TRANSPARENT MULTIJUNCTION ORGANIC PHOTOVOLTAICS

By

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ABSTRACT

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The widespread adoption of conventional solar cells based on inorganic semiconductors has been gaining traction in recent years but is still often hindered by high cost and lack of aesthetic appeal. Transparent organic semiconductor-based solar cells that selectively absorb in the UV and the NIR enable integration into building windows, automobiles, and consumer electronics in ways that traditional solar cells cannot. Moreover, integration onto existing infrastructure reduces the racking and installation cost. In this work, we investigate routes to improve the efficiency of transparent solar cells by utilizing multijunction architectures. A transfer-matrix optical interference model is developed as a framework to optimize the full device stack considering the angle-dependent PV performance that is critical for matching subcell photocurrents in series tandem solar cells. In addition, a new method of fine tuning energy levels of low-bandgap small molecules with infrared selective absorption was demonstrated using a series of organic heptamethine salts. By exchanging the counterion from a small, hard anion to a fluorinated weakly coordinating anion, the frontier energy of the salt is shown to shift without affecting the bandgap, thus enabling simultaneous optimization of photocurrent generation of photovoltage. We further utilize this tunability to develop heptamethine molecules with absorption as deep as 1600 nm, the deepest infrared photoresponse demonstrated to date with organic small molecules ideal for multijunction integration. Ultimately, transparent solar cells are an exciting new paradigm for solar deployment enabled by organic and excitonic semiconductors that offer a pathway to integrate solar onto virtually any surface without impacting the view.

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TABLE OF CONTENTS

LIST OF TABLES	vii
LIST OF FIGURES	viii
KEY TO ABBREVIATIONS	xi
KEY TO SYMBOLS	xviii
Chapter 1 – Introduction to Organic Photovoltaics	1
1.1 Organic semiconductors	2
1.1.1 Semiconductor basics	2
1.1.2 Organic molecular bonding	3
1.1.3 Electronic states and transitions	5
1.1.4 Energy transport in organic semiconductors	
1.2 Organic photovoltaics: working principles	
1.3 OPV background	
1.3.1. Early OPVs: 1980-2000	
1.3.2. Polymer OPVs.	
1.3.3. Small molecule OPVs: thermal evaporation.	
1.3.4. Solution processed small molecule OPVs	
1.3.5. Tandem OPVs	
	22
Chapter 2 – Introduction to Transparent Photovoltaics	
2.1 TPV mouvation	
2.2 TPV ligures of meril	
2.5 TPV background and state of the art.	
2.3.1 Spatially segmented FVS	
2.3.2 Semi-transparent solar concentrators and scattering concentrators	
2.3.5 Eurintescent solar concentrators and scattering concentrators	
2.3.4 VISIOIY transparent luminescent solar concentrators	34
2.5.5 Transparent electrodes	
2.4 1 Transparent conductive oxides	
2.4.1 Hansparent conductive oxides	
2.4.2 Olda-unit inclus	30
2.5 TPV efficiency limits	40
Chapter 3 – Experimental Techniques	
3.1 Thin film optical measurements: UV-Vis and VASE	
3.2 Heptamethine counterion exchange	
3.3 Purity assessment via high-resolution mass spectrometry	
3.4 Solar cell device fabrication	
3.5 Solar cell testing (JV-EOE)	
3.5.1 Current-voltage (JV)	
3.5.2 External quantum efficiency (EQE)	
	·····•-
Chapter 4 – Angle Dependence Modeling	

4.1 Motivation for angle dependent PV performance modeling	55
4.2 Optical interference modeling	57
4.3 Modifications for angular incidence	59
4.4 Verification of model (internal consistency and experimental)	
4.5 Application for real-world solar irradiance data	71
••	
Chapter 5 – NIR-Absorbing Organic Heptamethine Salts for TPV	74
5.1 Polymethine PV background	74
5.2 Counterion exchange effect on open-circuit voltage	75
5.3 Deep NIR (1600 nm) absorption.	
5.4 TPV demonstrations with organic salts	
Chapter 6 – Tandem TPV Optimization	
6.1 Tandem TPV background	
6.2 Simulations and contour mapping	
6.3 Experimental results	91
Chapter 7 – Conclusions and Outlook	
7.1 TPV efficiency: increase NIR EOE, multijunction TPV, better TE design	
7.2 TPV applications	
7.3 TPV scalability	
7.4 TPV lifetime	
7.5 Future applications: organic salts for cancer theranostics	
7.6 Final summary	
······································	
APPENDIX	
BIBLIOGRAPHY	

LIST OF TABLES

Table 2.1. Selected semi-transparent and transparent PV efficiencies.	.27
Table 4.1. Layer thicknesses (Å) to maximize J_{sc} and J_{sc^*} for 0° , 70° , or all angles of incidence	.67
Table 5.1. Device parameters and molecular properties for each salt	. 80
Table 6.1. Selected tandem semi-transparent OPV performance metrics	.90

LIST OF FIGURES

Figure 1.1. Hybridizations of carbon: sp, sp ² , and sp ³	-
Figure 1.2. Illustrations of σ and π bonds	-
Figure 1.3. Molecular structures of archetypal organic semiconductors used in organic solar cells	,
Figure 1.4. Formation of molecular bonding and antibonding orbitals in sp ² hybridized carbon)
Figure 1.5. Energy landscape for ground state S_0 and the first excited state S_1 as a function of nuclear coordinates for a molecule	
Figure 1.6. Singlets and triplets in organic molecules	,
Figure 1.7. Absorption spectra for organic and inorganic semiconductors9	,
Figure 1.8. Frontier energy levels for a series of acenes)
Figure 1.9. Förster and Dexter energy-transfer mechanisms	
Figure 1.10. Four steps to photocurrent generation in molecular organic solar cells	
Figure 1.11. JV curve for solar cell with PV performance metrics shown on it	,
Figure 1.12. Non-fullerene acceptor with 11.2% PCE)
Figure 1.13. Polymer triple junction tandem solar cell	
Figure 2.1. Transparent photovoltaic applications and the solar spectrum	
Figure 2.2. Survey of different TPV technologies as a function of AVT)
Figure 2.3. Examples of segmented solar cells	,
Figure 2.4. Examples of thin-film, semi-transparent solar cells	,
Figure 2.5. Scattering solar concentrators)
Figure 2.6. UV- and NIR-selective transparent solar cells	
Figure 2.7. Low bandgap donors	
Figure 2.8. High performance transparent solar cell module	,
Figure 2.9. Transparent luminescent solar concentrators	-
Figure 2.10. Thin silver and ITO comparison	,
Figure 2.11. Efficiency limits of TPVs)

Figure 3.1. Ellipsometry fitting for thin and thick films on silicon
Figure 3.2. Counterion exchange synthesis
Figure 3.3. High resolution mass spectra for Cy1-TPFB and Cy2-TPFB
Figure 3.4. Device architecture and layer patterns
Figure 3.5. Evaporator diagrams
Figure 3.6. Custom-built system assembly for two evaporation chambers and a nitrogen glovebox (Angstrom Engineering)
Figure 3.7. Diagram of spin-coating process
Figure 3.8. Photographs of JV testing setup
Figure 3.9. EQE for tandem PV
Figure 4.1. The position of the sun and the average yearly flux for PVs mounted in different configurations.
Figure 4.2. Conventional and inverted configurations for TPV
Figure 4.3. Schematic showing xyz coordinates for transfer matrix equations
Figure 4.4. Substrate corrections for optical interference simulation
Figure 4.5. Consistency check $A + R + T = 1$
Figure 4.6. Schematic showing how solar flux changes with incident angle
Figure 4.7. Predicted and experimental J_{SC} with respect to incident angle
Figure 4.8. Example J_{sc} contour plot where ClAlPc and C_{60} thicknesses are varied to maximize 0° J_{sc} for ITO thickness = 1000 Å in the conventional configuration
Figure 4.9. Simulated normalized J _{sc} under 1 sun illumination as a function of angle of incidence for two optimizations
Figure 4.10. Simulated absorption, reflection, transmission and IQE of 735 nm light as a function of incident angle in three optimizations
Figure 4.11. Simulated electric field profile for conventional and optically inverted ClAlPc-C ₆₀ TPVs70
Figure 4.12. Simulated electric field profile for normal and oblique incidence on ClAlPc-C ₆₀ TPVs70
Figure 4.13. Effect of improved angular dependence on yearly PV power output72
Figure 5.1. Molecular structure of Cy cation and anions used in Ref. [31]
Figure 5.2. Absorption and JV for Cy salts77

Figure 5.3. Cy-PF ₆ and Cy-TPFB alloying.	77
Figure 5.4. Cy1 and Cy2 salt structures, absorption, and mass spectra.	79
Figure 5.5. Device architecture, JV and EQE for Cy1 and Cy2.	79
Figure 5.6 Proposed energy level schematic for Cy1, Cy2, and C ₆₀	81
Figure 5.7. Interface gap change in Cy1 salt and band bending in Cy2-TPFB	81
Figure 5.8. V _{OC} and NIR EQE as a function of thickness for Cy1 and Cy2	82
Figure 5.9. Specific detectivity D* spectra for each deep NIR salt (Cy1 and Cy2)	85
Figure 5.10. Contour map of predicted J _{SC} and AVT for TPV with Cy-TPFB	86
Figure 5.11. Experimental optimization of Ag/Alq3 electrode for TPV with Cy-TPFB.	87
Figure 5.12. TPV demonstration with Cy-TPFB: JV, EQE, and transmission	87
Figure 6.1. Examples of managing electric field profiles in TPV	90
Figure 6.2. ClAlPc and SnPc tandem device.	91
Figure 6.3. ClAlPc and Cy-TPFB tandem devices.	93
Figure 6.4. Contour maps for transparent Cy-TPFB/C ₆₀ – ClAlPc/C ₆₀ tandem devices showing (a) AVT, (CRI, and (c) J_{SC} as a function of the middle MoO ₃ and the top ITO thicknesses.	(b) 95
Figure 6.5. Contour maps for transparent Cy-TPFB/C ₆₀ – ClAlPc/C ₆₀ tandem devices showing (a) AVT, (CRI, and (c) J_{SC} as a function of the ClAlPc and the Cy-TPFB layer thicknesses.	(b) 95
Figure 6.6. Dilute donor devices with ClAlPc, DBP, and TAPC.	96
Figure 6.7. ClAlPc BHJ and dilute C_{60} tandem devices	96
Figure 7.1. Examples of OPV lifetime1	01
Figure 7.2. Optical window of absorbance for biological tissue1	03
Figure 7.3. Types of photodynamic therapy	04
Figure 7.4. Optoelectronic tunability of Cy salts for therapy and for imaging	05
Figure 7.5. A549 cell viability with different concentrations of organic salts dissolved in DMSO 10	05
Figure A.1. Frontispiece for Advanced Optical Materials Volume 4, Issue 7 (July 2016)1	10

KEY TO ABBREVIATIONS

А	acceptor
Abs.	absorption
AFM	atomic force microscopy
AgNW	silver nanowire
Alq	short for "Alq ₃ "
Alq ₃	tris(8-hydroxyquinolinato)aluminum
AM1.5G	"air mass 1.5 global", also known as the solar spectrum on the surface of the Earth
AO	atomic orbital
a-Si	amorphous silicon solar cell
AZO	aluminum-doped zinc oxide
BBAR	broadband anti-reflection
BCP	bathocuproine
BDT	benzodithiophene
BF-DPB	N4,N4'-Bis(9,9-dimethyl-9H-fluoren-2-yl)-N4,N4'-diphenylbiphenyl-4,4'-diamine
BHJ	bulk heterojunction
BIPV	building integrated photovoltaics
BODIPY	boron-dipyrromethene
Bphen	bathophenanthroline
C12	alkyl group with twelve carbons
CIE	International Commission on Illumination
CIGS	cadmium indium gallium selenide
ClAlPc	chloroaluminum phthalocyanine
CoCB	cobalticarborane
Conv	conventional

CuPc	copper phthalocyanine
СҮ	1-(6-(2,5-dioxopyrrolidin-1-yloxy)-6-oxohexyl)-3,3-dimethyl2-((E)-2-((E)-3-((E)-2-(1,3,3-trimethylindolin-2-ylidene)ethylidene)cyclohex-1-enyl)vinyl)-3H-indolium chloride
Су	2-[2-[2-chloro-3-[2-(1,3-dihydro-3,3-dimethyl-1ethyl-2H-benz[e]indol-2- ylidene)ethylidene]-1-cylohexen-1-yl]-ethenyl]-3,3dimethyl-1-ethyl-1H-benz[e]indolium
Cy1	(1-Butyl-2-(2-3-2-(1-butyl-1H-benzo[cd] indol-2-ylidene)-ethylidene-2-diphenylamino- cyclopent-1-enylvinyl)-benzo[cd]indolium
Cy2	(1-Butyl-2- (23-2-(1-butyl-1H-benzo[cd]indol-2-ylidene)-ethylidene-2-phenylcyclopent- 1-enyl-vinyl)-benzo[cd]indolium
Cy7	2-[2-[2-chloro-3-[2-(1-ethyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)ethylidene]-1- cyclohexen-1-yl]ethenyl]-1ethyl-3,3-dimethyl-3H-indolium iodide
Cy7-P	3-Butyl-2-(2-[3-[2-(3-butyl-1,1-dimethyl-1,3-dihydro-benzo[e] indol-2-ylidene)-ethylidene]-2-chloro-cyclohex-1-enyl]-vinyl)-1,1dimethyl-1H- benzo[e]indolium hexafluorophosphate
D	donor
D-A	donor acceptor pair
DBP	dibenzoperiflanthene
DBR	distributed Bragg reflector
DC	direct current
DCM	dichloromethane
DCV	dicyanovinyl
DCV6T	α,ω -bis(dicyanovinyl-sexithiophene)-Bu(1,2,5,6)
DI	deionized
DMF	N,N-dimethylformamide
DMSO	dimethyl sulfoxide
DOS	density of states
DPP	diketopyrrolopyrrole
DSSC	dye-sensitized solar cell

DTDCTB	2-{[7-(5-N,N-ditolylaminothiophen-2-yl)-2,1,3-benzothiadiazol-4-yl]methylene} malononitrile
DTTz	2-((2-(5-(4-(diphenylamino)- phenyl)thieno[3,2-b]thiophen-2-yl)thiazol-5-yl)methylene)- malononitrile
ΔLUMO	energy difference between LUMO of donor and LUMO of acceptor
Ex	excitation
EPR	electron paramagnetic resonance
ESI	electrospray ionization
ETL	electron transport layer
F	fluorescence
F ₆ TCNNQ	hexafluorotetracyanonaphthoquinodimethane
F ₄ -ZnPc	fluorinated zinc phthalocyanine
f-CNT	free-standing multiwall carbon nanotube
FDA	Food and Drug Administration
FDPP	a DPP unit with a furan moiety used in place of thiophene
FPhB	tetrakis(4-fluorophenyl)borate
FRET	Förster resonance energy transfer
GO	graphene oxide
H_2Pc	phthalocyanine
Hb	hemoglobin
Hb-O ₂	oxyhemoglobin
НОМО	highest occupied molecular orbital
HTL	hole transport layer
IC ₆₀ BA	indene C ₆₀ bis adduct
ICG	indocyanine green
ICL	interconnecting layers for tandem solar cells
ІоТ	Internet of Things

IR	infrared
isc	intersystem crossing, also called "ISC"
ITIC	3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(4-
ITO	indium tin oxide
IZAO	indium zinc aluminum oxide
LC	liquid chromatography
LCD	liquid crystal display
LED	light emitting diode
Low-E	low emissivity
LSC	luminescent solar concentrator
LUMO	lowest unoccupied molecular orbital
MeOH	methanol
MDMO-PPV	poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene]
Me-PTC	N, N'-dimethyl-3,4,9,10-perylenedicarboximide
MJ	multijunction
МО	molecular orbital
NIR	near-infrared
NREL	National Renewable Energy Laboratory
OFET	organic field effect transistors
OLED	organic light-emitting diode
OptInv	optically inverted
OPV	organic photovoltaics
Р	phosphorescence
РЗНТ	poly,3-hexylthiophene
pBBTDPP2	poly[3,6bis(4'-dodecyl-[2,2']bithiophenyl-5-yl)-2,5-bis(2-ethylhexyl)-2,5-dihydropyrrolo [3,4-]pyrrole-1,4-dione]

PBDB-T	poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione)]
PBDTT-DPP	poly{2,6'-4,8-di(5-ethylhexylthienyl)benzo[1,2-b;3,4-b]dithiophene-alt-5-dibutyloctyl-3,6-bis(5-bromothiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4-dione
PBDTTT-C-T	2,6-Bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b'] dithiophene
PbPc	lead phthalocyanine
PC ₆₁ BM	(PCBM) poly-C61-butyric methyl ester
PC ₇₁ BM	poly-C71-butyric methyl ester
PCDTBT	poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'benzothiadiazole)]
PCPDTFBT	poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7-(5-fluoro-2,1,3-benzothiadiazole)]
PDT	photodynamic therapy
PEDOT	poly(3,4-ethylene dioxythiophene)
PET	polyethylene terephthalate
PFTBT	poly[2,7(9,9-didecylfluorene)-alt-5,5-(4',7'-di-2-thienyl-2',1',3'benzothiadiazole)]
PHJ	planar heterojunction
PID	proportional, integral and derivative control
PIDT-PhanQ	polyindaceno-dithiophene-alt-quinoxaline
PMHJ	planar mixed heterojunction
PMMA	polymethyl methacrylate
PSEHTT	poly[(4,4'-bis(2-ethylhexyl)dithieno-[3,2-b:2',3'-d]silole)-2,6-diyl-alt-(2,5-bis(3-(2-ethylhexyl)-thiophen-2-yl)thiazole[5,4-d]thiazole)]
PSS	polystyrene sulfonic acid
РТВ	series of polymers formed by combination of TT and BDT units
PTB7	poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]]
PTCBI	3,4,9,10-perylenetetracarboxylic bisbenzimidazole

PTT	photothermal therapy
PV	photovoltaics
PVD	physical vapor deposition
QCM	quartz crystal monitor
QToF	quadropole and time of flight detector, a type of tandem mass spec
Re	recombination
RF	radio frequency
SAM	self-assembled monolayer
SeDPP	DPP unit with a sulfur atom substituted by selenium
SEM	scanning electron microscopy
SJ	single junction
SnNcCl ₂	tin(IV) 2,3-naphthalocyanine dichloride
SnPc	tin phthalocyanine
SPR	surface plasmon resonance
SQ	Shockley Queisser, or squaraines dyes
STPV	semitransparent photovoltaic
Sub	substrate
SubNc	subnaphthalocyanine
TAPC	4,4'-cyclohexylidenebis[N,N-bis(4-methylphenyl)benzenamine]
ТСО	transparent conductive oxide
TCO _A	transparent conductive oxide acting as an anode (hole-collecting)
TCO _C	transparent conductive oxide acting as a cathode (electron-collecting)
TEM	transmission electron microscopy
TFM	tetrakis[3,5-bis(trifluoro methyl)phenyl]borate
TiOx	TiO ₂ , titanium dioxide

TLSC	transparent luminescent solar concentrator
TMM	transfer matrix method
TPV	transparent photovoltaics
TPFB	tetrakis(pentafluorophenyl)borate; could also be short for Cy-TPFB
TRIS	Δ -tris(tetrachloro-1,2-benzene diolato) phosphate(V). also called TRISPHAT or Δ -TRISPHAT
TRISPHAT	see "TRIS"
TT	thieno[3,4-b]thiophene
UV	ultraviolet
UV-Vis	ultraviolet-visible spectroscopy
VASE	variable angle spectroscopic ellipsometry
VIS	visible light
W ₂ (hpp) ₄	tetrakis(hexahydropyrimidinopyrimidine)ditungsten(II)
XRD	x-ray diffraction
ZnPc	zinc phthalocyanine

KEY TO SYMBOLS

Å	Angstrom, equivalent to 0.1 nm or 10^{-10} m
A	absorption; device area
a_B	exciton Bohr radius
A_{AL}	absorption in active layers
A_c	electron affinity
A_{CL}	absorption in contact layers
A_{TF}	absorption through the thin film stack
AVT	average visible transmission
AVT_0	average visible transmission with no solar spectrum weighting
С	speed of light
CRI	color rendering index
d	thickness of film
D^*	specific detectivity
Ε	energy, or electric field
E_B	exciton binding energy
$ E_{DA} ^2$	electric field intensity at the donor-acceptor interface
E_g	bandgap
EQE	external quantum efficiency
Eref	reference spectrum for mismatch factor, usually solar spectrum
E_S	solar simulation lamp (source) spectrum
f	fraction of s-polarized light
FF	fill factor
G(x)	exciton generation rate as a function of position x in optical interference model
h	Planck constant

ħ	reduced Planck constant
Ι	current
I_0	dark saturation current
I_c	ionization energy
I_G	interface gap, energy difference between HOMO of donor and LUMO of acceptor
I_{jk}	interface matrix between layers j and k
I_{ph}	photocurrent
IQE	internal quantum efficiency
j	layer index in optical interference model
J	current density
J_{MP}	current density at maximum power point
J_{SC}	short circuit current density
JV	current-voltage
k	Boltzmann constant, or the extinction coefficient
L	lightness (part of CRI calculation)
L_{C0}	charge carrier collection length
L_D	exciton diffusion length
L_j	layer matrix for layer <i>j</i>
\vec{M}	surface normal vector of solar cell module
MF	mismatch factor (spectral mismatch factor)
т	total number of layers in optical interference model
m_l	magnetic quantum number
m_r^*	reduced effective mass of exciton
m_s	magnetic spin quantum number
n	the principal quantum number; the lone pair electrons on oxygen or nitrogen; the ideality factor; the refractive index; or the exciton population density

n_0	refractive index of air
n _s	refractive index of substrate
ñ	complex index of refraction
$P(\lambda)$	photopic response, sensitivity of human eye to different wavelengths of light
PCE	power conversion efficiency
P_{Gen}	generated electrical power
Pin	incident optical power
q	elementary charge
Q	power dissipation rate
Q_A	normalized yearly power output of Device A, an unoptimized transparent solar cell
R	reflection; responsivity (A/W)
R_D	differential resistance of a solar cell in the dark at zero bias
r _{jk}	Fresnel reflection coefficient for interface between layer j and layer k
r_{jk}^p	Fresnel reflection coefficient for p-polarized light for interface <i>jk</i>
r_{jk}^s	Fresnel reflection coefficient for s-polarized light for interface <i>jk</i>
r_p	reflectivity of p-polarized light
r _s	reflectivity of s-polarized light
R_p	parallel (also called shunt) resistance
R_S	sheet resistance; reflection at the substrate-air interface; series resistance
R_{TF}	reflection through the thin film stack
r _{ab}	distance between molecules
S	the total spin; the solar spectrum photon flux (units of photons $nm^{-3} s^{-1}$); the Stokes shift; or the transfer matrix
Ŝ	position vector for the sun
So	ground state
S_1	first excited singlet state

S_2	second excited singlet state
S_{N}^{-1}	current spectral noise density
S_R	spectral response of reference photodiode
S_T	spectral response of test device; thermal (Johnson-Nyquist) noise
Т	transmission or temperature, depending on context
t	thickness
T_1	first excited triplet state
T_{50}	time for solar cell performance to decrease to 50% of initial value
T_{80}	time for solar cell performance to decrease to 80% of initial value
t _D	donor film thickness
t_f	final (calculated) thickness, used in calculating tooling factors
TF_{f}	final (calculated) tooling factor
TF_i	initial (guessed) tooling factor
T_{g}	glass transition temperature
t _i	initial (guessed) thickness, used in calculating tooling factors
t_{jk}	Fresnel transmission coefficient for interface between layer j and layer k
t^p_{jk}	Fresnel transmission coefficient for p-polarized light for interface jk
t^s_{jk}	Fresnel transmission coefficient for s-polarized light for interface jk
T_S	transmission at the substrate-air interface
T_{TF}	transmission through the thin film stack
и	chromaticity coordinate, one of two (u and v)
v	chromaticity coordinate, one of two (u and v)
V	voltage
V_{MP}	voltage at maximum power point
Voc	open circuit voltage

xxi

W	peak width
x	position vector in optical interference model
	Greek symbols:
α	azimuthal angle of solar cell module; absorption coefficient
$lpha_j$	absorption coefficient of layer j
β	tilt angle of solar cell module
δ_B	improvement in power generation of Device B (PV optimized for oblique incidence) over Device A
Δ	phase component of ellipsometric angle
3	permittivity
&r	relative permittivity, also called dielectric constant
\mathcal{E}_0	permittivity of free space
η	power conversion efficiency (see PCE)
η_A	absorption efficiency
η_{CC}	charge collection efficiency
η_{CT}	charge transfer efficiency
η_{ED}	exciton diffusion efficiency
θ	incident angle of solar cell on solar cell module
$ heta_0$	ambient incident angle
$ heta_j$	(incident) angle of light in layer j
$ heta_k$	(refraction) angle of light in layer k
κ	extinction coefficient, imaginary index of refractive index also notated as k
λ	wavelength
λ_{max}	peak absorption wavelength
\mathcal{V}_n	intramolecular vibrational mode
π	pi bonding orbital, 1 per double bond, 2 per triple bond

π^*	pi antibonding orbital
ρ	complex reflectance
σ	sigma bonding orbital, 1 per single, double or triple bond
σ*	sigma antibonding orbital
τ	exciton lifetime before recombination
arphi	zenith angle of the sun
Ψ	amplitude component of ellipsometric angle
ω	azimuthal angle of sun

Chapter 1 – Introduction to Organic Photovoltaics

Solar power is an attractive source of renewable energy because of the tremendous energy potential of sunlight reaching the earth. Traditional solar cells fabricated with inorganic semiconductors are important technologies for offsetting worldwide fossil fuel consumption. However, their adoption in various locations is often hindered by their high cost and lack of aesthetic appeal. To address the limitations of traditional photovoltaics (PV), various thin-film architectures have been developed based on materials such as amorphous silicon, CdTe, cadmium-indium-gallium-selenide (CIGS), organic semiconductors, and halide perovskites. Among these technologies, organic and other excitonic materials have the unique ability to selectively absorb ultraviolet (UV) and near-infrared (NIR) light without absorbing visible light. Because 70% of the solar photon flux is in the near-infrared ($\lambda > 700$ nm), efficient transparent solar cells can be made using excitonic materials.

In this chapter, we will introduce the working principles of organic photovoltaics, and summarize the status of transparent organic photovoltaics in the following chapter. Experimental methods used throughout the research in this thesis will be covered in Chapter 3; these include device fabrication and testing methods, as well as thin film analysis. Chapters 4-6 will cover three major projects completed for transparent PV development. The first of these, Chapter 4, discusses optical interference simulations for thin film PVs, specifically, how to modify the standard treatment for oblique incident angles, which are important for transparent PVs installed onto buildings. The next chapter, Chapter 5, will discuss the development of heptamethine salts for NIR OPVs with tunable energy levels and photoresponse out to 1600 nm. These materials expand the catalogue for transparent PVs and enable broader NIR absorption. Chapter 6 will cover the progress made on developing tandem OPVs and TPVs. Tandem, or multijunction, architectures were explored to improve the TPV power efficiency. The last chapter, Chapter 7, describes the outlook of transparent OPVs, as well as the cancer theranostic application of the heptamethine salts developed in Chapter 5.

1.1 Organic semiconductors

1.1.1 Semiconductor basics

Metals, semiconductors and insulators are distinguished by different bonding and band structures. In metals, the conduction band is partially filled with electrons, which gives them high conductivities. In semiconductors and insulators, the valence band is filled with electrons while the conduction band is completely empty. The energy difference between the top of the valence band and the bottom of the conduction band is called the bandgap (E_g) and is lower in semiconductors (0.5 – 3 eV) than in insulators (>3 eV). In semiconductors, an electron can be excited to the valence band via optical or thermal excitations. The excited electron is coulombically bound to the hole left behind in a quasi-neutral particle called the exciton. The binding energy (E_B) of the exciton is:

$$E_B = \frac{\hbar^2}{2m_r^* a_B{}^2}$$
(1.1)

where \hbar is the reduced Planck constant ($\hbar = h/2\pi$), m_r^* is the reduced effective mass of the exciton, and a_B is the exciton Bohr radius:

$$a_B = \frac{\hbar^2 \varepsilon}{m_r^* q^2} \tag{1.2}$$

q is the elementary charge, and ε is the permittivity ($\varepsilon = \varepsilon_r \varepsilon_0$). The relative permittivity ε_r (also called the dielectric constant) is the polarizability of a material and is related to its density. Because the dielectric constant is much larger for inorganic semiconductors ($\varepsilon_r = 11$ for Si) than in organic semiconductors ($\varepsilon_r = 2$ -4), the exciton radii and binding energies are very different. In inorganic semiconductors, the exciton Bohr radius is large (140 Å for GaAs) and the binding energy is small (4.2 meV for GaAs);[39] these excitons are called Wannier-Mott excitons. In contrast, organic semiconductors have small Bohr radii (5-10 Å) and large binding energies (0.5 – 1 eV); these excitons are called Frenkel excitons.

Semiconductors have electrical properties that can be modified by doping, which, for inorganic semiconductors, is done by adding an impurity atom with different numbers of valence electrons. If the impurity atom has more valence electrons than the atom it replaces, then it is an electron donor, and the semiconductor is said to be n-doped, where n stands for negative. In the opposite case, if the impurity atom

has fewer valence electrons, then it is called an electron acceptor, and the semiconductor is said to be positively p-doped with holes, which are electron vacancies. By combining p-type and n-type materials, electrical devices can be made with biasing (diodes, solar cells) and switching abilities (transistors). In an inorganic p-n junction, a p-type material is in contact with an n-type material. The excess holes from the ptype material diffuse into the n-type material, leaving behind a negative space charge at the junction. Similarly, the excess electrons from the n-type material diffuse into the p-type material, leaving behind a positive space charge. Eventually, the positive and negative space charge lead to the build-up of an electric field that stops the diffusion of holes and electrons. Doping and p-n junctions are accomplished differently in organic semiconductors, which will be described later.

1.1.2 Organic molecular bonding

Organic molecules consist of carbon atoms bonded to hydrogen. Carbon has a total of six electrons $(1s^2, 2s^2, 2p^2)$, two of which are in the inner shell and four of which participate in reactions and are called the valence electrons. Electrons have different types of atomic orbitals (AO) that correspond to the shape of their probability distributions. Carbon can have hybridized orbitals depending on the types of participating bonds. In methane (CH₄) the four valence electrons of carbon are in hybridized sp³ orbitals, four lobes that are 109.5 degrees apart and form a tetrahedron (Figure 1.1). The two electrons in the C-H bond have a probability distribution that exists between the two atoms: this is called a molecular orbital (MO). This type of bond is called a σ -bond or a σ -orbital (Figure 1.2). In ethene C₂H₄, each carbon is bonded to three atoms, one carbon and two hydrogens. The carbon atoms are double bonded to each other. In this case, one valence electron is in the 2p orbital and three valence electrons are sp²-hybridized, meaning that they exist in three coplanar lobes 120° apart. The carbon double bond consists of one sp² electron from each carbon and one 2p electron from each carbon. The two sp² electrons in the bond have a σ orbital, and the two 2p AOs are lobes that overlap above and below the molecular plane. The overlapping p orbitals are called a π bond or π orbital. Therefore, a double bond consists of one σ bond (two sp² electrons) and one π bond (two 2pz electrons). In carbon triple bonds (for example, ethyne C₂H₂), the four valence electrons of carbon consist of two 2p electrons and 2 sp-hybridized electrons, which are two separate lobes 180° apart



Figure 1.2. Illustrations of σ and π bonds.(a) In ethene (C₂H₄), both C atoms have p and sp² hybrid orbitals. The atoms are far apart, so atomic orbitals are shown. (b) The overlapping sp²-hybrid orbitals make a σ bond, and the overlapping p-orbitals make a π bond in the C=C double bond in ethene.

from one another in the molecular plane. The two carbons in this triple bond have one σ bond (two sp electrons) and two π bonds (two 2p_y and two 2p_z electrons). σ -bonds have shorter distances than π -bonds and maintain the molecular structure. π -bonds come from overlapping p_z-orbitals and are responsible for the interesting optical transitions in molecules. A molecule is "conjugated" when it has alternating single and double bonds. The position of the single and double bonds can be switched, leading to a resonant structure, and the π -orbitals (also called p-orbitals) are delocalized along the alternating single and double bonds. The delocalized p-orbitals allow for intramolecular charge transfer, and the overlap of p-orbitals across different molecules allows for intermolecular charge transfer via a hopping mechanism. At low



Figure 1.3. Molecular structures of archetypal organic semiconductors used in organic solar cells. $CuPc = copper phthalocyanine, P3HT = poly,3-hexylthiophene, PC_{61}BM = poly-C61-butyric methyl ester. temperatures, hopping occurs less frequently, and intermolecular charge transfer can occur by coherent charge transfer processes. Therefore, organic semiconductors can be described as a set of conjugated organic molecules and polymers with bandgaps between <math>0.3 - 3$ eV. Examples of organic semiconductors used in organic photovoltaics are shown in Figure 1.3.

1.1.3 Electronic states and transitions

The energy levels of an electron in a finite potential well are discretized. Similarly, an electron orbiting a positively charged nucleus occupies discrete energy levels. Because an electron has half-integral spin, it is considered a fermion. A photon, in contrast, has integral (zero) spin, making it a boson. By the Pauli exclusion principle, no two fermions can occupy the same quantum state. The electrons in an atom occupy a quantum state characterized by four numbers: the principal number n, the orbital number l, the magnetic quantum number m_l , and the magnetic spin quantum number m_s . As two atoms are brought closer together, their valence electrons cannot occupy the same quantum state, so their atomic orbital levels split into one bonding orbital (with lower energy) and one antibonding orbital (with higher energy). A bond is

therefore energetically favored to form, and the lower-energy bonding orbital is occupied with two electrons. Optical transitions take place for electrons in σ and π orbitals, as well as non-participating electrons (e.g., lone pair electrons on oxygen or nitrogen) called *n*. Typical transitions that can be excited with UV-visible light include: $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, where * indicates an antibonding orbital. The amount of energy split between the bonding and antibonding orbitals depends on how much the atomic orbitals overlap. Because the orbitals from each atom overlap significantly in a sigma bond, the energy minimized by the bond formation is greater, and the sigma bonding and antibonding orbitals are far apart. In contrast, the π and π^* orbitals is smaller. For organic molecules, the $\sigma \rightarrow \sigma^*$ transition is usually seen in UV light absorption, while $\pi \rightarrow \pi^*$ transitions can be activated by visible light. The smallest amount of energy needed to an excite an electron is the energy from the highest occupied molecular orbital (HOMO), which is the π orbital in this case, and the lowest unoccupied molecular orbital (LUMO), the π^* orbital (Figure 1.4).



Figure 1.4. Formation of molecular bonding and antibonding orbitals in sp² hybridized carbon. The highest occupied molecular orbital (HOMO) is the π bonding orbital, and the lowest unoccupied orbital (LUMO) is the π * antibonding orbital.



Figure 1.5. Energy landscape for ground state S_{θ} and the first excited state S_I as a function of nuclear coordinates for a molecule. Horizontal lines are vibronic substates, and vertical lines correspond to electrical transitions.

Electronic transitions in organic molecules need to consider vibrational and electronic states together because the atoms are smaller and their vibrational frequencies are larger.[39] Optical transitions result in electrons moving between vibronic states, the combination of vibrational and electronic states. The potential energy landscape for the ground state S_0 and the excited state S_1 for different nuclear coordinates (e.g., different interatomic distances for the two-atom case) is shown in Figure 1.5. Higher excited states $(S_2, S_3, ..., S_n)$ are possible for more electrons being excited to unoccupied molecular orbitals. Intramolecular vibrational modes are marked as v_n or v'_n . The Frank-Condon principle states that electron transitions happen faster than the nucleus can respond, resulting in vertical excitation ("Ex") and recombination ("Re") transitions in Figure 1.5. After excitation from v_0 to v'_1 , the electron eventually relaxes to the bottom of S_1 (v'_0), accompanied by a shift in the nuclear coordinates of the molecule. When the electron relaxes to the ground state, the energy can be emitted as either a photon (radiative decay) or a phonon (nonradiative decay).



Figure 1.6. Singlets and triplets in organic molecules. (a) Electron spin configurations for ground state S_0 , first excited singlet state S_1 , and first excited triplet state T_1 . Note that electron spins are opposing for singlet states and parallel in triplet states. (b) Jablonski diagram showing fluorescence and phosphorescence. Solid and dashed lines indicate radiative and nonradiative decay respectively.

Other types of electronic transitions can occur as well, and these can be summarized in a Jablonski diagram (Figure 1.6 (b)), which removes the nuclear coordinate axis. A single electron is called a doublet because the sum of its spin ($S = \Sigma m_s$) is $\frac{1}{2}$, and the multiplicity 2S + 1 is equal to 2. A pair of spin-opposite electrons has a total spin S = 0 and a multiplicity equal to 1, making it a singlet. A pair of spin-parallel electrons has a total spin of S = 1 and a multiplicity of 3, giving it the name triplet. The spin configurations of singlets and triplets in organic semiconductors are shown in Figure 1.6(a). Changes in total spin are not allowed by the conservation of spin and momentum, so transitions with $\Delta S = \pm 1$ are said to be spin forbidden. Despite being spin forbidden, spin flips can occur via spin-orbit coupling. Phosphorescent emission, which is a transition from T₁ to S₀, is spin forbidden and therefore occurs on a much longer timescale (μ s to ms) than fluorescence, which is a transition from S₁ to S₀ (ns).

Another consequence of the molecular nature is discrete and strong electronic transitions in photon absorption. As shown in Figure 1.7(a), absorption for organic semiconductors occurs as transitions to distinct states $(S_1, S_2 ... S_n)$ from the ground state (S_0) , where the optical bandgap E_G is the energy between S_0 and S_1 . In porphyrin systems, two absorption bands are known as the Q Band $(S_0 \rightarrow S_1)$ and the Soret Band $(S_0 \rightarrow S_2)$. The overlap (or similarity) of the vibrational modes of each orbital sub-state dictates the



Figure 1.7. Absorption spectra for organic and inorganic semiconductors. (a) Jablonski diagram for organic semiconductors highlighting the gap in density of states between top of S_1 and bottom of S_2 . This leads to two separate bands of absorption, as seen in the bottom left inset. The middle inset shows the vibronic substates in the S_1 and S_2 orbitals as a function of r_{ab} , the distance between molecules. (b) Jablonski diagram for an inorganic semiconductor showing absorption of all photons with energy above the bandgap.

strength of transition, leading to variations in the peak absorption intensity, which are highlighted in Figure 1.7(a) as "weak", "moderate", and "strong" transitions. In many acene and porphyrin molecules, these vibronic features can be resolved in absorption and emission spectra but are often broadened into featureless bands due to additional vibrational coupling and splitting in the solid state. Nonetheless, the gap between the S_1 and S_2 levels (and corresponding vibronic substates) can create a discontinuity in the density of states (DOS) that can be exploited to allow visible light transmission with selective NIR harvesting. This is in sharp contrast to the continuum in the density of states for traditional inorganic semiconductors (Figure 1.7 (b)), which leads to a continuously decaying absorption profile. The continuum of states for inorganic semiconductors arises from the periodicity in crystal structure and therefore the nuclear potential energy distribution (Bloch's theorem). In either class of materials, the excited state electron rapidly relaxes to S_1



Figure 1.8. Frontier energy levels for a series of acenes. From left to right: naphthalene ($C_{10}H_8$), anthracene ($C_{14}H_{10}$), tetracene ($C_{18}H_{12}$) and pentacene ($C_{22}H_{14}$). A_c is electron affinity and I_c is ionization energy. Figure adapted from Ref. [3] with permission.

via thermalization after a photon is absorbed into an S_n state.

The properties of organic semiconductors can be finely tuned via changes in the molecular structure, conjugation, and crystal structure. Bandgap engineering can be achieved by adjusting the conjugation length or by designing push pull molecules. The progression of the bandgap with conjugation is well demonstrated in the acene series where the addition of conjugated benzene rings starting from naphthalene to pentacene results in additional orbital energy level splitting that decreases the bandgap (Figure 1.8).[3, 40] Push pull molecules also rely on energy level splitting to decrease the bandgap and are composed of alternating electron donating and electron accepting units (D-A). When the D and A units are close, the highest occupied molecular orbital (HOMO) levels split, leading to a shallower HOMO level than either unit has. Similarly, the lowest unoccupied molecular orbital (LUMO) levels split and produce a deeper LUMO level. The bandgap of the D-A unit is thus narrowed by the HOMO-LUMO level splitting.



Figure 1.9. Förster and Dexter energy-transfer mechanisms. (a) Schematic of Förster energy transfer shown for singlets. D = donor, A = acceptor and * = excited state. (b) Schematic of Dexter energy transfer shown for triplets.

1.1.4 Energy transport in organic semiconductors

This section will cover the intermolecular transfer of excitons, the second important energy carrier in organic semiconductors. Excitons can move within a material via two main mechanisms: Förster and Dexter transfer. In Förster transfer, also called Förster resonance energy transfer (FRET), the exciton on the donor (D) undergoes long-range dipole-dipole coupling with the acceptor (A) molecule, and the energy non-radiatively transfers from donor to acceptor (Figure 1.9 (a)). This energy transfer can happen between similar or dissimilar molecules. The rate of FRET depends on 1) the distance between the donor and acceptor, 2) the amount of spectral overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor, and 3) the relative orientation of the emission dipole of the donor and the absorption dipole of the acceptor. For aligned D-A dipoles, FRET can occur between molecules up to 1-100 nm apart depending on the strength of the coupling.[39] On the other hand, Dexter transfer is highly distance sensitive, occurring typically at <1 nm length scales via direct orbital overlap. In Dexter transfer, two carriers move in concerted exchange: the electron in the donor LUMO moves to the acceptor LUMO, and an electron moves from the acceptor HOMO to the donor HOMO (Figure 1.9 (b)). Both singlet and triplet excitons may diffuse in Dexter transfer.



Figure 1.10. Four steps to photocurrent generation in molecular organic solar cells. (1) photon absorption, (2) exciton diffusion, (3) charge transfer, and (4) charge collection. (b) Blue arrows illustrate the movement of only the electron for clarity – for each electron collected at the anode there is one collected at the cathode.

1.2 Organic photovoltaics: working principles

A solar cell consists of a p-n junction sandwiched by two electrodes. This junction has a built-in voltage, and when light is incident on a solar cell, the excess carriers move from one electrode to the other due to the built-in electric field. Organic p-n junctions are distinct from inorganic p-n junctions because free carriers are not typically produced directly by light excitation. The photoexcited state that is separated by the built-in electric field in inorganic p-n junctions remains coulombically bound in organic materials, requiring an energetic driving force for dissociation greater than the exciton binding energy. In organic semiconductors, photocurrent production occurs in four distinct steps with different efficiencies: absorption (η_A), exciton diffusion (η_{ED}), charge transfer (η_{CT}), and charge collection (η_{CC}) (Figure 1.10). At a specific wavelength, a photon can be absorbed with efficiency η_A (absorption efficiency), promoting an electron from the HOMO to the LUMO. The exciton then diffuses to a heterojunction with efficiency η_{ED} (exciton diffusion length, which can vary from 10 to 20 nm in organic materials.[41] The exciton then separates into an electron on the acceptor material and a hole on the donor material with efficiency η_{CT} (charge transfer efficiency). The isolated charge carriers are then swept to the electrodes by the internal electric field or via diffusion with efficiency η_{CC} (charge collection efficiency).

$$V_{OC} = V_{OC} = V_{OC}$$

$$FF = \frac{V_{MP} J_{MP}}{V_{OC} J_{SC}}$$

$$\eta = V_{OC} J_{SC} FF / P_{in}$$

$$(V_{MP}, J_{MP})$$

Figure 1.11. *JV* curve for solar cell with PV performance metrics shown on it. The inner shaded box shows the maximum power producible, and the outer box shows the area of $J_{SC}*V_{OC}$.

In any diode (organic or inorganic), current flows in one direction. When light is incident on the diode, the current-voltage (I-V) relationship of the solar cell can be described as an exponential curve shifted by the photocurrent:

$$I = I_0 \left[\exp\left(\frac{qV}{nkT}\right) - 1 \right] - I_{ph}$$
(1.3)

Where I_0 is the dark saturation current, q is the elementary charge, V is voltage, n is the ideality factor, k is the Boltzmann constant, T is temperature, and I_{ph} is the photocurrent. The current is usually divided by the area of the device to give J, the current density. This makes it easier to compare devices with different areas and to calculate the incident power, which at 1 sun intensity is 100 mW/mm². The power conversion efficiency (*PCE* or η) of a solar cell can be calculated from the current-voltage (J-V) curve, which is collected by measuring the current through an illuminated solar cell while sweeping the voltage (Figure 1.11). The *PCE* is defined as the ratio of generated electrical power (P_{Gen}) to the total incident optical power (P_{in}) on the active area of the device:

$$\eta = \frac{P_{Gen}}{P_{in}} = \frac{J_{SC}V_{OC}FF}{P_{in}}$$
(1.4)

where J_{SC} is the short-circuit current density, V_{OC} is the open-circuit voltage, and *FF* is the ratio of the maximum power generated P_{Gen} to the product of J_{SC} and V_{OC} .
Photocurrent can be broken down into its spectral components by measuring the external quantum efficiency (*EQE*), which is the ratio of collected electrons to the number of incident photons. Since every photon produces up to one electron (in the absence of any carrier multiplication) regardless of the initial photon energy, integrating *EQE* over the solar photon spectrum *S* (units of photons/nm³-s) then yields the J_{SC} :

$$J_{sc} = q \int (EQE \times S) d\lambda \tag{1.5}$$

where *q* is the elementary charge. Equation 1.5 also is useful as a consistency check on the measurement of the J_{SC} . In OPVs, the *EQE* is the product of the four efficiencies described above: absorption (η_A), exciton diffusion (η_{ED}), charge transfer (η_{CT}), and charge collection (η_{CC}) efficiency. Internal quantum efficiency (*IQE*) is the fraction of collected charge carriers over the number of absorbed photons and is related to *EQE* by: $EQE = \eta_A * IQE$. For organic semiconductors, the exciton diffusion lengths range from 10-20 nm, which limits the thickness of the active layers to a similar range, and this tradeoff between absorption and exciton diffusion efficiency is known as the exciton diffusion bottleneck.

1.3 OPV background

Two approaches to making OPVs are to use small molecules or to use polymers. Small molecule organic semiconductors can be thermally evaporated or solution processed and have the benefit of ease of purification and good batch-to-batch consistency. Polymer OPVs are typically solution processed but require additional consideration of the final molecular weight and regioregularity. Thermal evaporation is a physical vapor deposition (PVD) technique requiring high vacuum. In this work, we utilized both approaches depending on the suitability for the active layer utilized. At this point it is not clear which approach (vacuum or solution) will ultimately be cheaper, but nearly all electronic devices are made by vacuum deposition.

In the following sections, we provide a brief overview of early OPVs polymer OPV development, thermally evaporated and solution processed small molecule OPVs, and tandem OPVs.

1.3.1. Early OPVs: 1980-2000.

The first organic solar cells consisted of a single organic thin film sandwiched between two metal electrodes with different work functions, but they had very low efficiencies (0.001 - 0.01%).[42, 43] In 1986, Tang demonstrated the first bilayer OPV (also called planar heterojunction) with an evaporated p-type phthalocyanine derivative and an n-type perylene derivative.[44] It had a breakthrough efficiency of around 1%. Around this time, conjugated polymers were developed and used in a single layer organic solar cell.[45] The next breakthrough was the use of C₆₀ in the bilayer solar cell, which enabled efficiencies over 2%.[46, 47] The higher electronegativity of C₆₀ and a high electron mobility made it energetically favorable for photoexcited electrons on the p-type organic thin film to transfer onto C₆₀, thus arriving at the naming convention of p-type (electron) donors and n-type (electron) acceptors.

1.3.2. Polymer OPVs.

A soluble derivative of C_{60} , phenyl- C_{61} -butyric acid methyl ester (PCBM), was developed in 1995 and used in a polymer bulk heterojunction device with 2.9% efficiency.[48] The bulk heterojunction structure, which was based off the dye-sensitized solar cell architecture, consisted of interpenetrating domains of the donor and acceptor to help overcome the exciton diffusion bottleneck. This was a critical step in improving the efficiency because the exciton diffusion length of the donor polymer poly-3hexylthiophene (P3HT) was ~10 nm, and a ~25 nm thick layer was needed to absorb most of the incoming light.[49] As a result, many photo-generated electron-hole pairs never reached a dissociating D-A interface and instead recombined. P3HT:PCBM bulk heterojunctions were developed in the early 2000s, with many studies focusing on control of morphology. Thermal annealing was shown to significantly improve efficiencies. Analytical techniques such as atomic force microscopy (AFM) and x-ray diffraction (XRD) confirmed that with thermal annealing: the PCBM fullerene molecules would diffuse out of P3HT:PCBM mixed domains, PCBM would self-aggregate, and P3HT polymers would line up with one another, forming crystallites.[50, 51] Essentially, with thermal annealing, phase segregation and crystallization would occur.[49] Notably, other donors and acceptors have been developed since P3HT and PCBM. P3HT has a bandgap of 1.6 eV, but devices with PCBM are limited to *Vocs* of ~0.6 V. Since then, low bandgap polymers



Figure 1.12. Non-fullerene acceptor with 11.2% PCE. (a) Device structure and molecular structure. (b) Absorption profiles of PBDB-T, PC₇₁BM, and ITIC. (c) Solution absorption of PBDB-T as a function of temperature. (d) Energy level schematic for PBDB-T/PC₇₁BM and PBDB-T/ITIC devices. Figure reproduced with permission from Ref. [12].

with higher photocurrents have been developed (PDCTBT, PTB7, etc.) to absorb in the NIR portion of the solar spectrum. Efforts to improve PCBM led to the development of PC₇₁BM, which has more absorption in the visible spectrum and absorption out to 700 nm.[52] However, fullerene-based acceptors overall have been challenging to replace due to their high electron mobilities. The HOMO/LUMO levels are hard to modify for fullerenes, and precise control of the energy levels is needed to optimize interface gaps (voltage) and Δ LUMO gaps (photocurrent). To overcome this, a record non-fullerene device was recently demonstrated with 11.2% PCE (Figure 1.12).[12] The new acceptor ITIC significantly differed from PCBM in its molecular structure, its primarily NIR absorption (peak at 710 nm, shoulder ~630 nm), and its higher HOMO and LUMO levels (3.78/5.51 vs. 3.98/5.96 for PCBM). The raising of the LUMO levels contributed to a higher interface gap and therefore V_{oc} . Polymer-based OPVs have crossed the 10% PCE threshold in research efficiencies.

1.3.3. Small molecule OPVs: thermal evaporation.

The first bilayer OPV used copper phthalocyanine, an evaporated small molecule, as the donor. Phthalocyanines, merocyanines, squaraines, diketyopyrrolopyrroles, borondipyrromethene, and isoindigo dyes are examples of the wide variety of small molecules that can be evaporated or spin-coated as donors for OPVs. Phthalocyanines consist of four isoindole groups linked together by nitrogen atoms, leading to a planar aromatic structure. A great deal of functionalization can be done either on the perimeter (e.g. adding sulfonate or carboxylate groups for water solubility) or in the center coordinating bivalent (+2) metal atom. The size and shape of the metal atom can lead to either planar (CuPc) or bent (PbPc, SnPc, ClAlPc) molecules. In the case of chloroaluminum phthalocyanine, the out-of-plane Cl atom changes the packing from cofacial to slip-stack, leading to a bathochromic shift in absorption which can be exploited in nearinfrared absorbing OPVs.[53] Subphthalocyanines, a smaller derivative of phthalocyanine molecules, have been used in solar cells with up to 3.0% PCE.[54] Merocyanines, another small molecule, have been used in solar cells with 3.9% PCE.[55] One of the earliest attempts to make push-pull molecules for OPV donors was in 2006 and introduced dicyanovinyl (DCV) electron withdrawing units to a 1-D oligothiophene.[56] Putting electron donating and electron withdrawing groups on the same molecule can promote intramolecular charge transfer and increase absorption.[53] Another push-pull molecule DTDCTB was coevaporated with C₇₀ to form a planar mixed heterojunction device with 7.9% PCE, a record for single junction evaporated small molecule OPV at the time.[57] More recently, an 8.0% efficient device was demonstrated using thermally evaporated small molecules in a ternary architecture (C_{70} , DTTz, and DTDCTB).[58]

1.3.4. Solution processed small molecule OPVs

Some small molecules decompose during thermal evaporation; for these materials, solution processing methods such as spin-coating and doctor blading are used to deposit uniform thin films. Merocyanines were cast from solution in a metal/dye/metal sandwich structure as early as 1978.[59] In dye sensitized solar cells (DSSCs), a mesoporous layer of TiO_2 is soaked in a solution containing small molecule photosensitizers; the first was demonstrated in 1991 with an efficiency of 7.1%.[60] Subnapthalocyanine

(SubNc) was spincoated to form amorphous thin films; the PCE of the devices were 1.5% after annealing at 120°C for 40 minutes.[61] Squaraines were spincoated with PCBM or use evaporated C_{60} for the acceptor and achieved up to 5.7% PCE after thermal annealing at 90°C.[62] Mainly, 1-D oligothiophene-based push pull molecules dominate among solution processed small molecule donors. A D-A-A planar mixed heterojunction (PMHJ) with C_{70} with 6.4% PCE, which was the record in 2009.[63] More recently, >11% PCE was obtained using a small molecule ternary-blend OPV.[64]

1.3.5. Tandem OPVs

A key approach to limit thermalization losses in OPV is to stack cells together in a tandem (or multijunction) OPV. There are predominately two types of tandem solar cells, solar cells connected in series and solar cells connected in parallel. For series tandem solar cells, the layers in both subcells can be deposited in a monolithic stack because the intermediate layer does not need to be externally contacted. The majority of tandem OPVs are monolithically configured in series because of the compatibility with single junction device fabrication processes. The open circuit voltage of a series tandem solar cell is the sum of the open circuit voltages of its subcells:

$$V_{OC,tandem} = V_{OC,bottom} + V_{OC,top} \tag{1.6}$$

and the photocurrent of the tandem device is limited by the subcell that produces less current (also called the limiting or current-limiting subcell):

$$J_{SC,tandem} = \min(J_{SC,bottom}, J_{SC,top})$$
(1.7)

Because of this condition, the currents produced in both the top and bottom subcells must be matched to maximize J_{SC} . This can be accomplished by tuning the absorber layer thicknesses in each subcell or tuning the thicknesses of optical spacer layers, which are transparent and conductive layers within the structure. Tuning the absorber layer thickness straightforwardly adjusts the number of photogenerated carriers within a subcell, and tuning the optical spacer layer thicknesses adjusts the intensity of the electric field profile across the structure, thereby allowing the maximum light absorption to occur near the donor-

acceptor interface. Because of the relatively large number of layers, tuning these thicknesses is a task greatly aided by simulations.

Between the two subcells in a tandem OPV is the intermediate layers, also called interstitial layers or the recombination zone. These layers are responsible for recombining photo-generated holes and electrons from the two subcells. As such, intermediate layers consist of hole transporting layer (HTL), a thin metal (to reset the work function and serve as recombination centers), and an electron transporting layer (ETL). Extra care must be taken for solution processed tandem OPVs to ensure that solvents used to spincast intermediate layers do not dissolve the first subcell. Other optimizations for the intermediate layers involve tuning the work function of the thin metal and improving the carrier mobilities in the ETL and HTLs by doping or other treatments.

The Shockley Queisser (SQ) limit for a single junction solar cell can be calculated based on thermodynamic limits. The ideal bandgap for a single junction solar cell is around 1.1-1.4 eV, leading to a maximum theoretical efficiency of 33% PCE.[65] The open circuit voltage depends on the bandgap E_g , but high J_{SC} requires absorption of many photons so there is a natural trade-off. A small bandgap leads to absorption of many photons, but because the electrons rapidly relax to the conduction band edge (in OPV, the LUMO level) upon photoexcitation, much of the energy of high-energy photons is lost. A large bandgap allows for more efficient collection of high-energy photons, but photons with less energy than the bandgap are not absorbed, leading to a loss in J_{SC} . A considerable amount of energy is lost in the thermalization of electrons excited by high-energy photons to the LUMO level. Using multiple subcells with complementary absorbers reduces thermalization loss and has been a traditional way to increase efficiencies for inorganic (Si, GaAs, etc.) as well as organic solar cells. Empirical limits for organic solar cells include a loss in voltage from the donor-acceptor heterojunction / energy offset required to dissociate excitons. Based on the trend of best reported PVs with a range of bandgaps, the highest achievable V_{OC} is approximately 80% of the SQ limit;[66] this heuristic, when combined with 75% EQE and 0.75 FF (the highest values demonstrated by OPV), a practical limit of 17% PCE was calculated for single junction OPVs.[66] For current-matched, two-junction OPVs, the empirical efficiency limit was calculated to be 24%, using

absorber bandgaps of 0.9 and 1.5 eV.[66] These efficiency limits show why tandem architectures are attractive for higher efficiency devices. The efficiency limits of transparent solar cells (both single junction and multijunction) are treated differently and will be described in more detail in Chapter 2.

The first tandem OPV was developed by Hiramoto et al in 1990 using a gold interstitial layer between two identical small molecule subcells (Me-PTC/H₂PC).[67] The voltage of the tandem device was almost double of the single junction (0.74 V vs. 0.44 V). From that point, the development of tandem OPVs has incorporated improvements made to single junction devices (by using a planar mixed heterojunction, for example)[68] while solving challenges inherent to tandem structures, such as managing optical interference by tuning optical spacer layers[69] and changing the work function of the metal in the interstitial layer.[70] As noted previously, solvent orthogonality is critical to managing polymer tandem solar cells. Although out of the scope of this thesis, polymer tandem OPVs have had an interesting developmental path. In 2005, Kawano et al demonstrated a tandem device with two polymer subcells, both consisting of bulk heterojunctions of MDMO-PPV with $PC_{61}BM$, and an intermediate layer of sputtered ITO and spincast poly(3,4-ethylene dioxythiophene):polystyrene sulfonic acid (PEDOT:PSS).[71] Polymer subcells were also combined with evaporated small molecule subcells: the first example developed by Dennler et al in 2006 used P3HT:PCBM and ZnPc:C₆₀ bulk heterojunction and had a PCE of 2.3%.[72] Then, in 2007, Gilot et al developed the first spincast intermediate layer for tandem polymer OPV using ZnO nanoparticles dispersed in acetone and pH-neutral PEDOT:PSS.[73] Triple junctions were also demonstrated in the study.

Recently, many studies of tandem OPVs have achieved efficiencies over 10%. In 2013, Liu et al demonstrated a solution processed small molecule tandem device with 10.1% PCE.[74] It had two identical subcells connected with a polyelectrolyte intermediate layer. Chen *et al* developed a solution processed triple junction device in 2014 with 11.5% PCE using absorbers with 1.4, 1.58 and 1.9 eV bandgaps.[9] The intermediate layers consisted of PEDOT:PSS / ZnO with spincast WO₃ layer on top of the middle subcell to align energy levels for hole transport from PTB to PEDOT (Figure 1.13).[9] The current record for tandem OPVs is held by the German chemical company Heliatek. They set a record efficiency of 13.2% in



Figure 1.13. Polymer triple junction tandem solar cell. (a) Device structure, (b) absorber optical constants, and (c) energy level schematic. Figure reproduced with permission from Ref. [9]. 2016 for a triple-junction tandem with in-house designed and thermally evaporated small molecule absorbers.[75]

In summary, organic semiconductors form the basis of organic electronic devices ranging from OPVs, organic light emitting diodes (OLEDs), organic field effect transistors (OFETs), and organic thermoelectrics. The main feature of organic semiconductors is the formation of Frenkel excitons due to their low dielectric constants. Their non-crystallinity results in a discontinuity in the density of states, giving rise to distinct absorption bands, which can be tuned to be outside of the visible spectrum. This feature can be used to make visibly transparent solar cells, which is the topic of the next chapter.

Chapter 2 – Introduction to Transparent Photovoltaics

Organic photovoltaics (OPV) have long offered the promise of low cost, flexible solar cells. While recent advances have led to efficiencies beyond 10%, the large scale commercial viability of OPVs as a replacement for traditional technologies remains an open question. In this chapter, we describe the emerging field of transparent photovoltaics (TPV) that uniquely exploit the excitonic nature of organic semiconductors. Transparent photovoltaics can create entirely new functionality and markets for solar deployment while complementing traditional opaque PV technologies. Moreover, TPVs provide a new and key motivation for reinvigorating research efforts into OPVs. In this chapter, we discuss the development of semi-transparent and transparent solar cells along with their key figures of merit, characterization strategies, and theoretical efficiency limits.

2.1 TPV motivation

Visibly transparent excitonic solar cells based on organic and excitonic semiconductors that selectively absorb in the ultraviolet (UV) and the near infrared (NIR) have recently been developed.[14] These new kinds of solar cells can enable solar PV integration into buildings, windows, greenhouses, automobiles, and consumer electronics (Figure 2.1(a)) and can turn essentially any surface into a power



Figure 2.1. Transparent photovoltaic applications and the solar spectrum. (a) Example applications for transparent photovoltaics, clockwise from upper-left: skyscraper windows, greenhouse windows, e-reader screens, and automobile windows. (b) AM1.5G solar spectrum in photon flux plotted with the photopic response, figure adapted with permission from Ref. [2].

generating surface. Integrating PVs into building and car structures produces electricity at the point of consumption, thereby reducing electricity transmission costs. Also, mounting PVs onto existing surfaces also reduces the racking cost associated with installing PVs. Despite not being able to absorb photons in the visible region, TPVs can still generate power using a significant portion of the solar spectrum. Approximately 10% of the photon flux is in the ultraviolet ($\lambda < 430$ nm) and 70% of the photon flux is in the infrared ($\lambda > 680$ nm), meaning that 80% of the solar spectrum is invisible to the human eye and can be used to generate electricity (Figure 2.1(b)).

2.2 TPV figures of merit

The approach to TPVs using wavelength selective harvesting around the visible spectrum allows for the highest possible combination of efficiency and clear transparency. For TPVs, three independent objective criteria are important in their performance: power conversion efficiency (η or *PCE*), average visible transmission (*AVT*), and color rendering index (*CRI*). Optimization of TPVs therefore requires the simultaneous consideration of all these metrics. In the absence of information on the *CRI*, the product of *PCE*AVT* can be utilized as a figure of merit to assess transparent device progress and overall system efficiencies (power generation and lighting efficiency).

Solar cell transparency is reported as the average visible transmission (*AVT*) weighted by the photopic response (sensitivity to different wavelengths of light, $P(\lambda)$) and, in some cases, also by the solar **photon** spectrum (AM1.5G, $S(\lambda)$). The standard definition accepted and reported in the window industry of *AVT* is described by:

$$AVT = \frac{\int T(\lambda)P(\lambda)S(\lambda)d\lambda}{\int P(\lambda)S(\lambda)d\lambda}$$
(2.1)

where the wavelength range is selected to cover the range of the photopic response. As a reference point, typical *AVT* requirements are 50-80% for architectural glass, 55-90% for automotive glass, and 80-90% for mobile electronics.[2] For integration onto displays where the solar spectrum weighting is less important, Equation 1.2 can be simplified by substituting S = 1. We assign the notation "*AVT*₀" for *AVT* with no solar

spectrum weighting. However, because the solar spectrum is roughly flat throughout the visible spectrum, the difference between AVT_0 and AVT is usually small enough to be negligible. The solar spectrum and the photopic response are both plotted for reference in Figure 2.1 (b).

The color rendering index (*CRI*), typically used in the lighting industry, quantifies the ability of a light source to faithfully reproduce the color of an object when compared to an illuminating reference light source (typically a blackbody radiator). The color temperature of the reference blackbody radiator is chosen so that its chromaticity is closest to that of the light source being tested. The *CRI* formalism can also be used to assess the impact of transmission through a surface to reproduce the color quality of the initial source color temperature (such as the solar spectrum, AM1.5G). A *CRI* > 90 is considered to be excellent for an illumination source.[76] Commercial cool-white fluorescent light typically have a *CRI* of \geq 70,[77, 78] and an incandescent bulb has a *CRI* of 100 due to being a blackbody radiator. To calculate *CRI*, eight test-color samples (CIE 1974) are "illuminated" by a reference spectrum. This illumination is characterized by lightness (*L*) and chromaticity (*u* and *v*), which make up the three-dimensional uniform color space CIELUV. The illumination of the eight test-color samples by the light transmitted through the solar cell (*S*(λ)*T*(λ)) is then calculated. The difference in *L*, *u*, and *v* between illuminating the eight test color samples with the sun or with the light transmitted through the solar cell is then corrected for chromatic adaption (the ability of the eye to discern the same color under different illumination conditions) and averaged into the *CRI* by the following expression:

$$CRI = \frac{1}{8} \sum_{i=1}^{8} (100 - 4.6\sqrt{(\Delta L_i^*)^2 + (\Delta u_i^*)^2 + (\Delta v_i^*)^2})$$
(2.2)

For reference, the *CRI* for any neutral density absorption profile (flat absorption through the visible) is 100 regardless of the reference illumination spectrum. The color coordinates are also useful in many applications where they can indicate the degree of coloring. For example, a^* and b^* are the chromaticity indices of the *perceptually* uniform color space CIELAB system which are related to the CIELUV coordinates *u* and *v*. Positive values of b^* (0 to 100) indicate a yellow coloring, and negative values of b^* indicate blue coloring, while positive a^* indicates red coloring, and negative a^* indicates green coloring.

The photon balance is an important consistency check for any solar cell, but it is particularly important for TPVs. The photon balance is:

$$A + R + T = 1 \tag{2.3}$$

where *A* is the absorption, *R* is the reflection, and *T* is the transmission of the entire device film stack at each wavelength. While reflection and transmission can be measured by standard spectrometers, absorption is more difficult to measure directly for thin film layers. To estimate *A*, it is important to recognize that there can be absorption in both the active layer (A_{AL}) and in the contact layers (A_{CL}) so that $A = A_{AL} + A_{CL}$. The active layer absorption can be obtained from the definition of the *EQE* ($IQE = EQE / A_{AL}$). Therefore, the photon balance becomes:

$$\frac{EQE}{IQE} + A_{CL} + R + T = 1 \tag{2.4}$$

It has been shown that A_{AL} can be measured directly by measuring the *EQE* under reverse bias where *IQE* can approach 100% via field-driven dissociation and carrier collection.[79] Measurements of *R* and *T* are generally straightforward but require careful attention for reference samples: *R* measurements need appropriate highly reflective reference mirrors with known reflectivity, and *T* measurements on thin-film devices should avoid the use of reference samples (unlike with solution measurements). We note that the measurement of A_{CL} is notably difficult because variations in the thin-film architecture will change thin-film optical interference and the amount of contact absorption. One solution is to model the entire device using transfer matrix modeling described in Section 4.2 to estimate A_{CL} . Nonetheless, because the *IQE* can reach 100% for some bulk heterojunction architectures and ultrathin planar devices,[80] the following balance should still be satisfied: EQE + R + T < 1. This consistency check confirms that neither *EQE* nor *T* of the entire device has been overestimated. We emphasize that this check should be reported for all semi-transparent and transparent devices (e.g. EQE, *R*, and *T* should be reported for each device) and applied to Eq. 2.4 like the photocurrent check in integrating the *EQE* using Eq. 1.5, which is listed as a necessary criterion for many journal publications including *Nature* journals.[81]



Figure 2.2. Survey of different TPV technologies as a function of *AVT***.** Si and GaAs efficiencies are included for reference. The green shaded portion is the combination of *AVT* and *PCE* that is enabled by wavelength selective approaches. Figure adapted from Ref. [1] with permission from the authors.

2.3 TPV background and state of the art

Several approaches to making semi-transparent PVs (STPV) have been explored since the first PVs were developed, including 1) spatially segmented photovoltaics, which involves spacing opaque PVs; 2) thin film solar cells, which can make semi-transparent PVs with tint; 3) scattering solar concentrators, which impart optical haze; and 4) luminescent solar concentrators, which can be adapted for both color and high transparency. In contrast, selectively absorbing organic materials have been used to make visibly transparent PVs. In general, we categorize PVs with AVT < 50% as "semi-transparent" (neutral, hazy, or colored) and AVT > 50% as "transparent" (neutral or tinted), analogous to the language used for transparent conductors. An overview of the performance (*PCE*) and transparency (*AVT*) for organic and inorganic TPV is provided in Figure 2.2. Selected results are tabulated in Table 2.1 for single-junction organic STPV/TPV. The research developments for each category are summarized below.

2.3.1 Spatially segmented PVs

Semi-transparent photovoltaics have applications in building-integrated photovoltaics (BIPV) either as facades or colorful architectural installations (e.g. being commercialized by Solaronix, Onyx Solar,

Device Structure	Voc (V)	J_{SC} (mA cm ⁻²)	FF	η (%)	AVT (%)	η (%) * AVT(frac.) (%)	Ref.
ITO/CuPc/PTCBI/BCP/Ag/ITO	0.45	2.5	0.55	0.62	26	0.16	[4]
ITO/TiO ₂ /P3HT:PC ₇₁ BM/PEDOT:PSS/	0.53	7.4	0.40	1.95	10.4*	0.20	[19]
Ag grid	0.00		0110	1.70	1011	0.20	[->]
ITO/ZnO/SO:PC ₆₁ BM/PEDOT:PSS	0.54	2.0	0.35	0.4	52*	0.21	[25]
(TLSC) CY in PMMA with edge- mounted Si solar	0.50	1.2	0.66	0.4	86	0.34	[5]
cells							
$ITO/W_2(hpp)_4 \text{ doped } C_{60}/C_{60}/$	0.56	3.8	0.595	1.3	28	0.36	[28]
ZnPc:C ₆₀ /F ₆ TCNNQ doped BF-DPB/							
f-CNT							
ITO/TiO ₂ /P3HT:PC ₆₁ BM/MoO ₃ /ITO	0.53	6.3	0.57	1.9	21.0*	0.40	[30]
AgNW/TiOx/ZnO/P3HT:PC61BM/	0.58	8.2	0.49	2.3	22.5*	0.52	[11]
PEDOT:PSS/GO/PEDOT:PSS							
ITO/MoO ₃ /Cy-TPFB/C ₆₀ /BCP/Ag/	0.69	2.5	0.53	0.9	61	0.54	[31]
MoO ₃ /ITO							
ITO/PEDOT:PSS/Cy7-P/C ₆₀ /Ag/Alq ₃	0.40	4.7	0.463	0.9	62.4*	0.56	[32]
ITO/PEDOT:PSS/PCDTBT:PC71BM/	0.85	9.2	0.481	3.9	21.5*	0.84	[33]
TiO _x /Al/ZnO:Al							
ITO/MoO ₃ /ClAlPc/C ₆₀ /BCP/ITO	0.71	4.2	0.46	1.3	65	0.85	[14]
BBAR/Quartz/ITO/MoO ₃ /ClAlPc/	0.78	4.7	0.46	1.7	56	0.95	[14]
C ₆₀ /BCP/ITO/DBR/BBAR							
ITO/MoO ₃ /DTDCTB/DTDCTB:C ₆₀ /	0.779	5.50	0.494	2.11	60.0	1.27	[34]
C ₆₀ /Bphen/Ag/MoO ₃							
ITO/PEDOT:PSS/	0.84	7.98	0.63	4.2	31.3*	1.31	[21]
PIDT-PhanQ:PC71BM/Surfactant/Ag							
ITO/MoO ₃ /DTDCTB/DTDCTB:C ₇₀ /	0.805	7.68	0.524	3.24	46.4	1.50	[34]
C ₇₀ /Bphen/Ag/MoO ₃							
ITO/PEDOT/PTB7:PC71BM/BCP/Ag/	0.733	10.0	0.70	5.6	28	1.57	[35]
(LiF/MoO ₃) ₃							
ITO/MoO ₃ /Cy7/C ₆₀ /Alq ₃ /Ag/Alq ₃	0.63	6.4	0.54	2.2	71.2*	1.57	[36]
ITO/ZnO/C ₆₀ -SAM/	0.76	11.9	0.62	5.6	29*	1.62	[37]
PBDTTT-C-T:PC71BM/MoO3/Ag							
ITO/ZnO/PCPDTFBT:PC71BM/	0.74	11.4	0.58	5.0	51.2*	2.56	[38]
PEDOT:PSS/Ag							
ITO/PEDOT:PSS/	0.77	9.30	0.56	4.0	64.3*	2.57	[22]
PBDTT-DPP:PC61BM/TiO2/AgNW							
(Ubiquitous Energy, Inc certified device)	0.68	2.35	0.59	5.1+	50.9	2.60	[1]

Table 2.1. Selected semi-transparent and transparent PV efficiencies.

**AVT* recalculated using transmission curves provided in references +measured at 0.185 suns



Figure 2.3. Examples of segmented solar cells. (a) Schematic of segmented PV. (b) Patterned electrode for a-Si solar cell, reproduced from Ref. [13]. (c) Photo of a café façade with segmented PV installed, reproduced from Ref. [20].

and Polysolar).[82, 83] Spatially segmented PVs are solar cells that achieve some transparency through the patterning of open spaces in the module (Figure 2.3) and have been investigated for over three decades. Any PV technology can, in principle, be spatially separated by mounting a spaced array of opaque modules onto a glass superstrate (e.g. being commercialized by Solar Constructions).[84] For less obstructive views, PVs can be segmented at the mm and µm scale by patterning material in stripes or grids via etching or laser ablation – the latter approach was used with Si PVs to create devices with 8-10% *PCE* and 10% *AVT*.[20, 85] A similar approach of spatial segmentation has been demonstrated for OPVs to create limited transparency.[19] Although spatial segmentation is a conceptually simple way to add transparency to highly efficient solar cells, transparency and power conversion efficiency cannot be simultaneously optimized for the highest *AVTs*.

2.3.2 Semi-transparent single junction thin film PVs

Like spatially segmented PVs, most PV technologies can also be made thin enough to transmit a fraction of visible light to make a STPV (Figure 2.4(a)). This approach generally leads to significant tinting due to non-uniform absorption profiles but has been widely demonstrated with a variety of PV technologies, including a-Si, CdTe,[86] CIGS,[87] quantum dots,[88] GaAs,[89], and organics. However, these approaches to semi-transparent PVs are less effective at the highest *AVT* values since much of the solar flux simply passes through the active layer. At lower *AVT*, this approach often this leads to red, brown, or yellow coloring with traditional semiconductors and a full spectrum of colors with organic semiconductors, which



Figure 2.4. Examples of thin-film, semi-transparent solar cells. (a) Schematic of thin-film, semi-transparent PV. (b, c) Demonstrations of semi-transparent organic solar cells adapted from Ref. [11] and [21], respectively.

could be advantageous in applications for colorful architecture. Nonetheless, semi-transparent solar panels based on crystalline and amorphous silicon have been produced on a commercial scale, and multiple studies have been conducted on their real (and simulated) power-generation on different buildings throughout the world.[90, 91]

Several semitransparent OPVs have been made using this approach. The archetypal small molecule copper phthalocyanine (CuPc)[44] was used with 3,4,9,10-perylenetetracarboxylic bis-benzimidazole (PTCBI) as an acceptor and indium tin oxide (ITO) as the transparent electrode for a device with *PCE* of 0.62% and *AVT* of 26%.[4] Similar results were obtained with a CuPc/C₆₀ heterojunction and a solution-processed silver nanowire (AgNW) mesh.[92] Another phthalocyanine, zinc phthalocyanine (ZnPc), was used as both the donor and as the high-index anti-reflection coating for a device with *PCE* 0.6% and *AVT* of 24%.[93] The archetypal polymer bulk heterojunction composed of poly-3-hexylthiophene (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) has been used in many studies of semitransparent polymer PV.[19, 94-96] For example, Ameri *et al* used a silver grid with an underlying layer of PEDOT:PSS to make P3HT:PC₇₀BM devices with 2% *PCE* and 10% *AVT*.[19] Because the peak absorption of P3HT (~550 nm) lies in the middle of the visible region, the visible transparency is reduced in these systems (Figure 2.4 (b)).[11]

Considerable efforts were made to develop polymers with smaller bandgaps for higher efficiency semitransparent and opaque devices.[97] The combination of the thieno[3,4-*b*]thiophene (TT) unit (weak acceptor strength; strong quinoidal resonance) and the large planar benzodithiophene donor gave rise to the



Figure 2.5. Scattering solar concentrators. (a) Schematic of scattering solar concentrator, modified from Ref. [5]. Incoming light is scattered and wave-guided to the edge-mounted solar cell. (b) Photo of a scattering concentrator window module, reproduced from Ref. [15].

PTB series, which had a bandgap of 1.6 eV and improved polymer-based solar cell performance from 4 to 6% *PCE*.[97, 98] Further improvements in side chain engineering, such as adding fluorine to the TT unit to deepen the HOMO level, led to the development of PTB7, a polymer that has enabled *PCEs* over 8% in both conventional and inverted architectures[99] and has been used in STPVs with 5.6% *PCE* and 28% *AVT*.[35, 100]

2.3.3 Luminescent solar concentrators and scattering concentrators

Luminescent solar concentrators and scattering concentrators are two types of solar concentrators that utilize a wave-guiding plate to focus light at the edges. In a luminescent solar concentrator photoluminescent chromophores, i.e. compounds or molecules that absorb and reemit light of a longer wavelength, are embedded in the wave-guiding plate. For scattering concentrators, light scattering particles are embedded in the plate (Figure 2.5 (a)). In both cases, a high-efficiency solar cell (e.g. Si or GaAs) is mounted at the edges to convert the concentrated light to electricity. The simple construction means that this approach can be very scalable, however, efficiencies have been modest (< 7%). Luminescent solar concentrators have been made using organic compounds, typically heavily colored since their inception.[101-103] In laboratory studies, scattering concentrators using TiO₂ nanoparticles have been made with 1.0% *PCE* and 85% transmittance with a device area of 2.5 cm²,[15, 104, 105] and a range of scattering particles have been demonstrated.[106] However, scattering concentrators face a fundamental



Figure 2.6. UV- and NIR-selective transparent solar cells. (a) Schematic of selectively UV and NIRabsorbing excitonic transparent solar cells from Ref. [1]. (b, c) Demonstrations of transparent organic solar cells adapted from Ref. [14]and [22], respectively.



Figure 2.7. Low bandgap donors. (a) Plot of solar spectrum overlaid with the normalized film absorption spectra of different low bandgap donors spanning a large near-infrared spectral range with NIR selective harvesting. (b) Molecular structures of the different low bandgap donors in (a).

tradeoff between transparency and *PCE*, and often exhibit larger losses at large device sizes due to outcoupling.[107]

2.3.4 Visibly transparent PVs

The development of visibly transparent solar cells based on selective harvesting of the invisible parts of the solar spectrum has emerged within the last 5-10 years. Wavelength selective TPVs offer the highest potential in combined *AVT* and *PCE* and requires three key components: 1) active layers with selective absorption potential in the UV and NIR, 2) highly conductive electrodes that are highly transparent throughout the solar spectrum, and 3) an overall device configuration that enables selective absorption in the active layers rather than in electrode layers (Figure 2.6 (a)). The highest reported efficiencies currently

range from 5% (single junction) to 8% (multijunction) (Table 6.1). The development of narrow bandgap small molecule (ClAIPc,[14] Cy,[32] etc.) and polymer (PBDTT-DPP,[22] PCPDTFBT,[38] etc.) donors with selective NIR harvesting was an important step to enabling high efficiency transparent solar cells. Shown in Figure 2.7 are the absorption spectra for free-standing films and molecular structures of key organic molecules and polymers with selective NIR harvesting.

The first TPV based on selective harvesting in the infrared was demonstrated using chloroaluminum phthalocyanine (ClAIPc).[14] C_{60} was used as the acceptor and sputtered ITO was used as the top and bottom electrodes to produce a *PCE* of 1.3% with an *AVT* of 65% (Figure 2.6 (b)) that was increased to a *PCE* of 1.7% and an *AVT* of 56% using a NIR selective transparent mirror. Because ITO was used as both the anode and cathode, metal oxide layers were utilized to obtain a high work function anisotropy and high photovoltages (>0.7 V).[14] TPVs have also been made using push-pull molecules such as DTDCTB, which consists of a thiophene electron-donating group and a benzothiadiazole (BT) electron-withdrawing group.[34] DTDCTB was thermally evaporated in a PMHJ structure, which has neat donor and acceptor layers on either side of the BHJ to aid in carrier collection. MoO₃ was used as the optical incoupling layer on top of a thin layer of Ag. The device has a high product of efficiency and *AVT*, with 60% *AVT* and 2.1% *PCE* for the device using C₆₀.

Several solution processable small molecule donors have also been used in TPVs including heptamethine salts,[31, 36] squaraines (SQs),[25, 108] and boron-dipyrromethene (BODIPY) derivatives.[109] Heptamethine salts in particular are uniquely tunable by anion exchange and blending that can precisely modulate the HOMO and LUMO levels by up to 1 eV,[31] which is desirable for aligning energy levels to balance electron transfer efficiency and interface recombination that can push performance towards the excitonic limit. This energy level tuning can also help to experimentally determine exciton binding energies and optimize the donor-acceptor LUMO level offset for maximum J_{SC} and V_{oc} .[110] Due to their small bandgaps and energy level tunability, heptamethine salts have been used in TPVs with high AVT (>70%) and *PCEs* of up to 2.2%.[36] Moreover, opaque tandem devices have been demonstrated using



Figure 2.8. High performance transparent solar cell module. (a) *JV* characteristics for Newport-certified high performance single junction transparent solar cell from Ubiquitous Energy using proprietary materials. (b) Transmission, reflection and *EQE* spectra for device in (a). (c) Photo of large-area, series-integrated module made using devices in (a).

heptamethines and trimethines with 4.3% efficiency,[111] making these a promising material set for tandem TPVs in the future.

High efficiency solution processed conjugated polymer TPVs have also been demonstrated based on poly(2,60-4,8-bis(5-ethylhexylthienyl)benzo-[1,2-b;3,4-b]dithiophene-alt-5-dibutyloctyl-3,6-bis(5bromothiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4-dione) (PBDTT-DPP) with PC₆₀BM as the acceptor.[22] PBDTT-DPP is composed of BDT donor units and DPP acceptor units (strong acceptor behavior with weak quinoidal resonance) with a peak polymer film absorption positioned at ~780 nm[97]. When combined with a composite AgNW electrode, a *PCE* of 4.0% and *AVT* of 64% was achieved, the highest combination of *PCE* and *AVT* for solution-processed single junction solar cells (Figure 2.6 (c)).

Recently, a certified *PCE* of 5.1% with 50.9% *AVT* was reported,[1] which is currently the highest combination of *PCE***AVT* for single junction devices (Figure 2.8). A highly transparent large area (10 cm x 10 cm) module was similarly demonstrated by combining these devices in series integration, which resulted in voltages over 100V under mid-day outdoor illumination.



Figure 2.9. Transparent luminescent solar concentrators. (a) Schematic of luminescent solar concentrators reproduced from Ref. [5]. Incoming light is absorbed and re-emitted by a luminophore embedded in a wave-guiding plate. (b) Absorption and emission spectra of luminescent dye with Stokes Shift *S* and peak width *W*. (c) Photo of a TLSC, from Ref. [5].

2.3.5 Transparent luminescent solar concentrators

Transparent luminescent solar concentrator (TLSC) are a related technology to TPV, which can exhibit high *AVT*, *CRI*, and defect tolerance (Figure 2.9 (a)). As with other LSCs, energy is guided over the device optically rather than electrically. TLSCs are composed of luminophores that absorbs either UV or IR light and **reemits** deeper NIR light. To minimize reabsorption of the emitted light, the Stokes shift of the luminophore (the difference between absorption and emission peak, in nm) should ideally be > 100nm (Figure 2.9(b)).[112] Reabsorption losses are also a primary limiting factor for the scale-up of TLSCs > 1 m². UV-absorbing inorganic luminophores with large down-conversion shifts (~400 nm) have been used for TLSCs with *PCE* > 0.5% and *AVT* > 85%.[113] However, due to the lower photon flux in the UV region of the solar spectrum, it is important to develop NIR-selective luminophores with large Stokes shifts for TLSCs as well. TLSCs using NIR-absorbing organic salts have been made with 0.4% *PCE* and 86% *AVT* (Figure 2.9(c)).[5] Looking ahead, the key challenges for TLSCs are associated with the design of luminophores with high luminescence efficiency, high Stokes shifts, and deeper NIR-selective harvesting.

2.4 TPV transparent electrodes

Transparent electrodes are a critical component of TPV devices as they are required in both the anode and cathode with both high and low work functions. Transparent electrodes have been made using transparent conductive oxides, ultra-thin metal films, conductive polymers, carbon nanotubes, and metallic nanowires. We summarize these key electrode materials that can be integrated into such devices and discuss considerations for their full optimization. Future advances in transparent electrodes will greatly aid the development and scalability of TPVs.

2.4.1 Transparent conductive oxides

Transparent conductive oxides (TCOs) have wide bandgaps, which lead to low absorbance in the visible spectrum. Indium tin oxide (ITO) is the most commonly used transparent electrode for thin film solar cells (OPV,[44] a-Si,[114] CdTe,[115] etc.), organic light emitting diodes (OLEDs),[116] LCDs,[117], and touchscreens. It has a combination of good transparency (~80% in visible wavelengths) and conductivities (sheet resistances of around 10-20 Ω/\Box) and accordingly has been used as a top electrode in many TPV studies. [4, 14, 30, 31] ITO is typically deposited via magnetron plasma sputtering but can also be deposited using pulsed laser deposition or solution deposition of nanoparticles. A high temperature (400-500°C) annealing step is typically used for ITO to achieve its maximum transparency and conductivity. The deposition of ITO is straightforward when deposited as the first/bottom electrode onto hard substrates like glass or steel, but it can be less compatible with flexible substrates due to the inherent brittleness of polycrystalline ITO and the high temperature annealing step. The ion bombardment of sputtering may damage underlying organic films, leading to lower device yields when ITO is used as a top electrode.[118] Barrier layers such as organics (e.g. CuPc), [119] metal oxides (MoO_3) , [30] or thin metals (Ag)[4] can be deposited prior to sputtering ITO to protect the underlying organic films. Low energy and oblique depositions of ITO have also been explored to minimize damage to underlying films. For example, ITO has been directly deposited onto organic layers using low operating powers of 7-25 W and RF sputtering at a low rate (0.05-0.3 Å/s).[14]

Another key consideration of using ITO (and many other conductors) is the potential for strong surface plasmon resonances (SPR) in the NIR, which commonly results in significant absorption at wavelengths in the range of 1100-2000 nm (Figure 2.10(a)). SPR are excited surface waves of conduction electrons found in any conductor. These oscillations and absorption features are highly sensitive to the dielectric environment, angle of excitation, conductivity, and density; thus, the SPR are also sensitive to



Figure 2.10. Thin silver and ITO comparison. (a) Transmission spectra for AgNW electrodes with different transparencies and sheet resistances with ITO as a reference. Note the pronounced IR absorption of the ITO electrode for $\lambda > 1200$ nm due to SPR. Graph reproduced from Ref. [7]. (b) Transmission spectra of ITO processed under different annealing conditions. Graph reproduced from Ref. [16] (c) SEM image of an AgNW electrode reproduced from Ref. [7]. (d) Normalized extinction coefficient for Ag nanoplates of different sizes, reproduced from Ref. [26].

the processing conditions (such as annealing, doping, etc.). This is highlighted in Figure 2.10(b) for ITO, where annealing in air can shift this SPR deeper in the IR. Ultrathin metals and metallic nanoparticles also often exhibit SPR in the visible and NIR and therefore also need to be carefully considered, while metal nanowires often have SPR deeper in the IR. As will be discussed in Section 2.5, the ideal bandgap for a completely transparent solar cell is around 1.1 eV, which corresponds to a wavelength of 1100 nm. Thus, SPR could result in considerable amounts of parasitic NIR absorption in the contact layers, which will be important to consider in future development of TPVs.

Alternative transparent conductive oxides have been considered for ITO due to the limited availability of In and cost. One example is zinc oxide, which is earth-abundant and can be doped with aluminum and gallium for increased conductivity. Aluminum-doped zinc oxide (AZO) has been used with TiO₂ and Al interlayers for poly[9'-hepta-decanyl-2,7carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'benzothiadiazole) (PCDTBT):PC₇₁BM solar cells to achieve 3.9% *PCE* with 21.5% *AVT*.[33] The 8 nm TiO₂ layer was spincoated on top of the mixed PCDTBT:PC₇₁BM layer for electron selectivity and protection during the sputtering process. The Al interlayer provided partial reflectance as well as chemical protection between the AZO and TiO₂. Schubert demonstrated a highly transparent gallium doped zinc oxide top electrode using pulsed laser deposition with an average transmission of 82.7% (400-800 nm) and sheet resistance R_S of 83 Ω/\Box .[120] By placing a metal shield between the target and the sample during PLD, direct line of sight ballistic particles were reduced that limited damage to the underlying organic films.

Amorphous sputtered oxides may also be suitable for flexible substrates. This was shown, for example, with InZnAlO (IZAO) where the resistance did not change over 10,000 bending cycles.[121] Additionally, the IZAO electrode showed high transmission ($AVT \sim 88\%$) and low sheet resistivities (85 Ω/\Box).[121] When used as a bottom electrode in P3HT:PCBM flexible devices on polyethylene terephthalate (PET), IZAO had higher efficiencies (2.5% vs. 1.9%) compared to cells with ITO and PEDOT:PSS.[121] Combining amorphous sputtered oxides like IZAO with methods to mitigate damage from sputtering could enable their use as both bottom and top electrode in rigid and flexible TPVs.

2.4.2 Ultra-thin metals

Ultra-thin metals are attractive candidates to replace ITO for their compatibility with roll-to-roll processes, low-temperature processing, and improved flexibility. They can be deposited using thermal evaporation, which causes less damage to underlying organic films compared to sputtering. However, ultra-thin metals face an inherent tradeoff between transparency and conductivity at low thicknesses and are in general less transparent than ITO except in the deep NIR spectrum ($\lambda > 1000$ nm) (Figure 2.10 (a)). Moreover, many metals such as Ag can often degrade over time via oxidation.[122]

The sheet resistance at low thicknesses increases due to the rise of electron scattering at surface and grain boundaries, which can be predicted for a variety of metals using the Fuchs-Sondheimer and Mayadas-Shatzkes models.[123] Ag films with thicknesses below 12 nm are not typically continuous or conductive,[124] but new approaches via seeding have enabled ultrasmooth and ultrathin metals.[125, 126] More recently, a flexible TPV using thin Ag as the electrode and PET as the substrate was demonstrated with little drop in performance after 1500 bending cycles at 2.7% tensile strain.[127]

The deposition of composite metal/semiconductor layers, originally conceived as a way to move the electric field intensity closer to the donor acceptor interface $(E_{DA})^2$, has become a widely-used method of making semi-transparent solar cells.[34, 36, 109, 128] In composite electrodes consisting of metal/semiconductor multilayers, the metal layer is generally used for lateral conductivity while the semiconductor functions both to select carriers and manage optical field profiles. O'Connor modeled the electric field intensity at the donor-acceptor interface for a generic capping layer as a function of index of refraction and thickness. [128] In the planar CuPc/ C_{60} device, an enhancement of 30% was seen in both the modeled $(E_{DA})^2$ for $\lambda = 470$ nm (absorption of C₆₀) and experimental J_{SC} for a capping layer consisting of 75 nm of aluminum hydroxyquinoline (Alq₃).[128] Véron used this approach in organic capping layer for enhanced light in/outcoupling in a semitransparent electrode of 12 nm Ag with 20 nm Alq₃ to make a transparent solar cell with 2.2% PCE and 71.4% AVT.[36] Inorganic semiconductors like MoO₃ can also be used to make transparent electrodes, as in the study by Lin that used an electrode of Ag $(14 \text{ nm}) / \text{MoO}_3$ (40 nm) in a DTDCTB:C₇₀ device that had 3.24% PCE and 46.4% AVT.[34] This approach could also be used to eliminate ITO from the device entirely since the bottom ITO can also be replaced by a semiconductor/metal electrode. This was done using MoO_3/Ag in the study by Wang[129] and MoO₃/Ag/MoO₃ was used to replace ITO as a bottom anode to make PCDTBT:PC₇₁BM solar cells with 4.4% PCE.[130] In this study, 2 nm of MoO₃ served as a seed layer for the 6 nm Ag, which was deposited onto -5°C substrates in order to prevent Ag interdiffusion. [130] A separate study by Schubert used a similar approach with 1 nm of Ca, Al, or Au as seed layers for the lateral-conducting Ag layer, [125] where the highest transparency electrode consisted of 3 nm MoO₃ / 1 nm Au / 7 nm Ag / MoO₃ 5 nm / Alq₃ 4 nm and has a peak transmittance of 83% at 580 nm and a resistivity of 19 Ω/\Box .

2.4.3 Polymers and conductive nanoparticles

As an alternative to the vapor deposition of oxides and metals, polymer-based conductors have been explored as transparent electrodes that can be deposited using spincoating or spraycoating. However, these polymer-based conductors typically exhibit lower conductivities and transparencies when compared to other alternative electrodes and may be incompatible on some systems due to solubilities or wettability of the active layers. PEDOT:PSS, which is typically used as an anode modification layer or can be used as a transparent electrode directly, is deposited via spincoating[131-133] spraycoating,[25, 134, 135], or vapor polymerization. For example, a transparent inverted OPV was made with the following structure: ITO/ZnO/SQ:PC₆₀BM/PEDOT:PSS, where ZnO was spincoated on from a sol-gel solution, the SQ:PC₆₀BM solution was spincoated and the low and high-conductivity formulations of PEDOT:PSS were spraycoated.[25] As PEDOT:PSS is an aqueous solution, it is difficult to spincoat onto hydrophobic organic surfaces. In these cases, dilution in isopropanol or surfactant additives can be used to achieve enhanced wetting. For example, a layer of AI4083 (lower conductivity formulation of PEDOT for interfaces) diluted in isopropanol and n-butanol was first spray coated, rendering it suitable for deposition of PH500 (high conductivity PEDOT).

Conducting nanoparticles can also be suspended in solution and spincoated or spraycoated to make transparent electrodes. Examples include silver nanowires (AgNW),[136-140] ITO nanoparticles,[22] graphene[141, 142] and carbon nanotubes.[28, 143, 144] These conducting nanoparticles usually need to be embedded in a conductive matrix or mechanically contacted to achieve higher conductivity. One example is the development of a composite AgNW electrode in TPVs, where the gaps between silver nanowires were filled with a spincoated layer of ITO nanoparticles.[22] Other hybrid electrodes have combined thin Ag, silicon nanowires, PEDOT:PSS, and Alq₃ to improve transmission over a long range of wavelengths, highlighting the potential benefits in incorporating multiple optimization strategies.[145]

2.5 TPV efficiency limits

The theoretical efficiency limits are useful in understanding the overall potential of TPVs and can be used to establish reasonable performance goals for different applications. Calculation of the efficiency limits of transparent solar cells starts with the Shockley-Queisser (also known as detailed balance) limit.[65] Every photon outside of the visible band with energy higher than the bandgap E_G is assumed to be absorbed and converted to an electron with 100% efficiency, setting the upper limit for J_{SC} . The electron then relaxes to the bandgap and is collected at the potential defined by the maximum voltage from the dark recombination rate of a black body radiator. For AM1.5G sunlight, the maximum efficiency for an opaque, single junction cell is 33.1%. We note that variations in this number have been reported due to slight variations and approximations in the solar spectrum used to perform the calculation.[2] The range of visible wavelengths for calculating the efficiency limit was defined to be 435-670 nm, where the *CRI* can be > 95



Figure 2.11. Efficiency limits of TPVs. Figures reproduced from Ref. [2]. (a) Calculated *CRI* and *AVT* values for ideal transmission curves with different UV and IR wavelength cutoffs. (b) Idealized step-function absorption curves for a solar cell with bandgap E_G . For a *AVT* of 10%, the absorption would be 10% from 435-670 nm, as shown by the dashed line. (c) Thermodynamic efficiency limits for TPVs with different *AVT*s as a function of their bandgap. (d) Thermodynamic efficiency limit for TPVs with different *AVT*s and number of junctions.

and the *AVT* can be > 99.5% (Figure 2.11(a)).[2] While it is possible to see wavelengths outside this range if bright enough (e.g. 370-435nm ad 670-750nm), these wavelengths do not strongly contribute to our perception of color rendering. (Figure 2.11(b)).[2] The idealized step-function absorption curves envisioned in Figure 2.11(b) can be achieved with molecular absorption profiles alone or enhanced with the use of 1D photonic crystals. The thermodynamic efficiency was calculated for varying bandgaps and for varying amounts of neutral absorption profiles in the visible (Figure 2.11(c)). A single junction transparent solar cell with 100% transparency has a theoretical efficiency limit of 20.6%.[2] This efficiency limit can be further increased via multijunction integration (as described in Section 1.3.5), where complementary bandgaps enable high energy photons to be absorbed in higher voltage subcells. Indeed, one of the biggest loss mechanisms in the single-junction efficiency limit is the thermal relaxation of hot electrons to the bandgap. For a transparent two, three, and infinite-junction solar cell with series integration and perfect photocurrent matching, the thermodynamic efficiency limits are 27.1%, 29.8%, and 37%, respectively (Figure 2.11(d)).[2]

Chapter 3 – Experimental Techniques

In this chapter, various experimental techniques used to characterize thin films, synthesize new compounds and fabricate organic solar cells will be discussed. Details of the device testing will also be described.

3.1 Thin film optical measurements: UV-Vis and VASE

Ultraviolet-visible spectroscopy (UV-Vis) is a technique used to characterize the transmission of either a thin film or a thin film stack. With UV-Vis, a light source consisting of broad spectrum light source (e.g. an incandescent bulb) is passed through a monochromator. The monochromatic light is split in two beams, one that goes through the thin film sample and one that is used as a reference for the intensity. A detector collects the intensity of the two beams of light and subtracts one from the other to get the transmission of the sample (0-100%). For thin-film transmission measurements, reference samples (e.g., clear glass slides) should not be utilized as in the case for solution transmission measurements. In solution measurements, a reference solution containing just the solvent can be utilized to subtract front/back and solvent reflections so that the transmission data can be straightforwardly converted to absorbance. The case for thin films is different and reflections cannot be simply subtracted due to the complex optical interference. Accordingly, no reference sample should be used for thin film measurements. The reflection of a thin film sample can also be measured via UV-Vis. For this measurement, a different sample mount is used with triangular mirrors. The sample beam first hits the mirror, then the sample, then the mirror, and is then finally collected at the detector. With the combination of experimental measurements for reflection and transmission, absorption spectra can be estimated Equation 2.3, A + R + T = 1. However, this assumes no scattering losses, which means that absorption can be overestimated by this method.

Variable angle spectroscopic ellipsometry (VASE) is another technique used to characterize thin film optical characteristics and nm-level thicknesses. Ellipsometry measures the change in polarization in light after it is reflected off a surface. A monochromatic beam of light is polarized and sent through a fiber optic directed at a thin film sample on a reflective surface. The light reflected off the sample is collected at



Figure 3.1. Ellipsometry fitting for thin and thick films on silicon. (a) Experimental Ψ for three different incident angles, 65°, 70° and 75° for 100 Å thick Cy-TPFB. Thickness was fit in transparent region ($\lambda > 1000$ nm). (b) Experimental Ψ and Δ for 70° incidence for 2000 Å thick TiO₂. Oscillations are visible for thicker films.

a detector, and, based on the phase difference and light attenuation of the reflected light, the ellipsometric angles Ψ (amplitude component) and Δ (phase component) can be calculated:[146]

$$\rho = \frac{r_p}{r_s} = \tan(\Psi) \, e^{i\Delta} \tag{3.1}$$

where ρ is the complex reflectance, r_p is the reflectivity of p-polarized light, and r_s is the reflectivity of spolarized light. Ψ and Δ are a polar description of the ratio of reflectance for p- and s-polarized light. The goal of the measurement is to obtain the optical constants n and k (refractive index and extinction coefficient, respectively) and the thickness d of the thin film sample. With three unknowns (n, k and d) and two experimental parameters (Ψ and Δ), it is not advisable to fit for all three at once. One approach is to measure Ψ and Δ for in a wavelength range where the film is transparent (k = 0) and fit for n and d. The wavelength dependence of n in the transparent region is given by the Cauchy Urbach model. Then, the thickness d is fixed, and n and k are calculated wavelength by wavelength from the transparent region. A model (Snell's laws, the Fresnel coefficients, and thin film interference equations) is then used to fit the optical constants n and k from Ψ and Δ . The measured thickness can be used to calculate the tooling factor (discussed in next section on device fabrication) of thermally evaporated materials, and the optical constants n and k can be used in optical interference models (see Section 4.2). The range of measurable thicknesses for ellipsometry is around 0.1 to 1000 nm. For thin (~100 Å) films, Ψ and Δ are relatively stable across the transparent region



Figure 3.2. Counterion exchange synthesis. (left) Photograph of 1-step counterion exchange synthesis. The more nonpolar Cy-TPFB (orange solid) precipitates out of a mixture of Cy-I and K-TPFB in 5:1 MeOH:DCM. (right) Dried silica plug after silica gel chromatography to separate unreacted Cy-I (dark band on top) from Cy-TPFB.

of the film (Figure 3.1 (a)). For thick (> 1000 Å) films, optical interference patterns can be seen in the form

of oscillations in Ψ and Δ (Figure 3.1 (b)).

3.2 Heptamethine counterion exchange

Heptamethine cations typically carry a +1 charge and is coordinated with a -1 anion, which can be a single ion (i.e., Γ) or a polyatomic ion (such as BF₄⁻). One example of the reaction is shown below for exchanging the counterion from I⁻ to tetrakis(pentaflurophenyl)borate (TPFB):



An example synthesis starts with equimolar amounts of potassium tetrakis(pentaflurophenyl)borate (K-TPFB, Boulder Scientific Company) and Cy-I (American Dye Source) which are dissolved in 5:1 methanol:dichloromethane (MeOH:DCM) at 10 mg/ml and stirred at room temperature for 15 minutes in ambient atmosphere. In this case, a solid orange precipitate forms due to the more nonpolar product Cy-TPFB being formed in a relatively polar solution of primarily methanol (Figure 3.2). The crude product is then collected using vacuum filtration and an MeOH wash. The crude product is redissolved in minimal DCM (~10 mg/ml) and poured through a plug of silica using DCM as eluent to remove impurities and

unreacted Cy-I. In silica gel chromatography, solvent is drawn through silica gel by a variety of methods (capillary motion, gravity or vacuum), and components of a mixture can be separated by polarity. The more polar reactant Cy-I binds to the silica gel, and the less polar product Cy-TPFB is eluted with the nonpolar DCM through the silica plug. The first fraction with similar color to Cy-I is collected (in this case, green), and excess DCM is removed in a rotary evaporator at 55°C for 20 min at atmospheric pressure.

3.3 Purity assessment via high-resolution mass spectrometry

Mass spectrometry is an analytical technique that identifies the mass over charge (m/z) ratio of a given compound. The goal of mass spectrometry is to obtain the molecular mass of a sample and any impurities. Mass spectrometry consists of three main components: an ionization source, an analyzer, and a detector. The ionization source used for our experiments was electrospray ionization (ESI), which means that a dilute (1-100 nM) solution is led to the end of a nozzle where a capillary voltage (1 kV or higher) is applied to create ions in solution. The solution is then mixed with a drying gas and sprayed, thereby generating gaseous ions. The next component is the analyzer, which for our experiments was both a quadrupole and a time of flight detector (QToF). This type of mass spectrometer containing two analyzers is called a tandem mass spectrometer and has higher resolution. A quadrupole consists of four rods, two of which are positive and two of which are negative. A varying voltage is applied onto the quadrupole such that only ions with certain m/z make it from one end to the other. In a time-of-flight analyzer, the ions are accelerated in a tube, and their m/z is known by when the ions arrive at a detector by gravity. The final component, the detector, is usually an electron multiplier.

Different elements have isotopes in varying relative abundances and each element will therefore generate a specific isotope pattern in mass spectrometry. Examples of isotope patterns for the cation and anion for Cy1-TPFB and Cy2-TPFB are shown in Figure 3.3.

The verification of cations and anions and ion purity assessment were performed using a Waters Xevo G2-XS QToF mass spectrometer coupled to a Waters Acquity ultra-high pressure LC system. Cations were analyzed in positive ion mode electrospray ionization, and anions were analyzed in negative ion mode



Figure 3.3. High resolution mass spectra for Cy1-TPFB and Cy2-TPFB. (a) Positive and (b) negative mode electrospray ionization for Cy1-TPFB. (c) Positive and (d) Negative mode electrospray ionization for Cy2-TPFB. Predicted isotopic abundance peaks for each compound were generated using the Isotope Model tool in MassLynx software.

ESI. Solutions were prepared in acetonitrile and directly injected for 2 minutes using an eluent of 50:50 water: acetonitrile. Mass spectra were acquired using a dynamic range extension over m/z 50 to 1,500, with mass resolution (M/ Δ M, full width-half maximum) of approximately 20,000. Other parameters include capillary voltage of 2 kV, desolvation temperature of 350°C, source temperature of 100°C, and desolvation gas (N₂) at 400 L h⁻¹. For ion purity assessment, solutions of the exchange precursors and products were prepared in acetonitrile with concentrations varying from 10 nM to 500 nM and analyzed by mass spectrometry as described above.

3.4 Solar cell device fabrication

Organic solar cells consist of two electrodes, a donor, and an acceptor. A typical solar cell device consists of ITO (transparent bottom electrode), MoO_3 (a transparent HTL), a donor, an acceptor (usually C_{60}), an electron transport layer called bathocuproine (BCP), followed by the cathode, which is silver or aluminum for opaque cells. For transparent devices, the top transparent electrodes used include ITO and Ag / Alq₃. The general device structure is shown in Figure 3.4 (a).

The active area for an organic cell is outlined by the overlap of the top and bottom electrodes because the organic layer has poor lateral conductivity compared to Si. The patterns used for the bottom ITO, organic layers, and top electrode are shown in Figure 3.4 (b). The bottom ITO layer is prepatterned onto 12 x 12 mm polished glass substrates (Xin Yan Tech). The pattern allows for ITO to be contacted easily during electrical testing. The organic layers (MoO₃ through BCP) are deposited by thermal evaporation through a stainless-steel shadow mask. The top electrode is deposited through another shadow mask, creating a pattern of six "fingers". Each finger is a different device, and this pattern allows for six 5.4 mm^2 devices to be made on each substrate. For organic layers that have higher conductivities, a shadow mask can be placed on top of the substrate during testing to define the device area.

The substrates need to be free of dust and organic residue before the deposition step. To accomplish this, a substrate cleaning procedure is used as follows. Substrates are sonicated for three minutes each in soap, DI water, and acetone. Then, the substrates are submerged in boiling isopropanol for three minutes and dried with nitrogen. Finally, the substrates are treated with oxygen plasma for 90 seconds and kept in



Figure 3.4. Device architecture and layer patterns. (a) Typical device structure for an OPV. Cy stands for cyanine, but could be any organic donor. (b) Different layer patterns used for ITO, organic layers, and the top electrode. The device area is outlined. This pattern for a 12-mm substrate makes six 5.4 mm² devices.



Figure 3.5. Evaporator diagrams. (a) Diagram of thermal evaporation chamber. The labelled parts are: (1) source boat, (2) copper heating agents, (3) source shutters, (4) QCM, (5) substrate shutters, (6) substrates, and (7) stage. (b) Schematic showing the positioning of the six evaporation sources and three QCM sensors.

a nitrogen-filled glovebox to prior to the subsequent deposition steps.

Thermal evaporation is a type of physical vapor deposition where source material is sublimed under vacuum. A simplified diagram for one evaporation source is shown in Figure 3.5(a). The source material (in powder form) is loaded into tungsten boats with a baffle design that emits sublimed material by line of sight to the substrate where it condenses. The tungsten boats are heated by copper filaments. The pressure is usually maintained at around 10^{-6} torr, which is achieved through a two-stage pump (a rough mechanical

pump and a cryopump). Between the active-layer and electrode deposition, layer masks are changed by unloading the substrates with a transfer fork into a nitrogen glovebox to prevent exposure to air before the device is completed or packaged. The position of the pump, transfer fork, evaporation chambers and nitrogen glovebox can be seen in Figure 3.6.

In thermal deposition, the deposition rate (usually 0.5 - 2 Å/s) is monitored using quartz crystal monitors (QCM) above each source. Quartz crystals resonate at specific frequencies that depend on the



Figure 3.6. Custom-built system assembly for two evaporation chambers and a nitrogen glovebox (Angstrom Engineering). A. EvoVac evaporation chamber. B. EvoVac cryopump. C. EvoVac helium compressor. D. Nitrogen glovebox. E. Solvent glovebox. F. AMOD evaporation chamber. G. AMOD cryopump. H. AMOD helium compressor.
total volume of thin film deposited on them. The electrical power delivered to the source boat for resistive heating is controlled using standard PID control. Once the deposition rate is stable, the substrate shutters open, allowing for a controllable deposition rate and a controllable thickness. QCMs are calibrated to relate the thickness arriving on the QCM to the thickness on the substrate by the ratio called the tooling factor (TF), given below:

$$\frac{t_i}{TF_i} = \frac{t_f}{TF_f} \tag{3.2}$$

where t_i is the initial measured thickness based on the initial guess of the tooling factor TF_i and t_f is the thickness measured on a reference substrate (usually undoped single-crystalline Si) using ellipsometry and TF_f is the calibrated tooling factor. The TF depends on the source material (density, Z-factor), boat position, and the overall boat-QCM-Substrate geometry. The Z-factor (also called Z-ratio) is the ratio of the acoustic impedance of quartz to that of the deposited material and is a correction factor in the frequency-change-to-thickness function. Accordingly, if a boat is repositioned or a QCM is moved, the TF needs to be remeasured. Because the QCM is calibrated, the co-deposition of multiple materials in a single layer should be reported as a vol. % (from the ratio of the deposition rates) and not as mass or molar %.

In our AMOD evaporation chamber (Angstrom Engineering), there are six thermal evaporation sources and three QCMs: each QCM is responsible for monitoring the deposition rates of two sources. The positioning of the six evaporation sources is shown in Figure 3.5(b). Different materials can be deposited at the same times because of this design; this process is referred to as codeposition and is necessary for creating bulk heterojunctions. The ratio of donor and acceptor can be varied using codepositon, providing a useful tuning parameter for improved film morphologies, doping, and device performances.

Some materials are unsuitable for thermal evaporation because they decompose at high temperatures prior to sublimation. For these materials, solution processing methods such as spin-coating and doctor blading can be used to deposit thin films from solution. In this research, spin-coating is used to deposit thin films of the heptamethine salts discussed in Chapter 5, which are too bulky for evaporation. In spin-coating, the substrate is held on a central axis by a vacuum chuck and rotated at around 2000-4000



Figure 3.7. Diagram of spin-coating process. (a) Solution is pipetted onto substrate. (b) The substrate is rotated, causing solvent to evaporate and shear off. (c) Particles left behind on the surface form a thin film.

rpm (Figure 3.7). A solution is pipetted onto the substrate either before or during the rotation; these are respectively called static or dynamic spincoating. The film is formed by a combination of solvent evaporation and solvent shearing. Using a high vapor pressure solvent (low boiling point) leads to fast solvent evaporation, creating thick, rough films. Using a low vapor pressure solvent (high boiling point) leads to solution that spin off the substrate and result in films that could be too thin. Therefore, the optimum solvent system can often be a mixture of a high and low vapor pressure solvents; for example, a mixture of 1:3 of dichloromethane (boiling point = 50° C) to chlorobenzene (boiling point = 131° C) was used as the solvent system for spincoating the heptamethine salts covered in Chapter 5. Spincoating speeds and times are other parameters that can be controlled for the spincoating process, with faster speeds and longer spin times creating thinner films. The parameters used for the heptamethine salts were 2000 rpm and 30 seconds of spin-coating time.

Opaque devices with a top electrode of 80 nm Ag are made for reference or control devices. For transparent devices, the top electrode is either ITO or a combination thin metal/semiconductor layer (e.g. Ag/Alq₃). Sputtering is used to deposit ITO, which has too high of a sublimation temperature to be deposited using thermal evaporation. In sputter deposition, plasma ions (Ar⁺ in our case) bombard a target of the material to be deposited, and the ejected atoms are ballistically transported under low vacuum (10^{-2} torr) to the substrate where they condense. As mentioned in Chapter 2, there are tradeoffs between using ITO or Ag/Alq₃ as the transparent electrode. ITO is more transparent and conductive, but the sputtering process can damage the underlying organic films and lead to low device yield. Low deposition rates (0.02 Å/s) are



Figure 3.8. Photographs of JV testing setup. (a) Calibrating the intensity of the xenon arc lamp for JV testing. (b) Substrate holder for testing. Gold pins contact different devices on the substrate. (c) Screenshot of Labview program used to interface with sourcemeter.

typically used to prevent this degradation from excessive high energy plasma ions. Ag/Alq_3 is less transparent but can be deposited at higher rates without damaging the organic films underneath.

3.5 Solar cell testing (JV-EQE)

3.5.1 Current-voltage (JV)

Obtaining the *JV* curve for a solar cell under 1-sun illumination allows us to calculate its power conversion efficiency (Figure 3.7). Current density (*J*) was measured as a function of voltage (*V*) using a Labview-controlled sourcemeter. The design of the electrode patterns allowed for independent and rapid testing of all the devices on a substrate. The illumination source was a xenon arc lamp calibrated for AM1.5G (100 mW/mm²) intensity using a NREL-calibrated Si reference cell with a KG5 filter to match the response of the Si cell to our testing cells (for details, see mismatch factor discussion in Section 3.5.2). AM 1.5G refers to the solar irradiance at the surface of Earth after being absorbed by air with a diameter of 1.5 times the thickness of the atmosphere and is a standard illumination source for PV testing.

3.5.2 External quantum efficiency (EQE)

The external quantum efficiency (*EQE*) for a solar cell is the ratio of collected electrons over incident photons for a given wavelength. *EQE* measurements are performed by illuminating the device area with monochromatic light from a tungsten halogen lamp chopped at specific frequency (200 Hz was used in our lab). The small current signal from the device is sent through a picoammeter and amplified by a lock-

in amplifier. The light intensity at the end of the IR-fiber was measured using a Newport calibrated Si diode for 350-800 nm and a Newport calibrated Ge diode for 800-1600 nm. The *EQE* can be integrated with the solar spectrum to give the J_{SC} , making it a good consistency check for the J_{SC} measured by *JV* testing, which is easy to overestimate. Errors in device area and illumination intensity can result in overestimations of J_{SC} .

EQE is also used for calculations of the spectral mismatch factor (*MF*), which accounts for the difference in the reference detector for setting the solar simulator power and the spectral response of the tested solar cell considering the non-ideal solar simulation source. The mismatch factor is used to correct the incident power P_{in} from 1-sun intensity ($PCE = J_{SC}*V_{OC}*FF / P_{in}*MF$). In practice, *EQE* is measured before *JV* to calculate *MF* and adjust the intensity of the simulation lamp. For example, if an *MF* of 1.05 were measured, then the intensity of the lamp would need to be decreased by 5% so that the incident power would be 1-sun (100 mW mm⁻²). To calculate *MF*, the *EQE* of a silicon reference cell with a known response is measured using the solar simulation lamp, as well as the *EQE* of the test device. The equation for *MF* is as follows:

$$MF = \frac{\int E_{ref}(\lambda) * S_R(\lambda) d\lambda}{\int E_{ref}(\lambda) * S_T(\lambda) d\lambda} * \frac{\int E_S(\lambda) * S_T(\lambda) d\lambda}{\int E_S(\lambda) * S_R(\lambda) d\lambda}$$
(3.3)

Where E_{ref} is the solar spectrum, S_R is the spectral response of the silicon reference photodiode, S_T is the spectral response of the test device, and E_S is the solar simulation lamp (source) spectrum. The silicon reference cell normally has photoresponse out to 1100 nm. We use a KG filtered silicon reference cell because the KG5 filter has low transmission in the infrared; the KG5-filtered reference cell has a more similar photoresponse to OPVs, and therefore, using it makes the *MF* closer to 1.[147]

In Figure 3.9(a), the set-up for EQE measurement of a multijunction solar cell is shown.[6] As in the single junction case, chopped monochromatic light is incident on the sample, and a lock-in amplifier amplifies the PV current responding to the same frequency as the chopping of the monochromatic light. To measure the EQE of an individual subcell (e.g. subcell 1) of a tandem solar cell, the other subcell (e.g. subcell 2) must be filled with carriers so that every carrier excited by the chopped monochromatic light in subcell 1 either is collected at the electrode or recombines with the carrier of the other type at the



Figure 3.9. *EQE* for tandem PV. (a) Set-up for *EQE* measurement of tandem PV. Optical bias lights pass through a neutral density filter to control for intensity before illuminating the sample. (b) Normalized absorption spectra of two active materials in Ref. [6], PFTBT:PCBM in wine and pBBTDPP2:PCBM in green. Figures reproduced from Ref. [6] with permission.

interconnecting layers (ICL, also called recombination zone or intermediate layers). The optical biasing

lights are un-chopped, so the current they generate in the solar cell are not amplified by the lock-in amplifier.

Neutral density filters and hot mirrors are used to easily switch which subcell is being optically biasing

different subcells.

Chapter 4 – Angle Dependence Modeling

Integrating transparent solar cells into building envelopes is a unique opportunity to reduce the levelized electricity cost of solar power. However, this integration requires a consideration of the angular dependence of these devices because illumination around the building envelope is rarely at normal incidence. In this chapter, we explain how we updated standard transfer-matrix equations to accurately model the quantum efficiency and optical properties under oblique illumination. We use this model to demonstrate the various angular performance characteristics possible for proof-of-concept optimizations of transparent planar-heterojunction solar cells and discuss considerations needed to fully account for optical, electrical, and positional configurations in this optimization.

4.1 Motivation for angle dependent PV performance modeling

The deployment of PVs in BIPV applications warrants the consideration of the angle-dependence



Figure 4.1. The position of the sun and the average yearly flux for PVs mounted in different configurations. (a) Schematic showing angles related to the position of the sun. S stands for the position of the sun, and M stands for the surface normal of the module. Adapted from Ref. [148]. (b) Table of average yearly flux for solar cells mounted in different positions in different U.S. cities. Adapted from Ref. [148].



Figure 4.2. Conventional and inverted configurations for TPV. Schematic showing device layer structure, illumination orientation, and incident angle h for the (i) conventional, (ii) optically inverted, (iii) electrically inverted, and (iv) optically and electrically inverted configurations. (TCO_A denotes the hole-collecting transparent anode, and TCO_C denotes the electron-collecting transparent cathode).

of both the solar flux and oblique angle device performance. In general, the photon flux follows a cosine decay as a surface is tilted away from a normal-incidence beam. However, the orientation of solar illumination varies throughout the day and year such that the average solar flux only drops modestly. This is in part because no surface stays at normal incidence for long without solar tracking and east/west facing surfaces can collect greater flux in the morning/evening. Figure 4.1 shows the average yearly solar flux for vertically mounted surfaces facing south, southeast, east (identical to west), and north in three northern hemisphere cities in the U.S. A comparable amount of solar flux is received for horizontal and vertically oriented surfaces over the year except in north facing vertical surfaces where there is no direct sunlight (only diffuse solar illumination). When combined around the entire surfaces of a building the overall vertical flux from east-west-south facings surfaces can be substantially greater than the horizontal or tilted fluxes. Transparent solar cells can also be oriented in multiple optically and electrically inverted configurations (Figure 4.2). Therefore, obtaining an accurate model for solar cell performance at oblique illumination angles and non-conventional device configurations is critical.

To further improve the efficiencies of OPV and TPV and reduce thermal losses, a multijunction approach is commonly employed.[2, 23] The photocurrent matching requirement of series-integrated subcells in multijunction PVs mandates a precise understanding of the angular performance of each subcell to ensure photocurrent matching across all angles. Previous efforts to model the angle dependence of conventional organic photovoltaics[149, 150] based on Ref. [151] lack clear descriptions of the correct angle-dependent model (e.g., fields and generation terms for both s- and p-polarizations) and do not show consistency checks necessary to assess the accuracy of these results. Here, we update the transfer matrix method (TMM), which has been widely used to model solar cell performance at normal illumination,[151, 152] to account for oblique illumination as a function of optical orientation, and we demonstrate complete self-consistency. We then model and optimize the performance of planar heterojunction (PHJ) TPVs under normal and oblique illumination for the two optical configurations.

4.2 Optical interference modeling

Complex optical interference effects arise because optimal layer thicknesses for organic and transparent PVs are typically in the range of 10-100 nm, which is the same order of magnitude as wavelengths of incident light. The resulting field profiles for thin film structures often resemble sinusoidal functions, rather than pure exponential decays of the Beer-Lambert equation. PV performance models that account for this optical interference are used in many thin-film solar cell studies to aid in efficiency optimization and understand angle dependencies. The transfer matrix model (TMM) is a popular model used to describe optical interference.[151, 152] TMM accounts for the complex interface reflections/transmission in a multilayer film stack. For a multilayer film stack with j = 1 to m layers and each layer having a complex index of refraction $\tilde{n}_j = n_j + i^*k_j$ and thickness d_j , the electric field propagated at an interface between layer j and k can be written as:

$$\begin{bmatrix} \bar{E}_{j}^{+} \\ \bar{E}_{j}^{-} \end{bmatrix} = I_{jk} \begin{bmatrix} \bar{E}_{k}^{+} \\ \bar{E}_{k}^{-} \end{bmatrix} = \begin{bmatrix} \frac{1}{t_{jk}} & \frac{r_{jk}}{t_{jk}} \\ \frac{r_{jk}}{t_{jk}} & \frac{1}{t_{jk}} \end{bmatrix} \begin{bmatrix} \bar{E}_{k}^{+} \\ \bar{E}_{k}^{-} \end{bmatrix}$$
(4.1)



Figure 4.3. Schematic showing xyz coordinates for transfer matrix equations. *E* refers to electric field, with E_i, E_r, and E_t referring to incident, reflected and transmitted electric field component respectively.

where the positive sign denotes propagation in the positive direction (+*x*, for example) and the negative sign is propagation in the negative direction (Figure 4.3). r_{jk} and t_{jk} are the Fresnel reflection and transmission coefficients respectively, with $r_{jk} = (\tilde{n}_j - \tilde{n}_k)/(\tilde{n}_j + \tilde{n}_k)$ and $t_{jk} = 2\tilde{n}_j/(\tilde{n}_j + \tilde{n}_k)$. The electric field propagating within a layer *j* can be described as:

$$L_{j} = \begin{bmatrix} e^{-i\xi_{j}d_{j}} & 0\\ 0 & e^{i\xi_{j}d_{j}} \end{bmatrix}, \xi_{j} = \left(\frac{2\pi}{\lambda}\right)\tilde{n}_{j}$$
(4.2)

The product of all the interface matrices I_{jk} and layer matrices L_j results in the transfer matrix S:

$$S = \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix} = \left(\prod_{n=1}^{m} I_{(n-1)n} L_n\right) I_{m(m+1)}$$
(4.3)

which is the relationship between the electric field coming into and out of the multilayer stack, as in:

$$\begin{bmatrix} \bar{E}_0^+ \\ \bar{E}_0^- \end{bmatrix} = S \begin{bmatrix} \bar{E}_{m+1}^+ \\ \bar{E}_{m+1}^- \end{bmatrix}$$
(4.4)

When these are combined with a 1-D exciton diffusion model, the exciton concentration profile can be calculated:

$$L_D^2 \frac{\partial^2 n(x)}{\partial x^2} - n(x) + \tau G(x) = 0$$
(4.5)

where L_D is the exciton diffusion length, *n* is the exciton density, τ is the exciton lifetime, and *G* is the exciton generation (or photon absorption) rate, which is proportional to the magnitude of the electric field

intensity $|E(x)|^2$. These models typically assume 100% charge transfer and 100% charge collection efficiencies, so the flux of excitons that diffuse to the D-A interface over the incident photon flux yields the *EQE* at each wavelength. The *EQE* can then be integrated to calculate the short circuit photocurrent density J_{SC} (Eq. 1.5). The most relevant applications of optical interference modeling for TPVs are 1) simulating the *A*, *R*, and *T* of a film stack at normal or oblique angle to verify the measured transmittance or internal quantum efficiency of an entire device film stack [37], 2) extracting the parasitic absorption losses in transparent contacts, 3) optimizing for photocurrent generation, and 4) designing layers for light management such as with 1D photonic reflectors (e.g. distributed Bragg reflectors).[14, 153] For optimizing device structures, electric field profiles are simulated as a function of position within the device while varying the thicknesses of various layers (electron or hole transport layers[28] or transparent electrode layers[34, 154, 155]) to optimize for high electric field intensity at the D-A interface to help overcome the exciton diffusion bottleneck. In practice, there are three or more independent objective criteria to maximize: efficiency, overall transparency, and color rendering.

4.3 Modifications for angular incidence

While the transfer matrix method has been described in detail in the literature, [156] we focus on corrections needed for oblique illumination and optical inversion. The electric fields of two adjacent layers j and k = j + 1 are related at their interface by a matrix consisting of the complex Fresnel reflection and transmission coefficients, r_{jk} and t_{jk} , which differ for s- and p- polarized light as:[157]

$$r_{jk}^{s} = \frac{\tilde{n}_{j}\cos(\theta_{j}) - \tilde{n}_{k}\cos(\theta_{k})}{\tilde{n}_{j}\cos(\theta_{j}) + \tilde{n}_{k}\cos(\theta_{k})}$$
(4.6)

$$t_{jk}^{s} = \frac{2\tilde{n}_{j}\cos(\theta_{j})}{\tilde{n}_{j}\cos(\theta_{j}) + \tilde{n}_{k}\cos(\theta_{k})}$$
(4.7)

$$r_{jk}^{p} = \frac{\tilde{n}_{j}\cos(\theta_{k}) - \tilde{n}_{k}\cos(\theta_{j})}{\tilde{n}_{j}\cos(\theta_{k}) + \tilde{n}_{k}\cos(\theta_{j})}$$
(4.8)

$$t_{jk}^{p} = \frac{2\tilde{n}_{j}\cos(\theta_{j})}{\tilde{n}_{j}\cos(\theta_{k}) + \tilde{n}_{k}\cos(\theta_{j})}$$
(4.9)

where \tilde{n}_j is the complex index of refraction for layer *j* (e.g. $n + i\kappa$), θ_j is the incident angle in layer *j*, and θ_k is the refraction angle in layer *k*. s- and p- polarization refer to the electric field oscillating parallel (p-) or perpendicular (s-) to the plane of incidence, which is the plane containing both the normal vector of the interface and the light propagation vector. The polarization dependence can be neglected in the normal incidence case (Eqs. 4.6-4.7 become equivalent to Eqs. 4.8-4.9) but not at oblique angles. Substituting Snell's law at each interface, $cos(\theta_j)$ can be expressed as a function of the ambient incidence angle, θ_0 , and ambient index of refraction, $n_0: cos(\theta_j) = \sqrt{1 - (n_0/\tilde{n}_j)^2 \sin^2(\theta_0)}$. In the notation of Ref. [7], power dissipation Q_j for s- and p-polarized light in the thin film layers are:

$$Q_j^s(x) = \frac{1}{2} c \varepsilon_0 \alpha_j n_j \left| E_j^z \right|^2$$
(4.10)

$$Q_j^p(x) = \frac{1}{2} c \varepsilon_0 \alpha_j n_j \left(\left| E_j^x \right|^2 + \left| E_j^y \right|^2 \right)$$
(4.11)

where *c* is speed of light, ε_0 is permittivity of free space, α_j is the absorption coefficient of layer *j*, n_j is the real index of refraction for layer *j*, and $E_j^{x,y,z}$ are the time and *y*-integrated Euclidean electric field components in layer *j* (Figure 4.3):[158]

$$E_{z,j} = \frac{1}{\sqrt{\cos\theta_0}} \left(t_{j,s}^+ e^{i\xi_j x} + t_{j,s}^- e^{-i\xi_j x} \right)$$
(4.12)

$$E_{y,j} = \frac{\cos \theta_j}{\sqrt{\cos \theta_0}} [t_{j,p}^+ e^{i\xi_j x} + t_{j,p}^- e^{-i\xi_j x}]$$
(4.13)

$$E_{x,j} = \frac{\tilde{n}_0 \sin \theta_0}{\tilde{n}_j \sqrt{\cos \theta_0}} \left[-t_{j,p}^+ e^{i\xi_j x} + t_{j,p}^- e^{-i\xi_j x} \right]$$
(4.14)

where $\tilde{n}_j \cos \theta_j = \sqrt{\tilde{n}_j^2 - n_0^2 \sin^2 \theta_0}$, $\xi_j = \frac{2\pi}{\lambda} \tilde{n}_j \cos \theta_j$, and $t_{j,p}^-$ is the same as t_j^- of Pettersson *et al* (Ref.

[151]) except that the interface matrix I_{jk} (that the total transfer matrix comes from) consists of the Fresnel complex reflection and transmission coefficients for p-polarized light (expressions for $t_{j,p}^+$, $t_{j,s}^-$, and $t_{j,s}^+$ are also defined by the total transfer matrix). The absorption coefficient is $\alpha_j = 4\pi\kappa_j/\lambda$, where κ_j is the imaginary index of refraction for layer *j*. Total power dissipation is then calculated by taking the sum of the s- and p-polarized power dissipations weighted by each fractional component of each polarization in

the incident light. Solar irradiance is unpolarized and therefore can be simulated with a 1:1 ratio of s- and p-polarized light. To account for the substrate, we derive incoherent corrections from Figure 4.4 for the conventional optical orientation with illumination through the substrate as:

$$R = R_S + \frac{T_S^2 R_{TF}}{1 - R_S R_{TF}}$$
(4.15)

$$T = \frac{T_S T_{TF}}{1 - R_S R_{TF}} \tag{4.16}$$

$$A = A_{TF} \frac{T_S}{1 - R_{TF} R_S} \tag{4.17}$$

And for the inverted optical orientation (illumination through the thin film) as:

$$R = R_{TF} + \frac{T_{TF}^2 R_s}{1 - R_s R_{TF}}$$
(4.18)

$$T = \frac{T_S T_{TF}}{1 - R_S R_{TF}} \tag{4.19}$$

$$A = A_{TF} \left(1 + \frac{T_{TF}R_S}{1 - R_{TF}R_S} \right)$$
(4.20)

where R, T, A are the reflection, transmission and absorption through the device at each wavelength; R_s , T_s are the reflection and transmission at the substrate-air interface (non-film side); and R_{TF} , T_{TF} , A_{TF} are the reflection, transmission, and absorption through the thin film layers. Once the reflection, transmission, and



Figure 4.4. Substrate corrections for optical interference simulation. Schematic showing the first three terms for reflection and transmission through the whole device. The clear block represents the substrate while the gray block represents the thin film layer stack. R_{TF} and T_{TF} are the reflection from and transmission through the thin film layers, and R_S and T_S are the reflection from and transmission through the substrate.

absorption are found for the thin film layer stack (R_{TF} , T_{TF} , and A_{TF}), a correction must be made to find the reflection, transmission, and absorption for the overall device (R, T, and A), which includes the substrate. The reflection and transmission associated with the substrate interface on the non-film side will be referred to as R_S and T_S and it is assumed the substrate always has negligible absorption. Light that is transmitted through the device consists of light that has been transmitted through the substrate and the thin film layer, as well as light that has been reflected multiple times before being transmitted through both substrate and thin film stack. Likewise, light that is reflected by the device consists of light that is reflected by the incident surface or has undergone multiple reflections within the substrate before being transmitted through the incident medium.

Given the exciton diffusion lengths (provided by Ref. [14]and Ref. [152]) and the position dependent Qj, it then becomes possible to solve the one-dimensional diffusion equation to calculate the external quantum efficiency (*EQE*) of the device. The short-circuit current density (J_{sc}) is subsequently calculated by integrating the convolution of the *EQE* and the solar spectrum S as $J_{sc} = \int (EQE * S) d\lambda$.

4.4 Verification of model (internal consistency and experimental)

To confirm the accuracy of the optical model (i.e., an internal consistency check), we show that A + R + T = 1 at all wavelengths, angles, and polarization combinations (see Figure 4.5) where A, R, and T are all *independently* determined from the calculated field profile:

Conventional

$$\begin{split} [A] + [R] + [T] &= \left[\frac{T_S}{1 - R_S(f|r^S|^2 + (1-f)|r^p|^2)} \cdot \sum_{j=1}^m \int \left(fQ_j^S + (1-f)Q_j^p \right) dx_j \right] \\ &+ \left[R_S + \frac{T_S^2(f|r^S|^2 + (1-f)|r^p|^2)}{1 - (f|r^S|^2 + (1-f)|r^p|^2)R_S} \right] + \left[\frac{(f|t^S|^2 + (1-f)|t^p|^2)T_S}{1 - R_S(f|r^S|^2 + (1-f)|r^p|^2)} \right] = 1 \end{split}$$
(4.21)

Optically inverted

$$\begin{split} [A] + [R] + [T] &= \left[\left(1 + \frac{R_S(f|t^{s|^2} + (1-f)|t^{p|^2})}{1 - R_S(f|r^{s|^2} + (1-f)|r^{p|^2})} \right) \cdot \sum_{j=1}^m \int \left(fQ_j^s + (1-f)Q_j^p \right) dx_j \right] \\ &+ \left[(f|r^s|^2 + (1-f)|r^p|^2) + \frac{R_S(f|t^s|^2 + (1-f)|t^{p|^2})^2}{1 - (f|r^s|^2 + (1-f)|r^{p|^2})R_S} \right] + \left[\frac{(f|t^s|^2 + (1-f)|t^{p|^2})T_S}{1 - R_S(f|r^s|^2 + (1-f)|r^{p|^2})} \right] = 1 \ (4.22) \end{split}$$



Figure 4.5. Consistency check A + R + T = 1**.** Left, center, and right panels show consistency check for different polarizations of light, and solid and dashed lines show it for normal and oblique incidence respectively. Device structure: Glass Substrate / 1200 Å ITO / 200 Å MoO₃ / 125 Å ClAlPc / 400 Å C₆₀ / 80 Å BCP / 1200 Å ITO).

where *m* is the total number of layers, Q_j is the power dissipated in the thin-film layer *j*, *x_j* is the position in layer *j*, *f* is the fraction of light that is s-polarized, $r^{s,p}$ are the Fresnel complex reflection coefficients for sand p-polarized light, $t^{s,p}$ are the Fresnel complex transmission coefficients for s- and p-polarized light, $r_0^{s,p}$ and $t_0^{s,p}$ are the Fresnel coefficients for the substrate-ambient interface, $T_S = (f|t_0^S|^2 + (1 - f)|t_0^p|^2) q_s/q_0$ in the conventional case and $T_S = (f|t_0^S|^2 + (1 - f)|t_0^p|^2) q_0/q_s$ in the optically inverted case, $R_S = (f|r_0^S|^2 + (1 - f)|r_0^p|^2)$, $r^p = S_{21}^p/S_{11}^p$, $r^s = S_{21}^s/S_{11}^s$ $t^p = 1/S_{11}^p$, $t^s = 1/S_{11}^s$ (as in Ref. [122]), $q_s = n_S \cos\theta_S = \sqrt{n_s^2 - n_0^2 \sin^2\theta_0}$, and $q_0 = n_0 \cos\theta_0$. The Fresnel coefficients for the substrate-

ambient interface for the case of conventional illumination are:

$$r_0^s = \frac{n_0 \cos(\theta_0) - n_s \sqrt{1 - (n_0/n_s)^2 \sin^2(\theta_0)}}{n_0 \cos(\theta_0) + n_s \sqrt{1 - (n_0/n_s)^2 \sin^2(\theta_0)}}$$
(4.23)

$$t_0^s = \frac{2n_0 \cos(\theta_0)}{n_0 \cos(\theta_0) + n_s \sqrt{1 - (n_0/n_s)^2 \sin^2(\theta_0)}}$$
(4.24)

$$r_0^p = \frac{n_0 \sqrt{1 - (n_0/n_s)^2 \sin^2(\theta_0) - n_s \cos(\theta_0)}}{n_0 \sqrt{1 - (n_0/n_s)^2 \sin^2(\theta_0)} + n_s \cos(\theta_0)}$$
(4.25)

$$t_0^p = \frac{2n_0 \cos(\theta_0)}{n_0 \sqrt{1 - (n_0/n_s)^2 \sin^2(\theta_0)} + n_s \cos(\theta_0)}$$
(4.26)

where n_s and n_0 are the refractive indices of the substrate and ambient, respectively. The Fresnel coefficients substrate-ambient interface for the optically inverted case are:

$$r_0^s = \frac{n_s \sqrt{1 - (n_0/n_s)^2 \sin^2(\theta_0)} - n_0 \cos(\theta_0)}{n_s \sqrt{1 - (n_0/n_s)^2 \sin^2(\theta_0)} + n_0 \cos(\theta_0)}$$
(4.27)

$$t_0^s = \frac{2n_s\sqrt{1 - (n_0/n_s)^2 \sin^2(\theta_0)}}{n_s\sqrt{1 - (n_0/n_s)^2 \sin^2(\theta_0)} + n_0\cos(\theta_0)}$$
(4.28)

$$r_0^p = \frac{n_s \cos(\theta_0) - n_0 \sqrt{1 - (n_0/n_s)^2 \sin^2(\theta_0)}}{n_s \cos(\theta_0) + n_0 \sqrt{1 - (n_0/n_s)^2 \sin^2(\theta_0)}}$$
(4.29)

$$t_0^p = \frac{2n_s\sqrt{1 - (n_0/n_s)^2 \sin^2(\theta_0)}}{n_s \cos(\theta_0) + n_0\sqrt{1 - (n_0/n_s)^2 \sin^2(\theta_0)}}$$
(4.30)



Figure 4.6. Schematic showing how solar flux changes with incident angle. (a) Assuming one photon is incident on area A_0 , the photon flux is $1/A_0$. (b) At incident angle θ , the area of illumination becomes A, which is greater than A_0 by a factor of $1/\cos(\theta)$.



Figure 4.7. Predicted and experimental J_{SC} with respect to incident angle. (a) Experimental data (squares) and corresponding simulation predictions (line) shown for normalized J_{sc} under conventional illumination as a function of incident angle for the device with structure: Glass Substrate / 1200 Å ITO / 100 Å ZnO / 300 Å C₆₀ / 150 Å ClAlPc / 1000 Å MoO₃ / ITO 1300 Å. (b) Simulated J_{sc} as a function of incident angle for five different top ITO layer thicknesses (x = 1000, 1200, 1400, 1600, 1800), where the structure is as follows: Glass Substrate / 1200 Å ITO / 200 Å MoO₃ / 125 Å ClAlPc / 400 Å C₆₀ / 80 Å BCP / (x) Å ITO).

We note that the performance under oblique illumination for all plots in this work is simulated assuming 1 sun photon flux (100 mW/cm²) at all incident angles for comparability. However, the flux on deployed PVs monotonically decreases with increasing incident angle (Figure 4.6) and varies widely with PV tilt angle, orientation, time of day, and location. Internal quantum efficiency (*IQE*) is also calculated from *A* as EQE = A * IQE, assuming 100% charge transfer and charge collection efficiency for both *IQE* and *EQE*.[156]

Transparent PHJ solar cells were first fabricated to measure *EQE* under oblique illumination and further confirm the accuracy of the model. Thin film layers of ZnO, C₆₀, chloroaluminum phthalocyanine (ClAlPc), MoO₃, and ITO were then deposited using thermal evaporation (for C₆₀, ClAlPc, and MoO₃) at a rate of 1 Å/s or DC magnetron sputtering (for ZnO and ITO) at a rate of 0.05 Å/s. The full experimental device stack was as follows: Glass Substrate / 1200 Å ITO / 100 Å ZnO / 300 Å C₆₀ / 150 Å ClAlPc / 1000 Å MoO₃ / ITO 1300 Å. The *EQE* spectrum was measured for this 60 mm² device (20 mm x 3 mm) under



Figure 4.8. Example J_{sc} contour plot where ClAlPc and C₆₀ thicknesses are varied to maximize 0° J_{sc} for ITO thickness = 1000 Å in the conventional configuration.

varying degrees of incidence ranging from 0° to 80°. *EQE* was also predicted from the derived model, using optical constants measured by variable angle spectroscopic ellipsometry (J. A. Woollam) and exciton diffusion lengths of 8 nm and 20 nm for ClAlPc and C₆₀, respectively. The *EQE* spectra were then integrated with the solar spectrum to calculate J_{sc} , which is normalized to the 0° incidence J_{sc} and plotted in Figure 4.7(a) along with the J_{sc} predicted by the model, verifying good accuracy between the model and experimental data. Using the transfer matrix model described and verified above, we investigate the performance of the archetypal TPV bilayer ClAlPc-C₆₀ PHJ solar cells described in Ref. [14]in various configurations and orientations. Here, we examine the conventional electrical configuration (Glass Substrate / ITO 1200 Å / MoO₃ 200 Å / ClAlPc (x) Å / C₆₀ (y) Å / bathocuproine (BCP) 80 Å / ITO (z) Å). We find that by varying the thickness of one layer alone, e.g. the top ITO layer, the angular response of J_{sc} can change from decreasing monotonically to exhibiting distinct angular maxima or reduced angular performance. To study these effects we optimize the thicknesses of three key layers of the device (the donor, acceptor and top ITO layers) simultaneously to maximize J_{sc} , which is proportional to power conversion efficiency

 $(PCE = J_{SC}V_{OC}FF$, where V_{OC} is open circuit voltage and assumed not to vary over the optimization thickness range), at various angles of incidence: *x* and *y* were allowed to vary from 100 to 800 Å, and *z* was varied from 400 to 2000 Å (a range of ITO thicknesses for which fill factor *FF* varies by less than 5%[14]). Optimum layer thicknesses were then obtained by generating contour plots of J_{SC} versus *x* and *y* and finding maximum J_{sc} in this three-parameter space (see Figure 4.8). The optimum layer thicknesses for maximum 0° J_{sc} , maximum 70° J_{sc} , and maximum $J_{sc,ave}$ for the conventional and optically inverted configurations are listed in Table 4.1, where 70° is the typical incident angle of light on a south-facing window at noon in the summer for East Lansing, MI (43° N. latitude),[159] and $J_{sc,ave}$ is the average of J_{sc} across all angles. The angle of illumination to optimize J_{sc} will depend on the application: for building-integrated TPVs, the performance under oblique illumination is more important than the performance at normal illumination because light that is incident on the building-integrated TPV will consist of more direct sunlight (roughly 70% of the incident spectrum[160]), which is mostly oblique illumination, than diffuse sunlight (the roughly 30% remaining), which impinges upon the device at all angles.

Fable 4.1. Layer thicknesses (Á)	to maximize J _{sc} and J _{sc} * for 0)°,	, 70°.	, or all angles of incidence
•/					/ I I

			ITO	MoO ₃	ClAlPc	C ₆₀	BCP	ITO
0 °	Conventional	J_{SC}	1200	200	125	400	80	1200
		Modified J_{SC}			125	225		1400
	Optically	J_{SC}	1200	200	150	275	80	400
	inverted	Modified J_{SC}			125	200		400
70 °	Conventional	J_{SC}	1200	200	125	475	80	1600
		Modified J_{SC}			125	250		1800
	Optically	J_{SC}	1200	200	150	250	80	400
inverted	inverted	Modified J_{SC}			125	175		400
All angles	All angles Conventional		1200	200	125	475	80	1200
		Modified J_{SC}			125	250		1600
	Optically	J_{SC}	1200	200	150	275	80	400
	inverted	Modified <i>J</i> _{SC}			125	175		400

 J_{sc^*} was modified from J_{sc} by multiplying it by charge collection efficiency, assuming a total charge collection length L_{c0} of 1000 Å for the donor/acceptor (see Eq. 4.32).



Figure 4.9. Simulated normalized J_{sc} under 1 sun illumination as a function of angle of incidence for two optimizations. (a) Devices with layer thicknesses optimized for maximum 0° J_{sc} for conventional case. (b) Devices with layer thicknesses optimized for maximum 0° J_{sc} for each case. (c) Devices with layer thicknesses optimized for 70° J_{sc} for each case. The normalization factor, 0° J_{sc} , is shown in the inset. Note that the illumination flux is held constant at all angles for comparison; the flux will vary with angle depending on geographical position, time of day, and orientation.



Figure 4.10. Simulated absorption, reflection, transmission and IQE of 735 nm light as a function of incident angle in three optimizations. (a) Devices with layer thicknesses optimized for maximum $0^{\circ} J_{SC}$ for conventional case. (b) Devices with layer thicknesses optimized for maximum $0^{\circ} J_{SC}$ for each case. (c) Devices with layer thicknesses optimized for 70° J_{SC} for each case.

In Figure 4.9, we plot relative J_{sc} as a function of incident angle, where the inset legend gives the magnitude of J_{sc} at 0° used for normalization. We also plot *A*, *R*, and *T* of a single wavelength of light (735 nm) as functions of incident angle, where 735 nm is the absorption peak of ClAlPc, the largest contribution to photocurrent among the active layers (Figure 4.10). In both figures, we include two approaches to thickness optimization: the devices in the left panel of Figure 4.9 have layer thicknesses optimized for 0°

 J_{sc} for the conventional configuration; devices in the center panel have thicknesses optimized for 0° J_{sc} for their respective configurations; and the devices in the right panel have layer thicknesses optimized for 70° J_{sc} for their respective configurations. Optimizing the thicknesses for the optically inverted configuration improved its normal incidence J_{sc} by 15% (moving from left to center panel), and optimizing the thicknesses for 70° J_{sc} improved the it by 5% for the conventional case and 0.1% for the optically inverted case (moving from center to right panel). The normalized J_{sc} in Figure 4.9 decreases sharply at high angles of illumination for all devices; however, optically inverted devices are shown to retain the normal incidence value over greater ranges of angles. The absorption curves show a similar trend of dropping off more quickly in the optimized conventional device. Losses to absorption at this wavelength (735 nm) come from increased reflection. Therefore, we note again that minimizing losses from reflection over all wavelengths is paramount for TPVs. The shift in reflection curves between the conventional and optically inverted devices can be explained by the different Brewster angles for the air-glass interface and the air-ITO interface: 55° and 62° , respectively. At angles lower than Brewster angle, the p-polarized component of light, which makes up 50% of solar irradiance, has a transmission that increases with higher incidence angles until it reaches 100% transmission at the Brewster angle, after which it begins to decrease, leading to a sharp increase in total reflection (reflection due to both s- and p-polarized components of light). This phenomenon also explains the different angles at which J_{sc} begins to drop off in Figure 4.9 for the conventional and optically inverted cases. Similar behavior around the Brewster angle has also been reported for polymer OPVs.[161]

To gain insight as to why devices optimized for optical inversion have better normal incidence performance and less-varying angular responses, we plotted the electric field profiles for $\lambda = 735$ nm, the peak absorbance of ClAlPc (Fig. 4.11). In the conventional illumination case, the top ITO layer was made thicker (1200 Å) to move the shoulder of the standing wave profile (which is largest in the bottom ITO layer where the photons first enter) closer to the donor-acceptor (D-A) interface. In the optically inverted orientations, moving the peak of the profile to the D-A interface is not as important as reducing the distance



Figure 4.11. Simulated electric field profile for conventional and optically inverted CIAIPc-C₆₀ TPVs. Simulations were done for $\lambda = 735$ nm, the peak absorbance of CIAIPc. $1 = MoO_3$, D = CIAIPc, $A = C_{60}$, and 2 = BCP. (a) Layer thicknesses optimized for illumination through substrate (b) Layer thicknesses optimized for illumination through thin film stack.



Figure 4.12. Simulated electric field profile for normal and oblique incidence on ClAlPc-C₆₀ TPVs. Simulations were done for $\lambda = 735$ nm, the peak absorbance of ClAlPc. $1 = MoO_3$, D = ClAlPc, $A = C_{60}$, and 2 = BCP. (a) Layer thicknesses optimized for illumination through substrate (b) Layer thicknesses optimized for illumination through thin film stack.

from the point of light entry to the D-A interface, so the optimum top ITO layer in these cases was 200 Å. These optically inverted devices have a less-varying angular response also due to the thin top ITO layer (Fig. 4.12); the increase in path length at oblique incidence spreads out the standing wave profile in an overall thicker device more than it does in the thinner devices optimized for optical inversion.

The TMM-based optimization for J_{sc} can be modified to account for electrical considerations by including the thickness-dependence of the 1) donor-acceptor charge collection lengths, 2) resistance of the electrode layer on the *FF* and 3) changes in the active layer bandgap.[162-164] While 3) is notably complex and well beyond the scope of the present work, we note that for 2), the *FF* was shown to be independent of the ITO cathode for thicknesses beyond 40 nm for small devices[14] and can be modeled for large area scaling as:[66, 165]

$$FF(d) = FF(R_S = 0, R_P = \infty) \left[1 - \frac{J_{SC}(d)R_S(d)}{V_{OC}}\right]$$
(4.31)

where d is the total active layer thickness, Rp is the parallel (also called shunt) resistance, and the series resistance, Rs, will be dependent on both the specific layer thickness and area. For 1), we can account for the influence of active layer thickness on charge collection efficiency under zero bias, as:[166]

$$\eta_{CC}(d, V = 0) = L_{C0}/d \cdot [1 - \exp(-d/L_{C0})]$$
(4.32)

where L_{C0} is the charge carrier collection length. For larger active layer thicknesses, the charge collection efficiency will decrease, which will reduce the optimum layer thickness. We show an example comparing optimizations with, and without, the charge collection correction in Table 4.1. Finally, we note that complete optimization would also consider the position of the sun (changing incident angle) and flux variations throughout the day for specific PV orientations/locations. Nonetheless, the demonstration of this model provides the starting point for analyzing such performance and optimization.

4.5 Application for real-world solar irradiance data

Proof-of-concept simulations were performed to quantify the impact of improving the angular performance of transparent solar cells.[148] Hourly sun position and solar irradiance data was collected from the National Solar Radiation Database and used to calculate the global tilted irradiance by the Hay model.[148] An unoptimized device (Device A) was compared with the device optimized for oblique incidence in Ref. [167] (Device B) (Figure 4.13 (a)). Both devices were used in several simulated configurations with different geographical locations, PV tilt angles, and PV facing direction. In Figure 4.13 (b), the yearly power output for a TPV in Lansing, MI is shown, normalized to the power output of a horizontal (tilt angle $\beta = 0^{\circ}$) TPV. The highest yearly power output was seen for a south-facing (azimuth angle $\alpha = 180^{\circ}$) TPV with a tilt angle of 30°. However, the vertically oriented TPV incorporated onto a building window ($\beta = 90^{\circ}$) had the lowest yearly power output across all PV facing directions. The yearly power output was calculated for Device B and compared to Device A, with the improvement plotted in Figure 4.13 (c). For a south-facing window ($\alpha = 180^{\circ}$, $\beta = 90^{\circ}$), the angular response of Device B increased the yearly power output by 15%, and for a north-facing window ($\alpha = 0^{\circ}$ or 360°), the improvement was closer to 17%.[148] These calculations show that the yearly power output of a solar cell can be increased by up to 15% and up to 40% elsewhere by reducing the angular roll-off of performance with no change to the normal incidence performance.

In summary, we extended the transfer matrix model to simulate the angular response of thin-film solar cells and demonstrated self-consistency of A+R+T=1 across all wavelengths, polarizations of light and angles of incidence. This model shows the range of angle-dependent performances in transparent planar heterojunction ClAlPc-C₆₀ solar cells under conventional illumination and optical inversion. Proof-of-



Figure 4.13. Effect of improved angular dependence on yearly PV power output. (a) Normalized responsivity for Device A (unoptimized) and Device B (optimized for improved angular roll-off). (b) Yearly power output of Device A in Lansing, MI with tilt angle β , where $\beta = 0^{\circ}$ is horizontal, and azimuthal angle α , where $\alpha = 180^{\circ}$ is south-facing. (c) Improvement in yearly power output in (b) by using Device B. All figures reproduced with permission from Ref. [148].

principle optimizations suggest that optically inverted structures can potentially provide enhanced angular performance and therefore have the potential to increase maximum power output around the building envelope. This work opens the door for many important advances and designs of thin-film transparent (and opaque) solar cells for installation in the building environment, facilitates subcell photocurrent matching in multijunction solar cells, and demonstrates the additional factors that should be considered for complete optimization in fixed deployment configurations.

Chapter 5 – NIR-Absorbing Organic Heptamethine Salts for TPV

Only a few organic photovoltaics and photodetectors have demonstrated photoresponse past 900 nm, an underutilized spectral region for tandem solar cells, transparent solar cells and infrared photodetectors. In this chapter, heptamethine salts with selective deep near-infrared (NIR) photoresponse are demonstrated with *EQE* cutoffs at $\lambda = 1400$ nm or 1600 nm, the deepest photocurrent generated by organic small molecules. Anion exchange is shown to deepen frontier orbital levels with minimal changes in absorption properties, leading to decreases in dark current, increases in open-circuit voltage (approaching excitonic limits), and increases in specific detectivity. Balancing exciton binding energy and charge transfer efficiency is shown to be key for enhancing the performance of very small bandgap NIR-absorbing devices. Organic heptamethine salts represent a pathway to inexpensive infrared solar cells and detectors and expand the catalog of existing donor materials for transparent and multijunction solar cells.

5.1 Polymethine PV background

Polymethines are a class of molecules consisting of an odd number of methine (C-H) groups that are connected by alternating single and double bonds. Trimethine, pentamethine, and heptamethines are commonly used in dyes and bio-imaging.[168, 169] The smaller polymethines (trimethine, pentamethine) typically have absorption in the visible spectrum due to a smaller degree of conjugation, and the larger polymethines (heptamethine, nonamethine) have smaller bandgaps and absorption in the NIR.[168]

Cationic polymethines can be synthesized by quarternization reactions of the nitrogen in the indole group. One of the five valence electrons on the nitrogen is shared with another carbon atom leaving it with a +1 charge. The aromatic rings on either side of the polymethine backbone can also play a role on the absorption profile of the dye. Functional groups can be added to the molecular structure for increased solubility in water (sulfonate and carboxylate groups) or in organic solvents (long alkyl chains). The center position of the heptamethine backbone also plays an important role. The electron withdrawing / donating group (Cl) on the center carbon atom can greatly affect the absorption profile by tuning the degree of

conjugation or bond length alteration. The three center carbon atoms may also be part of a cyclopentene or cyclohexene moiety, which can stabilize the structure via rigidity, and change the energies of vibronic states.

A review of organic salts primarily featuring polymethines was recently published [170] Here, we briefly summarize the introduction of these materials in PV applications. Polymethine PVs were first demonstrated using visibly absorbing trimethine and pentamethine salts (400-600 nm). A trimethine was used with a ClO₄⁻ anion by Meng *et al* in 2003 for an OPV with 0.25 V_{OC} and 0.1 % *PCE* using C₆₀ as the acceptor.[171] Several studies have since explored different hole transport layers, such as PEDOT:PSS (leading to a much higher V_{OC}),[172] TiOx (leading to smoother films and higher *PCE*s of 3.7%),[173] and MoO₃ (*PCE* = 2.9%).[174] Doping was also studied by air/oxygen for trimethine OPVs.[175]

Polymethines with greater degrees of conjugation (heptamethines and nonamethines) were used for near-infrared OPVs in 2009 when Bouit *et al* used a heptamethine salt as a bulk heterojunction donor with PCBM as an acceptor with 0.4% *PCE*.[176] Véron *et al* used a heptamethine salt to make higher efficiency NIR OPVs as well as transparent OPV.[36] However, very little was still known about the tunability of these compounds and it was often assumed that the anion played very little role. In the sections below, we challenge this notion and show that the anion can indeed play a significant role in the tunability of these compounds.

5.2 Counterion exchange effect on open-circuit voltage

Iodide (I⁻) is a common counterion after the quarternization reaction is completed using ammonium iodide (NH₄I). While the cation is the photoactive component, the counterion affects how the molecule aggregates in solution and thin films. For example, the solid packing was studied using single crystal diffraction for a heptamethine with PF₆⁻ anion and Δ -TRISPHAT anion.[36] A higher symmetry crystal structure was obtained for heptamethine coordinated with the Δ -TRISPHAT anion (monoclinic) than for the PF₆⁻ anion (triclinic).[36]

A study on the effect of counterion exchange on heptamethine OPV performance was carried out in our lab.[31] In the study, the heptamethine Cy and various counterions were investigated as shown in Figure 5.1. A variety of size counterion was tested, ranging from monoatomic iodide (I⁻) to polyatomic tetrakis pentafluorophenyl borate (TPFB⁻). Changing the counterion did not affect the thin film absorption or the optical bandgap (Figure 5.2(a)), but the frontier energy levels (HOMO and LUMO) of the molecule were affected. The change in energy levels could be seen from the different V_{oc} acquired by JV testing (Figure 5.2(b)). The device V_{oc} increases from 0.4 V (Cy-PF₆) to 0.7 V (Cy-TPFB), with no change in optical bandgap. V_{oc} is difficult to change without synthesizing new molecules, making this result particularly exciting. The magnitude of the V_{oc} change also resulted in a doubling of the device PCE, from 0.9% (Cy-PF₆) to 2.0% (Cy-TPFB). As mentioned previously in Chapter 1, the device V_{oc} depends on the interface gap, which is the difference between the HOMO of the donor and the LUMO of the acceptor. Because the device V_{oc} increased (donor HOMO shifted deeper) with no change in the optical bandgap (energy between HOMO and LUMO of the donor stayed the same), both the HOMO and LUMO levels of the donor shifted deeper by approximately 0.3 eV when going from the PF₆ to the TPFB anion.



Figure 5.1. Molecular structure of Cy cation and anions used in Ref. [31]. (a) Cy and (b) anions, (1) I⁻, (2) PF_6^- , (3) SbF_6^- , (4) Δ -TRIS⁻, and (5) TPFB⁻.



Figure 5.2. Absorption and *JV* for Cy salts. (a) Absorption spectra of spincoated Cy films (>12 nm) with different counterions. Solution absorption measured for methanol. (b) *JV* curve for OPV devices with Cy films with different counterions.



Figure 5.3. Cy-PF₆ and Cy-TPFB alloying. (a) V_{OC} as a function of molar fraction of Cy-TPFB, showing a roughly linear relationship. (b) Proposed energy schematic illustrating DOS of pure anions and mixed. Interface gap I_G of Cy/C₆₀ linearly varies with Cy-TPFB fraction.

Blending two heptamethines with different counterions (i.e., fractional alloying) is interestingly found to create intermediary energy level shifts resulting. in linear modulation of V_{OC} with molar concentration (Figure 5.3). This allowed for the fine tuning of the V_{OC} in devices, which represents a powerful tool for finely tuning the energy levels of a molecule without reverting to more complicated synthetic methods (the one-step counterion exchange synthesis is described in Chapter 3). Ultimately, this energy level tuning can be applied in a range of applications where energy level requirements are stringent for full optimization: 1) near infrared / transparent OPVs 2) OLEDs, 3) photocatalysts, and 4) and diagnostics and therapeutics (see Section 7.5).

5.3 Deep NIR (1600 nm) absorption

Organic semiconductors that absorb in the NIR, i.e. at $\lambda > 800$ nm, are promising for applications in broadband and transparent solar cells.[14, 22] Organic compounds with NIR photovoltaic response have been demonstrated including cyanines,[36, 163, 177-179] carbon nanotubes,[180] and polymers.[97, 181] However, *EQEs* in these studies have only extended to 1100 nm for SnNcCl₂ and 1450 nm for carbon nanotubes. Design strategies for redshifting the IR absorption of organic molecules have included increasing the conjugation[163, 182] and modifying the ligand structures to affect aggregation, crystal structure, and intermolecular proximities. However, once molecules are designed and integrated into optoelectronic devices, their performance typically suffers from arbitrary energy level alignments, resulting in lower-than-ideal open-circuit voltages, low carrier mobilities and diffusion lengths, and limited absorbance past 1000 nm. In this work, we synthesize a new series of heptamethine salts[183] with highest occupied molecular orbital (HOMO) levels that can be tuned by varying the anion electronegativity.[31, 36] These organic salts are used in photovoltaic and photodetector cells to demonstrate photoresponse at deep NIR wavelengths and open-circuit voltages nearing their excitonic limit. Using optical modeling and opencircuit voltage tuning[184, 185] we identify limiting factors for performance and strategies for performance enhancement.

Heptamethine salts Cy1 (1-Butyl-2-(2-[3-[2-(1-butyl-1H-benzo[cd]indol-2-ylidene)-ethylidene]-2diphenylamino-cyclopent-1-enyl]-vinyl)-benzo[cd]indolium, $\lambda_{max} = 996$ nm) and Cy2 (1-Butyl-2-(2-[3-[2-(1-butyl-1H-benzo[cd]indol-2-ylidene)-ethylidene]-2-phenyl-cyclopent-1-enyl]-vinyl)-benzo[cd]indolium, λ_{max} = 1024 nm) coordinated with the counterions tetrafluoroborate (BF_4) and tetrakis(pentafluorophenyl)borate (TPFB⁻) are shown in Figure 5.4(a). We focus on these molecules for their absorption ranges that extend to 1400 nm and 1600 nm for cations Cy1 and Cy2 respectively (Figure 5.4(b)). Figure 5.4(c) shows a summary of the m/z synthesis verification for the cation and anion masses. In previous studies, weakly coordinating anions like TPFB have been shown to modulate the frontier energy levels of organic cations used as donors in photovoltaic configurations, thereby increasing the open circuit voltage (V_{OC}) with little or no impact on the bandgap or absorption range.[31, 36, 176]



Figure 5.4. Cy1 and Cy2 salt structures, absorption, and mass spectra.(a) Chemical structures of the heptamethine salt cations (Cy1 and Cy2) and anions (BF₄⁻ and tetrakis pentafluorophenylborate, TPFB⁻). (b) Normalized thin film absorption (1-Transmission) of each organic salt. (c) Summary of high-resolution mass spectrometry m/z spectra for cations and anions used in this study. The multiple peaks and their relative heights represent the isotopic abundances of the constituent elements in the molecule.



Figure 5.5. Device architecture, *JV* and *EQE* for Cy1 and Cy2. (a) Device architecture used for photovoltaic and photodetector structures. (b) *JV* and (c) *EQE* curves for devices with salts with thicknesses of 12 nm (inset highlights the NIR *EQE*).

Salt	J_{SC} [mA cm ⁻²]	V _{oc} [V]	FF	Abs. edge [nm]	NIR EQE peak [%]	D* peak [Jones]	J ₀ [μA cm ⁻²]
Cy1-BF ₄	3.4 ± 0.3	0.13 ± 0.01	0.34 ± 0.01	1440	2.1	3.7 x 10 ⁹	48
Cy1-TPFB	1.9 ± 0.2	0.33 ± 0.01	0.49 ± 0.01	1460	1.1	5.3×10^{10}	0.014
Cy2-BF ₄	3.4 ± 0.3	0.15 ± 0.01	0.42 ± 0.05	1590	1.4	7.0 x 10 ⁹	7.0
Cy2-TPFB	1.7 ± 0.2	0.25 ± 0.01	0.40 ± 0.04	1500	0.8	1.7 x 10 ¹⁰	1.1

Table 5.1. Device parameters and molecular properties for each salt

Solar cell devices with the structure indium tin oxide (ITO)/10 nm MoO₃/t nm salt/40 nm C₆₀/7.5 nm bathocuproine (BCP)/80 nm Ag were prepared using the four salts as a function of thickness (Figure 5.5(a)). Donor layers of each organic salt were spin-coated from *N*,*N*-dimethylformamide (DMF) under nitrogen while other layers were thermally deposited in vacuum. The thickness for each salt was controlled by varying the solution concentration. For comparison purposes, the *JV* and *EQE* for devices with similar salt thicknesses (12±1 nm) are plotted in Figure 5.5(b-c) and average performance metrics are shown in Table 5.1. The fill factors (*FF*) for these devices, 0.3-0.5, are slightly low due to decreased shunt resistances from low-bandgap materials and series resistance from a potential interface barrier between the donor and MoO₃. The exchange of BF₄ for TPFB nearly doubles the *V_{oc}* from 0.13 to 0.33 V for cation Cy1 and 0.17 to 0.25 V for cation Cy2. This enhancement in the voltage is due to the shift in energy levels (Figure 5.6) and increased interface gap (Figure 5.7(a)). However, this exchange reduces the NIR *EQE* peak by more than 50% due to the substantial decrease in the donor-acceptor lowest unoccupied molecular orbital level offset (Δ_{LUMO}). To understand the effect of gradual shifts in interface gap on *EQE*, alloyed blends of Cy1- or Cy2-TPFB were prepared. The *V_{oc}* and *EQE* trends as a function of TPFB molar fraction are plotted in Figure 5.8(a).



Figure 5.6 Proposed energy level schematic for Cy1, Cy2, and C₆₀. Work functions and HOMO levels were extracted from ultraviolet photoelectron spectroscopy. LUMO levels were estimated by adding the optical bandgap and calculated exciton binding energies to the HOMO.



Figure 5.7. Interface gap change in Cy1 salt and band bending in Cy2-TPFB. (a) Energy schematic illustrating the deepening of the LUMO level and increase in interface gap (I_G) after counterion exchange from a small anion BF₄ to the bulky and weakly-coordinating anion TPFB⁻. (b) Schematic D-A band structure as a function of donor thickness (t_D).

The thickness trends of the pure salts are plotted in Figure 5.8(b), where V_{OC} either remains flat (Cy1-BF₄ and Cy2-BF₄) or decreases (Cy1-TPFB and Cy2-TPFB) with increasing thickness and EQE monotonically increases. In general, the V_{OC} is found to be independent of cyanine salt thickness in the 5-15 nm range. In some cases, open-circuit voltages for OPVs increase with thickness as parallel shunting pathways are eliminated by the formation of more complete films.[186] In the case of Cy1- and Cy2-TPFB, however, V_{OC} shows a modest decrease of 20% over the thickness range of 4 to 15 nm. Decreases in V_{OC}



Figure 5.8. V_{OC} and NIR *EQE* as a function of thickness for Cy1 and Cy2. (a) V_{OC} (left axis) and *EQE* (right axis) as functions of mole fraction TPFB for blends of (black) Cy1-BF₄ and Cy1-TPFB and (blue) Cy2-BF₄ and Cy2-TPFB at $t_D = 6$ nm. (b) *EQE* and V_{OC} as a function of donor thickness. Wavelength of *EQE* is shown in inset: 1200 nm for Cy1-BF₄ and Cy1-TPFB and 1350 nm for Cy2-BF₄ and Cy2-TPFB.

with increasing thickness have been attributed to (1) increased recombination due to presence of disorderinduced gap tail states,[187] (2) increased recombination due to electric field profile broadening[188] and (3) shifts in the interface gap due to band bending (Figure 5.7(b)).[189] Mechanisms (1) and (2) are unlikely due to the small thickness range (1 nm) over which the voltage drop occurs; thus, the V_{OC} decrease is most likely due to incomplete band bending in Cy1- and Cy2-TPFB devices as a function of thickness. In contrast, devices with Cy1- and Cy2-BF₄ have no thickness dependent photovoltage and therefore likely have smaller depletion widths stemming from either larger carrier densities or smaller dielectric constants.

Quantum efficiencies past 1000 nm have been limited in magnitude to < 15% even for many quantum dot systems.[163, 190] To identify the limiting factors in our NIR EQE, we examine the component efficiencies: η_A (absorption), η_{ED} (exciton diffusion), η_{CT} (charge transfer), η_{CD} (charge dissociation) and η_{CC} (charge collection). Through exciton diffusion and optical interference modeling, [152, 167] EQE curves were well fit for effective exciton diffusion lengths, which were calculated assuming 100% charge transfer, charge dissociation, and charge collection efficiencies. From this analysis, we find that the effective diffusion lengths in these four salts are all around 0.5-1 nm due to the modest EQEs. However, we also find that absorption profiles already reach 70% at the peak wavelength for Cy2-TPFB films that are only 25 nm thick, suggesting that these devices are not limited by absorption. With the extracted diffusion lengths, the optical interference model predicts that the EQE should decrease for all the tested salts with increasing thickness due to the inability of excitons to diffuse to the dissociating interface. This predicted trend of decreasing EQE is indeed seen experimentally in other larger gap cyanine salt devices.[31, 188] However, this behavior contrasts the experimental trends that show EQE monotonically increasing for donor layer thicknesses past 25 nm. This suggests that the intrinsic diffusion length is in fact longer than 0.5-1 nm and the EQE of these salts is instead limited by charge transfer, charge dissociation, or charge collection efficiency, at least one of which should not be modeled as 100%.

While there is not a clear method to directly distinguish between the component efficiencies (charge transfer, dissociation, and collection), we can infer insight about charge collection from other measurements. For example, since the experimental $C_{60} EQE$ peak ($\lambda = 430$ nm) does not decrease with increasing salt thickness and is similar in magnitude to other salt based OPVs with larger bandgaps,[31, 36] this implies that hole collection from excitons originating on C_{60} (which still have to transport through the donor salt) is not a limiting factor. Thus, devices are most likely limited by charge transfer or dissociation efficiency because of the tradeoff between the lowest unoccupied molecular orbitals of the donor and acceptor and the exciton binding energy.

To estimate the exciton binding energy, we turn to anion mixing experiments and look for the emergence of sharp cutoffs in the *EQE* (Figure 5.8(a)). Indeed, while there is a linear variation in the V_{OC}

that stems from a monotonic modulation of interface gap recombination, there is a sharp EOE cutoff at a molar fraction of 10% TPFB, suggesting that there is just enough energy (Δ LUMO) available at that concentration to efficiently overcome the exciton binding energy. The remaining quantum efficiency beyond this concentration likely stems from a combination of field- and temperature-driven dissociation.^[24] We can then estimate the energy available for exciton dissociation by subtracting the interface gap (calculated from the V_{oc})[66] from the optical bandgap, yielding exciton binding energies of ~0.55 eV for Cy1 and ~0.40 eV for Cy2, which is close to other reported values in organic molecules (0.2 to 1.4 eV).[191-193] These exciton binding energies make up roughly 50% of the optical bandgap ($\sim 0.8 \text{ eV}$), limiting the interface gap (and therefore V_{OC}) to modest values at which efficient exciton dissociation can still take place, despite the ability to achieve higher V_{OC} s. Moving forward, several strategies can be explored to decrease the exciton binding energy. For example, molecular modifications can be designed to enhance the delocalization of the electron/hole orbitals to increase the exciton radius,[194] e.g. via central methine substitution.[183] Another design strategy involves the coupling of smaller solubilizing groups or anions that allow for denser packing to increase the dielectric constant. [192, 195, 196] Thus, this presents an interesting design challenge for the future optimization of very small bandgap organic photoactive devices. To understand the ultimate potential of these material sets in photovoltaic applications, we modeled the EQE of a device with a 100 nm thick Cy2-TPFB layer having an exciton diffusion length of 100 nm, a 20 nm thick C_{60} layer, and charge transfer and charge collection efficiencies approaching 100%. Such a device would have an EQE of about 70-80% with a J_{SC} on the order of 25 mA/cm², and could be realized using a bulk heterojunction architecture and optimized energy level tuning. FF values can be increased from 0.3 to 0.65 (achievable for most organic systems) by optimizing the interface energetics through the selection of different transport layers or the modification of solvent and/or spincoating conditions. Combined with a slightly improved V_{OC} of 0.55 V, which is around the Shockley-Queisser excitonic limit, ideal devices would be around 10% efficient with high transparency and would be well suited for multijunction cells with complementary absorption.



Figure 5.9. Specific detectivity *D** spectra for each deep NIR salt (Cy1 and Cy2).

These salt-based devices are also shown to be viable for near infrared photodetectors.[197] Photodetector devices were fabricated with the same photovoltaic structure as those above. Specific detectivity (D^*) curves for each salt are plotted in Figure 5.9, where D^* is proportional to the *EQE* and inversely proportional to the differential resistance at zero bias.[198] Specific detectivity D^* (cm Hz^{1/2} W⁻¹) was calculated based on *JV* measurements at short circuit (V = 0). D^* is obtained from:

$$D^* = R \sqrt{A} S_N^{-1} \tag{5.1}$$

where *R* is responsivity in A/W, *A* is device area in cm², and S_N^{-1} is current spectral noise density in A Hz^{-1/2}. At room temperature and 0 V, the noise is dominated by thermal (Johnson-Nyquist) noise S_T (A Hz^{-1/2}), which is estimated as:

$$S_T = \sqrt{\frac{4kT}{R_D}} \tag{5.2}$$

where *k* is the Boltzmann constant (J K⁻¹), *T* is temperature (K), and R_D is the differential resistance of a solar cell in the dark at zero bias. Calculated *D**s are comparable to those of the limited reports in other organic systems[182, 198-200] and reach values of 6.5 x 10¹⁰ Jones at $\lambda = 1140$ nm and 1.7 x 10¹⁰ Jones at $\lambda = 1390$ nm for Cy1 and Cy2 salts respectively. This compares well to the very limited reports in organic systems, such as porphyrin tapes (2.3 x 10¹⁰ Jones at $\lambda = 1350$ nm)[182] and inorganic carbon nanotubes (8.8 x 10¹¹ Jones at $\lambda = 1350$ nm).[198] Exchanging the anion from Cy1-BF₄ to Cy1-TPFB increases the
detectivity by an order of magnitude from 3.7×10^9 to 5.3×10^{10} Jones, largely due to lower noise currents for devices with the TPFB anion. Compared to other organic systems, heptamethine salts have readily tunable properties via counterion or ligand exchange in addition to being easy to synthesize and fabricate. Moreover, they exhibit both broader and wavelength-specific photoresponsivity, which is promising for a range of applications in the near-infrared and visibly transparent photodetectors.

5.4 TPV demonstrations with organic salts

Because of the strong NIR absorption of the heptamethine salts we studied (Cy, Cy1, and Cy2), we decided to explore their use in transparent solar cells.[31] We began by performing optical simulations to optimize the thicknesses of the Ag / Alq₃ top electrode (Figure 5.10). The optimum combination of J_{SC} and AVT was found for thin layers of Ag (< 80 Å) and thick layers of Alq₃ (600 Å). Thicker layers of Alq₃ lead to both higher transparency and performance, pointing to the importance of managing electric fields and the shortcomings of only considering Beer Lambert's law. The contour map was experimentally confirmed



Figure 5.10. Contour map of predicted J_{SC} and AVT for TPV with Cy-TPFB. Device structure: 100 Å MoO₃ / 120 Å Cy-TPFB / 200 Å C₇₀ / 75 Å BCP / x Ag / y Alq₃. Black squares indicate experimental values.



Figure 5.11. Experimental optimization of Ag/Alq₃ electrode for TPV with Cy-TPFB. (a) JV, (b) EQE and (c) Transmission of TPVs with Cy-TPFB and 300 Å C₇₀ with different thicknesses of Ag and Alq₃ shown in legend (Å).



Figure 5.12. TPV demonstration with Cy-TPFB: *JV*, *EQE*, and transmission. (left) *JV* and (middle) *EQE* of Cy-TPFB in transparent and opaque devices with peak *EQE*s of 20 % and 25% respectively. (right) Transmission of the corresponding device stack with one NIR reflector attached (AVT = 50%).

using several points, shown as black boxes in Figure 5.10; the *JV*, *EQE*, and transmission curves for these devices are shown in Figure 5.11. Thicker layers of Ag (50, 80, and 120 Å were tried) yielded higher J_{SC} s, and thicker layers of Alq₃ yielded more transparent devices (compare 80/300 Ag/Alq₃ with 80/600 Ag/Alq₃), confirming both major trends shown by the optical interference calculations in Figure 5.10.

Shown in Figure 5.12 are transparent and opaque planar heterojunction devices based on Cy-TPFB with absorption in the 800-1000 nm range. The optimal opaque device structure was 10 nm MoO₃, 10-15 nm donor, 50 nm C₇₀, 7.5 nm bathocuproine (BCP), and 80 nm Ag. An efficiency of 2.7% was achieved with 25% external quantum efficiency between 800-1000 nm. For transparent devices, we replaced the Ag layer with a layer comprised of 8 nm Ag and 70 nm Alq₃ (optimized by optical interference simulations) and made the C₇₀ layer thinner (changed from 50 to 30 nm) to improve transmission. The highest

performance transparent device reached an efficiency of 2.0%, peak *EQE* of 20% between 800-1000 nm, and AVT = 50% with a NIR reflector attached to the glass substrate.

NIR-absorbing organic salts have the potential to enable highly efficient, tunable, and scalable TPVs. They have strong absorption in the near infrared, and their frontier energy levels can be easily shifted by exchanging the counterion. Counterion alloying can be done to meet stringent energy level requirements in TPVs and other applications such as OLEDs and cancer theranostics. Organic salts can also be deposited using solution processing methods, allowing TPV device fabrication to be scaled up. Increasing the EQE of these devices is a key challenge this material set faces; likely, a bulk heterojunction approach will need to be taken (blending Cy-TPFB with PCBM, for example). Using organic salts in a multijunction device can reduce thermalization losses; this approach will be discussed in the next chapter.

Chapter 6 – Tandem TPV Optimization

6.1 Tandem TPV background

In traditional tandem OPVs, complementary absorbing subcells are used to capture low/high energy photons with better matched low/high bandgaps to reduce thermalization losses. In semi-transparent tandem OPVs (5-8% *PCE*, Table 6.1), complementary absorbing subcells are also used, however, more emphasis is placed on absorption in the NIR. For example, an NIR absorbing (600-850 nm) subcell composed of 2-{[7-(5-N,N-ditolylaminothiophen-2-yl)-2,1,3-benzothiadiazol-4-yl]methylenemalononitrile (DTDCTB) and C₆₀ was combined with a visible-absorbing subcell composed of tetraphenyldibenzoperiflanthene (DBP) and C₇₀ for a semi-transparent tandem device with 5.3% *PCE* and 31% *AVT*.[17] In another study, two different NIR-absorbing polymers were used in a tandem TPV: PBDTT-FDPP-C₁₂ (film absorption max ~750 nm) and PBDTT-SeDPP (film absorption max ~800nm).[23] Using PC₆₁BM in both subcells resulted in a greenish tint, whereas substituting PC₇₁BM for PC₆₁BM in one of the subcells resulted in a neutral color due to the redshifted absorption of PC₇₁BM.[23] The use of PC₆₁BM in one subcell and PC₇₁BM in the other has been used in several tandem TPV studies since PC₇₁BM or C₇₀ can be used to obtain devices with higher *CRI* and *PCE*.[27, 29] Indeed, the highest combination of *PCE* and *AVT* for semi-transparent OPV to date uses PSEHTT:IC₆₀BA and PBDTT-DPP:PC₇₁BM, achieving 8.0% *PCE* with 41.7% *AVT*.[29]

6.2 Simulations and contour mapping

Predicting J_{SC} using optical interference modeling becomes especially important for tandem OPVs because photocurrent matching between subcells is essential for simple series-integrated structures and experimental optimizations are difficult to perform due to large number of variables and thicknesses. The overall performance is very sensitive to the thicknesses of the interconnect layers and the electrode thicknesses, which can all affect *PCE*, *AVT* and *CRI* differently. Example modeling results for a two-cell tandem incorporating bulk-heterojunction subcells of ClAIPc and tin phthalocyanine (SnPc) are shown in

			J_{SC}				η (%) *	
Front Subcell	Back Subcell	V_{OC}	(mA	FF	η	AVT	AVT(frac.)	Ref.
		(V)	cm ⁻²)		(%)	(%)	(%)	
F ₄ -ZnPc:C ₆₀	DCV6T:C ₆₀	1.54	5.2	0.61	4.9	19.8*	0.97	[10]
DTDCTB:C ₆₀	DBP:C ₇₀	1.70	6.2	0.51	5.3	31.8*	1.69	[17]
PBDTT-FDPP-C12:	PBDTT-SeDPP: PC71BM	1.47	8.4	0.59	7.3	34.0*	2.48	[23]
PC ₆₁ BM								
PIDT-PhanQ: PC ₆₁ BM	PCPDTFBT:PC71BM	1.70	5.81	0.67	6.7	38.6*	2.59	[27]
PBDTT-FDPP-C12:	PBDTT-SeDPP: PC ₆₁ BM	1.46	7.2	0.61	6.4	47.4*	3.03	[23]
PC ₆₁ BM								
PSEHTT:IC ₆₀ BA	PBDTT-DPP:PC71BM	1.62	7.62	0.64	8.0	41.7*	3.34	[29]
* 4 1 777 1 1 4 1 *		1 1 .	C					

Table 6.1. Selected tandem semi-transparent OPV performance metrics

**AVT* recalculated using transmission curves provided in references



Figure 6.1. Examples of managing electric field profiles in TPV. (a) Optical field profile management for a transparent semiconductor-metal-semiconductor electrode, of an STPV adapted from Ref. [154]. (b) Optical field profile simulation for the (LiF/MoO₃)₆ electrode of an STPV at different wavelengths, reproduced from Ref. [155]. (c) Example tandem TPV optimization, where the thickness of the interconnect layer and the top ITO cathode are varied to optimize *PCE*, *AVT*, or *CRI*.

Figure 6.1 (c) as a function of the interconnect and top transparent cathode thickness. This model is partially optimized for two of the eight key-parameters and indicates that an efficiency of > 6% with a transparency > 70% and *CRI* of ~85 for a two-cell junction is achievable. These simulations demonstrate the complex multidimensional optimization landscape that can emerge in these systems. Meiss also used the transfer matrix method to calculate the photocurrent of the limiting subcell for different thicknesses of the thin metal / semiconductor electrode (Ag / Alq₃) and demonstrated a tandem STPV with *PCE* of 4.9% and *AVT* of 19.8%.[10]

6.3 Experimental results

Given the importance of the tandem structure, we explored a range of subcell configurations for TPVs. The first architecture we explored used a subcell of ClAlPc/C₆₀ and SnPc/C₆₀, but of which contain donors that selectively harvest UV/NIR light ideal for TPV and transparent multijunctions ClAlPc has been demonstrated as an excellent candidate for TPVs,[14] and SnPc had been demonstrated as a good NIR solar cell and TPVs.[163, 201] SnPc and ClAlPc can both be thermally evaporated, which is advantageous for consistent processing in this study. Also, SnPc has deeper NIR absorption than ClAlPc by about 150 nm, so the two subcells can have complementary NIR absorption. The tandem device architecture is shown in Figure 6.2(a), where ClAlPc subcell was deposited first followed by the SnPc subcell. In Figure 6.2(b), the *JV* curves for the opaque devices are shown. The standalone "subcells" are devices made with ITO / MoO_3 / ClAlPc or Cy-TPFB / C₆₀ / BCP / Ag. The ClAlPc subcell device has a much higher V_{oc} (0.74 V) than the SnPc device (0.38 V), which is not surprising consider the smaller bandgap of SnPc. The V_{oc} of the tandem device (1.03 V) was almost equal to the sum of the V_{oc} s of the two subcells (0.74 + 0.38 = 1.12 V), indicating good balance of charge recombination in the interconnecting layers. However, the J_{sc} of the tandem device (0.026 mA mm⁻²) is less than half of either subcell J_{sc} (~0.06 mA mm⁻²). While the overall *PCE* of the tandem device (1.4%) was lower than that of the single junction ClAlPc device (2.4%), this



Figure 6.2. ClAlPc and SnPc tandem device. (a) Device architecture of $ClAlPc/C_{60} - SnPc/C_{60}$ tandem OPV. (b) *JV* of opaque devices with silver top electrode. *JV* is shown for tandem devices and $ClAlPc/C_{60}$ and $SnPc/C_{60}$ subcell devices. (c) *JV* of the tandem device with ITO top electrode.

architecture still shows promise considering the high voltages achieved. Photocurrent matching is the key challenge for this architecture, with no improvement seen by changing either SnPc or ClAlPc thicknesses. In Figure 6.2(c), the top silver electrode of the tandem device was replaced with 1000 Å of transparent sputtered ITO to make a transparent tandem OPV. These transparent tandem devices had a very low V_{oc} (0.49 V) compared to the opaque version (1.03 V), possibly due to the sputtering process of ITO causing partial shorts within the device stack. The *PCE* was lower by a factor of 4 (1.4% vs. 0.3%), so clearly more optimization is needed to successfully replace silver with ITO for transparent tandem devices.

We further explored another potential subcell based on the Cy-TPFB salt. Because of the higher V_{oc} of Cy-TPFB devices (0.7 V) compared to SnPc devices (0.4 V), SnPc was replaced with Cy-TPFB in the tandem architecture optimization. This tandem structure is shown in Figure 6.3(a). The Cy-TPFB subcell was deposited first to avoid damaging other layers with the spincoating process. Control subcell devices with ClAlPc and Cy-TPFB were also made with the structure ITO / MoO₃ / ClAlPc or Cy-TPFB / C₆₀ / BCP/ Ag. As seen in Figure 6.3(b), the ClAlPc and Cy-TPFB control devices have similar values for V_{oc} : 0.77 and 0.69 V, respectively. The V_{oc} of the tandem device is 1.38 V, which is close to the sum of the subcell V_{oc} s (0.77 + 0.69 = 1.46 V). This V_{oc} is significantly higher than the ClAlPc-SnPc tandem device (1.03 V). The J_{sc} of the ClAlPc and Cy-TPFB tandem device (0.033 mA mm⁻²) is also closer to the J_{sc} of the subcells (0.056 and 0.054 mA mm⁻² for ClAlPc and Cy-TPFB, respectively) than the ClAlPc and SnPc tandem device. As a result, the PCE of the tandem device (2.4%) was higher than that of the control subcell devices (2.1% for both ClAlPc and Cy-TPFB).

Optically biased *EQE* measurements were performed to determine which subcell was limiting the photocurrent. The experimental method was covered in Chapter 2; only brief highlights will be covered here. In Figure 6.3(c), the *EQE* spectra of the single-junction, control devices are shown. ClAlPc and Cy-TPFB have noticeably different absorption in the NIR, with the absorption peak of ClAlPc being at 735 nm and the absorption peak of Cy-TPFB being at 880 nm. Because there are regions where the absorption spectra do not overlap, each subcell can be illuminated separately: the ClAlPc subcell can be individually illuminated with 735 nm, and the Cy-TPFB subcell can be targeted with 940 nm. The *EQE* of the tandem



Figure 6.3. ClAlPc and Cy-TPFB tandem devices. (a) Device structure of tandem device with Cy-TPFB/C₆₀ and ClAlPc/C₆₀. (b) *JV* of a ClAlPc/C₆₀ device, a Cy-TPFB/C₆₀ device, and three tandem devices with different concentration solutions used for Cy-TPFB. (c) *EQE* of ClAlPc/C₆₀ and Cy-TPFB/C₆₀ devices. (d) *EQE* of tandem device with 11 nm of Cy-TPFB unbiased (blue curve), biased with 735 nm LED light (red curve), and biased with 940 nm bias (black curve).

device with and without optical bias is shown in Figure 6.3(d). The unbiased *EQE* curve is the lowest because at each point, the quantum efficiency of the subcell with lower current is being measured. When we optically bias one subcell in a tandem device, we fill it with excess carriers and measure the photocurrent in the other subcell. This is more representative of real-world conditions because in JV testing, all wavelengths of light are incident on the device at the same time. When the device is biased with 940 nm light, the photoresponse of the ClAlPc subcell is being measured (black curve), and when the device is biased with 735 nm light, the photoresponse of the Cy-TPFB subcell is measured (red curve). The

photoresponse of the CIAIPc subcell is higher overall, especially in the region of C₆₀ photoresponse (~400 nm); this imbalance causes a reduction of current density of the tandem device as seen in Figure 6.3(b). The integrated J_{SC} is 2.3 and 3.5 mA cm⁻² for the TPFB and CIAIPc subcells in the tandem device, respectively, while the measured J_{SC} for the tandem device was 3.0 mA cm⁻². These values are consistent with each other since we expect the current of the tandem device to be between the integrated J_{SC} of the subcell; when one subcell produces less current, a reverse bias is created by the other subcell to make it produce more current. Because the Cy-TPFB subcell was determined to be the current-limiting subcell, changes will need to be made to the device architecture to improve quantum efficiency within that subcell, which can be accomplished either by changing layer thicknesses or by adopting a bulk heterojunction.

To guide these experiments, simulations were performed to generate contour maps of the performance metrics J_{SC} , AVT, and CRI. The initial data shown above highlights the complex nature of optimizing and fully current matching these types of devices since there are eleven variables (each layer thickness is a variable). For clarity and visualization purposes, we focus on varying the middle MoO_3 , top ITO, ClAlPc and Cy-TPFB thicknesses since these have been identified as the most critical. The results of simulating AVT, CRI and J_{SC} are split into Figure 6.4 (varying MoO₃ and ITO) and Figure 6.5 (varying ClAlPc and Cy-TPFB). Changes in MoO_3 and ITO result in significant changes in AVT (0.75 to 0.80) and CRI (85% to 95%), meaning a total improvement of 10% in optical properties is possible with complete optimization. In electrical performance, J_{SC} varied from 2.1 to 2.6 mA cm⁻², which marks a potential improvement of 25%. For changes in ClAIPc and Cy-TPFB, with thicker layers, the AVT intuitively decreases as there is more overall absorption across the spectrum. CRI is less sensitive but also starts to decrease above a certain ClAlPc thickness because of tail absorption in the visible region. For the J_{SC} optimization, we find that thicknesses near the exciton diffusion lengths for the two materials is ideal, which is well known in the OPV field. Based on these contour maps, the AVT and J_{SC} can potentially be improved by more than 20% just by small changes in thickness variations. Experimental device fabrication is needed to confirm these trends; however, these contour maps represent a starting point and a guide to optimization. Full optimization will require simulation across the entire multivariable space, utilizing larger



Figure 6.4. Contour maps for transparent Cy-TPFB/C₆₀ – ClAlPc/C₆₀ tandem devices showing (a) AVT, (b) CRI, and (c) J_{SC} as a function of the middle MoO₃ and the top ITO thicknesses. For these simulations, Cy-TPFB and ClAlPc thicknesses were both held constant at 200 Å.



Figure 6.5. Contour maps for transparent Cy-TPFB/C₆₀ – ClAIPc/C₆₀ tandem devices showing (a) *AVT*, (b) *CRI*, and (c) J_{SC} as a function of the ClAIPc and the Cy-TPFB layer thicknesses. For these simulations, the middle MoO₃ and the top ITO thicknesses were held constant at 100 and 1200 Å, respectively. Explain why the range was limited for the thickness of Cy-TPFB and that a larger range would expose optical interference effects (e.g. starting to be seen in the CRI at 400 Å Cy-TPFB).

supercomputers or genetic algorithms for sampling.

Another approach for tandem TPVs is a C_{60} -only subcell capable of harvesting just the UV part of the solar spectrum with a higher voltage. These C_{60} -only devices generally only work well when the C_{60} is dilutely doped (5 volume %) with a donor, for example 1,1-bis-(4-bis(4-methyl-phenyl)-amino-phenyl)cyclohexane (TAPC).[202] Several donors can be used to dilutely dope C_{60} , but TAPC has less tail absorption in the visible light compared to other donors such as ClAlPc and DBP (Figure 6.6). The working principle of these devices is that the exciton dissociates within the doped C_{60} layer almost immediately, and the electron and hole mobility of C_{60} is high enough to allow for efficient ambipolar charge collection. This device has high quantum efficiency (50-60%) in the UV (300-400 nm) region (see Figure 6.7(a)), as well



Figure 6.6. Dilute donor devices with ClAIPc, DBP, and TAPC. (a) Device structure and molecular structure for chloroaluminum phthalocyanine (ClAIPc), dibenzoperiflanthene (DBP), and 1,1-bis-(4-bis(4-methyl-phenyl)-amino-phenyl)-cyclohexane (TAPC). (b) *JV* and (c) *EQE* of devices with 5% volume doping (donor:acceptor).



Figure 6.7. CIAIPC BHJ and dilute C₆₀ **tandem devices.** (a) EQE of a single junction, 5% TAPC:C₆₀ device and of a CIAIPC BHJ device. (b) Device structure of an opaque tandem device with TAPC:C₆₀ front subcell and CIAIPC BHJ back subcells. (c) JV of TAPC:C₆₀ – CIAIPC BHJ tandem device and the TAPC:C₆₀ and CIAIPC BHJ subcells.

as high V_{oC} (~ 1.0 V). The combination of this subcell with ClAlPc/C₆₀ in tandem devices has resulted in good V_{oC} summations of the subcells: 0.92 V for TAPC:C₆₀, 0.80 V for ClAlPc BHJ, and 1.65 V for the tandem device (compare with 0.92 + 0.80 = 1.72 V) (Figure 6.7(b) and (c)). Moreover, 1.65 V is the highest V_{oC} for a tandem device achieved thus far in this study. However, optically biasing the individual subcell is challenging because every wavelength absorbed by the TAPC:C₆₀ subcell is also absorbed by the ClAlPc/C₆₀ subcell. This complicates the process of determining the current-limiting subcell and requires more manual tuning of probe light intensity during *EQE* measurements and *a posteriori* simulations to predict the photocurrent contributions from each subcell. Nevertheless, the high quantum efficiency and V_{oC} of the dilutely doped C₆₀ subcell make it a promising candidate for further study in tandem TPVs. The multijunction architecture is attractive for making higher voltage devices and reducing thermalization losses. As discussed in Chapter 2, the theoretical efficiency limit for a transparent solar cell increases from 20% PCE to 27% PCE going from a single-junction to a two-junction device. We tested a variety of subcells (ClAlPc/C₆₀, SnPc/C₆₀, Cy-TPFB/C₆₀ and TAPC:C₆₀) for OPVs, finding that good voltage summations could be obtained with using an ICL of 50 Å BCP / 1-5 Å Ag / 50 Å MoO₃. More simulations and experimental work will be needed to current match the subcells in TPV architectures, i.e. using a transparent top electrode.

Chapter 7 – Conclusions and Outlook

In this chapter, future work in approaching the efficiency limits for efficient transparent organic solar cells will be discussed. Also, challenges to face for large scale commercial adoption of the technology will be considered.

7.1 TPV efficiency: increase NIR EQE, multijunction TPV, better TE design

Key challenges for improving the efficiency of transparent solar cells include increasing the quantum efficiency in the ultraviolet and near infrared, optimizing the architecture of multijunction TPVs, and designing better performing transparent electrodes for better scalability. The lifetime is arguably just as important of an important performance metric as PCE because the power generated over the lifetime of the device is PCE * lifetime; accordingly, it will be discussed in its own section, Section 7.4. The limiting factor in current TPVs is the exciton diffusion efficiency since most of the exciton diffusion lengths of donors are small (< 10 nm), which limits the thickness (and therefore absorption) or charge collection efficiency for the near-infrared absorbing donor layer. To increase the exciton diffusion efficiency, the morphology of the donor/acceptor blend needs to be improved. The morphology can be affected by changing deposition conditions, such as changing solution compositions, deposition rates and substrate temperatures. Different post-deposition treatments such as thermal or solvent annealing can also be explored. To analyze morphological changes, SEM, TEM, and small-angle XRD can be used. Another area of development lies in the design of the molecular structure of the absorber. New donors or acceptors can be synthesized with different absorption spectra, higher carrier mobilities, lower exciton binding energies, and better processability (solubility in the case of solution processable molecules). Different strategies like extending the conjugation, using the push-pull approach on a single molecule, and improving π - π stacking can be used to accomplish these various objectives.

Multijunction solar cells have been demonstrated to be a reliable way to improve efficiency for many types of solar cell. The optimization of multijunction transparent solar cells will require more modeling and experimental studies to port tandem organic solar cell development techniques to tandem transparent solar cells. Extensive modeling and optical cavities can be used to create double passes of both UV and NIR light in the solar cell, increasing the absorption and the quantum efficiency. Experimental studies will be needed to optimize the interconnecting layers between junctions and to tune absorber thicknesses in the individual subcells.

Transparent electrodes for transparent solar cells have been thus far dominated by ITO for the bottom layer. For the top electrode, the requirement of a layer with compatible processing methods with the underlying layers has made conventional ITO sub-optimal. However, ITO replacements have not been as transmissive or conductive, so transparent top electrode development remains a key challenge for transparent solar cells.

Sputtered oxides have potential for high transparencies, and with different dopants, the conductivities can be improved. Moreover, with different deposition techniques, such as eclipsed PLD, damage to the underlying film can be prevented. AgNWs are highly conductive but have surface plasmon resonances that lead to absorption in the near infrared. For solution processed transparent electrodes, a combination of conductive oxides and silver nanowires will likely be necessary.

7.2 TPV applications

TPVs can be deployed over large amounts of surface area previously inaccessible for solar energy harvesting. With approximately 4 billion m² of glass surface area in the United States alone,[203, 204] TPVs are capable of offsetting a significant fraction of energy consumption in buildings and generating electricity close to the point of use while also reducing heating loads similar to low-emissivity (low-E) coatings. Combined with the 8 billion m² of rooftop surface area suitable for PV installation,[205] TPVs can serve as an important complement to rooftop photovoltaics.

Smart windows are a particularly attractive starting point for TPVs because of their low power demands. A 2% *PCE* TPV is sufficient to keep even a north-facing smart window powered indefinitely. In addition, the maximum *AVT* of most smart windows is only around 70% with varying degrees of *CRI* and color tint. These thresholds are already within the demonstrated capabilities of the newest TPV architectures.

Beyond power generation, TPVs can also serve as viable replacements for low-E window coatings which reflect NIR light responsible for carrying heat.[206] Low-E coatings are used to offset cooling loads, or the amount of energy required to cool a given area. By instead harvesting the NIR light for power generation, these technologies can simultaneously offset cooling load while contributing energy to the building.

Consumer electronics such as e-readers are great near-term targets for TPVs due to their large volumes, low power requirements, and common exposure to lighting and sunlight. TPVs could allow devices to recharge while in use, allowing manufacturers to minimize battery size to keep devices thin. Internet of Things (IoT) devices such as electronic shelf labels are another near-term possibility. These and other IoT devices that are becoming integral components in smart building, retail space, and home networks feature low enough power consumption that they can already be powered by preliminary TPVs.

TPVs are also ideal components for future all-electric and solar-powered vehicles,[207, 208] where high *AVT* (55-90%) is key for coating over windows and preserving aesthetic freedom. While a completely coated vehicle would require *PCEs* of 10-15% to provide 10-20 miles worth of travel (~3-3.5 mi./kW-hr) from a typical charge on a sunny day, modern TPVs are applicable on smaller scales such as internal fans or smart windows. These simple features would allow vehicles to cool themselves while parked in the sun without draining the battery.

7.3 TPV scalability

Scaling up and integrating TPVs for given commercial applications requires the simultaneous consideration of *PCE*, *AVT*, and *CRI*. Entry into architectural applications typically require *PCE* > 3-5% to appreciably offset energy consumption in a building, and the *AVT* should generally be > 60% for non-tinted windows.[209] While some inorganic semitransparent PV technologies are applicable here, they should be neutrally colored (high *CRI*) to avoid adverse effects on the circadian rhythms of inhabitants.[210] Low-power smart windows and electronic displays can be powered with *PCEs* > 2%, but the latter require *AVTs* > 80% and *CRI* > 90 so as not to interfere with the view. Preliminary TPVs can already meet many of these metrics as discussed above, and higher performance devices are likely to continue emerging.

7.4 TPV lifetime

Lifetime is a key consideration to any PV technology and needs to be longer than the application lifetime or the cost/energy payback time to become commercially viable. Organic and excitonic materials are well known to be sensitive to oxygen and moisture [211]. Despite these potential sensitivities, commercialized organic light emitting diodes (OLEDs) made from similar materials exhibit lifetimes on the order of decades[212] and a number of OPV lifetimes are now reaching into 5-20 years. Organic PV performance often has a region of fast decay (also known as the burn-in) followed by a region of slower decay and can overall be fitted to a biexponential equation or a combination of exponential and linear decay



Figure 7.1. Examples of OPV lifetime. (a) OPV performance decay over time with three primary regimes: burn-in, long-term, and failure. Reproduced from [8]. (b) Polymer (PCDTBT:PCBM) OPV lifetime in an oxygen and moisture-free environment. Reproduced from Ref. [18]. (c) Performance parameter decay curves over 4400 hrs. for encapsulated polymer OPV in indoor 1-sun testing conditions. Reproduced from [24]

(Figure 7.1 (a)).[213] When encapsulation fails, there is often a quick decay in performance until the device no longer functions at all.[8] PV lifetimes are typically reported as T_{80} (or T_{50}), which is defined as the time for performance to decrease to 80% (or 50%) of either the initial performance or the performance after the burn-in. When the length of the experiment is less than T_{80} or T_{50} , the rate of decay is extrapolated to calculate T_{80} and T_{50} . Primary degradation mechanisms often include moisture or oxygen diffusion in the active organic layer, which can lead to photo-oxidation of organic layers (e.g. via triplet quenching to generate singlet oxygen), oxidation of electrodes (e.g. Ag), and crystallization of low T_g (glass-transition temperature) buffer layers.[8, 213-215] Structural changes in the morphology, particularly for nanostructured bulk heterojunctions can also result from thermal fluctuations and the presence of moisture or other solvents. Many of the potential stability issues can be overcome with encapsulation between glass panels or thin-film encapsulation (for flexible applications).[216] For encapsulated PCDTBT:PCBM devices held under 1-sun illumination in a controlled moisture- and oxygen-free environment, projected T₈₀ lifetimes of up to 20 years were demonstrated (Figure 7.1 (b)).[18] The same polymer, PCDTBT, had a projected T_{80} of 6.2 years when tested under ambient, indoor 1-sun conditions (Figure 7.1 (c)).[24] Changing the active layer morphology from planar to bulk heterojunction has generally been shown to increase OPV lifetime due to reduction of the probability of generating new trap-states from exciton-exciton and exciton-polaron interactions, which are reduced by the increased exciton dissociation efficiency and leads to lower exciton concentrations.[217]

Nonetheless, when considering lifetime and stability it is often equally important to determine the required lifetime for a given application. If the application lifetime is longer than the PV lifetime, then the ease of replacing the PV module becomes the key question. Mobile electronics are often replaced at least once every 10 years, and most smart phones are replaced as frequently as every 2-3 years. For these applications, a TPV could be pre-coated onto or beneath display screens. In contrast, for architectural applications, no PV technology will last as long as a building or window. In this case, TPVs could be



Figure 7.2. Optical window of absorbance for biological tissue. Hb = Hemoglobin, $Hb-O_2 = Oxyhemoglobin$. The shaded portion is the absorption range of Cy salts.

applied as laminates to the inside or outside of windows, which would then allow for cost-effective replacement.

7.5 Future applications: organic salts for cancer theranostics

Inspired by the fine tuning afforded by organic salts, we have begun to investigate the potential to translate our solar cell materials to cancer diagnostic probes and therapeutics. Organic salts that absorb and fluoresce in the infrared can be used as bioimaging agents due to the NIR optical window in biological tissue that, to date, has been underutilized (Figure 7.2). They can also be used as cancer therapy drugs, killing tumor cells by generating reactive oxygen species (ROS) or by producing local thermal stress. Fluorescent molecules have been used clinically as a bioimaging agent since the FDA approved indocyanine green (ICG) for use in humans in 1959.[183, 218] It was shown to preferentially accumulate in tumor cells because of the mitochondrial membrane potential.[219] More recently, ICG and other polymethines have been explored as theranostic drugs, i.e. the combination of tumor diagnosis as well as tumor killing (therapy).[220, 221] Theranostic drugs are attractive as they combine multiple functions into one drug, but bright imaging and cytototoxicity are hard to optimize for the same molecule.



Figure 7.3. Types of photodynamic therapy. (a) Optical processes leading to the formation of peroxide (O_2^{-}) and singlet oxygen $({}^{1}O_2)$. A = Absorption, F = Fluorescence, P = Phosphorescence, ISC = intersystem crossing. (b) Illustration of how the excited triplet state on the dye triplet state (T_1) transfers an electron to ground state oxygen $({}^{3}O_2)$ to create singlet oxygen $({}^{1}O_2)$.

There are two main types of cancer therapy, photodynamic therapy (PDT) and photothermal therapy (PTT) (Figure 7.3). In PDT, the dye absorbs light and then creates a reactive oxygen species (ROS). ROS examples include superoxide (O_2) , peroxide (H_2O_2) , hydroxyl radicals (OH^-) and singlet oxygen $({}^1O_2)$, and they are generated during normal cell metabolism and can be found in larger amounts when the cell is under stress. ROS causes damage to different membranes as well as to DNA, leading to cell death. In PDT a photon is absorbed creating an excited singlet state on the dye. The excited state can then dissociate to oxidize molecular O₂ and form superoxide, or can undergoes intersystem crossing to the triplet state and energy transfer to ground state triplet oxygen to create singlet oxygen. These two types of therapy can be distinguished by electron paramagnetic resonance (EPR) because triplet states with the spins going the same way have a specific magnetic signature. [222] Photothermal therapy (PTT) is another type of therapy that is considered for these molecules where dyes accumulated in the tumor absorbs NIR light, reradiates this energy as heat (as opposed to light), which then damages to the surrounding cell environment. Because the formations of different ROS have different redox potentials, being able to tune the energy levels of the Cy could allow us to turn on or off cytotoxicity at will. Having a facile way to change the phototoxicity of a cationic dye is a powerful tool to be able to kill tumors (high phototoxicity) and produce bright images (low phototoxicity) using the same molecule.



Figure 7.4. Optoelectronic tunability of Cy salts for therapy and for imaging. The ball-and-stick model and Connolly surfaces of the anions are shown: hexafluorophosphate (PF_6^-), tetrakis(4-fluorophenyl)borate (FPhB⁻); cobalticarborane (CoCB⁻); tetrakis (pentafluorophenyl) borate (TPFB⁻); tetrakis[3,5-bis(trifluoro methyl)phenyl]borate (TFM⁻); Δ -tris(tetrachloro-1,2-benzene diolato) phosphate(V) (TRIS⁻). Figure courtesy of Prof. Sophia Lunt.



Figure 7.5. A549 cell viability with different concentrations of organic salts dissolved in DMSO. (left) cell viability for cultures kept in the dark. (right) cell viability for cultures illuminated with NIR flashlight centered at 850 nm with daily ~10 minute treatments showing unprecedented tunability (figure courtesy of Prof. Sophia Lunt).

Preliminary work now being carried out with our collaborator (Prof. Sophia Lunt) has shown that anion exchange can dramatically change the cytotoxicity of the Cy salt (Figure 7.4).[31] Unlike Cy-I and Cy-PF₆ which are cytotoxic at even small concentrations of 1-5 μ M in the dark, Cy-FPhB is found to be highly photocytotoxic, causing cell death only when exposed to NIR light (Figure 7.5). These are attractive for laser treatments of tumors as they can now provide true double selectivity through the use of both the dye and light. By deepening the HOMO and pairing the Cy salt with TRIS or TPFB, initial data has found that the salt can become entirely nontoxic even at much higher concentrations of >20 μ M in dark and in light, making it attractive for non-toxic in-vivo cellular imaging. The range in tunable toxicity of the Cy dye allows it to be used for both bright imaging as well as for photo-activated therapy, making it an exciting new platform in biomedical engineering. Future work will need to explore this systems in actual mammalian systems *in vivo* with a variety of cancer types and conditions.

7.6 Final summary

Transparent solar cells are an exciting new paradigm for solar deployment specifically enabled by organic and excitonic semiconductors. They offer a pathway to integrate solar onto virtually any surface without impacting the view or aesthetics and open new applications that have been less accessible to traditional semiconductors. By selectively harvesting the invisible parts of the solar spectrum it is possible to achieve the highest possible combination of efficiency and transparency. Optical interference, low bandgap donors, and transparent electrodes have all been critical to the optimization of TPVs thus far. Record transparent solar cells have already reached *PCEs* of >5% with 60% *AVT*, enabling deployment over the smart windows and low-power electronic displays of today. It is likely that TPVs will eventually approach OPV record efficiencies above 10% while also imparting a high degree of visible transparency. To reach this lofty goal, there is still a need to develop a broader catalog of donors and acceptors that absorb outside of the visible spectrum while simultaneously exhibiting high exciton diffusion lengths, charge carrier mobilities, and lifetime. These important design strategies, combined with the development of new transparent multijunction architectures, will enable higher energy applications for TPVs in the future and

complement traditional PVs in the quest to offset a significant fraction of our energy needs with renewable energy.

APPENDIX

List of publications from this thesis

- 1. Young, M., Traverse, C. J., Pandey, R., Barr, M. C., and Lunt, R. R., *Angle dependence of transparent photovoltaics in conventional and optically inverted configurations*. Applied Physics Letters, 2013. **103**(13): p. 133304.
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- 8. Traverse, C. J., Young, M., Patrick, T., Bangsund, J., Bates, M., Chen, P., Redoute, A., Wingate, B., Lunt, S. Y., Anctil, A., and Lunt, R. R. *Anions for Near-Infrared Selective Organic Salt Photovoltaics*. In preparation.
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- 10. Lunt, R. R., Lunt, S. Y., Broadwater, D., Young, M. and Bates, M. 2017. *Tunable Luminescent* Organic Salts For Enhanced Imaging And Photodynamic Therapy. Filed Aug 8, 2017.

Notes:

Large portions of Chapter 2 will be published in 2018 as a book chapter entitled "Chapter 1: Transparent Photovoltaics" in *World Scientific Handbook of Organic Electronics, Volume IV.*

The Frontispiece for Organic Heptamethine Salts for Photovoltaics and Detectors with Near-Infrared Photoresponse is shown on the next page.



Figure A.1. Frontispiece for Advanced Optical Materials Volume 4, Issue 7 (July 2016). Corresponding article: Organic Heptamethine Salts for Photovoltaics and Detectors with Near-Infrared Photoresponse.

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