ENVIRONMENTAL ASSESSMENT OF TRANSPARENT PHOTOVOLTAICS

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ABSTRACT

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Transparent organic photovoltaics (TPV) can harvest energy from the near-infrared (NIR) and ultraviolet region of the solar spectrum and could be used in new applications such as windows. In addition to producing electricity, the transparent organic solar cell absorbs in the NIR region and could reduce the cooling energy demand of buildings during summer. Organic photovoltaic (OPV) is an emerging technology, developed mostly to replace fossil fuel energy, aimed to reduce greenhouse gases emissions. As OPV technology is reaching commercialization, it is essential to quantify its environmental impacts and ensure that new issues are not created. Life cycle assessment (LCA) is often used to compare energy technologies and identify environmental concerns, but this process is challenging for emerging technologies due to lack of inventory data. To guide future transparent OPV development, this work (1) demonstrates a new iterative methodology to evaluate and guide OPV material manufacturing that combines LCA and green chemistry approaches, (2) evaluates the energy saving from organic TPV in window and skylight applications in various cities, and (3) assesses the impact of organic TPV on urban heat island effect.

The methodology was used to identify "hotspots," which correspond to the processes that have the highest impact for chloroaluminum phthalocyanine (ClAlPc) manufacturing. An optimized process that reduces the environmental impact by 3%, the cost by 9% and chemicals hazard by 23% compared to the current process was demonstrated. The impact of TPV during the use phase was studied using ClAlPc based devices in window application. The building energy performance was shown to improve by up to 20 % due to heating and cooling energy saving. The energy saving varies with climate since NIR absorption by TPV in a window is more efficient in a warmer climate. The use of TPV in the window application in an urban area could further reduce the energy demand of buildings. The net energy saving by the TPV application in the urban area was calculated to be higher than in rural area by up to 2 GJ per month.

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KEY TO ABBREVIATIONS

1-CINP: 1-chloronaphthalene	GWP: Global warming potential		
2,4-DCA: 2,4-dichloroanisole	ITO: Indium tin oxide		
AE: Atom economy	LCA: Life cycle assessment		
AlCl ₃ : Aluminum chloride anhydrous	LCI: Life cycle inventory		
BCP: Bathocuproine	MoO ₃ : Molybdenum(VI) oxide		
BIPV: Building integrated photovoltaic	M-Pcs: Metallophthalocyanines		
BOS: Balance-of-systems	NEB: Net environmental benefit		
C ₆₀ : C60 fullerene	NH4Cl: Ammonium chloride		
CBECS: Commercial Buildings Energy	NIR: Near-infrared		
CED C 1	NOx: Nitrogen oxides		
CED: Cumulative energy demand	OPV: Organic photovoltaics		
CIAIPc: Chloroaluminum phthalocyanine	PA: Phthalic anhydride		
CuPc: Copper phthalocyanine	PCE: Power conversion efficiency		
DBU: 1,8-Diazabicyclo[5.4.0]undec-7-ene	PM: Particulate matter		
DEG: Diethylene glycol	PMI: Process mass intensity		
eGrid: emissions & Generation Resource Integrated Database	PN: 1,2-dicyanobenzene		
EIA: U.S. Energy Information	PV: Photovoltaic		
Administration EPBT: Energy payback time	QSAR: Quantitative structure-activity relationship models		
EQE: External quantum efficiency	SHGC: Solar heat gain coefficient		
EROI: Energy return on energy invested	SO ₂ : Sulfur dioxide		
GHGs: Green housegases	SRR: Skylight to roof ratio		
GHS: Globally Harmonized System	TMY: Typical Meteorological Year		

TPV: Transparent OPV UHI: Urban heat island effect UV: Ultraviolet UWG: Urban weather generator

WDI: Water demand indicator

WWR: Window to wall ratio

Chapter 1 Introduction

1.1 Introduction

Future energy solutions should not create new environmental, social, and cost problems. Electricity generation from fossil fuels, such as coal, natural gas, and fuel oils, is not desirable for a long-term goal. Environmental impacts related to these non-renewable sources of electricity include the release of a large amount of greenhouse gases (GHGs).¹ To solve the issue, interest in renewable energy has increased, and the most promising renewable source is solar energy because of over hundred thousand terawatts of potential energy from sunlight.² Advancing photovoltaic (PV) technology over time has resulted in interest for alternative photovoltaics, such as organic photovoltaics (OPV). OPV are soon to be commercialized because of their benefits such as flexibility, low weight, and low cost.^{3,4}

Currently, electricity generated in the U.S. relies on the use of coal and natural gas. Also, coal-fired electricity generation increases air pollution due to mercury, sulfur dioxide (SO₂), nitrogen oxides (NOx), and particulate matter (PM) emissions.⁵ The next fifty years are critical in order to replace conventional energy sources to renewable energy in order to reduce the environmental impact of electricity production. According to the U.S. Energy Information Administration (EIA), the net coal-fired electricity generating capacity has decreased by around 60 gigawatts (GW) from 2011 to 2016 to comply with the U.S. Environmental Protection Agency's Mercury and Air Toxics Standards.⁶ Electricity generation from renewable energy should reach 1,650 billion kilowatt-hours (BkWh) by 2050 and should become the second largest source of electricity as shown in Figure1-1.⁶



Figure 1-1. Net electricity generation from select fuels (Adapted from Annual Energy Outlook 2018, EIA, 2018)⁶



Figure 1-2. Renewable electricity generation, including end-use generation (Adapted from Annual Energy Outlook 2018, EIA, 2018)⁶⁶

The amount of renewable energy produced from wind, geothermal, and hydroelectricity are expected to remain similar while PV would increase until 2050 as shown in Figure 1-2.⁶ Interest in building integrated photovoltaic (BIPV) application has increased due to its potential economic

and environmental benefits.⁷ Reducing land use for PV deployment is a major economic benefit of BIPV in an urban area, and BIPV application could also achieve microclimate improvement.⁷

Building sector contributed to over 50% of total energy use in high-income cities (Tokyo, New York, Seoul, Greater London, Singapore, Berlin, and Bologna) in 2008. The energy use in the building sector was associated with building maintenance and operation.⁸ Buildings are complex systems, and their energy consumption is affected by local climate, occupancy profiles, and consumer preferences.⁹ Figure 1-3 shows the primary energy use for electricity generation and final world electricity demand for each sector. A key solution for urban sustainable energy is to increase the energy efficiency of the building energy system and/or to increase low carbon electricity production in a city where land is limited, which can mostly be attained using BIPV.



Figure 1-3. Energy use for power generation and total electricity demand in 2010 (Adapted from Transition to Sustainable Buildings, IEA, 2013)⁹

Although it is difficult to estimate, windows are most likely responsible for 5% to 10% of the total energy consumed in buildings in OECD countries.¹⁰ It is essential to develop high-performance windows with low thermal transmittance and climate-appropriate solar heat gain coefficient (SHGC) to reduce energy consumption. Efforts have focused on multiple glazed

windows (triple or quadruple) with multiple low-E coatings, exotic inert gases, such as krypton and xenon to develop high-performance windows. However, these windows are generally too expensive, and additional work is required to find an inexpensive solution to reduce the energy consumption of windows.¹⁰

Transparent OPV (TPV) offers an opportunity to produce electricity and improve building energy performance at the same time. The absorption from TPV can be tuned from ultraviolet (UV, <435 nm) to near infrared (NIR, >670 nm) range of the solar spectrum. TPV in window applications could control the inward flow of solar heat and reduce cooling energy demand while the absorbed solar energy can be used to produce electricity while performing the original function of windows because of its transparency.¹¹ Although there are benefits of OPV applications, the potential impacts from OPV material manufacturing are not well understood.

Previous work has used life cycle assessment (LCA) to evaluate the impact associated with fullerenes synthesis¹², a common acceptor material in OPV as well as various small molecules and polymer organic solar cells³ based on cumulative energy demand (CED). The energy requirement for OPV manufacturing was 50 % lower than for manufacturing conventional inorganic photovoltaics.³ While the potential energy benefit of OPV compared to inorganic solar cells has been established, the impact of transparent photovoltaics has not been studied.

One limitation of LCA in its application to emerging technology which uses new chemicals is the lack of inventory information. An approach to reduce the environmental and health impacts of chemicals and help develop alternative chemical process is green chemistry. The framework of green chemistry includes all stages of the chemical life-cycle and tries to reduce the intrinsic hazard of chemical products by design.¹³ Applying green chemistry to the new chemical is relatively

simple compared to LCA because green chemistry metric is designed to use stoichiometry or mass balance to evaluate environmental performance.¹⁴

1.1.1 Motivation

Energy solutions developed today should remain desirable in the future. As organic solar cells are getting closer to commercialization, it is imperative to investigate the potential unintended consequences in both the manufacturing and use phases of the organic solar cells. LCA considers all stages from raw material extraction (cradle) to the ultimate return of the material to the earth (grave). The cumulative environmental impacts from all stages in the product are imperative since they allow the evaluation of trade-offs in product and process selection. Performing LCA during the development process can lead to design solutions with lower environmental, cost, and health impacts.

Sustainability considers the economic, social, and environmental aspects altogether. Developing technology for only photovoltaic efficiency without considering embodied energy and environmental impacts should be avoided. Building renewable energy infrastructure requires environmental costs to help choose appropriate materials for photovoltaic technologies.^{15,16} It is also better to use environmentally benign chemicals and reduce the amount of waste during the manufacturing of OPV material, since prevention is better than remediation. A holistic approach to evaluating the sustainability of OPV material process has not been established, but it could play a significant role as the first step for maximizing net benefit of OPV application.

TPVs have the potential to be affordable by using low-cost materials and to be integrated into the infrastructure of the built environment, thereby reducing installation costs and balance-of-systems (BOS).¹¹ Currently, the assessment of the environmental performance of PV is limited to

the traditional function and application of PV by only considering the module, BOS, and electricity generation. The tradeoff between PV efficiency and energy inputs, such as cumulative energy demand (CED) in perspective of energy performance, has been studied and formulated as metrics such as energy payback time (EPBT) and energy return on energy invested (EROI).¹⁷ However, TPV generates electricity and contributes to management of building energy demand by NIR absorption. The NIR absorption by TPV has not been well evaluated. However, switching from a conventional double-pane window to a semi-transparent PV made of amorphous silicon as a window has been found to reduce the building energy demand up to 15 %.¹⁸ Integrating the benefit from TPV in the window application to current methods of PV evaluation is required to make a clear comparison with existing renewable energy applications. Combining the energy saving and the electricity production to evaluate the benefit of TPV is needed to compare with other renewable energy options.

Urban areas account for about 64 % of the global primary energy use and produce 70 % of the world carbon dioxide emissions.¹⁹ Serious action to reduce the energy burden needs to be done, and some cities such as Aspen, Colorado, and Burlington, Vermont already use only renewable energy. Others, such as San Diego, California, aim to be 100% powered by renewable sources by 2035.¹⁹ The use of TPV in window application could help fulfill this goal of renewable energy in the urban area. An additional impact of energy use in the urban area is due to waste heat from anthropogenic activities and solar radiation which cause urban heat island effect (UHI). UHI can potentially affect communities by increasing energy demand during summertime peak, air conditioning costs, air pollution, greenhouse gas emissions, etc.²⁰ Large-scale deployment of BIPV in urban areas, such as rooftop or façade application, has been studied for microclimate impact, and studies conclude that PV application could reduce local temperature because solar energy is

converted to electricity ^{21,22} As a similar application, studying the impact of TPV in urban area is required to ensure that TPV does not further increase UHI effects.

1.2 Background

1.2.1 Green Chemistry

Green chemistry is known for its twelve principles (summarized in Table 1-1) and metrics¹³ which are general guidelines to reduce the environmental impact of chemical synthesis. The framework of green chemistry requires to (1) consider all stages of the chemical life-cycle, (2) reduce the intrinsic hazard of chemical products by design, and (3) use green chemistry as a cohesive system of principles or design criteria.¹³

As an example of green chemistry metrics and applications, the E-factor (Equation 1-1) is used to describe fine chemical (chemical category of OPV materials) processes, due to a large amount of waste generated from solvent use.²³ Similarly, a pharmaceutical company reported that the wasted materials were mainly from solvent use as reaction medium or work-ups. The contribution from solvent use was up to 35 to 50 % material use in a pharmaceutical process.²⁴ This issue is the motivation for searching for green solvents that reduce environmental impacts on fine chemical and pharmaceutical manufacturing²⁵, and most pharmaceutical companies have adopted green chemistry approach.²⁶

$$E - factor = \frac{Mass \ of \ byproduct \ (waste)}{Mass \ of \ desired \ product}$$
(1-1)

Although there are many studies reporting efforts on adopting green chemistry approaches in the pharmaceutical area, green chemistry applications in OPV area have been little reported. Previous study discusses strategies for producing conjugated polymers using green chemistry toward sustainable OPV.¹⁵ This paper criticizes the current research focused on renewable energy that consideration of embodied energy and environmental impacts is often absent. It further suggests guidelines to produce little waste, avoid protecting groups, use catalysts, generate environmentally benign byproducts, and consume less energy with exemplary polymer synthesis pathways.¹⁵

No.	Principle	Description		
1	Prevention	It is better to prevent waste than to treat or clean up waste after it has been created		
2	Atom economy (AE)	E) Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product		
3	Less hazardous chemical syntheses	Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment		
4	Designing safer chemicals	Chemical products should be designed to effect their desired function while minimizing their toxicity		
5	Safer solvents and auxiliaries	The use of auxiliary substances (e.g., solvents, separation agents, and others) should be made unnecessary wherever possible and innocuous when used		
6	Design for energy efficiency	Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure		
7	Use of renewable feedstocks	A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable		
8	Reduce derivatives	Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible because such steps require additional reagents and can generate waste		
9	Catalysis	Catalytic reagents (as selective as possible) are superior to stoichiometric reagents		
10	Design for degradation	Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment		
11	Real-time analysis for pollution prevention	Analytical methodologies need to be further developed to allow for real-time, in- process monitoring and control prior to the formation of hazardous substances		
12	Inherently safer chemistry for accident prevention	Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fire		

Table 1-1. Twelve principles of green chemistry and description (Adapted from Mulvihill, 2011)²⁷

1.2.2 Life Cycle Assessment

Life cycle refers to the lifespan of a product and/or process and includes raw material extraction, material processing and manufacturing, assembly, product use, and end of life as shown in Figure 1-7(a).²⁸ LCA is a systematic approach and consists of goal definition and scope, inventory analysis, and impact assessment, and interpretation as illustrated in Figure 1-7(b).^{28,29}



Figure 1-4. (a) Cradle to grave Life Cycle Assessment and (b) LCA framework according to ISO standards 14040 and 14044(Adapted from Anctil and Fthenakis, 2011).²⁸ © 2011 Annick Anctil and Vasilis Fthenakis. Originally published in Life Cycle Assessment of Organic Photovoltaics under CC by 3.0 license. Available from: DOI: 10.5772/38977

LCA can be applied to determine the potential environmental impacts from any product, process, or service. The accuracy and detail of the data collected during the life cycle inventory (LCI) are important and will determine the accuracy and quality of the analysis. The life cycle impact assessment (LCIA) identifies a link between the product or process and its potential impacts. Finally, interpretation evaluates the results of LCI and LCIA and communicate the results effectively.²⁹

1.2.3 Transparent Organic Photovoltaic Applications

Technologies of TPV have recently emerged with excitonic materials that selectively harvest electricity from UV and NIR radiation. Materials used to fabricate TPV include organic small molecules and organic salts.^{30,31} For TPV devices with small molecules, NIR-selective TPV was demonstrated in 2011 with chloroaluminum phthalocyanine (ClAlPc) as the donor and C₆₀ fullerene (C₆₀) as the acceptor between two transparent conductive electrodes (indium tin oxide, ITO). The power conversion efficiency (PCE) of the demonstrated device was $1.3\pm 0.1\%$ with average visible transmittance (AVT) of 65%.³⁰ Theoretical PCE of TPV is 20.6 % with 100% AVT

for a single junction device, and could reach about 30% PCE and 100% AVT with three to four junctions devices.¹¹

The performance of small molecule OPV relies on material purity. A study reports that PCE of solar cell made of copper phthalocyanine (CuPc) varies from 0.26 ± 0.01 % to 1.4 ± 0.1 % based on the purity of CuPc.³² The purification of OPV material is critical to the embodied energy of OPV device, which is an evaluating criterion of environmental performance of PV. For example, the purification of C₆₀ to reach electronic grade purity doubles the embodied energy.¹²

Chapter 2 Alternative Chloroaluminum Phthalocyanine Synthesis

2.1 Alternative Synthesis Pathway

Chloroaluminum phthalocyanine (ClAlPc) is of particular interest for TPV since it absorbs only in the near-infrared region. It allows the solar cell to be transparent, which is important for applications such as power-generating windows.^{11,30} While metal phthalocyanines are common small molecules widely used in the dye industry,³³ the required high purity for solar applications³² makes it a fine chemical. The most common precursors of phthalocyanine are phthalic anhydride (PA) and 1,2-dicyanobenzene (phthalonitrile, PN). PN can be produced from *o*-xylene under ammoxidation process at 480°C. The yield is 80-85%.³⁴ The other precursors are metal salts, and aluminum chloride anhydrous (AlCl₃) is used to synthesis ClAlPc. Manufacturing process of AlCl₃ is by chlorinating molten aluminum at 670-850°C, and the yield is over 90 %.³⁵

The reaction of ClAlPc from PN and PA is carried out using either heating mantle or microwave reactor (CEM Corporation Discover SP). In ClAlPc synthesis, the molar ratio of PN or PA to aluminum ion is fixed to 4:1 and mixed in reaction media.^{33,36,37} High boiling point solvent is required for all synthesis because of the high reaction temperature (230°C). Synthesizing methods of ClAlPc are reported in limited number of publications since the material is not typically utilized in the dye industry which consumes most metallophthalocyanines (M-Pcs).³⁸⁻⁴⁰ The summary of the synthesis pathway of ClAlPc and reaction condition is shown in Figure 2-1,^{33,36,37} and is used to calculate atom economy (AE) that evaluates the environmental performance of the synthesis pathway based on stoichiometry.⁴¹



Figure 2-1. (a) Synthesis pathway of chloroaluminum phthalocyanine from phthalonitrile and phthalic anhydride (b) reaction condition and reactants of chloroaluminum phthalocyanine

As a screening process, the environmental performance of the synthesis pathway of ClAlPc is evaluated using green chemistry metrics. AE is the conversion efficiency of a chemical process considering all atoms in the reactants and the desired products produced as shown Equation 2-1.

$$AE (\%) = \frac{mol \ wt. \ of \ desired \ product}{\sum (mol \ wt. \ of \ reactants)} \times 100$$
(2-1)

Synthesis pathways of ClAlPc from either PN or PA showing atom utilization of reactants are shown in Figure. 2-2 and Figure. 2-3. The pathway from PN results in higher AE because most reactants are converted to ClAlPc while PA pathway uses urea only as a nitrogen source (Figure 2-3, orange color), and residual atoms are wasted. Therefore, ClAlPc synthesis via PN would be desirable in term of environmental performance so that further optimization of ClAlPc process starts from PN pathway.



Figure 2-2. Synthesis pathway of chloroaluminum phthalocyanine via phthalonitrile showing atom utilization of reactants



Figure 2-3. Synthesis pathway of chloroaluminum phthalocyanine via phthalic anhydride showing atom utilization of reactants

As evidence of byproduct formation during ClAlPc synthesis from PN and PA, the energy inputs from a microwave reactor and images at certain temperatures are recorded. Figure 2-4 shows continuous energy input until around 80°C, and then intermediates start to form ClAlPc with an exothermic reaction that is recognized with the trend of cumulative energy input. Meantime, ClAlPc synthesis from PA shows the opposite trend of cumulative energy input compared to the ClAlPc synthesis from PN. The images show color changes from orange to green and eventually purple. Bubbles are observed during temperature increase and are suspected to be hydrochloric acid gas, due to the reaction of aluminum chloride with moisture.⁴² The formation of hydrochloric acid gas results in loss of chlorine ion during reaction, so the yield of ClAlPc from PA is only around 25 %.



Figure 2-4. Reaction energy input of chloroaluminum phthalocyanine synthesis from phthalonitrile under microwave reactor and pictures of the synthesis at each reaction stage (1. initial mixture of reactants, 2. intermediate reaction, 3. chloroaluminum phthalocyanine in 1-chloronaphthalene)



Figure 2-5. Reaction energy input of chloroaluminum phthalocyanine synthesis from phthalic anhydride under microwave reactor and pictures of the synthesis at each reaction stage (1. initial mixture of reactants, 2-4. intermediate reactions, 6. chloroaluminum phthalocyanine in 1-chloronaphthalene)

The source of reaction energy is of interest from the green chemistry perspective, which corresponds to *#6 design for energy efficiency* from Table 1-1. M-Pcs have been synthesized using microwave reactor, and the reaction time is five to ten min ^{43–45}. The experiments required 40 minute which is longer than other M-Pcs but significantly shorter than six hours when using the heating mantle method⁴⁶. For microwave synthesis, polar solvents are required because heating is based on molecular rotation⁴⁷, and the comparison of conventional and microwave reactor is shown in Table 2-1.

Table 2-1. Summary of reaction energy source, conventional and microwave reactors: principle, advantages, and disadvantages



Current ClAlPc processes use toxic and hazardous solvents, and thus there are opportunities to reduce health and environmental impacts. Extra filtration and solvent reflux are minimized to reduce the energy input from reference method.⁴⁶ The similar boiling point of toluene and D.I. water interrupts with solvent recovery and results in more energy consumption for solvent

recovery. Acetone is used as a substitute of toluene because it has lower boiling point, reducing the energy consumption for solvent recovery. The reference and alternative processes are shown in Figure 2-6. Trichlorobenzene is the most common reaction media in copper phthalocyanine synthesis, but production of polychlorinated biphenyl as a toxic byproduct has been reported.^{37,48,49} ClAIPc process uses 1-chloronaphthalene which has the same concern and should be replaced.



Figure 2-6. Flow diagram of chloroaluminum phthalocyanine processes: (a) reference process using a heating mantle⁴⁶ and (b) alternative process using a microwave reactor

Chapter 3 Evaluation of CIAIPc Synthesis Methods for Transparent Organic Photovoltaic 3.1 Introduction

Metal phthalocyanines (M-Pcs) have been widely used as electron donor material in organic photovoltaic (OPV).⁵⁰ Especially, chloroaluminum phthalocyanine (ClAlPc) is of particular interest for OPV since it absorbs only in the near-infrared (NIR) region.^{30,51–54} It allows the solar cell to be transparent which is important for applications such as power-generating windows. For this type of application, the merit of the solar cell is not solely a function of device efficiency but also transparency. The focus of this research is ClAlPc for which there is limited reported synthesis methods since the material is not typically utilized in the dye industry that consumes most M-Pcs.^{39,40}

Two precursors have been mainly used to synthesis M-Pcs: (1) phthalonitrile (PN) and (2) phthalic anhydride (PA), as shown in Figure3-1. Although it is known that PN produces higher purity M-Pcs, PA is preferred for copper phthalocyanine (CuPc) synthesis by the dye industry because of low cost, phthalic anhydride being about 100 times cheaper than phthalonitrile.³⁷ However, the PA process increases impurity in M-Pcs, which reduces the efficiency in OPVs. A previous study showed that power conversion efficiency of donor-acceptor bilayer solar cell based on CuPc increase from $0.26 \pm 0.01\%$ to $1.4 \pm 0.1\%$ with increasing purity.³² The same study also identified metal-free phthalocyanine as a potential impurity in CuPc using mass spectrometry which reduces hole mobility and device efficiency.³²



Figure 3-1. Metal phthalocyanines synthesis from (1) phthalonitrile (PN) and (2) phthalic anhydride (PA)

For the PN process, phthalonitrile directly forms chloro-substituted CuPc, which may impact the efficiency in OPVs. Christie and Deans showed the pathway of chloro-substituted copper phthalocyanine, up to Cl4-CuPc using spectroscopic analysis.^{37,55} It is important to mention that chloro-functionalized Pcs lead to smaller HOMO-LUMO gap and also lower LUMO.³⁵

The goal of this work is to establish the trade-off between material purity, device efficiency and material cost based on the synthesis precursors.

3.2 Experimental Procedure

3.2.1 Material Synthesis

The reaction of ClAlPc from PN and PA is carried out using microwave reactor, CEM Corporation Discover SP, at 230 °C. Microwave-assisted synthesis of M-Pcs is not a common method, but it has advantages of reducing reaction time and increasing reaction yield. The ratio of reactants is followed by the previous study as shown in Table 3-1.⁵⁶ Additional washing is performed for PA process with sulfuric acid and sodium hydroxide solution in low concentration (0.1M). The yields of ClAlPc from PN and PA processes are $81\pm5\%$ and $24\pm7\%$ respectively.

Since the goal for this study is to produce low-cost OPV materials, further purification, such as thermal gradient sublimation, is not performed to evaluate if the initial ClAlPc purity is sufficient for OPV applications directly.

Table 3-1. Sample description of chloroaluminum phthalocyanine synthesis from phthalonitrile

 and phthalic anhydride

	Precursor	Time and Temp.	Molar Ratio of reactants	Solvent
PN-1	phthalonitrile	40 min 230 °C	PN:AlCl ₃ 4:1	1-chloronaphthalene Acetone
PA-1	phthalic anhydride	40 min 230 °C	PA:Urea:AlCl ₃ 4:12:1 (NH4)2MoO4 as catalyst	1-chloronaphthalene Acetone
PA-2	The same batch with PA-1 with additional acid/base wash			0.1M H ₂ SO ₄ 0.1M NaOH

3.2.2 UV-visible Spectroscopy

ClAlPc samples from PN, PA and TCI America (98 % purity for reference) are dissolved in ethanol (EtOH) through 15 min of sonication. Undissolved phthalocyanine and impurities are separated by 22 μ m syringe filter. UV-vis spectra of extracts are measured through UV 2600 Spectrometer, Shimadzu, in range of 400 nm to 800 nm.

3.2.3 HPLC-MS Spectroscopy

Waters Xevo G2-XS UPLC-MS is used to analyze mass spectrum of ClAlPc samples. Mass spectra are obtained by electrospray ionization of extracts and column separation through 5% H₂O and 95 % acetonitrile as eluent.

3.2.4 Cost Analysis

The cost of ClAlPc from PN and PA processes is estimated using the price of reactants and solvents from chemical vendors. The reference price is determined as the sales price of chemical for the largest quantity to reflect reality from Sigma Aldrich, Molbase, and TCI America.^{57–59}

3.2.5 Solar Cell Fabrication and Tests

The device architecture is ITO (1200Å, pre-patterned) / MoO₃ (100Å) / ClAlPc (150Å) / C_{60} (300Å) / BCP (75Å) / Ag (1000Å) shown in Figure 3-2. Layers are deposited using a growth rate of ~1 Å/s. Reference for ClAlPc is from TCI America 98%, and C_{60} 99.9% is from MER corporation. Device characteristic J_{sc}, V_{oc}, FF, and device efficiency are measured as a function of voltage (V) (Keithley 2420) under AM1.5G solar simulation (xenon arc lamp) where the intensity was measured using a NREL-calibrated Si reference cell with KG5 filter. External quantum efficiency (EQE) measurements are performed under a monochromatic incandescent halogen lamp calibrated using a Newport Si detector.



Figure 3-2. Energy level diagram and structure for the solar cell based on chloroaluminum phthalocyanine and C₆₀

3.3 Result and Discussion

3.3.1 UV-visible Spectra

UV-vis spectra of ClAlPc dissolved in ethanol are shown in Figure 3-3. UV-vis spectrum of M-Pcs is known to exhibit strong Q-band at 600 to 700 nm due to π - π transitions.⁶⁰ ClAlPc-reference and PA solutions have maximum peak at 670 nm, but for the PN solution which has a lower pH, the peak is at 677 nm. It is reported that acidic solutions results in red-shifts due to M-Pc protonation.⁶⁰



Figure 3-3. UV-vis spectrum of chloroaluminum phthalocyanine: ClAlPc-reference (green solid), ClAlPc-phthalonitrile (blue dash-dot), and ClAlPc-phthalic anhydride (red dash)

3.3.2 HPLC-MS Spectra

In Figure 3-4, mass chromatograms of ClAlPc show one strong peak at 7 min of retention time with 580.16 mass charge ratio (m/z) for all samples except PA-1 samples for which there is a peak at 4 min with 487.12 m/z, suggesting significant amount of impurity. This impurity is efficiently removed by acid/base solution as shown as PA-2 in Table 1 and Figure 3-4. — PA-1

and PA-2 are synthesized in the same batch, but PA-2 is washed with acid/base solution. All samples do not match exactly the expected m/z for ClAlPc, which is 574.96 but a slightly higher value of 580.16. The difference could be a result of chlorine ion lost during ionization which would result in phthalocyanine adducts with acetonitrile which would correspond to the observed value. Isotope distribution is also used to verify material purity, and PN and PA samples match the 98% purity ClAlPc reference from TCI America.



Figure 3-4. Mass chromatogram (left) and isotope distribution (right) at 580.16 m/z of chloroaluminum phthalocyanine: ClAlPc-Reference (green), ClAlPc-Phthalonitrile (blue), ClAlPc-Phthalic anhydride-1 (deep red) and Phthalic anhydride-2 (red)

3.3.3 Cost Analysis

The cost of ClAlPc from PN and PA process is significantly lower than reference ClAlPc from TCI America. Although phthalic anhydride is a hundred-fold cheaper than phthalonitrile, PN

process produces cheaper ClAlPc since yield of PA process is much lower than PN process, 24 % compared to 81 % as shown in Figure 3-5. Also, the price of ClAlPc is directly associated with the price of solvents, which use similar amounts for both processes.



Figure 3-5. Cost analysis of chloroaluminum phthalocyanine: ClAlPc from phthalic anhydride (PA process) and phthalonitrile (PN process) compared to purchased ClAlPc from TCI America

3.3.4 Photovoltaic Performance

Characteristics of ClAIPc devices from PN and PA processes are illustrated in Figure 3-4 and 3-5 and summarized in Table 3-2. PA process leads to the lowest device performance. The PA process requires urea addition as a source of nitrogen to form 1,3-Diiminoisoindoline, but the urea decomposes to not only ammonia gas but also many other byproducts at high temperature, such as biuret, cyanuric acid, and ammelide etc.⁶¹ Therefore, the PA process inevitably results in lower purity of ClAIPc which results in lower device efficiency. Since the devices from PN-1 sample show the highest energy conversion efficiency but yields the lowest number of working devices, we report data as both the best devices and median device performance, which show lower energy conversion efficiency although all devices work (Table 3-2). Also, external quantum efficiency
(EQE) of replication shows lower ClAlPc response and rare C_{60} response (Figure. 3-7). Either impurity or degradation of ClAlPc could affect to device performance, but it is hard to diagnose the failure of device since we did not further characterize devices.

Table 3-2. Photovoltaic performance parameters of optimal chloroaluminum phthalocyanine devices: ClAlPc-Reference (TCI America), phthalonitrile (PN-1), and phthalic anhydride (PA) cells

ClAlPc Source	Jsc (mA/mm ²)	Voc (V)	FF	Efficiency (%)	Yield
TCI America	0.05 ± 0	0.78 ± 0	0.50 ± 0	2.1±0.1	8/8
PN-1 Best	0.06	0.76	0.42	2.0	-
PN-1 Replication	0.03±0	0.06 ± 0	0.42 ± 0	0.80 ± 0.02	8/8
РА	0.02 ± 0	0.58 ± 0.01	0.24±0	0.20 ± 0.02	7/8



Figure 3-6. Representative current density-voltage characteristics of solar cells based on ClAlPcreference (green solid), ClAlPc-phthalonitrile-1 best (blue dash-dot) and phthalonitrile-1 replication (deep blue dash) and ClAlPc-phthalic anhydride (red dot)



Figure 3-7. External quantum efficiency of solar cells based on ClAlPc-reference (green solid), ClAlPc-phthalonitrile-1 best (blue dash-dot) and phthalonitrile-1 replication (deep blue dash) and ClAlPc-phthalic anhydride (red dot)

3.4 Conclusion and Future Work

Two precursors of ClAIPc, phthalonitrile and phthalic anhydride, are studied to evaluate tradeoff between material purity, device efficiency, and material cost. The results show that UVvis and mass spectra of ClAIPc from PN and PA processes are in agreement with reference material. The cost of ClAIPc from two processes are significantly lower than ClAIPc from chemical vendor, and PN process produces three-fold cheaper ClAIPc than PA process due to high yield. Based on photovoltaic fabrication and tests, we observe two different results from ClAIPc-PN devices. The best device from PN sample shows similar energy conversion efficiency with the reference device although fabrication yield is low. For PA samples, all devices work, but have low energy conversion efficiency due to impurities from urea decomposition. Future studies will identify trace impurities of ClAIPc from PN process and explore synthesis pathways to improve initial purity of ClAIPc.

Chapter 4 Fine Chemical Process Toward to Sustainable Organic Photovoltaic

The previous chapters discuss the experimental and simulation method to synthesize CIAIPc and to fabricate CIAIPc solar cell, and to assess life cycle assessment of OPV. Those methods are applied in this chapter to assess fine chemical process to evaluate environmental, cost, and chemical hazard impacts and demonstrating iterative design approach. As described in the motivation, establishing a holistic evaluation method for OPV material process is important to develop sustainable energy solution. This work has been published as E. Lee, C. Andrews, and A. Anctil, "An Iterative Approach to Evaluate and Guide Fine Chemical Processes: An Example from Chloroaluminum Phthalocyanine for Photovoltaic Applications", *ACS Sustainable Chem. Eng.*, **2018**, 6 (7), pp 8230–8237. Additional information regarding data source for life cycle assessment, synthesis process, material purity, and evaluation criteria for CIAIPc processes is available in the appendix.

4.1 Introduction

Fine chemicals are complex, single, and high purity chemical substances produced in limited quantities (up to 1000 MT per year) at a high price (>\$ 10/kg) for use in the pharmaceutical, agrochemical, animal health, pigment, and electronic industries.⁶² One method that can be used to reduce the environmental impact of fine chemical manufacturing is green chemistry, which is well -known for its 12 principles.¹³ They are general guidelines to reduce the environmental impact of chemical synthesis, for example, by reducing byproduct and derivatives, increasing energy efficiency, and encouraging safer chemical use. The framework of green chemistry requires (1) considering all stages of the chemical life cycle, (2) trying to reduce the intrinsic hazard of chemical products by design, and (3) using green chemistry as a cohesive system of principles or

design criteria.¹³ Another method to reduce the impact of a product is life cycle assessment (LCA) which is a comprehensive method for assessing impacts associated with the whole life cycle of a product, from material extraction (cradle) to final disposition (grave). LCA quality is dependent on the accuracy of mass and energy flow information collected to construct the life cycle inventory. To remain competitive, the fine chemical industry rarely publishes detailed information through patents or journal article publications. Energy consumption directly associated with one chemical is also difficult to assess since fine chemicals are produced in multipurpose plants where equipment and facilities are shared between production lines and are used for multiple chemicals.⁶³

In addition to academia, pharmaceutical and chemical companies have established various sustainability methods that combine aspects of LCA and green chemistry to guide their product development.^{64–66} A total of 19 methods is summarized and compared to the proposed methodology in Table A1 of appendix. Existing methods for industrial applications require extensive data collection to either perform a full LCA or calculate company specific impacts. At the other end of the spectrum, lab scale methods tend to use simplified impact assessment focusing on the manufacturing stage of the process, without consideration of upstream chemicals used as LCA would do. To the knowledge, there is no screening method to evaluate the impact of manufacturing and upstream chemicals on the basis of environmental impact, cost, and chemical hazard criteria that can be used to guide chemical development at the lab scale.

LCA is a useful tool to evaluate chemical and pharmaceutical processes as long as the inventory of all chemicals and processes already exists, which is not the case for most new chemicals. Also, the characterization factors which are necessary to calculate the environmental and health impacts are also often missing. Without characterization factors for certain chemicals in the LCA database, the assessment will underestimate the impact. Green chemistry principles can help identify issues associated with new chemicals regarding toxicity and material efficiency and can be used to complete the information from the life cycle assessment. This work proposes a new evaluation method to rapidly screen potential environmental, health, and cost impacts for fine chemicals with limited LCA information that can be used by both industry and academia. The goal of this study is to demonstrate the use of an iterative sustainability methodology that combines process-based LCA and green chemistry metrics to evaluate and guide fine chemical synthesis.

The proposed method is applied to small molecules which are used in organic photovoltaics (OPV).⁶⁷ Current OPV research focuses on reducing cost and increasing the efficiency of solar cells, and environmental and health impacts from OPV materials are mostly unknown.^{68,69} The basic structure of OPV requires mixing a donor and an acceptor material,⁷⁰ such as metal phthalocyanine (M-Pc) as a donor and fullerenes as an electron acceptor.^{71,72} Chloroaluminum phthalocyanine (ClAIPc) is of particular interest for OPV since it absorbs only in the near-infrared region. It allows the solar cell to be transparent, which is important for applications such as power-generating windows.^{11,30} While metal phthalocyanines are common small molecules widely used in the dye industry,³³ the required high purity for solar applications³² makes it a fine chemical. Current prices for high purity (98%) ClAIPc is \$157/g⁷³ compared to \$55/g for lower purity (85%).⁷⁴ The price difference can be attributed to the energy intensive purification process necessary for electronic applications.¹²

The proposed methodology is iterative and follows the steps shown in Figure 4-1(a). It begins with the synthesis of ClAlPc which will be considered the baseline, using the conditions reported in a published patent.³⁸ During the synthesis, the direct energy, chemical consumption, and yield are measured to build the life cycle inventory. The material needs to meet the purity requirement for OPV applications and is characterized using UV-Vis and HPLC mass spectroscopy. Impact

assessment which uses a combination of green chemistry impact factors and LCA is performed using the life cycle inventory. The process is evaluated based on the three impact categories shown in Figure 4-1(b). The "hotspot" is identified as the chemical or process which has the highest contribution for one or more of the impact categories. An alternative is developed using green chemistry principles and compared to the baseline. The iterative method is repeated until an alternative that simultaneously reduces the environmental, cost and chemical hazard is found.

As shown in Figure 4-1(b), the goal is to design for sustainability and therefore the alternatives need to reduce all impact categories and avoid trade-offs. For example, designing for lower cost, could have the unintended consequence of increasing the chemical hazard and environmental impacts.



Figure 4-1. (a) Proposed iterative methodology and (b) sustainability method and categories

4.2 Method

4.2.1 Life Cycle Assessment for Fine Chemicals Process

The study includes all stages from raw material extraction to the production of 1 kg of ClAlPc to meet purity requirement of OPV application. The use of LCA software facilitates the compilation and analysis of the inventory data and for this project, SimaPro (Pre Consultants,

Netherlands), is used, in combination with inventory data from existing databases (Ecoinvent 3.3 and US-EI from DATASMART)^{75,76} previously published literature, and data collected during the chemical synthesis. Inventory data for new chemicals is estimated using default values and stoichiometric reactions based on previously published guidelines.^{63,77,78} The standard transportation distance for chemicals is adapted to reflect the U.S conditions using the average mileage of commodity flow survey.⁷⁹ Additional details on inventory assumptions and life cycle assessment are available in Table A2. The goal is to combine life cycle assessment method for existing chemicals with green chemistry metrics to assess the impact of material synthesis and rapidly screen potential concerns. All 12 green chemistry principles are considered to be included since they were not meant to be independent goals.¹³ Care is taken to not duplicate information from the life cycle assessment with green chemistry metrics but rather complement it.

Sustainable chemical process design requires reducing the environmental, economic and social impacts simultaneously. Since the objective is to provide fast screening of chemical process only sub-categories that can be assessed at this stage of product development are used. Table 4-1 summarizes the metrics and sub-criteria selected in the methodology. Environmental impacts are commonly assessed using LCA, and therefore, for existing chemicals, those sub-categories are chosen and complemented with green chemistry metrics. For economics assessment, the production rate provides an estimate of maintenance and facility use in addition to the life cycle cost of raw materials. Finally, for the social impact, the only aspect that can be characterized and minimized during R&D is the intrinsic hazards of the chemicals to workers. Therefore, chemical hazard is used as our third impact category although both exposure and toxicity assessments of chemicals should be considered for risk characterization.

In Table 4-1, only two principles are used as sub-criteria because LCA methods are chosen instead. Four principles are not applicable, including #4: *Designing safer chemicals* and #10: *Design for degradation* since we do not want to change the chemical. The other five principles such as #5: *Safer solvents and auxiliaries* are used to guide alternative synthesis rather than in the evaluation stage (Table 4-1).

Table 4-1. Summary of green chemistry metrics and LCA impact categories used in the assessment methodology and to guide alternative synthesis

	Green C		hemistry	Life cycle assessment		
Principle (#)		Principle (#)	Metrics or tool	Impact category	Method	
x imental		F + Waste prevention (1)	E-Factor: amount of waste	E1: global warming potential (GWP)	Tool for reduction and assessment of chemicals and other environmental impacts (TRACI) 2.1- U.S. 2008 normalization ⁸⁰	
y Inde	nviro	E4. Waste prevention (1)	generated /kg of product	E ₂ : Cumulative energy demand (CED)	CED 1.09 ⁸¹	
ethodolog	Е			E3: water demand indicator (WDI)	Water accounting and vulnerability evaluation (WAVE) ⁸²	
stainability Met Chemical hazard		H₁-H₄: Inherently safer chemistry for accident prevention (12)	NFPA 704 standard (0-4 score): H1: health hazard H2: flammability hazard H3: reactivity hazard H4: special hazard			
S. St				C1: Life cycle cost	Price of petroleum, coal, and natural gas as raw material inputs	
	Ŭ			C ₂ : Production rate	Reaction capacity based on vessel size and time per batch	
	SIS	Atom Economy (2)	Atom economy: formula weight (FW) of atoms utilized/ FW of all reactants in percentage			
	ynthe	Less Hazardous chemical synthesis (3)	Globally Harmonized System ⁸³			
	c ann	Safer Solvents and Auxiliaries (5)	GSK Solvent Selection Guide ⁸⁴	Environmenta	I E ₁ : Global Warming Potential E ₂ : Cumulative Energy Demand E : Water Demand	
	lterna	Design for Energy Efficiency (6)	Ambient temperature and pressure process	E ₃ , Water Demand E ₄ : E-factor		
Guide A		Reduce derivatives (8)	Atom economy: FW of atoms utilized/ FW of all reactants in percentage			
icable	Catalysis (9)	M-Pc synthesis with organic base 85				
	Designing safer Chemicals (4)	Preferred molecular design to reduce chemical toxicity	Cost	Chemical Hazard (NFPA score)		
	Use of renewable feedstock (7)	Raw material or feedstock should be renewable	C ₁ : Life cycle cost C ₂ : Production rate	H_1 : Health hazard H_2 : Flammability hazard H_3 : Reactivity hazard		
Not appli		Design for degradation (10)	Designing Small Molecules for Biodegradability ⁸⁶		H₄: Special hazard	
		Real-time analysis for pollution prevention (11)	Real-time, in-process monitoring and control prior to the formation of hazardous substances			

Weighting and normalization are used to convert each sub-criterion to one dimensionless impact category unit and, for this work, all sub-criteria are given equal weight. The baseline process is given a 100% score for each category to allow relative comparison of the alternatives.

4.2.2 Selection of Impact Category for Sustainability Assessment

4.2.2 1 Environmental Impact

Global warming potential (GWP) (E_1) and Cumulative energy demand (CED) (E_2) are common environmental impact indicators with a well-established methodology. If inventory data is not available, the new materials inventory guidelines mentioned before are used but those methods are limited to CED and GWP.

For water use, the water demand indicator (WDI) (E₃) is a LCA metric that includes water consumption from chemical process and utility input which is not accounted for in the E-factor. Although E-factor have recently included water use ⁸⁷, the evaluation method follows the original definition of the E-factor and does not. The green chemistry metrics listed in Table 4-1 are calculated in Table A6 and used to develop alternative ClAlPc process.

The first of the green chemistry principles, *#1: waste reduction*, is key to reducing the environmental impact of chemical process. It is calculated using the E-Factor (E4) which is the mass balance based on actual process of wasted material.^{2,88} Similarly, process mass intensity (PMI) is defined as the ratio between quantity of raw materials involved in the process and quantity of product in kg. PMI includes water use and therefore E-factor is used as an impact category instead since water consumption is already calculated from the WDI.^{2,35}

4.2.2 2 Chemical Hazard

Chemical hazard is used to estimate the social impact. According to the World Business Council For Sustainable Development (WBCSD), workers' occupational health risks and safety are considered a mandatory topics in social life cycle metrics for chemical products.⁸⁹ The recommended method for LCA human health impact is the consensus model USEtox developed by UNEP/SETAC and based on the on the potential toxicity impacts and emission of chemicals.⁹⁰ This method cannot be used since ClAIPc processes include uncharacterized chemicals with unknown toxicity and emissions. EPI suite and ECOSAR use quantitative structure-activity relationship models (QSAR) to respectively estimate the environmental fate and aquatic ecotoxicity of chemicals. Their use is limited to organic chemicals since chemical descriptors are not suitable for inorganic molecules and organometallics such as aluminum chloride and ClAlPc used in our alternative processes.^{91,92} For these reasons, only green chemistry metrics are considered for chemical hazard: #3: Less hazardous chemical synthesis, #5: Safer solvents and auxiliaries, and #12: Inherently safer chemistry for accident prevention. Principles 5 and 3 are used to guide alternative synthesis, and principle 12 is used to evaluate chemical hazard (Table 4-1). H₁-H₄ are based on the NFPA 704: standard system for the identification of the hazards of materials for emergency response. NFPA 704 standard is based on acute exposure to chemicals, such as fire, spill or similar emergency. It provides information regarding the health, flammability reactivity, and special hazards of materials that are assessed by short-term and acute exposure and use a rating system from 0 to 4, where 0 is low hazard.³⁸ The Globally Harmonized System (GHS) is also a classification and labeling system but it covers additional aspects such as chronic toxicity and environmental hazard. However, an overall score is not provided even though it can be done as demonstrated by the GSK solvent guide⁸⁴ where a decision tree was used to assess health hazard. Based on the decision tree methodology, the health hazard score is determined by occupational exposure limits (OELs) or GHS Hazard and Precautionary risk phrases. If a chemical does not have an OEL value and is annual production is less than 1,000 tons/yr, the health hazard score is 4 out of 10. In the ClAIPc case, most health hazard score for chemicals used in the processes would receive this score since their annual production is lower than the 1,000 tons/yr. Therefore, the NFPA 704 standard is selected to reflect actual health hazard.

The hazards scores for each chemical are multiplied by the mass of chemical used to produce 1kg of ClAlPc and then normalized based on the baseline score. Health (H₁) and flammability (H₂) hazards are each weighted as each 1/3, but reactivity (H₃) and special (H₄) hazards are equally weighed 1/6 respectively since the oxidizing property of chemicals is responsible for both the reactivity and the special hazards scores.

4.2.2 3 Cost

Cost is characterized by C₁, the life cycle cost and C₂ the production rate (Table A7 and A8) There are no green chemistry metrics that directly assess the cost of the process although some have used PMI as an indicator.²⁴ PMI is based on the mass of chemicals, including water, not the specific chemical price and therefore the use of expensive chemicals, in particular for fine chemicals is not well reflected by the metric.

4.2.3 Material Synthesis and Data Collection

The baseline process for ClAlPc is based on a patent³⁸ and uses a heating mantle. Alternatives processes are numbered as P1-P5 which correspond to the order in which they are developed (Table 4-2). The reaction of ClAlPc from phthalonitrile (PN) and phthalic anhydride (PA) is

carried out using either heating mantle or a microwave reactor (CEM Corporation Discover SP). In the M-Pc synthesis, the molar ratio of PN or PA to metal ions is fixed to 4:1.^{33,36,37} The source of metal ion is aluminum chloride (AlCl₃), and PN or PA are mixed with the metal salt in reaction media. High boiling point solvents are needed for all synthesis because of the high reaction temperature (230°C). For microwave synthesis, polar solvents are required because heating is based on molecular rotation.⁴⁷ 1-chloronaphthalene (1-ClNP), 2,4-dichloroanisole (2,4-DCA), and diethylene glycol (DEG) are used as reaction media. Auxiliaries such as urea, ammonium chloride (NH₄Cl), and 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) are added for P2-P5. Table A2 provides details about the synthesis conditions. Direct energy demands, such as electricity from the reactor and vacuum pump, and chemical consumption are recorded during the synthesis of ClAIPc. To better reflect industrial process, the theoretical energy demand for the baseline process is calculated using previously reported method⁷⁷ and converted to steam.

For material characterization, ClAlPc samples and reference (TCI America 98 %) are dissolved in ethanol through 15 min of sonication. Undissolved phthalocyanine and impurities are removed using a 22 µm syringe filter.⁶⁰ UV-vis spectrum of extracts is measured using UV-Vis 2600 Spectrometer, Shimadzu. Waters Xevo G2-XS UPLC-MS is used to analyze the mass spectrum of ClAlPc samples. Mass spectra are obtained by electrospray ionization of extracts and column separation with 5% H₂O and 95 % acetonitrile as eluent. Additional details on material characterization are available in Table A8-S9.

Dracasa	Energy course	Precursor		Reaction media		Auxiliaries		Rxn.
Process	Energy source	Туре	Use (g)	Туре	Use (g)	Туре	Use (g)	Time
Baseline	Heating mantle	PN : AlCl ₃	1.80:0.47	1-CINP	10.75	•	•	6 hr
1	Microwave	PN: AlCl ₃	1.80:0.47	1-CINP	10.75	•	•	40 min
2	Microwave	PA : AlCl ₃	1.80:0.41	1-CINP	5.44	Urea	2.19	40 min
3	Microwave	PN: AlCl ₃	1.80:0.47	2,4-DCA	6.79	Urea	0.54	40 min
4	Microwave	PN: AlCl ₃	1.80:0.47	2,4-DCA	6.79	NH4Cl	0.54	40 min
5	Microwave	PN : AlCl ₃	1.80:0.47	DEG	6.66	DBU	2.48	40 min

Table 4-2. Reaction condition and chemical use for ClAlPc processes

4.3 Result and Discussion

4.3.1 Methodology Assessment

The iterative method is shown in Figure 4-1 (a) is used for ClAlPc synthesis and alternative processes developed are summarized in Table 4-1. Figure 4-2 (a) illustrates the iterative process and the identified hotspots for the baseline, P1, P4, and P5 as examples. Figure 4-2 (b)-(e) shows the impact assessment for each proposed alternative compared to either the baseline or the previous best chemical synthesis process. The impact for each category is fixed at 100% which correspond to the baseline score to facilitate comparison between the proposed alternatives. Summary of the score for each process is available in Table A9. The following sections summarize the alternative processes from the baseline to P5.

Baseline to Process 1. The baseline process is a well-established pathway for ClAlPc synthesis using solution processing and has the highest yield at 84%, but high yield is not necessarily synonymous with a sustainable process. The two main concerns or "hotspots" from the baseline process are the reaction time (six hours) which impacts production rate as well as the toxicity of the reaction media. The purity requirements for OPV application are also not met due to partial chlorination of ClAlPc, which can be considered an impurity (Figure A9).

To address these issues, the use of microwave rather than heating mantle and alternative solvents is considered, based on reported conditions for other M-Pc.^{44,93,94} P1 uses microwave reaction rather than heating mantle but keeps all the other conditions as the baseline. The reaction time is reduced from six hours to 40 min which is an improvement compared to the baseline, but longer than the five to ten minutes reported for other M-Pcs.^{44,93}



Figure 4-2. (a) Summary of hotspots determined by iterative evaluation, and (b)-(e) evaluation of alternative ClAlPc processes based on environmental, chemical hazard and cost impacts

The microwave reaction increases both the environmental and the cost impact as shown in Figure 4-2(b). The microwave process is faster, which increases the production rate by 27 % even when considering a smaller reaction volume (3.5 L for microwave reactor versus 20 L of pilot scale reactor). However, the electricity consumption in the microwave process is higher and the chemical yield lower (73% vs 84%) compared to the baseline which results in a 31% increase in environmental impact. The cost impact does not change significantly.

Baseline to Process 2. Since P1 increases the environmental impact, but result in no reduction in cost, the second alternative pathway (P2) considers alternative precursors for ClAlPc. PA is used by the dye industry to synthesize CuPc because of its low cost.³³ The bulk chemical of PA is three times cheaper than PN⁷⁴ and therefore could significantly lower ClAlPc price. In the Porphyrin Handbook, various ClAlPc processes are summarized including reaction condition and yield, but none of process uses PA as a precursor.³⁶ Unfortunately, P2 reaction yield is only 25% (Table A5) and the impact for all 3 categories increases. Previous work by our group has shown that ClAlPc synthesis from PA produces impurities due to urea decomposition that reduces photovoltaics device efficiency (Figure A8).⁹⁵ Using PA does not seem like a suitable pathway for ClAlPc synthesis since it reduces material purity while increasing environmental and cost impacts. Therefore, P2 is excluded from Figure 4-2 and the next iterative step is based on P1.

Process 1 to Process 3. The initial process modification P1 tried to address one of the two hotspots from the baseline process, the long reaction time but the use of microwave resulted in an increased electricity consumption. The second hotspot which is the toxicity of 1-CINP is considered for P3 using the green chemistry principle *#3: Less Hazardous Chemical Synthesis.*

Chlorinated naphthalene is known to be toxic to aquatic environment and has been prohibited for industrial use in Japan due to its persistency in aquatic environment.^{96,97} The fifth green

chemistry principle: *safer solvents and auxiliaries* is used to find alternative solvents using solvent selection guides.^{84,98}

Replacement of 1-CINP is difficult due to the high reaction temperature. Based on the CHEM21 solvent selection guide, anisole would be a good alternative solvent but has a boiling point of 155.5 °C. It has been reported that using anisole instead of a phenoxy derivatives for CIAIPc synthesis produces a high crystallinity compound.⁹⁹ We select 2,4-dichloroanisole (2,4-DCA) as an anisole alternative since it has a boiling point of 285 °C. For the baseline and P1 synthesis, extra volume of solvent was used to prevent chlorination of phthalocyanine, but it limits the reaction volume per batch and therefore the production rate. To prevent partial chlorination of CIAIPc, 30 w/w % of urea is added while reducing the volume of 2,4-DCA.^{33,37,55}

P3 compared to P1 reduces the chemical hazard by 23 % but both environmental and cost impacts increase (893% and 352% respectively). The increase in environmental impact is associated with high CED and GWP due to the upstream process of 2,4-DCA. The chlorination of anisole requires large volumes of organic solvents and acetic acid, which is responsible for 40% of the CED and GWP impacts of 2,4-DCA. The importance of LCA in our method is demonstrated for P3 since it provides insight on the impact from the upstream stages which is not considered by green chemistry alone. Another issue from the 2,4-DCA synthesis is filtration. The crude ClAlPc solution becomes viscous after the reaction is completed and the separation requires a larger volume of organic and inorganic solvents compared to the baseline method which increases the E-factor and water demand.

In term of cost, P3 raw material cost is 637 % higher than the baseline due to the 2,4-DCA cost and the extra amount of washing solvents. Overall the cost of P3 is 352% that of the baseline

due to a higher production rate and lower use of reaction media which counterbalance the higher raw material cost. The material characterization using HPLC-MS shows the same impurity observed in P2 (Figure A8). Therefore, P4 focuses on another source of ammonium to solve the purity issue.

Process 3 to Process 4. The use of urea as a reaction auxiliary in P2 and P3 results in insoluble byproducts which cannot be filtered out due to the decomposition of urea between 200-250 °C.⁶¹ The alternative source of ammonium for P4 is ammonium chloride due to its high boiling point (338 °C). The salt is stable and soluble in water after reaction which allows its removal during filtration. P4 solves the impurity production from urea decomposition, in addition, to increase the yield by 10% compared to P3. The environmental and cost impacts of P4 are lower than for P3 but remains much higher than the baseline (733 % and 284 % respectively) as shown in Figure 4-2(c). So far, the transition from baseline to P4 results in a reduction in chemical hazard but increases the environmental and cost impacts. Therefore, the approach demonstrates the potential of creating new issues while developing alternative synthesis if we focus on a single issue. The concern with the toxic solvent has not been solved since 2,4-DCA used in P3, and P4 shifts the problem from chemical hazard to environmental and cost impacts. The next step is therefore to reduce the environmental and cost impacts which are associated with 2,4-DCA synthesis.

Process 4 to Process 5. To find an alternative to 2,4-DCA, GSK's green solvent list is used. Both ethylene glycol and diethylene glycol (DEG) are listed on the list and have the same score but the boiling point of ethylene glycol is lower than the required reaction temperature.⁸⁴ DEG is chosen DEG as reaction media and DBU as a proton acceptor for P5, corresponding to *#9: Catalysis.* The CED and GWP associated with the upstream processes of DEG and DBU is smaller than 1-CINP although direct energy use from microwave is higher. In P5, a single washing solvent, methanol which is a safer solvent (principle #5), reduces the overall environmental impact by reducing the e-factor and WDI. DEG is a co-product of ethylene glycol, which is produced in large quantity globally¹⁰⁰ and therefore is cheaper than 2,4-DCA and 1-CINP. Using chemical produced in large quantity has the advantage that toxicity of the chemical has been tested since it is required for all chemicals with a production higher than 1,000 tons per year.¹⁰¹ The use of DEG as reaction media reduces the environmental and cost impacts compared to P4 while chemical hazard remains similar as shown in Figure 4-2(d).

4.3.2 Overall Evaluation

Using this iterative method, the baseline process is modified to P5 which reduces the environmental, cost and chemical hazard impacts as shown in Figure 4-2(e). The identification of the hotspot for each process effectively guided alternative processes. In P2, atom economy might be used as a screening criterion for chemical reaction selection but used alone it can lead to synthesis methods with higher environmental impact due to lower yield which results in additional material and energy use from the upstream process. For microwave reactor, microwave is known to reduce reaction time for phthalocyanine synthesis^{44,102,103}, but scaling up is challenging due to the high power consumption. Although industrial scaling up for microwave reactor is not considered in our study, there is a commercial microwave plant in Japan which suggest that microwave could be used at an industrial scale to produce ClAlPc.^{104,105}

The location is important for CED and GWP since the main contributor to these impact categories is electricity which depends on the portion of fossil fuel in the electricity mix.¹⁰⁶

Chemical production is energy intensive and energy-related environmental impact can account for almost half and sometimes up to 80% of GWP.¹⁰⁷ Figure 4-3 compares the CED impact from some of the processes considered. For P1 and P5, the electricity consumption from the microwave has the highest impact when considering the chemical synthesis and separation. For P4, as previously discussed, the solvent upstream process is more important than the direct energy consumption.



Figure 4-3. Cumulative energy demand for baseline, 1-chloronaphthalene (P1), 2,4-dichloroanisole (P4), and diethylene glycol (P5) ClAlPc processes

In addition to the direct electricity consumption, the relative contribution of other factors to CED is illustrated in Figure 4-4 for the baseline and P5 for all stages from basic chemical, synthesis, and separation. The direct electricity consumption (orange in Figure 4-3) and transportation is excluded from the figure to emphasize the impact of chemicals. In Figure 4-4, the upstream process of 1-CINP has higher CED impact compared to the combination of DEG and DBU (865 MJ compared to 560MJ).



(b)

Figure 4-4. Sankey diagram of the cumulative energy flow for ClAlPc synthesis from (a) the baseline and (b) diethylene glycol and DBU (P5) excluding transport and electricity

This work developed of a new methodology that combine LCA and green chemistry metrics to evaluate and guide fine chemical manufacturing. A secondary contribution is the creation of life cycle inventory for the four processes developed for ClAlPc based on a microwave reactor. Finally, a new method P5 is developed to produce ClAlPc which reduces simultaneously the environmental impact by 3%, the cost by 9% and chemicals hazard by 23% compared to the baseline process while producing high quality material that can be used for organic photovoltaics application.

Chapter 5 Building Energy Model for Life Cycle Assessment of Transparent Organic Photovoltaic in Window Application

This work includes a simulation of the building energy demand by TPV in window application. The material of TPV used in this chapter is ClAlPc which is discussed in the previous chapters.

5.1 Introduction

The energy consumption from fossil fuel is becoming an important issue due to resource depletion. In the United States, fossil fuels are the largest source of energy for electricity generation by about 63%.¹⁰⁸ The primary energy consumption from the residential and commercial building sectors is about 50%.¹⁰⁹ An approach to solve this large-scale energy demand in the building sector could be building-integrated photovoltaics (BIPV) application. BIPV are integrated directly into facades or other surfaces of a building so that they replace conventional building materials and save the energy used in a building. A previous study suggests the use of Transparent PV (TPV) as a window for future energy solution since TPV can optimize both average visible transmission (AVT) and power conversion efficiency (PCE), thereby providing sufficient energy for the U.S. electricity consumption.¹¹ The same study also estimates 5 to 7 billion square meter of the glass surface in the U.S., and there will be an additional 100 GW if TPV with 15% PCE were applied as window and skylight to the glass surface.¹¹ Using TPV in window application could manage energy demand of building by absorption of near-infrared radiation, which is felt as heat. The function of heat management by semi-transparent PV has been studied and has resulted in saving energy from air conditioning.^{110–113} According to the Commercial Buildings Energy Consumption Survey (CBECS) from the U.S. Energy Information Administration (EIA), electricity use is higher in the summer due to the cooling and ventilation while the use of natural gas is mainly for heating during winter.¹¹⁴ TPV in window application can mitigate these patterns of energy use since electricity generation in summer will be higher. Natural gas use could also be saved by internal reflection of longer wavelength radiation related to heat energy in a particular area with a mild climate.

The use of semi-transparent PV for heat management has been evaluated based on annual electricity cost¹⁸ and building energy demand.^{18,111,112,115} According to previous studies, semi-transparent PV application helps to reduce cooling energy demand in a warm climate but increases heating energy demand in cold climate because less solar energy radiates into the building. Most studies assess silicon-based solar cell such as amorphous silicon PV^{18,111,112,115}, micromorph silicon PV¹¹¹, and only one paper considers organic PV¹¹² with limited information regarding optical properties (60% absorption and 30 % transmittance) and PV efficiency (3% PCE). All PV studied in previous studies are semi-transparent PV that have low visible transmittance of around 10 to 20%.

There is only one experimental study that demonstrates the benefit of semi-transparent PV¹¹⁵, whereas other studies use simulation software of building energy demand, such as EnergyPlus managed by the National Renewable Energy Laboratory (NREL). A study considers the thermal balance of PV application in a building energy system that accounts for solar radiation transformed into electricity¹¹², while others use PV optical properties such as window properties in the simulation. All papers do not consider the lifetime of the window and PV so that analysis is based on annual energy demand. Similar to the window application of PV, there is an LCA study applying PV as adaptive shading.¹¹⁶ The concept of the PV application is not as a window, but as the shading application, and it shows that such application reduces cooling and heating energy

demand. The LCA is based on 20 years' application of adaptive shading by PV application, and the system boundary includes PV, balance of systems (BOS), building operation, and disposal. The study assesses GWP, and other six major ReCiPe midpoint indicators (TAP, FEP, HTP, MDP, and POFP).

This chapter discusses the energy demand of commercial building-applied TPV and reports the building energy simulation data of medium office from reference building structure developed by U.S. Department of Energy (DOE) by using EnergyPlus. The results of building energy demand will be used as background data for assessing net energy benefit (NEB) of TPV application for 20 years' lifetime through LCA.

5.2 Method

The goal of this task is to assess building energy demand for evaluating net energy benefit (NEB) of transparent organic photovoltaics (TPV) in window application based on the simulation of building energy demand. The overall framework of this study includes material production, module manufacturing, and module use as illustrated in Figure 5-1(a), but the contribution of this chapter is limited to the use of TPV module as a window.

TPV are fabricated on glass substrates that are pre-coated with 120 nm thick of indium-tinoxide (ITO) as a function of the transparent anode. Molybdenum(VI) oxide (MoO₃, 10 nm), chloroaluminum phthalocyanine (ClAlPc, 15 nm), fullerene (C₆₀, 30 nm), and bathocuproine (BCP, 7.5 nm) are sequentially deposited through thermal evaporation. Then indium tin oxide (ITO, 100 nm) cathode is rf-sputtered directly onto the organic layer.³⁰ Since the ClAlPc-based device has high-visible transparency of > 55%, it could substitute the original function of windows. The busbar and silver grid are assumed to be applied in the system for expanding laboratory scale data of TPV to real application. Total coverage of the busbar and grid is 11% of the window area with 3 nm thick titanium and 70 nm thick silver based on previous literature of transparent electrodes.¹¹⁷



Figure 5-1. System diagram shows: (a) scope of simulations in building system simulation and photovoltaic simulation for TPV application in window, (b) system boundaries of life cycle assessment including material production and module manufacturing, and module use of TPV as windows and skylights, (c) scenarios of TPV application. **baseline** window composites of 3mm glass and 13 mm air gap; **glass TPV** that contains the active layer of TPV represents window replacement; **Plastic TPV** encapsulated with PET film is a scenario of retrofitting window.

Clear double pane window is used for the baseline simulation for window or skylight structure¹⁸, and Figure 5-1(b) illustrates the baseline and the two alternatives considered for TPV, the first case with TPV located inside the double pane window and the second case with TPV encapsulated with PET film. Since TPV is based on organic material, it could degrade under

oxygen or moisture conditions.¹¹⁸ Therefore, TPV is either deposited inside of the two panes of the window (glass TPV) or encapsulated with the film (plastic TPV) as shown in Figure 5-1(c).

5.2.1 Selection of study area

The selected cities are Detroit, MI, Los Angeles, CA, Phoenix, AZ, and Honolulu, HI, since they represent a range of solar insolation conditions, climate zones, energy cost and environmental impact of electricity production. These factors will influence the benefit of both PV electricity production and building energy balance. Figure 5-2 shows the climate conditions of the cites selected as study areas.

Figure 5-2. Annual climate conditions (global horizontal irradiance, relative humidity, and dry bulb temperature) of study areas

Global horizontal irradiance (GHI) is the total irradiance from the sun that is the sum of direct irradiance and diffuse horizontal irradiance. Honolulu has the highest GHI, followed by Pheonix, then Los Angeles, and Detroit. The dry bulb temperature varies more in Detroit and Pheonix while it does not vary much in the other locations. The relative humidity is relatively higher in the three cities of Detroit, Los Angeles and Honolulu, while Pheonix is dry, especially in summer.

		Detroit, MI	Los Angeles, CA	Phoenix, AZ	Honolulu, HI
	Latitude	42.33	33.90	33.44	21.31
Grid	eGrid region ¹⁰⁶	RFCM	CAMX	AZNM	HIOA
Climate zone	IECC 2015 119	5A	3C	2B	1A
	Thermal Criteria ¹²⁰	3000 < HDD $18^{\circ}C \le 4000$	HDD 18°C ≤ 2000	3500 < CDD $10^{\circ}C \le 5000$	5000 < CDD 10°C
Insolation	Fixed tilt(deg.) 0/90, (Annual average, kWh/m ² /day) ¹²¹	3.8/2.9	4.9/3.5	5.7/4.0	5.4/2.9

Figure 5-3. Summary of study areas based on the electricity grid and climate zone. eGrid is a source of data on the environmental characteristics of electric power generated in the U.S. Thermal criteria classify IECC climate zone based on degree days.

Figure 5-3 summarizes climate zone, emissions & Generation Resource Integrated Database (eGrid) sub-regions in 2016¹⁰⁶, and solar insolation.¹²¹ The climate zone from 1 to 8 is

determined by temperature variations represented as heating degree days (HDD) and cooling degree days (CDD)¹²⁰, but zone 8 is excluded in Figure 5-3 since it is only for Alaska which is not included in the study area selection. The degree days are a measurement of the demand for energy needed to heat or cool a building.¹²² The climate zones are then divided into moist (A), dry (B), and marine (C) subregions based on mean temperature and precipitation.¹²⁰

5.2.2 Simulation for Building Energy Demand and Electricity Production

EnergyPlus and the DOE reference buildings are used to simulate building energy demand. EnergyPlus is an energy analysis and thermal load simulation program and calculates the heating and cooling loads to maintain the setpoints of thermal control through heating, ventilation, air conditioning (HVAC) system.¹²³ It calculates the energy demand of the buildings from the heat and mass balance and building system simulations. Thermal properties of building exteriors, such as envelopes and windows (Table 5-2), are used to calculate the heat and mass balance, and the energy demand of building based on electricity and natural gas is determined based on the specified size and type of HVAC system (Table 5-1).¹²⁴

Another simulation software used to calculate electricity production from TPV in window application is RETScreen. RETScreen is a clean energy management software for energy efficiency and renewable energy. The performance of a photovoltaic system is influenced by design elements, such as the amount of solar radiation on PV, the type and area of PV, its power conversion efficiency, and its slope and azimuth (physical orientation). The power conversion efficiency of TPV is assumed to be 10% as considered by the previous study,¹¹ and the other details of electricity production simulations, such as the slope of skylight and PV areas, are summarized in Table 5-1.

The simulation method for building energy demand follows previous work and uses default values for building internal loading.¹⁸ Building geometry and heating sources are modified from the DOE reference building of post-1980 construction¹²⁴ through SkechUp Pro 2017 to obtain the desired window to wall ratio (WWR) or skylight to roof ratio (SRR) (Table 5-1). The thermal characteristics of building envelop are listed in Table 5-2. The glazing system is assumed to be double-pane glazing system as shown in Figure 5-1(c).

	Medium	office	Small office		
Building geometry	33 m	50 m	Angle of skylight (roof): 21°		
DV application	Building orien	ation: south	Building orientati	on: south	
HVAC System type	Variable Air Volume (VAV) with re-heat		Packaged single-zone (PSZ)		
Heat ¹²⁴	1	Natural gas heating and	l electric heating coil		
Cooling ¹²⁴		Direct expansion	n cooling coil		
Window to wall ratio or skylight to roof ratio (%)	67.8		14.9		
Window area (m ²)	938.2 (S 1340.3 (S	938.2 (SEW) / 1340.3 (SEWN) 81.0 (S)			
	S1: OPV in window	S2: OPV in PET film	S1: OPV in window	S2: OPV in PET film	
PV area (m²)	SEW: 835.1 SEWN: 1193.0 Subarea S and N: 357.9 E and W: 238.6	SEW: 799.0 SEWN: 1141.4 Subarea S and N: 342.4 E and W: 228 3	72.1 (S)	68.9 (S)	

Table 5-1. Simulation inputs for building energy demand and TPV application

The mid-size office reference building is modified to a maximized WWR and used to study window application. TPVs are applied to windows in all directions. Since TPV application to the north could result in lack of solar radiation passing through building inside and thus increase overall energy demand of the building, a simulation case without the north window (SEW versus SEWN) is considered. The small-size office for skylight application is also modified to incorporate a skylight onto the south roof and attic space is integrated to the office area as shown Table 5-1 (building geometry). In the EnergyPlus simulation, the azimuth orientation for both types of building is assumed to be south, and the weather data for study locations is imported from EnergyPlus website to obtain climate data and schedule of building operation. ¹²⁵

Study Area		Envelop thermal transmittance (U-factor, W/m ² .K)				
	Climate	Roof		Wall		
	Zone	Medium office ¹²⁴	Medium office ¹²⁴ Small office Medium office		¹²⁴ Small office ¹²⁴	
		Insulation entirely	Attic and other	Steel frame Wall	Mass Wall	
		above deck	Attic and other	Steel Hume Wan	iviuss vvun	
Detroit	5A	0.30	0.31	0.47	0.57	
Los Angeles	3C	0.57	0.63	1.25	5.68	
Phoenix	2B	0.26	0.27	1.36	2.33	
Honolulu	1A	0.42	0.46	5.68	5.68	

Table 5-2. Thermal properties of envelope used for DOE reference building in each study area

In EnergyPlus simulation, three spectral properties of a window which are transmittance, front reflectance, and back reflectance, are required as input parameters to calculate the building energy demand. The TPV in window application transmits visible radiation and absorbs near-infrared radiation to generate electricity. The electricity generation by TPV in window application is not currently supported in EnergyPlus, and the absorbed radiation is considered as heat and emitted indoors. Therefore, the absorbed radiation that could generate electricity causes an extra heat flowing into the window and thus results in an overestimation of required cooling energy. To solve this issue, a previous study suggested adding an additional reflectance on the front surface of the outside glass followed by energy conversion efficiency of solar cell.¹¹² Thus, an additional reflectance is added as a function of wavelength according to external quantum efficiency (EQE)

of TPV (Equation 5-1). EQE is defined as the ratio of the number of electron output by the solar cell to the incident photon of a given wavelength.¹²⁶ Therefore, the additional reflectance avoids radiation in EnergyPlus simulation which corresponds to the same amount of energy converted by TPV, and the modified optical properties for EnergyPlus simulation is shown in Figure 5-4.

$$R_{EP}(\lambda) = R(\lambda) + (1 - (A_{TPV \text{ layer}}(\lambda) + EQE(\lambda))$$
(5-1)

Figure 5-4. Optical properties of transparent photovoltaic as input of EnergyPlus simulation: (a) front illumination (b) back illumination

Heating sources used in DOE reference building are mainly electricity and natural gas (Table 4-2), but the geographical characteristics of the sources is not considered in each reference building model. In LCA, the impacts from the source of heating are critical since there is different environmental impacts between electricity and natural gas based on the study areas. Therefore, the simulation considers an additional modification to reflect the actual heating source based on the CBECS database from EIA. The selected number of buildings for each study area and their major heating source are summarized in Table 5-3, and the portion of major heating source is allocated

to the heating energy demand in EnergyPlus simulation by modifying the energy efficiency of a furnace in HVAC system.

	Data source					
Heating Source	(House ¹²⁷				
	Detroit	Los Angeles	Phoenix	Honolulu		
# of building (n)	95	103	12	312,625		
Electricity	7.4%	46.6%	57.1%	3.5%		
Natural gas	91.6%	46.6%	35.7%	33.5%		
Others	1.0%	6.8%	7.2%	63.0%		

Table 5-3. Heating source of the office building in study area assessed from CBECS database

5.3 Result and Discussion

5.3.1 Simulation for Building Energy Demand and Photovoltaic

Two different buildings models are used as illustrated and described in Table 4-1. The medium office model is used for the window application while the small office model is used for skylight application. The medium office building has 68% WWR, and the small office has 15 % SRR where TPV are applied as the window and skylight respectively. For HVAC system of both buildings, a heating appliance is assumed to use both natural gas and electricity to account for regional differences while air conditioning equipment uses only electricity as shown in Table 5-3.

Figure 5-5 summarizes the annual building energy demand and the electricity production for TPV for both window and skylight application. For the climate dependence of energy demand, most of the energy demand in Detroit is from heating while the other three locations require cooling demand dominantly. The energy demand from fans is not sensitive to climate effect because both heating and cooling need to be distributed all over the building. In terms of building type, there is more energy demand in medium office because of larger size compared to the small office, whereas the trends of heating and cooling demands show a discrepancy. Medium office requires more heating than the small office, and it is presumed to be because of lower heat transfer efficiency from the larger building size and HVAC system. Meanwhile, the portion of fan energy demand is larger in the small office. The loading of fan is increased because the attic space is integrated with the office area to simulate effects of TPV skylight regarding energy demand of HVAC system as mentioned in the Methods section.

Figure 5-5. Monthly energy demand for baseline building and electricity production by TPV application. Baseline building is installed double pane window, and power conversion efficiency of TPV for electricity production is 10 %.

The dotted line with square symbols for electricity production represents the SEWN application compared to the SEW as shown as a solid line with triangle symbols in Figure 5-5. Los Angeles, Phoenix, and Honolulu have a similar trend of energy demand with dominant cooling demand, but the electricity production from TPV is similar between Los Angeles and Honolulu

and higher in Phoenix because of the latitude. The energy production in Detroit is significantly lower during the winter, but the addition of TPV on the north side increases electricity production during the summer.

5.3.2 Assessment of Building Energy Demand by TPV Application

The annual energy saving for TPV application in windows is shown in Figure 5-6(a). Both glass and plastic TPV reduce the energy demand from electricity and natural gas use. Depending on the study area, the portion of energy saving varies due to climate and the source of heating and cooling equipment. In Detroit, annual energy saving is lower than other cities because there is only a smaller opportunity for electricity saving by TPV application because of the cold climate condition that consumes less electricity for air conditioning in summer. However, natural gas saving in winter allows energy saving in Detroit to be comparable to other cities. It implies an internal heat reflection of TPV window could save heating energy demand.

Figure 5-6. Annual energy saving of TPV application in window for medium office: (a) glass TPV (b) plastic TPV, with application of TPV in SEWN (south, east, west, and north) direction

For plastic TPV, up to 4% of electricity saving is reduced due to the placement of TPV inside the building as shown in Figure 5-6 (b). When TPV is placed inside the building, the portion of solar radiation that is absorbed by TPV but not converted to electricity is re-emitted into the building, and this results in more cooling energy demand compared to glass TPV. In Figure 5-6 (a) and (b), the decrement of electricity saving in warmer climates (Los Angeles, Phoenix, and Honolulu) is lower than the decrement in cold climate (Detroit). Overall, energy saving from plastic TPV application is still more than 10% of total energy consumption.

Figure 5-7. Annual energy saving of TPV application in skylight for small office (a) glass TPV (b) plastic TPV

For the skylight application of TPV as shown in Figure 5-7, electricity demand is reduced in all locations, but natural gas consumption increases in Detroit. The difference in electricity saving between the glass and plastic TPV applications differs by about 5%. Although net energy saving is positive, the increased use of natural gas lowers the benefit of skylight TPV in Detroit. It shows the trade-off between PV electricity generation and building energy saving. ASHRAE standard 90.1, The Energy Standard For Buildings Except Low-Rise Residential Building, recommends that the SRR be less than 5 % because of energy conservation efficiency.¹²⁸ The ratio is intended to maximize electricity production for this case study, but care needs to be taken under cold climate to make sure both energy saving and electricity generation are considered to optimize SRR.

Chapter 6 TPV Application in Urban Area: Urban Heat Island Effect and Its Consequential Environmental Impact on Building Sector

This work is an extension from the previous chapter to assess the specific advantage of TPV in an urban area. The same building model and TPV are extended to an urban weather simulation. A key point of this chapter is that the energy saving from TPV application contributes to urban climate improvement by reducing heat from the HVAC wasted to the urban energy system. Meanwhile, there is additional energy saving that could be achieved by TPV application under the elevated temperature due to human activities including building in an urban area compared to a rural application of TPV. It suggests that TPV application in an urban area does not create adverse impacts. Reduction of waste heat from buildings would be considered a net environmental benefit although it is not directly quantified in an LCA study.

6.1 Introduction

Currently, 54 % of the population lives in urban areas in the world, and it will increase to 66% by 2050.¹²⁹ Over 50% of the total energy consumption is from the maintenance and operation of building in high-income cities.⁸ BIPV could provide renewable electricity with minimal land use.

As discussed in the previous chapter, transparent photovoltaics (TPV) allow to substitute building window and perform similarly to heat management film also known as low-e film. With TPV application in the medium office, about 10% of the internal energy demand could be saved from HVAC operation. Energy use in an urban area, such as from building operation, is also related to microclimate through the urban energy balance. Total energy gain within the urban area is the sum of waste heat from anthropogenic activities and solar radiation. The excessive waste heat
causes urban heat island effect (UHI), which increase the urban temperature by around 10°C to 15°C during daytime.¹³⁰ UHI can potentially affect communities by increasing energy demand during summertime peak, air conditioning costs, air pollution, greenhouse gas emissions, etc.²⁰ The building performance can also be affected by UHI which would further increase the cooling energy demand by up to 15% under mid-latitude climate in the U.S. because of the warmer temperature.¹³¹ Due to this reason, building standards such as ASHRAE Standard 90.1 could be inefficient since thermal insulation requirements of the standards underestimate UHI effect.¹³¹ TPV application reduces cooling energy demand by absorbing NIR so that the net energy benefit of building under urban climate could have even more benefits than what was reported in Chapter 4.

To assess local climate, a simulation coupling urban climate and anthropogenic activities is essential. Urban weather generator (UWG) was developed by Massachusetts Institute of Technology in 2011. The function of the model is to simulate urban climate from rural climate by incorporating urban characteristics. The model can be used alone for assessment of local climate or also be integrated into building energy simulations.¹³² Further effort on developing building energy model in UWG was achieved in 2016 by including the DOE commercial building data.¹³³ The data includes sixteen different building types with three construction eras (pre-1980 construction, post-1980 construction, and new construction). In term of energy use, the model takes into account operation schedules for lighting, plugged-in electrical equipment, occupancy, and gas equipment.¹³³ This work assesses the UHI effect by TPV application in the urban area by using UWG and simulates building energy demand from EnergyPlus with the pre-developed building structure of medium office from the previous chapter.

6.2 Method

The goal of this task is to assess the simultaneous impacts of UHI effect and energy benefit by TPV application in an urban area. The overall framework of the urban weather simulation and the scenario of building simulation is illustrated in Figure 6-1. UWG models the energy balance between elements representing particular urban characteristics, heat flux from human activity, solar radiation, and heat exchange from a rural area to an urban area.^{132,133} The building geometry and TPV application scenario are integrated into the model according to Table 5-1 and Figure 5-1(c).



Figure 6-1. Description of Urban weather Generator (UWG) model,¹³² and adoption of DOE reference building applied TPV in window (model mechanics are adapted from http://urbanmicroclimate.scripts.mit.edu). Reference weather data from the weather station is simulated to generate urban weather data by reflecting urban characteristics including land use, wind speed, a reflection of solar radiation, traffic, and waste heat from the building.

Selected city of this case study is Los Angeles. It represents a realistic case of UHI²², and California aims to add additional renewables to cover the energy demand from electricity grid by 2035.¹⁰⁶ The assessment periods are in August and December to assess the impacts from heating and cooling energy demand. The input parameters for UWG include urban characteristics summarized in Table 6-1. Except for the building type, other parameters use the default value representing characteristics of a large city.¹³² The density of buildings in UWG are classified into three categories: high-dense, mid-dense, and low-dense. The density determines the number of building per estimated floor area. The high-dense scenario is selected to assess impacts from TPV application to the windows of 48 buildings. From Chapter 5, clear window and glass TPV application are selected to compare impact in urban and rural areas. The thermal parameters (Ufactor and SHGC) for the glass TPV and clear window are calculated from EnergyPlus and imported as input parameters for UWG simulation (Table 6-1). The rural temperature profile is obtained from Typical Meteorological Year 2 (TMY2), which is a data set derived from the 1961-1990 National Solar Radiation Data Base, at Los Angeles International Airport, and input into the UWG simulation.

	Urban Characteristics	Value	Unit
Microclimate	Urban Boundary Layer Height - Day	1000	m
Parameters ¹³³	Urban Boundary Layer Height - Night	50	m
	Average Building Height	12	m
Urban	Building Density	0.54	-
Characteristics ¹³³ Vertical to Horizontal Ratio		0.48	-
	Road Albedo	0.08	
Duilding Type	Medium office with glass TPV application	2.62/0.60	U-factor/SHGC
bunding Type	Medium office with clear double pane window	2.74/0.76	U-factor/SHGC
Vagatation	Urban Area Veg. Coverage	0.19	-
Vegetation Dependence ¹³³	Latent Fraction of Tree	0.5	-
rarameters	Rural Road Vegetation Coverage	0.8	-

Table 6-1. Urban Weather Generator Parameters as the inputs of simulation for generating urban temperature profiles

From the original UWG model, calculation of the solar heat gain to buildings is modified to reflect electricity generation by TPV. It is similar to the modification described in Chapter 5 that avoided a certain amount of solar radiation based on external quantum efficiency. In the UWG model, TPV efficiency of 10% is assumed to be excluded in the simulation of building energy balance by adjusting SHGC.

6.3 Result and Discussion

6.3.1 Comparison of Urban and Rural Temperature

The temperature variation in Los Angeles in August based on TMY2 (rural) and the simulation result (urban) is shown in Figure 6-2. During the summer season, compared to the urban temperature, the rural temperature is lower by about 3°C at solar noon (~12:30 pm) and less than 1°C at daybreak. TPV application does not change the overall temperature, but small changes are observed at the peak of the day. The urban air temperature with the TPV application is slightly lower than the reference glass window, and it suggests that solar radiation harvested for electricity generation contributes to the mitigation of UHI.



Figure 6-2. Temperature variation in Los Angeles based on rural scenario (green dot line) and urban: baseline (solid black line) and urban: TPV (red dash line) scenarios during the summer season for a month (Aug.)

During the winter season, the temperature difference between the rural and urban climate varies more than during the summer season. The daily maximum temperature in the rural location is similar to the urban location while minimum temperature is lower by up to 5°C as shown in Figure 6-3. The trends in temperature difference are typical of UHI characteristic during winter, since built surface absorbs heat during daytime and releases heat in the night. Therefore, the temperature in the urban location is higher than the rural location.¹³⁴ The urban climate change for the TPV application is found to be negligible.



Figure 6-3. Temperature variation in Los Angeles based on rural scenario (green dot line) to urban: baseline (solid black line) and urban: TPV (red dash line) scenarios during the winter season for a month (Dec.)

6.3.2 UHI Intensity in Urban Area and Waste Heat from HVAC System

Based on the temperature variation, UHI intensity is calculated and shown in Figure 6-4. The calculation of UHI intensity follows the same methods from the previous work and is determined as the averaged air temperature difference between urban and rural areas.¹³⁵ In Figure 6-4, area above the line indicating 0 shows the existence of UHI effect. In the summer season, UHI occurs during the whole day, and the most intense time is at solar noon when the sun is at the highest position (Figure 6-4). There is an absence of UHI before noon in winter, and most intense UHI occurs before sunrise. In both seasons, the impact from TPV application on UHI effect is found to be negligible. Research reports show that rooftop solar application in Los Angeles shows no adverse impacts on air temperature and UHI effect, and there is a potential benefit of cooling air temperature by up to 0.2 °C.²² The reported result is similar to results for TPV in window application.



Figure 6-4. Urban heat island intensity in Los Angeles during (a) summer season (Aug.) and (b) winter season (Dec.)

In the UWG model, the urban temperature is calculated from rural temperature by additional sensible heat flux generated in the urban area as shown in equation 6-1.¹³³

$$H_{urb} = Q_{sens,road} + Q_{traffic} + Q_{veg} + \sum_{i=1}^{N} (Q_{sens,wall,i} + Q_{sens,window,i} + Q_{vent\&infil,i} + Q_{waste,i} + Q_{roof,i})$$
(6-1)

Where,

Hurb: urban heat flux

Qsens, road: sensible heat from road, per urban area

Qtraffic: Sensible heat flux from non-building anthropogenic heat, per urban area

Qveg: Sensible heat flux from vegetation, per urban area

Qsens, wall: Sensible heat flux from wall, per urban area

Qsens, window: Sensible heat flux from window, per urban area

Qsens, vent&infil: Sensible heat flux from ventilation/infiltration, per urban area

Q_{sens, waste}: Sensible heat flux from waste heat (including. HVAC, gas), per urban area Q_{sens, roof}: Sensible heat flux from roof, per urban area

N: building types simulated

With equation 6-1, the potential of UHI mitigation by TPV application could be explained. TPV application reduces the energy demand of HVAC including cooling and heating. Figure 6-6 illustrates the monthly average waste heat from HVAC per urban area. In summer, there is more waste heat because of more cooling energy demand in the daytime. Comparing clear window (baseline) to TPV application, the reduction of waste heat is higher in the daytime while there is no difference in waste heat after sunset. The same trend is shown in winter, but the temporal patterns and magnitude of waste heat are different due to climate. Therefore, the concept of waste heat helps to explain the UHI intensity graph (Figure 6-4) showing a little reduction of urban temperature in summer. In this case study, the medium office is only simulated for TPV application in Los Angeles, and it shows that the reduction of waste heat is not enough to lower the urban temperature. However, a comprehensive assessment of UHI mitigation can be achieved if the realistic data regarding type and number of buildings are allowed.



Figure 6-5. Emission of waste heat from HVAC to the urban area in (a) summer season (Aug.) (b) winter season (Dec.)

6.3.3 Energy Saving by TPV Application in Rural and Urban Areas

TPV application in the urban area compared to rural location has more benefits due to warmer temperature caused by UHI. Figure 6-8 shows the monthly energy saving in GJ by TPV application in the rural and urban area. The building energy demand of a single medium office building with TPV application is simulated by using the climate data from both the Los Angeles International Airport (rural characteristics) and the UWG simulation (urban characteristics). There is electricity saving in both summer and winter of up to 2 GJ, from air conditioning and fan operations. Since the climate in the urban area is warmer than rural climate during summer as shown in Figure 6-2, there is more saving during the summer. The natural gas saving is negligible because of climate and schedule of heating operation based on the regular working hours for a commercial building.



Figure 6-6. Comparison of monthly energy saving for TPV application in window for urban and rural scenarios in Los Angeles during summer (Aug.) and winter (Dec.) seasons

In this chapter, the TPV application in the urban area is discussed with microclimate and building energy demand simulations. TPV application shows no adverse impacts on air temperature, and there is a potential benefit of cooling the urban air temperature because of the reduced waste heat. It is contrary to a previous study showing the UHI effect induced by a large solar power plant in Arizona.¹³⁶ The absorbed solar radiation that is converted to electricity reduces the building energy demand so that the overall energy balance in an urban area results in cooling the air temperature. The building consumes more energy under UHI effect. However, the consumption can be reduced with TPV application by up to 2 GJ/month in the urban area compared to the application in the rural location.

Chapter 7 Conclusions

OPV material process is improved by using the iterative evaluation method developed in this work which is based on green chemistry and life cycle approach. The material produced from the new process reduces the overall impact of OPV device, especially TPV made of ClAlPc. The application for window reduces the energy demand of building and waste heat from HVAC system, and shows potential for urban climate improvement. These benefits would be considered as net environmental benefit of TPV application and could be quantified with a projection of overall impacts through life cycle assessment.

In Chapter 2, synthesis pathways of ClAlPc are established by applying green chemistry principles and metrics. The work identifies a greener pathway for ClAlPc synthesis by starting from phthalonitrile as the precursor. The atom economy of phthalonitrile pathway is about 30% higher than that of phthalic anhydride pathway. The phthalic anhydride pathway has a theoretical yield of 60%, however, because of byproduct generation during intermediate step, the actual yield lowers to 25%. The application of microwave reactor to the phthalonitrile pathway reduces reaction time from six hours to 40 minutes that suggests better energy efficiency and yield.

Chapter 3 evaluates the performance of OPV devices from ClAlPc synthesized from different processes. Two precursors of ClAlPc, phthalonitrile and phthalic anhydride, are studied to evaluate the tradeoff between material purity, device efficiency, and material cost. The results show that UV-vis and mass spectra of ClAlPc from phthalonitrile and phthalic anhydride processes are in agreement with the reference material. The best device from phthalonitrile sample shows similar energy conversion efficiency with the reference device although the fabrication yield is low. For phthalic anhydride samples, all devices work, but have low energy conversion efficiency

due to impurities from urea decomposition. The results of Chapter 2 and 3 are used as baseline of evaluation method developed in Chapter 4.

A new methodology is developed by combining LCA and green chemistry metrics to evaluate OPV material processes. Through the experimental work basis of Chapter 2, the hotspot of baseline process of ClAlPc was identified as toxic solvent use and high energy demand. Applying the iterative evaluation method could solve issues related to each intermediate process regarding environmental, cost, and chemical hazards. Finally, a new process using diethylene glycol under microwave reactor is developed to produce ClAlPc which reduces the environmental impacts by 3%, the cost by 9% and chemicals hazard by 23% simultaneously compared to the baseline process, while producing high-quality material that can be used for OPV application.

The application of TPV made of CIAIPc is assessed to evaluate the energy benefit of power generating window. The energy benefit is a key aspect of TPV application, and it will be used for use phase input data in LCA for net environmental benefit of TPV application for windows over its lifetime. The building energy demand simulation of the medium office and the small office identifies energy benefit in locations representing different climates and environmental impacts from the electricity grid. The reduction of cooling energy demand in all study location and type of applications results in annual energy saving while the natural gas demand in Detroit shows contrary trends by application type. The window application saves natural gas while skylight application consumes more natural gas due to heat loss from the skylight. However, overall net energy benefit is notable for both applications in term of energy saving and PV electricity generation. The energy saving from HVAC by TPV application in windows is seen under cold climate condition as well, even though the cold climate condition, such as Detroit, requires higher heating energy demand.

The last part of the work is related to Chapter 5, but the application considers not only location but also urban impact as well. TPV application for a window in an urban area could result in additional benefits in terms of saving land use and reducing waste heat contributing to UHI effect. Also, the energy saving of the TPV application in the urban area is higher than the application in the rural area up to 2 GJ per month. The overall result implies that TPV window in the urban area reduces energy demand and has additional potential for deployment of renewable energy devices and mitigation of UHI effect, leading towards urban sustainability.

TPV application in window studied in chapter 5 and chapter 6 provides motivating research questions for future study. Regarding cooling energy demand, the absorption profile of TPV plays an essential role since NIR absorption reduces energy demand. Regarding the TPV absorption, the next step in this subject is to study different types of TPV that harvest electricity from different regions of the solar spectrum. The requirement of thermal transmittance of a building is recommended by climate conditions, to save energy in both cooling and heating, and thus there could be optimal configurations of TPV specific to climate conditions. The applications of TPV in window are only limited to office buildings in chapter 4 and chapter 5. In chapter 5, waste heat from HVAC could be reduced by TPV application since TPV application aids to reduce energy demand from HVAC used in the office buildings. HVAC systems vary depending on the purpose and type of building. Therefore, the benefit of TPV application from the reduction of waste heat from HVAC will differ. Various types of building exist in an urban area, and application of TPV to each building will result in benefit of differing magnitude and temporal patterns. Another study for TPV application will be to study TPV in windows of all the different DOE commercial reference buildings to assess the patterns of energy saving and reduction of waste heat from HVAC. APPENDIX

APPENDIX

1. Summary of Evaluation Methods for Chemicals

In Table A1, 19 studies regarding evaluation method for chemical process are summarized by their principles, method, and application area, and evaluation criteria. Most studies cover environmental impact while either LCA or own metrics partially cover health and cost impacts. The purpose of application widely covers from lab scale experiment to industrial application in addition to educational purpose and synthesis plan. The methods for lab scale experiment are based on point system or own metrics^{137–139} for simplicity. Screening methods aim to develop chemical process in early stage so that wide evaluation criteria are considered depending on own purpose of application while the system boundary of evaluation is generally limited in the process (gate to gate) similar to the lab scale evaluation. Among the studies considering green chemistry principles, only few studies include cost analysis ^{137,140–142}, and it is presumed due to the reason that the 12 Green Chemistry principles do not explicitly include the economic aspect. The evaluation approach aims to fine chemicals process that involve complex organic molecules and requires high purity. Therefore, it is important to include our system boundary from cradle to gate so that the evaluation method could identify and prevent unintended impacts associated with environmental, cost and chemical hazard from upstream process with iterative approach.

Paper	Principle	Method	Purpose of Application	Evaluation criteria	Ref.
Our method	LCA; Green chemistry	Iterative approach based on streamlined LCA and green chemistry metrics	Screening method for fine chemicals	CED; Global warming potential; water demand; chemical and electrical cost; E- factor NFPA 704	-
Koller et al., 2000	EHS (Environmental, Health, and Safety)	Mass balance	Screening method for fine chemicals	Safety; Health; Environment	143
Saling et al., 2002 (Eco-efficiency, BASF)	LCA	LCA (Cradle to grave) Cost analysis	Industrial application for manufacturing	CED; Emission; Material depletion; Risk; Toxicity; cost	64
Eissen and Metzger, 2002 (EATOS)	Green chemistry	Mass balance	Screening method	Mass index; E-factor	144
Gonzalez and Smith, 2003 (GREENSCOPE, EPA)	Green chemistry	Own metrics based on process	Bench to process level application for decision making	Efficiency (material); Environment; Energy; Economics	140
Aken et al., 2006 (EcoScale)	Green Chemistry	Penalty points given in evaluation criteria	Lab scale evaluation	Yield; Cost; Safety; Technical steps (reaction, work-up, purification)	137
Curzons et al., 2007 (FLASC, GSK)	LCA; EHS	LCA (Cradle to gate) Hierarchical Cluster Analysis (HCA) Principle Component Analysis (PCA)	Industrial application for manufacturing	Energy; GHGs; Fossil fuel; Acidification Eutrophication; photochemical ozone creation potential; Total organic carbon	65
Ribeiro et al., 2010 (Green Star)	Green chemistry	Score given in evaluation criteria	Lab scale evaluation	Score for each 12 Green chemistry principles	138
Mercer et al., 2012 (Multivariate Method)	Green chemistry; LCA	Own metrics based on chemical reaction	Lab scale evaluation for education purpose	Acidification; Ozone depletion; Smog formation; Global warming; Human toxicity; Persistence; Bioaccumulation; Abiotic Depletion	139
Andraos, 2012 (Benign index, CareerChem)	Green Chemistry	Own metric (BI) based on process	Screening method for chemical reaction and synthesis plan	Acidification-basification; Ozone depletion; Smog formation; Global warming; Inhalation toxicity; Ingestion toxicity; Bioconcentration; Abiotic resource	145
Russell and Shiang, 2012 (DCSFT)	LCA; Questions	Score based on justification	Planning for industrial application	Economic; Social; Resource use; Water; Green House Gases; Organization	66
Andraos, 2013 (Safety/Hazard Indices, CareerChem)	Safety; Hazard	Own metric (SHI) based on chemical properties	Screening method for chemical reaction and synthesis plan	Flammability; corrosiveness (gas and liquid); oxygen balance; hydrogen generation; explosive vapor; explosive strength; impact sensitivity; risk phrase; occupational exposure limit; dermal absorption; skin dose	146
McElroy et al., 2015 (CHEM21)	Green chemistry; LCA; EHS	Score based on GHS and chemical properties	Methodology for bench scale to manufacturing	Evaluation criteria considering sustainability varies up to Each stage	142

Table A1. Summary of existing method for fine chemical evaluation

Table A1 (cont'd)

Eckelman, 2016	Green Chemistry LCA	LCA (Cradle to gate) Own metric (inherent toxicity, i*)	Screening method for inherent chemical toxicity	Ingestion non-cancer and cancer; inhalation non-cancer and cancer	147
Alder et al., 2016 (GSK's solvent sustainability guide)	Green Chemistry; LCA; EHS	LCA (Cradle to gate) Score based on GHS and chemical properties	Solvent selection guide	Boiling point; incineration; recycling; biotreatment; VOC emission; aquatic impact; air impact; health hazard; exposure potential; safety; LCA	84
Mercado et al., 2016 (GREENSCOPE extension)	Green Chemistry; EHS	Synergistic approach of WAR Algorithm, GREENSCOPE. and SustainPro tools	Industrial application for sustainability assessment	GREENSCOPE: Efficiency (material); Environment; Energy; Economics WAR Algorithm: ozone depletion, global warming, smog formation, acid rain formation, human toxicity, ecotoxicity SustainPro: energy consumption, waste of material, costs, capacities, time, and efficiency	141
Smith et al., 2017	Green Chemistry; LCA	LCI (gate to gate)	Life cycle inventory analysis of chemical manufacturing	Emission; energy; mass	148
Kreuder et al., 2017 (CGM, MilliporeSigma)	Green chemistry	Green Chemistry metrics; own metrics	Screening method for industrial chemicals	Resource use; Energy efficiency; Human and environmental hazard	149
Song et al., 2017	LCA	QSAR; Machine learning	Screening method	CED; Acidification; GHGs; Eco- indicator 99; Human health; Ecosystem	150
iSUSTAIN™ Green Chemistry Index v2.0	Green Chemistry	Green Chemistry metrics; own metrics;	Industrial application for sustainability assessment	Green chemistry index within 12 Green Chemistry principles	151

2. Detailed Methodology

2.1. ClAlPc Synthesis

Baseline and five alternative processes to demonstrate the iterative process based on evaluation of sustainability are introduced in the main chapter (Table 1-1). However, detailed information regarding to upstream process are omitted so that Table A2-A5 illustrates the material flow and resource use within system boundary. White boxes are new inventory data, and gray boxes correspond to information from existing inventory data while black boxes are direct emission from process. The most common precursor of phthalocyanine among phthalic acid and its derivates is 1,2-Dicyanobenzene (phthalonitrile, PN), and PN is produced from *o*-xylene under ammoxidation process at 480°C. The yield is 80-85%.³⁴ Another precursor determining a type of metal phthalocyanine is metal salts, and thus aluminum chloride anhydrous (AlCl₃) is used to synthesis chloroaluminum phthalocyanine (ClAlPc) in our experiment. AlCl₃ are produced by chlorinating molten aluminum at 670-850°C, and yield is over 90 %.³⁵Other information of chemical production is summarized in Table A2.

The reaction of ClAlPc from phthalonitrile (PN) and phthalic anhydride (PA) is carried out using either heating mantle or a microwave reactor (CEM Corporation Discover SP). In ClAlPc synthesis, the molar ratio of PN or PA to aluminum ion is fixed to 4:1.^{33,36,37} AlCl₃ and PN or PA are mixed with the metal salt in reaction media. High boiling point solvent is required for all synthesis because of the high reaction temperature (230°C).



Figure A1. Flow diagram of the baseline process



Figure A2. Flow diagram of P1



Figure A3. Flow diagram of P2



Figure A4. Flow diagram of P3



Figure A5. Flow diagram of P4



Figure A6. Flow diagram of P5

2.2. Material Characterization

UV-vis spectrometry and HPLC-MS are used to validate purity of ClAlPc samples for OPV application. Samples are dissolved in ethanol with 15 min of sonication and filtered through 22 μ m syringe filter⁶⁰, and reference (TCI America 98 %) is compared to the samples. All samples have the same maxima in the UV-vis spectrum with the reference at 670 nm although spectrum maxima of P1 is at 675 nm that is due to acidity of sample.⁶⁰

HPLC-MS results show more informative chemical identification since impurities of baseline, P2, and P3 are identified at different m/z and retention time. As shown in the Table A9, HPLC-MS spectrum at 7.13 min has peak at 614.12 m/z, and it implies that additional chlorine ion is in chemical structure by attack by a nucleophile.^{38,55} Meanwhile, P2 and P3 have peak at 487.17 m/z, and the common feature of both processes is the use of urea as nitrogen source. Urea decomposition is previously studied and known as that the thermal decomposition at around 200 °C results to produce less soluble derivatives.⁶¹ Therefore, it is fair assumption that the derivatives remain after the separation process of ClAlPc.



Figure A7. UV-vis spectra of ClAlPc samples



Figure A8. HPLC-MS spectra of ClAlPc samples (at 6.81 min)

3. Data Source for Evaluation Methods

3.1. Materials for Life Cycle Assessment

Table A2. Data	sources for	materials and	energy used	1 in the	inventorv	analysis
I ubic I imi Dutu	5041005 101	inaterials and	energy abec		meencory	anaryono

	Details					
1,2-dicyanobenzene	Ammoxidation process. o-xylene is converted to 1,2-	34				
	dicyanobenzene by reaction with gaseous ammonia and oxygen					
Aluminum chloride	Chlorination of molten aluminum with chlorine gas	35				
Naphthalene	Refining process of coal tar	152				
1-chloronaphthalene	Stoichiometric reaction equation	77,78				
Anisole	Methylation of sodium phenoxide with dimethyl sulfate	153				
Sodium phenoxide	Phenol is converted to sodium phenoxide by reaction with	153				
1	sodium hydroxide					
2,4-dichloroanisole	Chlorination of anisole by reaction with sodium chlorate					
Caprolactam	Oxidation of cyclohexane process in China					
1,8-Diazabicyclo	Synthesis of bicyclic amidines from caprolactam by using ¹					
(5.4.0)undec-7-ene	acrylonitrile					
Utility input for	Utility input for chemicals with no specific information is					
reaction and workout	assumed to be 1.2 kg/kg of steam, 0.7 MJ/kg of electricity, 70					
	kg/kg of cooling water, and 0.06 Nm ³ /kg of nitrogen gas per kg					
	of product					
Utility input for	Utility input for solvent regeneration is assumed to be 1.5 kg/kg	78				
solvent regeneration	of steam, 0.2 MJ/kg of electricity, 80 kg/kg of cooling water, and					
	0.01 Nm ³ /kg of nitrogen gas per kg of product					
Transportation	Average distance for basic chemicals in the U.S: 69 km truck, 43					
(chemical)	km train, barge 27 km, and pipeline 18km					
Transportation	Average distance for gases in the U.S: 107 km truck, 8 km train,	157				
(nonflammable gas)	barge 6 km, and pipeline 5 km					

3.2. Chemical Identification and Hazards from NFPA

No.	Chemicals	CAS	Health	Flammability	Reactivity	Special
1	1,8-Diazabicyclo(5.4.0)undec-7-ene	6674-22-2	3	1	0	0
2	1-chloronaphthalene	90-13-1	2	1	0	0
3	2,4-Dichloroanisole	553-82-2	0	1	0	0
4	Acetic acid	64-19-7	3	2	0	0
5	Acetone	67-64-1	2	3	0	0
6	Acrylonitrile	107-13-1	3	3	0	0
7	Alumina	1344-28-1	2	0	0	0
8	Aluminum	7429-90-5	0	3	3	0
9	Aluminum chloride	7446-70-0	3	0	2	0
10	Ammonia, liquid	7664-41-7	3	0	0	0
11	Ammonium chloride	12125-02-9	2	0	0	0
12	Anisole	100-66-3	0	2	0	0
13	Bauxite	1318-16-7	1	0	0	0
14	Benzene	71-43-2	2	3	0	0
15	Bituminous coal	2684C (SRM)	1	3	0	0
16	Caprolactam	105-60-2	2	1	0	0
17	Chlorine, liquid	7782-50-5	3	0	0	1
18	Chloroaluminum phthalocyanine	14154-42-8	0	0	0	0
19	Coal tar	1991 (SRM)	1	1	0	0
20	Crude oil	2721 (SRM)	2	3	0	0
21	Diesel	68334-30-5	1	2	0	0
22	Diethylene glycol	111-46-6	0	1	0	0
23	Dimethyl sulfate	77-78-1	4	2	0	0
24	Ethyl acetate	141-78-6	2	3	0	0
25	Fuel grade uranium (Uranium dioxide)	1344-57-6	3	0	0	0
26	Gasoline	8032-32-4	1	3	0	0
27	Hydrochloric acid	7647-01-0	3	0	0	0
28	Hydrogen peroxide	7722-84-1	3	0	2	1
29	Hydrogen, liquid	1333-74-0	3	4	0	0
30	Hydroquinone	123-31-9	2	1	0	0
31	Lignite coal	1415-93-6	1	1	1	0
32	Limestone	1d (SRM)	1	0	0	0
33	Liquefied petroleum gas (propane)	74-98-6	2	4	0	0
34	Metallurgical coke	65996-77-2	1	1	0	0
35	Methanol	67-56-1	2	3	0	0
36	Naphthalene	91-20-3	2	2	2	0

Table A3. Chemical identification and NFPA score of materials used in ClAlPc processes

37	Natural gas	68410-63-9	1	4	0	0
38	Nickel	7440-02-0	2	3	3	0
39	Nitric acid	7697-37-2	3	0	2	1
40	Nitrogen, liquid	7727-37-9	3	0	0	1
41	Oxygen, liquid	7782-44-7	3	0	0	1
42	Petroleum coke	64741-79-3	1	1	0	0
43	Petroleum refining (Petroleum ether)	8032-32-4	2	4	0	0
44	Phenol	108-95-2	3	2	0	0
45	Phthalic anhydride	85-44-9	2	1	0	0
46	Phthalonitrile	91-15-6	2	1	0	0
47	Potassium chloride	7447-40-7	0	0	0	0
48	Pyrolysis gasoline	68606-10-0	1	3	0	0
49	Quicklime (Calcium oxide)	1305-78-8	3	0	0	0
50	Residual fuel oil	68476-33-5	2	2	0	0
51	Sodium chlorate	7775-09-9	1	0	2	1
52	Sodium chloride	7647-14-5	1	0	0	0
53	Sodium hydroxide	1310-73-2	2	0	0	0
54	Sulfur	7704-34-9	2	1	2	0
55	Sulfuric acid	7664-93-9	3	0	0	0
56	Toluene	108-88-3	2	3	0	0
57	Urea	57-13-6	0	0	0	0
58	Xylene	1330-20-7	2	3	0	0

Table A3 (cont'd)

Table A4. Chemical hazard weighed to material consumption for ClAlPc manufacturing based on input from technosphere

Process	Health	Flammability	Reactivity	Special
Baseline	1.39	3.12	0.06	0.03
P1	1.66	2.70	0.11	0.05
P2	1.62	2.97	0.05	0.02
P3	1.77	2.95	0.02	0.01
P4	1.76	2.97	0.02	0.01
P5	1.53	2.84	0.03	0.03

Process	Health	Flammability	Reactivity	Special
Baseline	2.07	2.28	0.20	0.09
P1	2.07	2.29	0.20	0.09
P2	2.01	2.61	0.08	0.03
P3	2.18	2.47	0.03	0.02
P4	2.18	2.47	0.03	0.02
P5	1.89	2.24	0.06	0.05

Table A5. Chemical hazard weighed to material consumption for ClAlPc manufacturing based on input from technosphere except energy source (grey in Table A2.)

3.3. Summary of Green Chemistry Metrics and Solvents Use

Table A6. Green chemistry metrics of proposed processes and solvents use

Process	AE %	RME %	PMI	E-factor	E-factor (water use)	Yield %		Solvent	use (g)	
Pacalina	80.02	74.80	16 15	8 15	16.60	84 20	Toluene	Ace	tone	Water
Dasenne	89.02	/4.09	40.45	0.45	10.09	04.20	31.22	29.	.81	14.00
D1	80.02	6176	52 00	0.02	10.45	72 80	Toluene	Ace	tone	Water
P1	89.02	04.70	33.00	9.95	19.45	/2.80	31.22	29	.31	14.00
D2	50.52	0.95	200 56	12 60	720.10	24.00	Acetone	Water	H_2SO_4	NaOH
P2	39.32	9.85	508.50	43.08	/29.19	24.80	79.20	195.37	1.86	0.40
D2	80.02	26.52	107 15	70 77	25766	50.54	Acetone	Water	H_2SO_4	NaOH
P3	89.02	30.32	487.43	38.77	557.00	50.54	79.2	186.20	9.80	4.00
D4	00.02	42.02	100.00	22.12	207 71	(0)((Acetone	Water	H_2SO_4	NaOH
P4	89.02	43.83	406.09	32.12	297.71	00.00	79.2	186.20	9.80	4.00
D5	80.02	(2)	20.16	0 1 1	0.11	70 72		Meth	anol	
P3	89.02	02.03	29.10	8.11	8.11	/0./2		31.	65	

3.4. Cost of Crude Oil, Coals, and Natural Gas

The price of petroleum, coal, and natural gas from life cycle inventory to consider the cost of chemicals and energy. The reference prices of fossil fuels are retrieved from Energy Information Administration (EIA) for the average of most recent data (Table A7). For C₂, the production rate of ClAlPc is modeled on either a pilot scale conventional reactor (20L) or microwave reactor (3.5L) based on previous studies (Table A8).^{158,159} Comparing the production rate is important because it provides an estimate of use and maintenances of facility.

	unit	Price (\$)	Period
Crude oil	kg	0.41	09/17-02/18
Bituminous	kg	0.05	01/16-12/16
Lignite	kg	0.02	01/16-12/16
Anthracite	kg	0.10	01/16-12/16
Gas natural	m ³	0.14	09/17-02/18

Table A7. Reference cost of crude oil, coals, and natural gas

Table A8. Production rate of baseline and alternative processes

	Reactor	Production rate (kg/hr)
Baseline	Pilot 20L	0.41
P1	Microwave 3.5L	0.56
P2	Microwave 3.5L	0.24
P3	Microwave 3.5L	0.60
P4	Microwave 3.5L	0.73
P5	Microwave 3.5L	0.58

3.5 Sustainability Score Summary

Table A9. Summary of sustainability scores for all methods

Process	Environmental (%)	Cost (%)	Chemical hazard (%)
Baseline	100	100	100
P1	131	100	108
P2	613	84	408
P3	893	77	352
P4	733	77	284
P5	97	77	91

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