does not influence the effects of “dry” or “extra-dry” PEDOT:PSS procedures on device lifetime.
While it is not ideal that the metal halide bulb’s spectra could not mimic the ultraviolet aspects of solar aging, it provides an opportunity to investigate non-ultraviolet degradation mechanisms, which will be relevant as UV-resistant organic molecules or UV-blocking substrates are employed in the future. Fortunately, the modular design permits replacement of the bulb with a UV-emitting light source, which could further decouple UV-driven degradation from other degradation sources, or a more advanced light source which can fully replicate the solar spectrum could be installed.
Chapter 6
Conclusions and Future Work

In my work, I have uncovered several structure-property relationships of BsubPcs and related compounds, as well as several other phenomena related to their incorporation into OPVs, and built testing systems which will permit the discovery of further relationships. My primary areas of focus were exploring the various device engineering strategies that are enabled by the versatile \( \mu\text{-oxo-(BsubPc)}_2 \) molecule, characterizing the degradation of OPVs using several different BsubPc donor molecules, determining the impact of bay chlorination on the properties of OPVs containing Cl-\( \text{C}_n\text{BsubNc} \) molecules prepared by various synthetic routes, and the development of high-throughput automated OPV testing systems.

I characterized the differences between Cl-BsubPc and the \( \mu\text{-oxo-(BsubPc)}_2 \) dimer in a donor configuration with a \( \text{C}_{70} \) acceptor, finding \( \mu\text{-oxo-(BsubPc)}_2 \) to have superior \( J_{SC} \) and inferior \( V_{OC} \) with an overall higher efficiency. My further work with charge cascade devices, leveraging \( \mu\text{-oxo-(BsubPc)}_2 \)'s energy levels to use it as an ambipolar interlayer, demonstrated substantial improvements of FF and \( J_{SC} \) with no increase to overall device thickness. Mixed layer Cl-BsubPc:\( \mu\text{-oxo-(BsubPc)}_2 \) devices mitigated low \( V_{OC} \)'s via an intriguing organic alloying effect, which yielded \( V_{OCs} \) intermediate to those shown by neat layers of either molecule alone while retaining much of the \( \mu\text{-oxo-(BsubPc)}_2 \)'s superior \( J_{SC} \) and improving FF beyond those of either type of neat-layer device. With the exception of a Cl-\( \text{Cl}_6\text{BsubPc}:\mu\text{-oxo-(BsubPc)}_2 \) energy cascade device, all \( \mu\text{-oxo-(BsubPc)}_2 \)-containing devices were superior to all Cl-BsubPc devices. With this work, building on the efforts of my colleague Dr. Castrucci, I demonstrated the superior performance and versatility of the novel \( \mu\text{-oxo-(BsubPc)}_2 \) molecule across a spectrum of device engineering strategies. We recommended further investigation of mixed-layer BsubPc-based devices due to their ability to enhance device metrics via organic alloying. I also suggest that a lifetime study be carried out on this compound, to ensure it offers a competitive long-term stability. I finally advise the exploration of analogous molecules to \( \mu\text{-oxo-(BsubPc)}_2 \), utilizing the robust chemical versatility of the BsubPc family to further improve the ability of this already-promising molecule.
I carried out a rooftop device lifetime study with three BsubPc compounds containing various axial substitutions, all paired with fullerene. This study met ISOS-O3 level testing guidelines on the great majority of the standard’s metrics, achieving the robust standard established by consensus in the field. My results demonstrated the need for such testing: while the PhO-BsubPc compound showed the most promising performance immediately after fabrication, it degraded much more rapidly than the robust Cl-BsubPc. I attributed this to the ease of hydrolysis of the phenoxy group in comparison to that of the chloro group. I also found a “burn-in” effect wherein all devices suffered a rapid drop in efficiency on their first day of testing. After fabricating a BsubPc-free OPV using an α-sexithiophene donor, I demonstrated that this phenomenon was due to the fullerene acceptor rather than the BsubPc donor. From this study, I concluded that the axial substituent of a BsubPc strongly affects its lifetime when it is employed as a donor material, supporting the findings of my colleague David Josey who found the same when employing BsubPc as an acceptor. I highlighted the importance of improving encapsulation to protect highly-performing but easily-degraded molecules such as PhO-BsubPc, and recommended that alternative materials to the ubiquitous fullerene acceptor be pursued, in order to avoid burn-in effects.

I next tested sets of increasingly chlorinated Cl-ClₙBsubNc molecules as donor materials paired with C₇₀ acceptors, continuing the work of my colleague Dr. Jeremy Dang who explored them as acceptor materials in PHJ devices. Dr. Dang synthesized each batch of molecules via a different synthetic route, which impacted the distribution of variously chlorinated molecules in each mixed alloyed composition of Cl-ClₙBsubNc. Another colleague of mine, Dr. Minh Dang, tested the same molecules paired with PC₇₁BM in a bulk heterojunction (BHJ) device design. By comparing the results of my PHJ devices using Cl-ClₙBsubNc as a donor with Dr. J. Dang’s acceptor PHJs and Dr. M. Dang’s donor BHJs, I found compelling evidence that the superior fill factor of more-chlorinated Cl-ClₙBsubNc mixed alloyed compositions was due to an increased exciton diffusion length. Notably, the current record-holding small-molecule PHJ OPV, Cnops et al.’s 8.4% efficient device, contained a Cl-ClₙBsubNc interlayer, in addition to a Cl-BsubPc layer. A new record could be set using a highly-chlorinated Cl-ClₙBsubNc interlayer prepared by a nitrobenzene synthesis route, rather than a less chlorinated composition of the sort that is currently available commercially, and I recommend that this possibility be investigated.
My final major project was the development of automated OPV lifetime testing systems, including an artificial solar simulator. This was done to facilitate the bulk testing of various OPVs, and will continue to be of value to the Bender laboratory after my departure. It will allow the relatively easy identification of further structure-property relationships as they relate to OPV degradation, with regard to our laboratory’s more laborious prior methodology. The automated measurement systems are now deployed in our rooftop testing apparatus, and the artificial aging chamber, in its first experiment, gave insight into how our substrate drying procedures can impact device lifetime. Its results also suggested that the burn-in experienced by fullerene-containing devices is driven by shorter wavelengths of light. This indicates that fullerene could be protected with a UV-blocking substrate, enabling better fullerene-containing OPV performance in outdoor settings. While this raises the subject of using UV-blocking substrates on OPVs in general to protect other UV-vulnerable molecules, I maintain my Chapter 3 recommendation that fullerene be replaced. This is because it would be preferable to use a molecule which can harvest all incoming light rather than blocking a portion, and also because fullerene is made by a poorly-scaling plasma arc synthesis method.

With the efforts detailed above, I have made contributions to the informed development of superior OPV materials by identifying degradation-based structure-property relationships, demonstrated various device engineering strategies which enhance the performance of OPVs using BsubPc-based donor materials, and improved our laboratory’s capacity to identify further such relationships in the future via automated testing systems. This work advances several fronts on which research must proceed to realize the full potential of the versatile boron subphthalocyanine molecular family, and organic photovoltaics in general.
References


Appendices

7.1 Appendix A: Materials and Methods Sections

7.1.1 Experimental Section for Chapter 2: Characterization of \(\mu\)-oxo-(BsubPc)\(_2\) in Multiple Architectures of Organic Photovoltaic Devices: Comparing Against and Combining with Cl-BsubPc

The following text is the Experimental section of the titular paper, as published by ACS Applied Materials & Interfaces. This section was primarily authored by Dr. Castrucci, as referenced in Chapter 2.

Molybdenum(VI) oxide (Sigma-Aldrich, 99.98% trace metals basis), TPBi (Lumtec), and silver paint (PELCO, Conductive Silver 187) were purchased and used as received. \(\alpha6T\) (Sigma-Aldrich) and \(C_{60}\) and \(C_{70}\) (SES Research, 99.5%) were purchased and purified once by train sublimation before use. Cl-BsubPc and \(\mu\)-oxo-(BsubPc)\(_2\) were synthesized as previously reported,\(^7\) and purified twice by train sublimation before use.

For the UPS measurements, \(\mu\)-oxo-(BsubPc)\(_2\) films were evaporated from an alumina crucible using a transfer arm evaporator (TAE) described by Greiner et al.\(^6\) The films were deposited on a highly oriented pyrolitic graphite (HOPG) substrate to a thickness of approximately 12 nm, using typical small organic molecular film density, as measured by a calibrated quartz crystal microbalance (QCM). This thickness was chosen so as to avoid charging effects, as well as any substrate-induced interaction. The base pressure in the chamber was approximately 1x10\(^{-8}\) Torr. The films were then \textit{in-situ} transferred to a PHI5500 Multi-Technique System to perform the photoemission using a non-monochromated He I\(\alpha\) (hv=21.22eV) source. All measurements were done at a take-off angle of 88 degrees and the sample was held at a bias of -15 V with respect to the spectrometer. The pressure in the analysis chamber was approximately 1x10\(^{-9}\) Torr.

The Work Function was calculated according to: \(\varphi = 21.22 - \text{SEC}\), where SEC is the secondary electron cut-off. The HOMO-Fermi energy difference was taken as the intersection of the HOMO edge with the background noise, with the Fermi energy being calibrated to 0 eV binding
energy. The ionization energy (IE) is then simply the sum of the work function and HOMO-Fermi energy difference.

OPV devices were fabricated on 25 mm by 25 mm glass substrates coated with indium-tin oxide (ITO) having a sheet resistance of 15 Ω per square (Thin Film Devices, Inc.). The ITO was pre-patterned, leaving 8 mm from one side as uncoated glass. Substrates were cleaned by successive sonications in detergent and solvents, followed by 5 minutes of atmospheric plasma treatment. PEDOT:PSS was spin-coated onto the substrates, 500 rpm, 10 s; 4000 rpm, 30 s. Substrates were baked on a hot plate at 110 °C for 10 minutes, and then transferred into a nitrogen atmosphere glove box (O₂ < 10 ppm, H₂O < 10 ppm). Substrates were transferred to a custom-built thermal evaporation system attached to the nitrogen glove box without exposure to ambient conditions. All subsequent device layers were thermally evaporated at ~1.0 A/s and a working pressure of ~1 x 10⁻⁷ Torr for organic layers and ~1 x 10⁻⁶ Torr for silver. Silver electrodes were evaporated through a shadow mask, defining 0.2 cm² as the active area for each device. A transfer back to the glove box was required between the electron transport and silver layers to change the shadow masks.

Mixed donor layers were achieved through co-deposition from separate crucibles. To ensure the correct material ratio, a well-loaded crucible was brought to its targeted deposition rate and monitored until steady state had been held for at least ten minutes. The second crucible, previously held just under its onset evaporation temperature, was then further heated to achieve the desired combined deposition rate. The material ratio in the film was thus set according to the rate of deposition of each material.

Layer thickness and deposition rates of evaporated films were monitored using a quartz crystal microbalance calibrated against films deposited on glass where film thickness was measured with a KLA-Tencor P16+ surface profilometer. Solid film absorbances were measured using a Perkin-Elmer Lambda 1050 spectrometer with the films deposited at device relevant thicknesses on glass slides.

To enhance the electrical contact during testing, silver paint was applied to the ITO and metal electrode contact points and left to dry for 20 minutes. Devices were kept in the nitrogen-filled glove box throughout testing. Voltage sweeps of the devices were performed under full illumination by a 300W Xe arc lamp (Oriel) with an AM 1.5G filter, and the corresponding
currents were measured with a Keithley 2401 Low Voltage SourceMeter. Light intensity was calibrated to 100 mW/cm² with reference to a calibrated silicon photodetector. Wavelengths scans at 10 nm intervals were performed using an in-line Cornerstone™ 260 1/4 m Monochromator and the corresponding currents were measured using a Newport Optical Power Meter 2936-R and converted to external quantum efficiencies using a reference wavelength scan of a calibrated silicon photodetector.

All p-values reported are the results of single sided t-tests comparing the parameters with a null hypothesis of the parameter with the larger average value exceeding the parameter with the smaller average value. When an average value is reported followed by a range of values, that range of values denotes the 95% confidence interval. All error bars in figures show a 95% confidence interval for the y-axis values.

7.1.2 Materials and Methods Section for Chapter 3: Boron Subphthalocyanines as Electron Donors in Outdoor Lifetime Monitored Organic Photovoltaic Cells

The following text is the Materials and Methods section of the titular paper, as submitted to Solar Energy Materials and Solar Cells.

All BsubPc compounds (Cl-, Ph-^4^, and PhO-BsubPc^6^) were synthesized and purified internally according to our established procedures. The C_{60} was purchased from SES Research, and α-6T was bought from Lumtec. These compounds were all purified via train sublimation. Bathocuproine (BCP) was purchased from Sigma Aldrich, molybdenum (VI) oxide (MoOx) from Strem Chemicals, and silver from R. D. Mathis Company, all of which were used as-received. PEDOT:PSS from Heraeus was filtered with 0.22μm syringe filters. Devices with an area of 0.2cm² were constructed on ITO-coated glass, using a spin-coated PEDOT:PSS layer, a MoOx hole transport layer, and a BCP electron transport layer. BsubPc donor layers were 10nm thick, α-6T layers were 50nm thick, and fullerene layers were 30nm thick, all in accordance with past optimized devices. Deposition of organic molecules and metals was performed via evaporation from boron nitride crucibles with a chamber pressure of approximately 1x10^{-7} torr, using a calibrated QCM used to monitor thickness. Devices were encapsulated against atmosphere using a surficial 100nm MoOx buffer layer followed by Ossila encapsulation epoxy and a thin sheet of glass. This resulted in the device structure shown in Figure 1. Devices
underwent initial current-voltage (J-V) testing before removal from the glovebox. This process used a Keithley 2401 SourceMeter, with light provided via an Oriel 300W xenon arc lamp using an AM1.5G filter. Intensity was set to 100mW/cm² using a calibrated silicon photodiode.

OPV cells were then placed outside for roughly six hours daily, taken indoors at night or to avoid precipitation. Constant current monitoring used USB data acquisition devices, with OPV cells facing due south. A tilt angle of roughly 43.7° was used, corresponding to the latitude of the University of Toronto. Temperature was recorded using a thermocouple on the back of a device substrate. Solar irradiance data was gathered via a pyranometer placed parallel to the ground several meters away. Irradiance values were transformed to those for a 43.7° tilted array using the model developed by Erbs et al., as implemented programmatically by Josey et al. Daily J-V curves were recorded each morning using the same method as the initial post-fabrication test. Humidity, air temperature, wind speed, and wind direction, were recorded simultaneously in accordance with ISOS-O3 standards, and are plotted in Figures S1 and S2 of the SI. An image of the rooftop testing apparatus can be found in Figure S4 of the SI.

7.1.3 Materials and Methods Section for Chapter 4: The mixed and alloyed chemical composition of chloro-(chloro)$_n$-boron subnaphthalocyanines dictates their physical properties and performance in organic photovoltaics

The following text is the Materials and Methods section of the titular paper, which will be largely similar to the text to be submitted to Materials Today.

The various BsubNc mixed alloy compositions, excepting the commercially purchased material, were synthesized and purified internally using our previously developed procedures recorded by Dang et al., and C$_{70}$ was bought from SES research. These materials were each purified further via train sublimation. Bathocuproine (BCP) from Sigma Aldrich, silver from R. D. Mathis Company, and PC$_{70}$BM from American Dye Source were used at commercial purity.

PEDOT:PSS was purchased from Heraeus and filtered using 0.22μm syringe filters during spin-coating.
Devices were fabricated on glass substrates measuring 25mm by 25mm, with an indium tin oxide coating offering a sheet resistance of 15 Ω per square (Thin Film Devices, Inc.). The coating was pre-patterned to leave 8mm of one side bare, in order to provide an anode-contact region. The substrate cleaning process relied on sonication in detergent and solvents and plasma treatment. The PEDOT:PSS hole transport layer was spin-coated onto the substrate at 500 RPM for ten seconds, then 1000 RPM for 30 seconds. Moisture was removed by baking at 110°C for ten minutes, at which point samples were transferred to a nitrogen-purged glovebox containing less than 10 ppm of H₂O and O₂.

The thermal evaporation system was linked to the glovebox to enable transfer, deposition and subsequent testing without exposure to atmosphere. PHJ device layers were deposited at 1 Å/s, with a vacuum pressure of 1 x 10⁻⁷ torr for organic layers and 1x10⁻⁶ torr for the silver cathode. Silver was deposited through a shadow mask, resulting in a 0.4cm² active area for each device. Small, isolated strips of silver were deposited on the exposed ITO anode to enable consistent electrical contact. Samples were transferred from vacuum to the glovebox and back in order to change from the organic mask to the silver mask. The resulting devices have the following architecture: Glass/ITO/PEDOT:PSS/Cl-ClnBsubNc/C₇₀/BCP/Ag.

*The following paragraph on BHJ fabrication was authored primarily by Dr. Minh Dang*

BHJ devices were fabricated on equivalent PEDOT:PSS/ITO substrates to those used by the PHJ devices. PC₇₀BM was first solubilized in 1,2-dichlorobenzene (ODCB) to form a solution with a concentration of 25 mg/ml. The solutions were heated at 45 °C for 2 hours. Cl-ClnBsubNcs were then added to the PC₇₀BM solutions to form a Cl-ClnBsubNc:PC₇₀BM with a 1 to 5 concentration ratio. The resulting solutions were heated at 45 °C overnight. The active layer was prepared by spin-coating the photoactive blend onto the PEDOT:PSS at 1000 rpm for one
minute, with the solution kept at 60 °C during the spin-coating process. Additionally, the
substrates of ITO/PEDOT:PSS were already set to be spinning when the photoactive blend was
dropped. The resulting active layer was annealed at 120 °C for 10 minutes. The devices were
completed with the same vacuum-deposited BCP/Ag electrode as was used by the PHJ devices.
The resulting devices have the following architecture: Glass/ITO/PEDOT:PSS/Cl-
ClnBsubNc:PC70BM/BCP/Ag.

Accumulated layer thickness during deposition was monitored using a quartz crustal
microbalance, which was first calibrated again neat films deposited on glass. The thicknesses of
these films were characterized with a KLA-TencorP16+ surface profilometer. Current-voltage (J-
V) testing of completed devices was undertaken in the glovebox environment, using an Oriel
300W xenon arc lamp with an AM1.5G filter for 100mW/cm² light. J-V sweeps were conducted
using a Keithley 2401 SourceMeter. AFM imaging was carried out on a Veeco Dimension 3000
microscope, with a 2um x 2um scan area.

7.2 Appendix B: Supplemental Information Sections

7.2.1 Supplemental Information for Chapter 2: Characterization of μ-oxo-
(BsubPc)2 in Multiple Architectures of Organic Photovoltaic Devices:
Comparing Against and Combining with Cl-BsubPc

The following text is the Supplemental Information of the titular paper, as published by ACS
Applied Materials & Interfaces. It contains work by both co-authors in approximately equal
proportion.
**Figure S1.** Absorption spectrum (pink) of a 50 nm μ-oxo-(BsubPc)₂ film on a glass slide overlaid with the solar irradiance (gray = orbit, black = sea level) spectrum.
Figure S2. Ultraviolet photoelectron spectroscopy of a film of μ-oxo-(BsubPc)2. (a) Identification of the HOMO to Fermi gap. (b) Identification of work function by way of secondary electron cut-off.

\[ \text{UPS } h\nu = 21.22 \text{eV} \]

\[ (\text{HOMO}-E_F) + \text{Workfunction} = \text{HOMO}-E_{\text{vac}} \]

\[ = 5.9 \pm 0.05 \text{ eV} \]

(a)

\[ \text{HOMO}-E_F = 1.45 \text{ eV} \]

(b)

\[ \text{Workfunction} = 21.22 - \text{SEC} \]

\[ = 4.45 \text{ eV} \]
Table S1. Material energy levels used to construct Figure 3. Work function, and HOMO and LUMO energy levels are reported relative to the vacuum level. LUMO energies are calculated as HOMO energy less the optical gap. Optical gap determined from absorption onset of 50 nm solid films of each material on glass slides.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Work Function (eV)</th>
<th>$E_{\text{HOMO}}$ (eV)</th>
<th>Optical Gap (eV)</th>
<th>$E_{\text{LUMO}}$ (eV)</th>
<th>$E_{\text{HOMO}}$ - Work Function (eV)</th>
<th>Work Function - $E_{\text{LUMO}}$ (eV)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu$-oxo- (BsubPc)$_2$</td>
<td>4.5</td>
<td>5.9</td>
<td>1.9</td>
<td>4.0</td>
<td>1.4</td>
<td>0.5</td>
<td>This work</td>
</tr>
<tr>
<td>Cl-BsubPc</td>
<td>5.0</td>
<td>5.6</td>
<td>2.1</td>
<td>3.5</td>
<td>0.6</td>
<td>1.5</td>
<td>1</td>
</tr>
<tr>
<td>$\alpha$6T</td>
<td>3.9</td>
<td>4.9</td>
<td>2.2</td>
<td>2.7</td>
<td>1.0</td>
<td>1.2</td>
<td>2</td>
</tr>
<tr>
<td>C$_{60}$</td>
<td>4.6</td>
<td>6.3</td>
<td>1.9</td>
<td>4.4</td>
<td>1.7</td>
<td>0.2</td>
<td>1</td>
</tr>
<tr>
<td>C$_{70}$</td>
<td>-</td>
<td>6.2</td>
<td>1.7</td>
<td>4.5</td>
<td>-</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Cl-Cl$_{6}$- BsubPc</td>
<td>-</td>
<td>5.9</td>
<td>2.1</td>
<td>3.8</td>
<td>-</td>
<td>-</td>
<td>4</td>
</tr>
</tbody>
</table>
**Table S2.** Mean device parameter comparison for reference devices containing TPBi electron transport layers and devices containing bathocuproine (BCP) electron transport layers (ETLs). Cascade and bilayer cells were tested. The standard deviation (SD) of each value is shown in parentheses. Device structure is ITO/PEDOT:PSS/MoOₓ(5 nm)/Donor/C₇₀(30 nm)/ETL/Ag(80 nm).

<table>
<thead>
<tr>
<th>Donor/dₓ nm</th>
<th>ETL/dₓ ETL</th>
<th>Jₓc (SD)/mA cm⁻²</th>
<th>Voc (SD)/V</th>
<th>FF (SD)</th>
<th>ηₓ (SD)/%</th>
<th>No. of cells tested</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl-BsubPc/10</td>
<td>BCP/10</td>
<td>4.1(0.13)</td>
<td>1.08(0.01)</td>
<td>0.51(0.02)</td>
<td>2.3(0.12)</td>
<td>20</td>
</tr>
<tr>
<td>Cl-BsubPc/10</td>
<td>TPBi/3</td>
<td>4.6(0.11)</td>
<td>1.08(0.01)</td>
<td>0.52(0.01)</td>
<td>2.6(0.09)</td>
<td>12</td>
</tr>
<tr>
<td>Cl-BsubPc/2.5, μ-oxo/7.5</td>
<td>BCP/10</td>
<td>5.7(0.08)</td>
<td>0.87(0.01)</td>
<td>0.61(0.01)</td>
<td>3.0(0.05)</td>
<td>14</td>
</tr>
<tr>
<td>Cl-BsubPc/2.5, μ-oxo/7.5</td>
<td>TPBi/3</td>
<td>5.9(0.17)</td>
<td>0.87(0.02)</td>
<td>0.64(0.02)</td>
<td>3.3(0.17)</td>
<td>14</td>
</tr>
</tbody>
</table>
**Figure S3.** J-V curves for comparison of BCP ETL performance to TPBi ETL performance in bilayer and cascade devices. Shaded regions show the 95% confidence interval for the current flux. Device structure is ITO/PEDOT:PSS/MoO$_x$ (5 nm)/Donor/C$_{70}$ (30 nm)/ETL/Ag (80 nm).

Numerical data is tabulated in Table S2.
**Table S3.** Mean device parameter comparison for optimization of $\mu$-oxo as an electron donor. The standard deviation (SD) of each value is shown in parentheses. Device structure is ITO/PEDOT:PSS/ Donor/Acceptor/TPBi(3 nm)/Ag(80 nm).

<table>
<thead>
<tr>
<th>Donor/d$_{D}$/nm</th>
<th>Acceptor/d$_{A}$/nm</th>
<th>J$_{sc}$ (SD)/mA cm$^{-2}$</th>
<th>V$_{oc}$ (SD)/V</th>
<th>FF (SD)</th>
<th>η$_{p}$ (SD)/%</th>
<th>No. of cells tested</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu$-oxo/10</td>
<td>C$_{60}$/30</td>
<td>-3.6 (0.26)</td>
<td>0.80 (0.14)</td>
<td>0.36 (0.03)</td>
<td>1.0 (0.21)</td>
<td>12</td>
</tr>
<tr>
<td>$\mu$-oxo/20</td>
<td>C$_{60}$/20</td>
<td>-2.3 (0.22)</td>
<td>0.70 (0.12)</td>
<td>0.27 (0.02)</td>
<td>0.43 (0.07)</td>
<td>12</td>
</tr>
<tr>
<td>$\mu$-oxo/30</td>
<td>C$_{60}$/10</td>
<td>-1.2 (0.16)</td>
<td>0.45 (0.26)</td>
<td>0.25 (0.03)</td>
<td>0.13 (0.07)</td>
<td>12</td>
</tr>
</tbody>
</table>
Figure S4. J-V curves for investigating of μ-oxo as an electron donor. Shaded regions show the 95% confidence interval for the current density. Device structure is ITO/PEDOT:PSS/Donor/Acceptor/TPBi(3 nm)/Ag(80 nm). Numerical data is tabulated in Table S3.
**Table S4.** Mean device parameter comparison for investigating μ-oxo as an electron donor with MoOₓ hole extraction layer. The standard deviation (SD) of each value is shown in parentheses. Device structure is ITO/PEDOT:PSS/MoOₓ/Donor/Acceptor/TPBi(3 nm)/Ag(80 nm).

<table>
<thead>
<tr>
<th>Donor/dD</th>
<th>Acceptor/dA</th>
<th>J_sc (SD)/mA cm⁻²</th>
<th>V_oc (SD)/V</th>
<th>FF (SD)</th>
<th>η_P (SD)/%</th>
<th>No. of cells tested</th>
</tr>
</thead>
<tbody>
<tr>
<td>μ-oxo/5</td>
<td>C₆₀/30</td>
<td>-4.0 (0.15)</td>
<td>0.84 (0.02)</td>
<td>0.56 (0.06)</td>
<td>1.9 (0.27)</td>
<td>7</td>
</tr>
<tr>
<td>μ-oxo/8</td>
<td>C₆₀/45</td>
<td>-3.9 (0.13)</td>
<td>0.90 (0.003)</td>
<td>0.59 (0.01)</td>
<td>2.0 (0.07)</td>
<td>7</td>
</tr>
<tr>
<td>μ-oxo/10</td>
<td>C₆₀/60</td>
<td>-3.1 (0.13)</td>
<td>0.88 (0.07)</td>
<td>0.48 (0.36)</td>
<td>1.3 (0.20)</td>
<td>9</td>
</tr>
</tbody>
</table>
Figure S5. J-V curves for optimization of µ-oxo as an electron donor with MoOₓ hole extraction layer. Shaded regions show the 95% confidence interval for the current density. Device structure is ITO/PEDOT:PSS/MoOₓ/Donor/Acceptor/TPBi(3 nm)/Ag(80 nm). Numerical data is tabulated in Table S4.
Table S5. Mean device parameter comparison for optimization of acceptor and donor layer thicknesses in μ-oxo/C70 devices. The standard deviation (SD) of each value is shown in parentheses. Device structure is ITO/PEDOT:PSS/MoO₃(5 nm)/Donor/_acceptor/TPBi(3 nm)/Ag(80 nm). The “5nm μ-oxo” device was fabricated with 5nm of TPBi instead of 3nm, leading to a drop in $V_{OC}$.

<table>
<thead>
<tr>
<th>Donor/dₐ</th>
<th>Acceptor/dₐ</th>
<th>J_{SC} (SD)/mA cm⁻²</th>
<th>$V_{OC}$ (SD)/V</th>
<th>FF (SD)</th>
<th>$\eta_{P}$ (SD)/%</th>
<th>No. of cells tested</th>
</tr>
</thead>
<tbody>
<tr>
<td>μ-oxo/5</td>
<td>C₇₀/30</td>
<td>5.8(0.06)</td>
<td>0.69(0.04)</td>
<td>0.55(0.01)</td>
<td>2.2(0.13)</td>
<td>14</td>
</tr>
<tr>
<td>μ-oxo/10</td>
<td>C₇₀/30</td>
<td>6.3(0.14)</td>
<td>0.91(0.01)</td>
<td>0.48(0.02)</td>
<td>2.7(0.15)</td>
<td>15</td>
</tr>
<tr>
<td>μ-oxo/16</td>
<td>C₇₀/30</td>
<td>5.3(0.03)</td>
<td>0.92(0.01)</td>
<td>0.41(0.01)</td>
<td>2.0(0.06)</td>
<td>10</td>
</tr>
<tr>
<td>μ-oxo/10</td>
<td>C₇₀/20</td>
<td>5.1(0.19)</td>
<td>0.91(0.01)</td>
<td>0.49(0.04)</td>
<td>2.3(0.11)</td>
<td>13</td>
</tr>
<tr>
<td>μ-oxo/10</td>
<td>C₇₀/30</td>
<td>6.3(0.14)</td>
<td>0.91(0.01)</td>
<td>0.48(0.02)</td>
<td>2.7(0.15)</td>
<td>15</td>
</tr>
<tr>
<td>μ-oxo/10</td>
<td>C₇₀/40</td>
<td>5.1(0.23)</td>
<td>0.90(0.01)</td>
<td>0.52(0.01)</td>
<td>2.4(0.16)</td>
<td>18</td>
</tr>
</tbody>
</table>
**Figure S6.** J-V curves for optimization of donor and acceptor layer thicknesses in bilayer devices. Shaded regions show the 95% confidence interval for the current flux. Device structure is ITO/PEDOT:PSS/MoO₃(5 nm)/Donor/Acceptor/TPBi(3 nm)/Ag(80 nm). For varied C₇₀ acceptor thickness, the donor layer is 10 nm of μ-oxo. For varied μ-oxo donor thickness, the acceptor layer is 30 nm of C₇₀. The “5nm μ-oxo” device was fabricated with 5nm of TPBi instead of 3nm, leading to a drop in Vₜₜₜ. Numerical data is tabulated in Table S5.
Table S6. Mean device parameter comparison for optimization of donor layer thicknesses in Cl-
BsubPc/μ-oxo/C70 charge cascade devices. The standard deviation (SD) of each value is shown
in parentheses. Device structure is ITO/PEDOT:PSS/MoOx(5 nm)/Donors (10nm)/C70(30
nm)/TPBi(3 nm)/Ag(80 nm).

<table>
<thead>
<tr>
<th>Donor/donor nm</th>
<th>$J_{sc}$ (SD)/mA cm$^2$</th>
<th>$V_{oc}$ (SD)/V</th>
<th>FF (SD)</th>
<th>PCE (SD)/%</th>
<th>Cells Tested</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl-BsubPc/10</td>
<td>4.6(0.11)</td>
<td>1.08(0.01)</td>
<td>0.52(0.01)</td>
<td>2.6(0.09)</td>
<td>12</td>
</tr>
<tr>
<td>Cl-BsubPc/7.5, μ-oxo/2.5</td>
<td>5.6(0.04)</td>
<td>0.91(0.01)</td>
<td>0.60(0.01)</td>
<td>3.0(0.08)</td>
<td>16</td>
</tr>
<tr>
<td>Cl-BsubPc/5, μ-oxo/5</td>
<td>5.7(0.09)</td>
<td>0.89(0.01)</td>
<td>0.63(0.02)</td>
<td>3.2(0.14)</td>
<td>17</td>
</tr>
<tr>
<td>Cl-BsubPc/2.5, μ-oxo/7.5</td>
<td>5.9(0.17)</td>
<td>0.87(0.02)</td>
<td>0.64(0.02)</td>
<td>3.3(0.17)</td>
<td>14</td>
</tr>
<tr>
<td>μ-oxo-(BsubPc)$_2$/10</td>
<td>6.3(0.14)</td>
<td>0.91(0.01)</td>
<td>0.48(0.02)</td>
<td>2.7(0.15)</td>
<td>15</td>
</tr>
</tbody>
</table>
Figure S7. J-V and EQE curves for optimization of Cl-BsubPc/μ-oxo/C70 cascade devices. Shaded regions show the 95% confidence interval for the current flux or external quantum efficiency. Device structure is ITO/PEDOT:PSS/MoO₃(5 nm)/Donors (10 nm)/C₇₀(30 nm)/TPBi(3 nm)/Ag(80 nm). Numerical data is tabulated in Table S6.
7.2.2 Supplemental Information for Chapter 3: Boron Subphthalocyanines as Electron Donors in Outdoor Lifetime Monitored Organic Photovoltaic Cells

The following text is the Supplemental Information of the titular paper, as submitted to Solar Energy Materials and Solar Cells.

**ISOS-O3 Testing Additional Details:** ISOS-O3 testing standards were met on all metrics except the following: Maximum Power Point (MPP) resistor loading was done at the ISOS-O1 level, since resistances were not adjusted to track the MPP as the OPVs degraded over time. EQE monitoring, which is optional at the ISOS-O2 level, was only fully implemented for BsubPc-containing devices, and t80 EQEs were not taken on PhO-BsubPc and Ph-BsubPc devices. Air temperature and humidity were monitored at a 6 meter distance instead of the recommended 1.2m for ISOS-O3 testing. Location of testing was 43°39'31.7"N, 79°23'45.6"W, between September 10 and November 26 of 2015 for BsubPc devices, and September 9 and November 28 of 2016 for α-sexithiophene devices.
Figure S1: Air temperature (°), relative humidity (%), wind speed (m/s) and wind direction (°) data for α-sexithiophene/C₆₀ photovoltaic devices. For wind direction measurements, 90 degrees corresponds to wind from the east, 180 from the south, and so on.
Figure S2: Air temperature (°), relative humidity (%), wind speed (m/s) and wind direction (°) data for boron subphthalocyanine/C₆₀ photovoltaic devices. For wind direction measurements, 90
degrees corresponds to wind from the east, 180 from the south, and so on. Meteorological data was recorded on an hourly-average basis in the month of November 2015.

Figure S3: Post-Fabrication (t0) and Post-Aging (ts50 or ts80) EQEs of BsubPc devices.
Figure S4: Photograph of apparatus on roof of University of Toronto’s Wallberg building. Sample holders mounted to frame with electrical contacts, pyranometer on rail at right.
7.2.3 Supplemental Information for Chapter 4: The mixed and alloyed chemical composition of chloro-(chloro)ₙ-boron subnaphthalocyanines dictates their physical properties and performance in organic photovoltaics

The following text is the Materials and Methods section of the titular paper, which will be largely similar to the text to be submitted to Materials Today.

**Figure S1.** Effect of solvent on PHJs with solution-deposited commercial Cl-ClₙBsubNc layers. “CB” indicated chlorobenzene solvent was used, and “ODCB” indicates ortho-dichlorobenzene.

**Figure S2.** J-V plot for various device structures from the initial characterization process, with legend sorted chronologically. Some alterations affected $J_{SC}$ substantially, but fill factor was not substantially improved until the Cl-ClₙBsubNc layer was made thinner.
References


Copyright Acknowledgements

The text displayed in Chapter 2 is published in ACS Applied Materials & Interfaces under the title “Characterization of μ-oxo-(BsubPc)₂ in Multiple Architectures of Organic Photovoltaic Devices: Comparing Against and Combining with Cl-BsubPc.”

At the time of this writing, the in-progress papers detailed in Chapters 3 and 4 are not copyrighted by a journal, but following publication in journals their text will be subject to any applicable restrictions.