

TRANSPARENT SINGLE JUNCTION  
SMALL MOLECULE PHOTOVOLTAICS

By

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## ABSTRACT

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Photovoltaics offer a viable solution to our growing energy needs. Conventional solar panels can meet these needs if installed over a large enough area, however achieving this is difficult due to high installation costs and lack of aesthetic appeal. Visibly transparent photovoltaics that selectively absorb ultraviolet and near-infrared light allow seamless integration over previously inaccessible surfaces such as windows or electronic displays, and can thus complement existing solar deployment in a significant way. Enhancing commercial viability for a greater range of these applications requires high power conversion efficiency, a large catalog of wavelength-selective photoactive materials, and long lifetime. In this work, we investigate several approaches toward complete optimization for these important devices. We first explore alternative electrode materials as a replacement for a widely used organic buffer layer which can improve device durability. Next, we demonstrate near-infrared selective organic molecular salts that exhibit uniquely decoupled absorption and molecular orbital energy level tunability. The effects of anion exchange on the solubilities and surface energies of the collective salts are also explored. We further investigate the structural effects of several near-infrared selective molecules and salts to identify key metrics to guide the design of long lifetime materials. This is the first comprehensive lifetime study on devices featuring organic salts with varied counterions. As a result, we show dramatically enhanced device lifetimes of over 7 years under typical solar illumination, exceeding the lifetimes of most mobile electronic devices. This work provides a roadmap to enhance the performance and robustness of transparent photovoltaics that can enable wide scale deployment.

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## KEY TO ABBREVIATIONS

|                   |                                                                                                                |
|-------------------|----------------------------------------------------------------------------------------------------------------|
| A                 | acceptor                                                                                                       |
| AC                | alternating current                                                                                            |
| AFM               | atomic force microscopy                                                                                        |
| Alq <sub>3</sub>  | aluminum hydroxyquinoline                                                                                      |
| AM1.5             | air mass 1.5, solar spectrum at the surface of the Earth                                                       |
| AZO               | aluminum-doped zinc oxide                                                                                      |
| BAPV              | building-applied photovoltaic                                                                                  |
| BCP               | bathocuproine                                                                                                  |
| BHJ               | bulk heterojunction                                                                                            |
| BIPV              | building-integrated photovoltaic                                                                               |
| BOS               | balance of systems                                                                                             |
| C <sub>60</sub>   | spherically shaped fullerene molecule with 60 carbon atoms                                                     |
| C <sub>70</sub>   | ellipsoid shaped fullerene molecule with 70 carbon atoms                                                       |
| C <sub>60</sub> I | C <sub>60</sub> -(N,N-dimethylpyrrolidinium iodide)                                                            |
| CB                | chlorobenzene                                                                                                  |
| CBH               | CB <sub>11</sub> H <sub>12</sub>                                                                               |
| CBD               | chemical bath deposition                                                                                       |
| CIELab            | International Commission on Illumination "Lab" colorspace defined by<br>lightness and chromaticity coordinates |
| CIGS              | copper indium gallium selenide                                                                                 |
| ClAlPc            | chloroaluminum phthalocyanine                                                                                  |

|                 |                                                                                                                                                                |
|-----------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------|
| ClPhB           | tetrakis(4-chlorophenyl)borate                                                                                                                                 |
| CoCB            | C <sub>4</sub> B <sub>18</sub> Co                                                                                                                              |
| CuPc            | copper phthalocyanine                                                                                                                                          |
| Cy <sup>+</sup> | 2-[2-[2-chloro-3-[2-(1,3-dihydro-3,3-dimethyl-1-ethyl-2H-benz[e]indol-2-ylidene)ethylidene]-1-cyclohexen-1-yl]-ethenyl]-3,3dimethyl-1-ethyl-1H-benz[e]indolium |
| D               | donor                                                                                                                                                          |
| DBR             | distributed Bragg reflector                                                                                                                                    |
| DC              | direct current                                                                                                                                                 |
| DCM             | dichloromethane                                                                                                                                                |
| DIM             | diiodomethane                                                                                                                                                  |
| DMF             | dimethylformamide                                                                                                                                              |
| DNA             | deoxyribonucleic acid                                                                                                                                          |
| DOS             | density of states                                                                                                                                              |
| FCB             | B <sub>12</sub> F <sub>12</sub>                                                                                                                                |
| FPhB            | tetrakis(4-fluorophenyl)borate                                                                                                                                 |
| FRET            | Förster resonant energy transfer                                                                                                                               |
| HOMO            | highest occupied molecular orbital                                                                                                                             |
| ICBA            | indene-C <sub>60</sub> bis-adduct                                                                                                                              |
| IoT             | Internet of Things                                                                                                                                             |
| ITO             | indium tin oxide                                                                                                                                               |
| IZAO            | indium aluminum zinc oxide                                                                                                                                     |
| IZATO           | indium aluminum zinc tin oxide                                                                                                                                 |

|           |                                                                                                                                                    |
|-----------|----------------------------------------------------------------------------------------------------------------------------------------------------|
| LCD       | liquid crystal display                                                                                                                             |
| LSC       | luminescent solar concentrator                                                                                                                     |
| LUMO      | lowest unoccupied molecular orbital                                                                                                                |
| MeOH      | methanol                                                                                                                                           |
| NIR       | near-infrared                                                                                                                                      |
| NPD       | N,N'-di(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine                                                                                     |
| NREL      | National Renewable Energy Laboratory                                                                                                               |
| OLED      | organic light emitting diode                                                                                                                       |
| O&M       | operating and maintenance                                                                                                                          |
| OPV       | organic photovoltaic                                                                                                                               |
| P3HT      | poly(3-hexylthiophene-2,5-diyl)                                                                                                                    |
| 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 |
| PCBM      | phenyl-C <sub>61</sub> -butyric acid methyl ester                                                                                                  |
| PDT       | photodynamic therapy                                                                                                                               |
| PEDOT:PSS | poly(3,4-ethylenedioxythiophene) polystyrene sulfonate                                                                                             |
| PHJ       | planar heterojunction                                                                                                                              |
| PhB       | tetraphenylborate                                                                                                                                  |
| PID       | proportion integration derivative parameters for process control                                                                                   |
| PMHJ      | planar mixed heterojunction                                                                                                                        |
| PTCBI     | perylene-tetracarboxylic bisbenzimidazole                                                                                                          |
| PV        | photovoltaic                                                                                                                                       |

|        |                                                              |
|--------|--------------------------------------------------------------|
| QCM    | quartz crystal monitor                                       |
| QD     | quantum dot                                                  |
| QD-LED | quantum dot light emitting diode                             |
| RMS    | root mean square                                             |
| ROS    | reactive oxygen species                                      |
| SAM    | System Advisor Model                                         |
| SEM    | scanning electron microscopy                                 |
| SiNc   | silicon naphthalocyanine                                     |
| SQ     | Shockley-Queisser                                            |
| TCO    | transparent conductive oxide                                 |
| TF     | tooling factor                                               |
| TFM    | tetrakis[3,5-bis(trifluoromethyl)phenyl]borate               |
| TPFB   | tetrakis(pentafluorophenyl)borate                            |
| TPV    | transparent photovoltaic                                     |
| TRIS   | $\Delta$ -tris(tetrachloro-1,2-benzendiolato)phosphate(V)    |
| UPS    | ultraviolet photoelectron spectroscopy                       |
| UV     | ultraviolet                                                  |
| VIS    | visible                                                      |
| X      | placeholder for the anion paired with a $\text{Cy}^+$ cation |
| XRD    | X-ray diffraction                                            |

## KEY TO SYMBOLS

|                      |                                                        |
|----------------------|--------------------------------------------------------|
| $A$                  | optical absorption                                     |
| $a$                  | crystal lattice constant                               |
| $\text{\AA}$         | angstrom unit, 0.1 nm                                  |
| $a^*$                | red and green chromaticity coordinate                  |
| $A_c$                | electron affinity                                      |
| $A_{\text{contact}}$ | parasitic absorption from electrode (contact) material |
| $AVT$                | average visible transmission                           |
| $b^*$                | blue and yellow chromaticity coordinate                |
| $CRI$                | color rendering index                                  |
| $d$                  | distance between two molecules                         |
| $E_B$                | exciton binding energy                                 |
| $E_{BE}$             | electron binding energy                                |
| $E_C$                | conduction band energy                                 |
| $EDL$                | exciton diffusion length                               |
| $E_G$                | semiconductor bandgap                                  |
| $E_K$                | electron kinetic energy                                |
| $EQE$                | external quantum efficiency                            |
| $E_{\text{ref}}$     | reference photon spectrum in mismatch calculation      |
| $E_S$                | laboratory device measurement lamp spectrum            |
| $E_V$                | valence band energy                                    |
| $F_D$                | donor molecule fluorescence spectrum                   |
| $FF$                 | fill factor                                            |

|          |                                                                       |
|----------|-----------------------------------------------------------------------|
| $h$      | Planck constant, $4.135 \times 10^{-15}$ eV-s                         |
| $I_c$    | ionization potential                                                  |
| $I_G$    | interface gap, offset between donor LUMO and acceptor HOMO            |
| $IQE$    | internal quantum efficiency                                           |
| $J$      | current density, current per unit area                                |
| $J_{mp}$ | current density at maximum power point on $J$ - $V$ curve             |
| $J_s$    | solar cell reverse saturation current                                 |
| $J_{sc}$ | short circuit current density                                         |
| $K$      | normalization constant in Dexter transfer                             |
| $k$      | optical extinction coefficient                                        |
| $k_B$    | Boltzmann constant, $8.617 \times 10^{-5}$ eV/K                       |
| $k_D$    | Dexter exciton transfer rate                                          |
| $k_F$    | Förster exciton transfer rate                                         |
| $L$      | four-point probe sample length                                        |
| $L^*$    | luminosity color coordinate                                           |
| $LCOE$   | levelized cost of energy                                              |
| $LUE$    | light utilization efficiency                                          |
| $MF$     | mismatch factor                                                       |
| $m_r$    | reduced effective electron mass                                       |
| $n$      | number of vibronic states; index of refraction; diode ideality factor |
| $P$      | photopic response                                                     |
| $PCE$    | power conversion efficiency                                           |
| $P_{in}$ | incident power                                                        |

|          |                                                                     |
|----------|---------------------------------------------------------------------|
| $q$      | elementary charge                                                   |
| $R$      | optical reflection                                                  |
| $R_0$    | Förster radius                                                      |
| $r_B$    | Bohr radius                                                         |
| $R_E$    | electrical resistance measured via four-point probe                 |
| $R_f$    | front-face optical reflection off an LSC                            |
| $R_p$    | solar cell parallel resistance                                      |
| $R_s$    | solar cell series resistance                                        |
| $S$      | electron spin state                                                 |
| $S_0$    | ground state                                                        |
| $S_1$    | first singlet excited state                                         |
| $S_2$    | second singlet excited state                                        |
| $SPF$    | AM1.5 solar photon flux spectrum                                    |
| $S_R$    | reference silicon photodiode EQE spectrum for mismatch calculation  |
| $SS$     | Stokes shift                                                        |
| $SS_1$   | small Stokes shift in Figure 2.12                                   |
| $SS_2$   | large Stokes shift in Figure 2.12                                   |
| $S_T$    | device EQE spectrum for mismatch calculation                        |
| $T$      | optical transmission                                                |
| $T_1$    | first triplet excited state                                         |
| $T_{50}$ | time over which a solar cell degrades to 50% of initial performance |
| $T_{80}$ | time over which a solar cell degrades to 80% of initial performance |
| $t_D$    | donor thickness                                                     |

|          |                                                                           |
|----------|---------------------------------------------------------------------------|
| $t_f$    | measured layer thickness from ellipsometry                                |
| $TF_f$   | calculated tooling factor                                                 |
| $TF_i$   | initial tooling factor estimate                                           |
| $t_i$    | nominally measured thickness from initial deposition                      |
| $V$      | voltage                                                                   |
| $V_{mp}$ | voltage at maximum power point on J-V curve                               |
| $V_{oc}$ | open circuit voltage, or photovoltage                                     |
| $W$      | four-point probe sample width                                             |
| $W_D$    | depletion width                                                           |
| $x$      | blended layer thickness used for BHJ and PMHJ optimization                |
| $y$      | blended layer volumetric concentration used for BHJ and PMHJ optimization |

### Greek symbols:

|                 |                                                                  |
|-----------------|------------------------------------------------------------------|
| $\Delta E^*$    | color difference between normal and off-angle optical reflection |
| $\varepsilon$   | permittivity                                                     |
| $\varepsilon_0$ | permittivity of free space                                       |
| $\varepsilon_r$ | dielectric constant (or relative permittivity)                   |
| $\eta_A$        | PV absorption efficiency                                         |
| $\eta_{Abs}$    | LSC absorption efficiency                                        |
| $\eta_{CC}$     | PV carrier collection efficiency                                 |
| $\eta_{CT}$     | PV charge transfer efficiency                                    |
| $\eta_{ED}$     | PV exciton diffusion efficiency                                  |
| $\eta_{Opt}$    | LSC optical efficiency                                           |

|               |                                                                                             |
|---------------|---------------------------------------------------------------------------------------------|
| $\eta_p$      | power conversion efficiency                                                                 |
| $\eta_{PL}$   | LSC luminescent efficiency                                                                  |
| $\eta_{PV}^*$ | efficiency of a solar cell edge-mounted to an LSC                                           |
| $\eta_{RA}$   | LSC reabsorption suppression efficiency                                                     |
| $\eta_{Trap}$ | LSC waveguiding efficiency                                                                  |
| $\kappa$      | dipole orientation factor                                                                   |
| $\lambda$     | optical wavelength                                                                          |
| $\nu$         | vibrational mode in the ground state; frequency of light                                    |
| $\nu'$        | vibrational mode in the first singlet excited state                                         |
| $\pi$         | pi bonding orbital                                                                          |
| $\pi^*$       | pi antibonding orbital                                                                      |
| $\rho$        | resistivity                                                                                 |
| $\rho_S$      | sheet resistance                                                                            |
| $\sigma$      | sigma bonding orbital                                                                       |
| $\sigma^*$    | sigma antibonding orbital                                                                   |
| $\sigma_A$    | acceptor molecule optical absorption cross section                                          |
| $\sigma_D$    | normalized overlap of donor molecule emission and absorption molecule<br>absorption spectra |
| $\tau$        | exciton lifetime                                                                            |
| $\Phi_D$      | work function of an electron detector used for UPS                                          |
| $\Phi_S$      | work function of a sample measured with UPS                                                 |
| $\chi$        | effective orbital radius                                                                    |
| $\Omega$      | Ohm, unit of electrical resistance                                                          |

## Chapter 1 – Organic Photovoltaics

Solar harvesting photovoltaics (PVs) are highly appealing renewable energy technologies because of the tremendous potential contained in sunlight. While PVs based on inorganic semiconductors have become highly efficient over the years, solar deployment can be greatly expanded if transparent surfaces are made accessible for PV applications. Organic photovoltaics (OPVs) offer a low-cost alternative to conventional solar cells. These devices utilize organic semiconductors which can be designed to selectively absorb ultraviolet (UV) and near-infrared (NIR) light to enable aesthetically pleasing, highly transparent photovoltaics (TPVs) unachievable with traditional solar technologies.

In this chapter, we discuss organic semiconductor physics as well as the development of early small molecule organic PVs. In Chapter 2, we review the development of TPVs and their relevant figures of merit, performance limitations, and key challenges. Chapter 3 describes relevant experimental techniques utilized in this work for fabricating, measuring, and analyzing small molecule single junction TPVs. Chapters 4-7 cover four experimental projects key to TPV development. In Chapter 4, an inorganic replacement for bathocuproine will be demonstrated for use as the cathode side buffer layer. Applications of alternative transparent top electrodes as replacements for indium tin oxide are also described. In Chapter 5 we explore the performance of molecular salt-based NIR-selective devices and the effects of the anion on physical properties of salts and salt films. Bulk and planar mixed heterojunction architectures utilizing three NIR-selective donors are investigated in Chapter 6. Chapter 7 covers the results of a study on the effects of the NIR-selective donor on device lifetime. Chapter 8 describes potential TPV applications, new approaches for transparent bulk heterojunction architectures, alternative transparent

electrodes, organic salt applications in luminescent solar concentrators, and potential applications in cancer treatment.

## **1.1 Organic and excitonic semiconductors**

### ***1.1.1 Overview of semiconductors***

In terms of electronic properties, materials can be classified as metals, semiconductors, or insulators. Metals exhibit high electric conductivity because of mobile delocalized electrons in the conduction band. Semiconductors and insulators exhibit valence bands filled with ground state electrons and unfilled conduction bands in the ground state. The energetic separation between these two bands is known as the bandgap ( $E_G$ ). A semiconductor exhibits  $E_G$  of approximately 0.2-3 eV while an insulator tends to exhibit values  $> 3$  eV and is generally non-conductive.

Photons with energies lower than  $E_G$  are transmitted through semiconductors, while those with energies greater than  $E_G$  are absorbed. The energy of an absorbed photon is transferred to a ground state electron which is promoted to the conduction band, leaving an unoccupied state, or a hole, in the valence band. An identical process can also occur for thermal excitations with energy  $> E_G$ . Excited electrons are considered free charge carriers at room temperature in most inorganic semiconductors, however free charge carrier generation in organic semiconductors is less trivial due to low dielectric constants. In an organic semiconductor, an excited electron remains coulombically bound to a hole and the pair is known as an exciton, discussed below.

For most semiconductors, some thermally excited electrons occupy the conduction band edge at room temperature. These electrons, the position of the vacuum level, and the density of states for a given semiconductor determine a statistical distribution of charges with an average energy known as the work function. For an intrinsic semiconductor, the work function is located

in the middle of the band gap, indicating an equal occupation of holes and electrons in the valence and conduction bands respectively. This can be altered through the controlled addition of impurities into the semiconductor lattice in a process called doping that can be used to control the conductive properties of a given semiconductor as desired.

An extrinsic semiconductor is one that has a work function positioned away from the middle of the bandgap. This is controlled through the doping of either electron donating or electron withdrawing elements with respect to the semiconductor. For example, if silicon (group IV) is doped with a group III element with fewer valence electrons such as boron, the work function will be adjusted toward the valence band and the silicon will become p-type (more free holes than electrons). Conversely, if a group V element such as phosphorus is instead used as the dopant, the work function will be moved toward the conduction band and the silicon will become n-type (more free electrons than holes). If doped at a high enough concentration, the work function will be positioned at either the conduction or valence band and the semiconductor will become degenerate and function as a metal. Indium tin oxide (ITO), which is simply the semiconductor  $\text{In}_2\text{O}_3$  degenerately doped n-type with tin, exhibits a high enough conductivity that it is routinely used as a transparent electrode in photovoltaic and light emitting devices.

If an n-type and p-type semiconductor are brought into contact, excess electrons and holes from the respective materials will diffuse into the other due to a space charge formed near the interface. As charge carriers diffuse, an electric field forms and opposes the space charge. The process stops when equilibrium between the space charge and electric field is reached. A potential gradient formed around the interface of the p and n-type semiconductors at equilibrium permits current to travel in only one direction. This basic diode, known as a p-n junction, is illustrated in

Figure 1.1 and enables many electronic devices such as integrated circuits, transistors, and photovoltaics. In organic photovoltaics, the p-type and n-type semiconductors serve as the electron donor and acceptor respectively. An exciton formed in either material diffuses to the donor/acceptor interface, and the energetic offset between the two materials drives dissociation into free charge carriers that are swept to the outer electrodes by the potential gradient. Since the

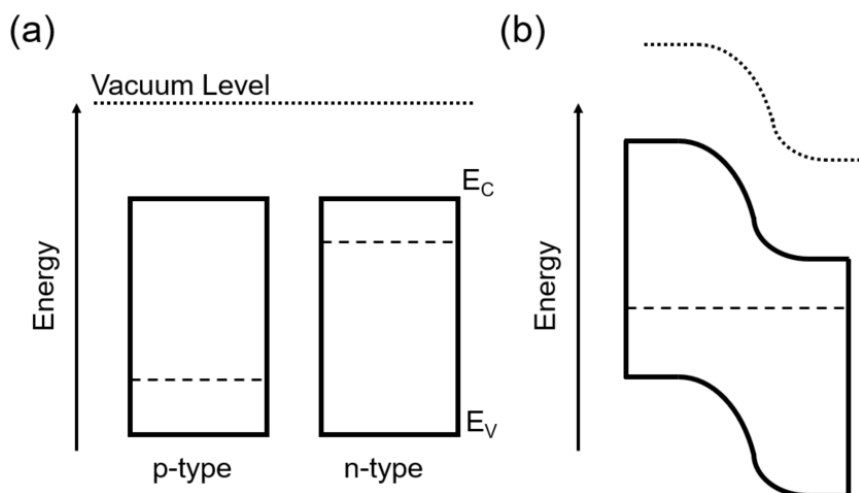


**Figure 1.1. Formation of a p-n junction.** (a) A p-type and n-type semiconductor with work functions indicated by the dashed lines. The conduction and valence bands ( $E_C$  and  $E_V$  respectively) are indicated for the n-type material. (b) The newly formed p-n junction from the joined semiconductors in panel (a) at equilibrium.

electron and hole dissociate to the acceptor and donor respectively, these materials are required to exhibit substantial electron or hole mobilities to enable efficient charge extraction at the outer electrodes.

### 1.1.2 Molecular bonding

Organic semiconductors are materials that consist of both carbon and hydrogen and exhibit electrical properties that make them potentially suitable for a range of semiconductor applications.

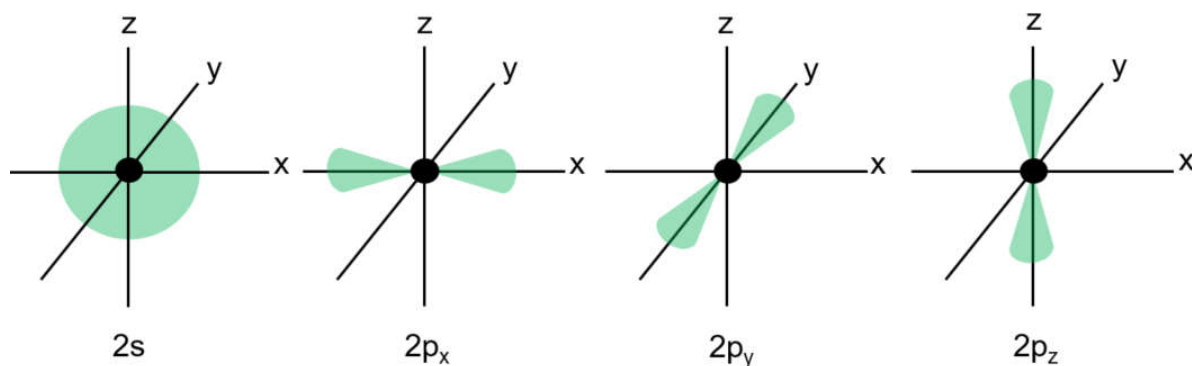


**Figure 1.2. Atomic orbitals.** Atomic 2s and 2p orbitals (green) are shown oriented around an atom (black). The 1s orbital was omitted for clarity because it exhibits the same shape as the 2s orbital.

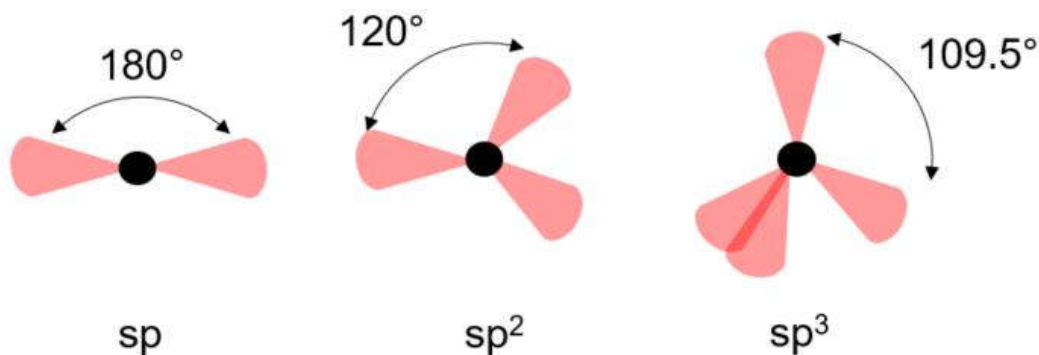


**Figure 1.3. Carbon hybridization.** Hybrid  $sp$ ,  $sp^2$ , and  $sp^3$  orbitals (red) shown around carbon atoms (black).

The arrangement of electrons in various orbitals is known as the configuration, where carbon exhibits a configuration of  $1s^2 2s^2 2p^2$ . Expanding this to describe individual 2p orbitals, ground state carbon has a configuration of  $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$ . 1s and 2s orbitals are spherically shaped charge distributions while the 2p orbitals are figure-eight shaped lobes oriented  $90^\circ$  from each other on either the X, Y, or Z axes in cartesian space around the nucleus. These atomic orbitals are shown in Figure 1.2. The electrons in the 1s and 2s orbitals are known as the core electrons while those in the 2p orbitals are valence electrons. Because the 2p orbitals each contain at most one electron but can hold up to two, electrons can be shared with non-filled orbitals from other atoms,

resulting in covalent bonds. In the ground state, carbon can make two covalent bonds consisting of shared electrons in the 2p orbitals.

Interatomic forces involved in bonding can compensate for the energetic differences between the carbon 2s and 2p orbitals, resulting in hybrid orbitals (Figure 1.3). The exact hybridization depends on how the 2s and 2p orbitals mix. The mixing of the 2s and one 2p orbital results in two sp hybrid orbitals oriented 180° from each other. When 2s and two 2p orbitals mix, three sp<sup>2</sup> orbitals form in a triangular configuration oriented 120° apart. Finally, when the 2s orbital mixes with all three 2p orbitals, four sp<sup>3</sup> orbitals separated in a tetrahedral configuration 109.5° apart are formed.

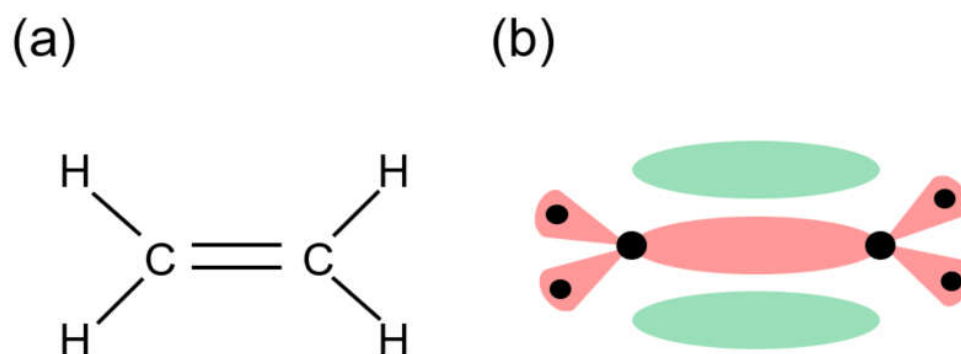


**Figure 1.4. Ethene structure and bonding.** (a) Chemical structure for ethene (C<sub>2</sub>H<sub>4</sub>). (b) Bonding configuration for ethene. The  $\sigma$  bonds (red) are formed from the overlapping sp<sup>2</sup> hybrid orbitals while the  $\pi$  bond (green) is formed from the overlapping non-hybridized 2p<sub>z</sub> orbitals.

The number of bonds a carbon atom can form is determined by the number of hybrid and remaining 2p orbitals. If two 2p or hybrid atomic orbitals on the same axis between two carbon atoms are filled, the resulting molecular orbital is known as a  $\sigma$  orbital, while two filled atomic orbitals on parallel axes make a molecular  $\pi$  orbital. These molecular orbitals are respectively associated with  $\sigma$  and  $\pi$  covalent bonds. As an example, in ethene (C<sub>2</sub>H<sub>4</sub>), two sp<sup>2</sup> hybridized carbon atoms are each bonded to the other carbon and two hydrogens. Two sp<sup>2</sup> orbitals in each

carbon are shared with the other carbon and two hydrogens in  $\sigma$  bonds, and the remaining non-hybridized  $2p_z$  orbitals are shared between the carbons in  $\pi$  bonds. An illustration of the carbon bonds in ethene is shown in Figure 1.4. In more complex molecules with alternating single and double bonds, also known as conjugation, electrons in  $\pi$  orbitals can become delocalized, allowing for intramolecular and intermolecular charge transfer.

### 1.1.3 Electronic states and transitions

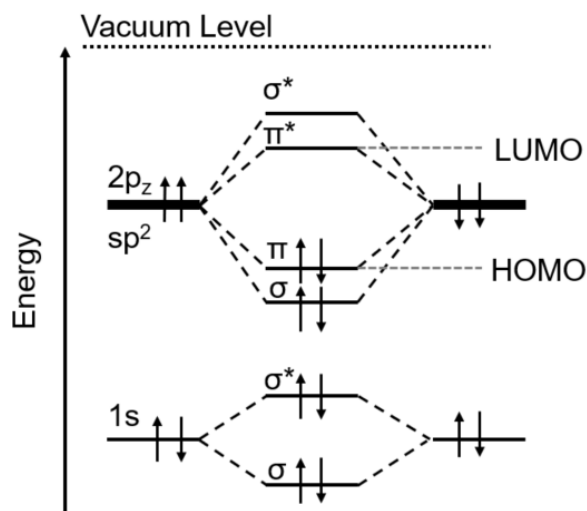


**Figure 1.5. Ethene energy levels.** Simplified energy schematic illustrating the formation of the HOMO and LUMO from orbital splitting between carbon atoms in ethene, where the bonding  $\pi$  orbital is the HOMO and the antibonding  $\pi^*$  orbital is the LUMO.

Atomic orbitals between bonding atoms induce energy states based on the amount of charge overlap between the respective orbitals and the Pauli exclusion principle, which states that no two identical fermions such as electrons can occupy the same quantum state. Turning once again to ethene, the  $\sigma$  molecular orbitals from the  $sp^2$  hybrid atomic orbitals occur along the internuclear axis and exhibit high charge overlap. Because of the Pauli exclusion principle, the  $\sigma$  orbitals are separated into strongly bonding  $\sigma$  and antibonding  $\sigma^*$  orbitals, where the antibonding orbital exhibits a higher energy state than the bonding orbital (Figure 1.5). The electrons will then

fill the lower energy bonding orbital and leave the antibonding orbital empty, inducing an attraction between the two nuclei. Since the  $2p_z$  atomic orbitals interact outside the internuclear axis, there is comparably little charge overlap. While the  $\pi$  molecular orbital is split into bonding and antibonding  $\pi$  and  $\pi^*$  orbitals analogous to the  $\sigma$  orbitals, the amount of energetic separation in this case is lower. Ultraviolet (UV) light is typically required to induce a  $\sigma \rightarrow \sigma^*$  transition while  $\pi \rightarrow \pi^*$  transitions can usually be induced with visible or infrared light. The  $\pi$  orbital also contributes little attractive force due to the overlap in electron density taking place far away from the nuclei. Because of the lower energetic separation between the  $\pi$  and  $\pi^*$  orbitals, the bonding  $\pi$  orbital is the highest occupied molecular orbital (HOMO), while the lowest orbital with higher energy states, the antibonding  $\pi^*$  orbital, constitutes the lowest unoccupied molecular orbital (LUMO). These are also known as the frontier orbitals and serve as the organic or molecular analogs to the valence and conduction bands respectively.

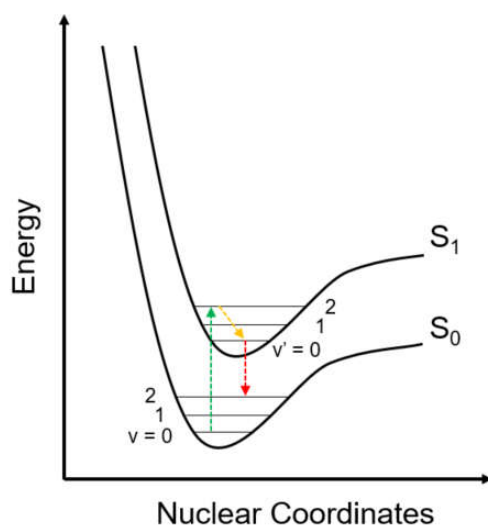


**Figure 1.6. Energetic state transitions.** Potential energy as a function of nuclear coordinates showing the  $S_0$  and  $S_1$  states along with their vibronic states ( $v$  and  $v'$  respectively). Also shown are an example excitation (green dashed arrow) from  $S_0$  to  $S_1$ , thermalization (orange) to the lowest vibronic state in  $S_1$ , and recombination (red) to  $S_0$  resulting in photon or phonon emission.

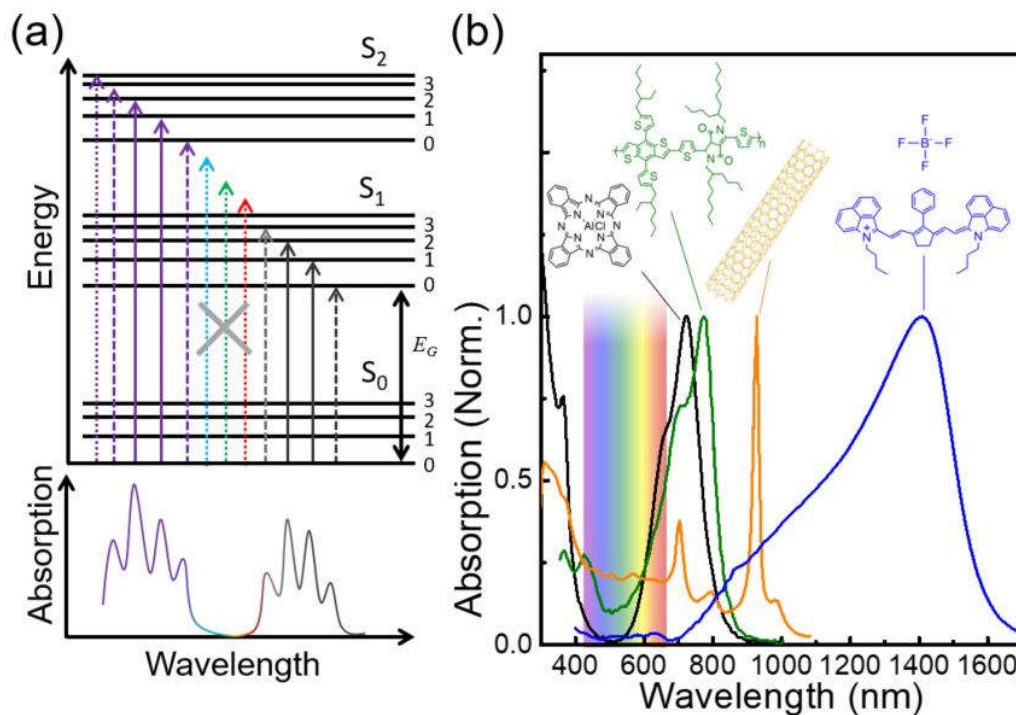


**Figure 1.7. Selective optical absorption.** (a) An energy schematic for an excitonic material. The overlap of vibrational modes determines the intensity of absorption, which may be weak (dotted arrows), moderate (dashed arrows), or strong (solid arrows). The gap between excited molecular orbitals creates a discontinuity in the density of states, yielding a band of transmitted light. (b) Absorption profiles of NIR-selective harvesting films including: small molecule, chloroaluminum phthalocyanine (black), polymer, PBDTT-DPP (green), nanotube, a (9,1) carbon nanotube (orange), and organic salt cation (1-Butyl-2-(2-3-2-(1-butyl-1H-benzo[cd]indol-2-ylidene)-ethylidene-2-phenylcyclopent-1-enyl-vinyl)-benzo[cd]indolium) paired with  $\text{BF}_4$  (anion) (blue).

The ground ( $S_0$ ) and excited ( $S_I$ ) states for a given molecule are each separated into discrete vibronic states, labeled as  $v$  and  $v' = 0, 1, 2 \dots n$  respectively where  $n$  is the total number of vibronic states available to be occupied by electrons. According to the Franck-Condon principle, electron excitation occurs over a time scale that is practically instantaneous compared to the response of atomic nuclei. This therefore results in a vertical transition to a higher excited state. The electron then relaxes via thermalization to the lowest available vibronic state ( $v' = 0$ ) in  $S_I$ , which may also result in a transition in the nuclear coordinates or shift in the equilibrium position of the nuclei, before recombining to  $S_0$ . Recombination can result in the emission of either a photon or phonon

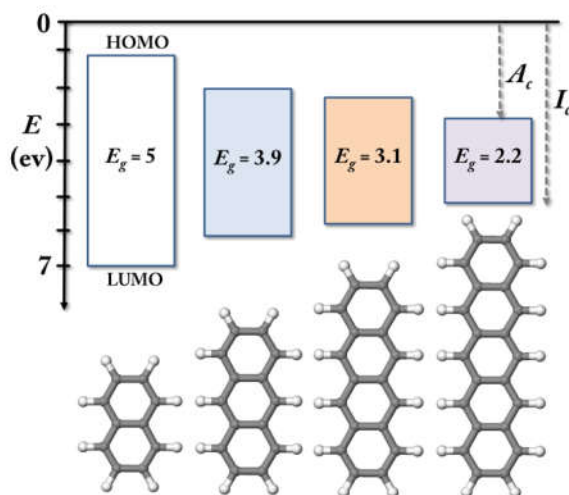


**Figure 1.8. Bandgaps for acene molecules.** Bandgap is adjusted as conjugation is increased from naphthalene (left) to pentacene (right). Electron affinity ( $A_c$ ) and ionization potential ( $I_c$ ) are also highlighted. Figure reproduced with permission from Ref. 6.

(heat) with energy equal to that lost by the electron between the  $S_1$  and  $S_0$  states. Photon and phonon emission are also known as radiative and non-radiative decay respectively. The excitation, thermalization, and recombination processes are illustrated in Figure 1.6.

The electronic transitions discussed above also describe the optical absorption characteristics of organic and excitonic semiconductors as shown in Figure 1.7. The energetic difference between  $S_0$  and  $S_1$  is referred to as  $E_G$ , where photons with energy  $> E_G$  are absorbed, and the gaps between excited states such as  $S_1$  and  $S_2$  can result in bands of optical transmission between isolated absorption peaks (Figure 1.7a). This contrasts with inorganic semiconductors that exhibit continuous densities of states (DOS) above  $E_G$  resulting in continuous absorption at higher photon energies. This unique property of organic semiconductors can be exploited to allow visible light transmission and UV/NIR-selective absorption by controlling the molecular structure (Figure 1.7b). By modifying  $E_G$  and the discontinuity of states it is possible to tune the solar harvesting outside of the visible band and into the NIR. The bandgap can be modified by controlling  $\pi$ - $\pi$  conjugation and designing push pull molecules. Acene molecules offer a simple application of  $\pi$ -

$\pi$  conjugation, where adding conjugated benzene rings to naphthalene reduces the bandgap, shown in Figure 1.8. Push pull molecules are designed with the addition of alternating electron donor and acceptor units. Both design techniques achieve lower bandgaps by inducing splitting of the HOMO and LUMO, resulting in a shallower HOMO and deeper LUMO.

### 1.1.4 Excitons

As discussed above, a newly excited electron remains coulombically bound to a hole in the valence band or HOMO, and the neutral electron-hole pair is known as an exciton. An exciton exhibits a binding energy of:

$$E_B = \frac{\hbar^2}{2m_r r_B^2} \quad (1.1)$$

where  $\hbar$  is the reduced Planck constant ( $\hbar = h/2\pi$ ),  $m_r$  is the reduced effective exciton mass, and  $r_B$  is the exciton Bohr radius, given as:

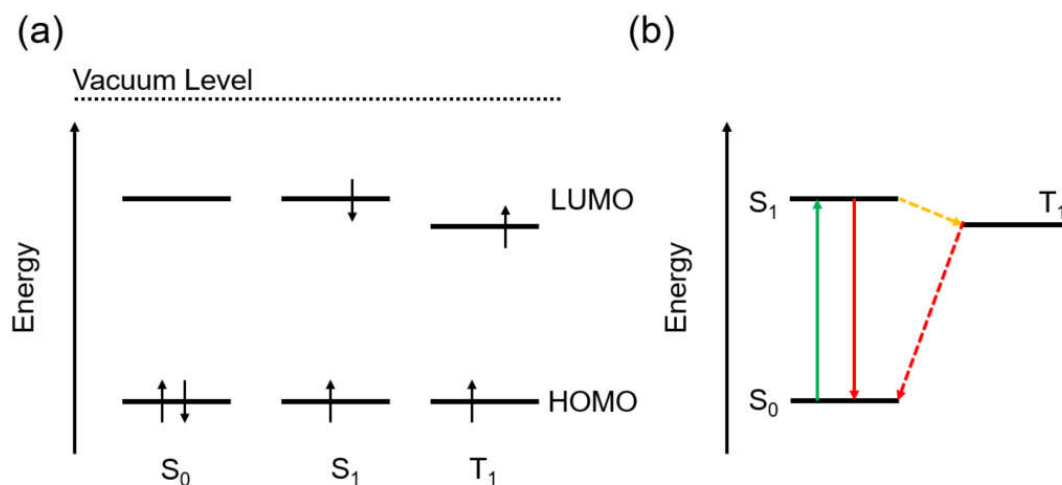


**Figure 1.9. Singlet and triplet excitons.** (a) Energy schematic illustrating the spins of electrons in the ground state ( $S_0$ ), singlet excited state ( $S_1$ ), and triplet excited state ( $T_1$ ). (b) Simplified Jablonski diagram illustrating singlet and triplet excitation (green solid arrow) and recombination (red arrows). Fluorescence (recombination from  $S_1$ ) is indicated by the solid red arrow. Intersystem crossing to  $T_1$  to form a triplet is shown by the orange dashed arrow while phosphorescence (recombination from  $T_1$ ) is shown by the red dashed arrow.

$$r_B = \frac{\hbar^2 \epsilon}{m_r q^2} \quad (1.2)$$

where  $q$  is the elementary charge and  $\epsilon$  is the permittivity which itself is defined as  $\epsilon = \epsilon_r \epsilon_0$ , where  $\epsilon_r$  is the dielectric constant and  $\epsilon_0$  is the permittivity of free space. The binding energy is inversely proportional to the Bohr radius and dielectric constant, meaning that excitons formed at high electron-hole separations will have lower binding energy and dissociate more readily. Because of this, excited states formed within inorganic semiconductors such as Si ( $\epsilon_r = 11.7$ ,  $E_B = 14.7$  meV) can be dissociated from excitations at room temperature (25.7 meV) directly into free carriers, while those formed in organic semiconductors ( $\epsilon_r = 2-4$ ,  $E_B = 0.1-1$  eV) require additional energetic driving forces to dissociate.

Excitons are classified according to their Bohr radii as Frenkel, charge transfer, or Wannier-Mott excitons. Wannier-Mott excitons are typically formed in inorganic semiconductors at low temperature and are characterized by a Bohr radius that is larger than the lattice constant of the material. Frenkel excitons are localized to a single molecule and formed in organic semiconductors. Charge transfer excitons are an intermediate case between Frenkel and Wannier-Mott excitons and occur when the electron and hole occupy adjacent molecules in certain events such as dissociation in organic photovoltaics, discussed later.

In addition to Bohr radii, excitons are classified according to electron spin states. The excited electron in the antibonding orbital, while bound to a hole, also forms a two-particle system with the remaining electron from the bonding orbital. These two electrons have opposite spins,  $S = \frac{1}{2}$  and  $-\frac{1}{2}$ , which sum to 0. This results in a multiplicity  $2S + 1$  equal to 1 and the exciton is therefore referred to as a singlet. By the same concept, two electrons with identical spins sum to 1

and result in a multiplicity of 3. The exciton formed in this case is then known as a triplet. Both exciton types are illustrated in Figure 1.9a.

Transitions such as  $S_0 \rightarrow S_1$  are spin-allowed since they do not involve changes in momentum (otherwise known as spin flips), however singlet to triplet transitions such as  $S_1 \rightarrow T_1$  are spin-forbidden because they violate the conservation of momentum. These transitions become weakly allowable through spin-orbit coupling, where the change in spin angular momentum is compensated by an opposite change in orbital angular momentum, allowing the total angular momentum to be conserved. To differentiate photoemission from singlet and triplet recombination, photons emitted from  $S_1 \rightarrow S_0$  transitions are known as fluorescence while those emitted from  $T_1 \rightarrow S_0$  transitions are referred to as phosphorescence. Because phosphorescence is spin-forbidden, it occurs on timescales (milliseconds) orders of magnitude longer than fluorescence (nanoseconds). Singlet and triplet transitions are illustrated in Figure 1.9b.

### 1.1.5 Exciton diffusion

Excitons migrate between organic molecules via hopping or coherent mechanisms. One common nonradiative hopping process that supports singlet exciton diffusion is known as Förster resonant energy transfer (FRET) where an exciton diffuses through a semiconductor via dipole-dipole coupling until the exciton either dissociates at an energetic interface or recombines. In this case, the energy of the excited electron in a donor molecule is transferred to an electron in the HOMO of an acceptor molecule, promoting it to the LUMO (Figure 1.10a). The exciton transfer rate between donor and acceptor molecules is given by the Förster expression:<sup>21</sup>

$$k_F = \frac{1}{\tau} \left( \frac{R_0}{d} \right)^6 \quad (1.3)$$

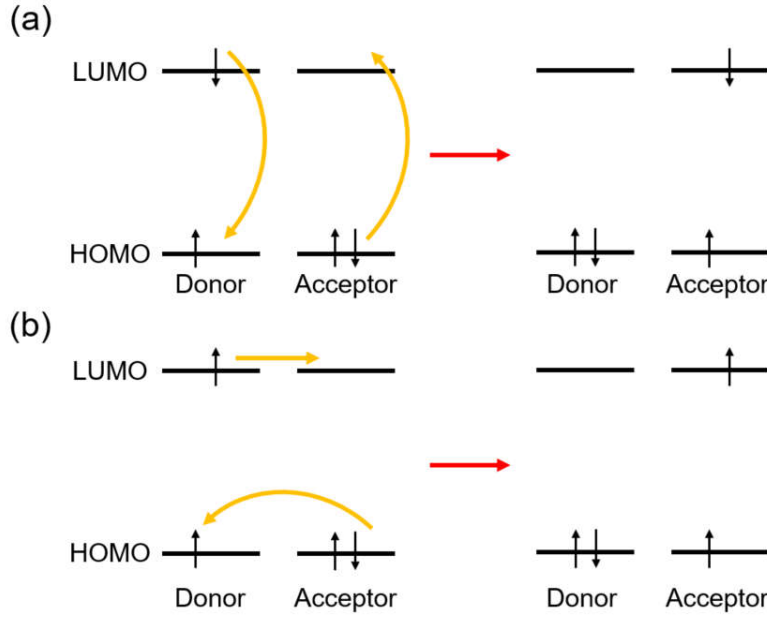


**Figure 1.10. Förster and Dexter transfer.** Schematics of Förster (a) and Dexter (b) transfer mechanisms shown for singlet and triplet excitons respectively.

where  $d$  is the distance between the two nearest neighbor molecules,  $R_0$  is the Förster radius (the distance at which the probability of exciton transfer is 50%), and  $\tau$  is the exciton lifetime. The Förster radius  $R_0$  can be expressed in terms of experimentally measurable spectroscopic parameters as:<sup>22</sup>

$$R_0^6 = \left( \frac{9\Phi_F}{128\pi^5 n^4} \right) \kappa^2 \int \lambda^{-4} F_D(\lambda) \sigma_A(\lambda) d\lambda \quad (1.4)$$

where  $\Phi_F$  is the fluorescence quantum yield,  $n$  is the index of refraction of the donor material,  $\kappa$  is the dipole orientation factor (approximately  $0.845\sqrt{0.66}$  for amorphous films),  $\lambda$  is the optical wavelength,  $F_D$  is the fluorescence spectrum of the donor molecule, and  $\sigma_A$  is the absorption cross section of the acceptor molecule. The exciton diffusion length (distance traveled by an exciton before recombination) is then given in terms of FRET parameters as:<sup>23</sup>

$$EDL = \sqrt{\frac{\kappa^2 \Phi_F}{8\pi n^4} \left( \frac{\sigma}{d^4} \right)} = \frac{1}{\sqrt{6}} \left( \frac{R_0^3}{d^2} \right) \quad (1.5)$$

The *EDL* is directly proportional to the Förster radius and inversely proportional to the intermolecular spacing. A high *EDL* can then result from either dense molecular packing or an optimized overlap integral between  $F_D$  and  $\sigma_A$  (Equation 1.4). Large molecules with low packing densities can therefore still exhibit high *EDLs* if they also exhibit significant emission and absorption overlap.

In the case of triplet excitons, diffusion is typically described by Dexter transfer. Triplet transfer is not an allowed dipole-dipole transition due to the requirement of a spin-flip (this can be seen experimentally in the very low triplet absorption cross sections). Dexter transfer is more akin to the charge transfer of electrons, where one electron moves from the donor LUMO to acceptor LUMO while another electron moves from the acceptor HOMO to the donor HOMO (Figure 1.10b). This transfer rate is dictated by the degree of wavefunction or orbital overlap between the transferring molecules. While singlet diffusion is also possible via Dexter transfer, FRET is usually the more favored mechanism due to a faster transfer rate. The rate of Dexter transfer is expressed as:<sup>24</sup>

$$k_D = \frac{2\pi}{\hbar} \frac{K}{d^2} \sigma_D e^{-\frac{2d}{\chi}} \quad (1.6)$$

where  $\sigma_D$  is the normalized overlap of the donor and acceptor emission and absorption spectra,  $K$  is a normalization constant, and  $\chi$  is the effective orbital radius of the final and initial electronic states. The *EDL* given in Equation 1.5 can be expressed in terms of Dexter parameters as:<sup>23</sup>

$$EDL = \sqrt{\frac{\tau K \sigma_D}{3\hbar}} \exp\left(-\frac{d}{\chi}\right) \quad (1.7)$$

The *EDL* in the context of Dexter transfer is heavily dependent on the distance to the nearest neighboring molecule ( $d$ ), where a greater separation yields a lower diffusion length. This

is due to the overlap of intermolecular orbitals acting as energetic bridges between molecules. The exciton relaxes nonradiatively (energy is lost as heat) as it diffuses intermolecularly to available vibronic states. If molecules are separated at a great distance, this orbital overlap is reduced, yielding slower rates for diffusion before recombination.

Another diffusion mechanism, known as "trivial transfer", is independent of intermolecular distance as it involves the exciton recombining radiatively to emit a photon. The photon can then be absorbed by a neighboring molecule, creating a new exciton. The *EDL* for trivial transfer is given as:<sup>25</sup>

$$EDL = \sqrt{\left(\frac{1}{6\alpha^2}\right)\left(\frac{\Phi}{1-\Phi}\right)} \quad (1.8)$$

where  $\Phi$  is the luminescence quantum yield of the donor and  $\alpha$  is the absorption coefficient of the acceptor. Because trivial transfer relies completely on optical absorption and emission characteristics, high quantum yields approaching unity allow for *EDLs* approaching infinity.

## 1.2 Organic and excitonic photovoltaics

### 1.2.1 Working principles

A conventional OPV architecture consists of the anode, normally ITO, followed by the donor, acceptor, and the cathode. This donor-acceptor bilayer photoactive architecture is commonly referred to as a planar heterojunction (PHJ). The order of photoactive layers can also be inverted such that the first electrode serves as the cathode to suit the fabrication requirements of the device. Hole and electron transport layers which often sandwich the donor and acceptor layers each consist of a wide band gap material with energy levels aligned so that only holes or electrons are favored to traverse them while excitons or oppositely charged particles are blocked.

The top transport layer (deposited directly before the top electrode) also serves as a buffer layer and protects the underlying layers during the deposition of the top electrode and throughout the lifetime of the device. These material properties along with layer thicknesses have a dramatic effect on the power conversion efficiency (*PCE*) through the balance of maximizing optical absorption and excitonic losses.

The *PCE* of a given device is the ratio of generated power ( $P_{Gen}$ ) to incident power ( $P_{in}$ ), and is extracted from the current per unit area ( $J$ ) in response to applied voltage ( $V$ ). The *PCE* is calculated from the short circuit current density ( $J_{sc}$ , the y-intercept of a  $J$ - $V$  curve), open circuit voltage ( $V_{oc}$ , the x-intercept of a  $J$ - $V$  curve), the fill factor ( $FF$ , the ratio between the maximum power point of a  $J$ - $V$  curve and the product of  $J_{sc}$  and  $V_{oc}$ ), and  $P_{in}$  as

$$PCE = \frac{P_{Gen}}{P_{in}} = \frac{J_{sc}V_{oc}FF}{P_{in}} \quad (1.9)$$

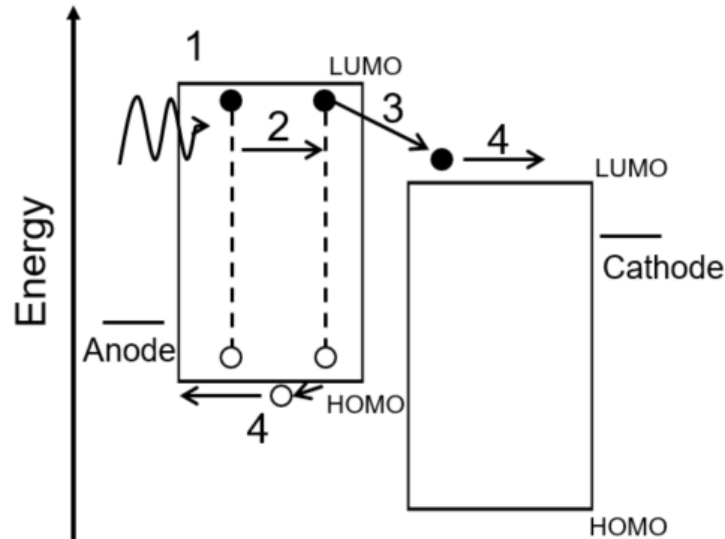


**Figure 1.11. Photocurrent generation.** Illustration of the conversion of light into free charge carriers in a planar heterojunction, broken down into critical steps: (1) photon absorption, (2) exciton diffusion, (3) charge transfer, and (4) carrier collection.

Another key metric used to understand photocurrent generation is the external quantum efficiency (*EQE*), defined by the ratio of extracted electrons to incident photons. Integration of the *EQE* at each wavelength in the spectrum yields  $J_{sc}$ :

$$J_{sc} = q \int (EQE * AM1.5) d\lambda \quad (1.10)$$

where AM1.5 is the solar photon flux. This integration offers an important consistency check for the measured  $J_{sc}$  and connects the internal mechanism for the quantum efficiency of generating charge with measurable electrical properties. *EQE* is determined over a process of four steps. In the first step, a photon is absorbed by either the donor or acceptor material, exciting an electron from the HOMO to the LUMO forming an exciton. In the second step the exciton diffuses through the semiconductor until it either recombines or reaches the interface between the donor and acceptor materials. The exciton is energetically favored to dissociate at this interface in the third step due to the offset energy levels of the donor and acceptor materials. From the donor (acceptor) material at this interface, the electron (hole) hops to the LUMO (HOMO) of the acceptor (donor). In the final step, the newly separated electron and hole are driven toward the outer electrodes by the built-in potential gradient from the p-n junction discussed earlier and are collected to produce current. These steps are illustrated in Figure 1.11. The *EQE* is summarized by the component efficiencies of absorption ( $\eta_A$ ), exciton diffusion ( $\eta_{ED}$ ), charge transfer ( $\eta_{CT}$ ), and carrier collection ( $\eta_{CC}$ ) as  $EQE = \eta_A \eta_{ED} \eta_{CT} \eta_{CC}$ . Since organic materials tend to exhibit exciton diffusion lengths (*EDLs*) of 10-20 nm, the thicknesses of photoactive layers are approximately limited to this range. The internal quantum efficiency (*IQE*), the ratio of extracted electrons to absorbed photons, is related to the *EQE* as  $IQE = EQE/\eta_A$ . The *IQE* describes the efficiency of converting a generated exciton into collected charge carriers, and is important for analyzing various charge recombination mechanisms.

### 1.2.2 Early small molecule OPV demonstrations

Although there has been significant work in OPVs containing both small molecule and polymer-based photoactive materials, small molecules are especially enticing because they can be designed to enable both the solution deposition and thermal vapor deposition of thin films. This high level of flexibility in device fabrication serves as the primary motivation for the use of small molecules in the TPVs developed in this work. In this section, we briefly review relevant milestones in the development of small molecule-based OPVs that are applied toward TPV development in later chapters.

The first efficient small molecule OPVs were fabricated in 1978 by solution depositing merocyanine in an electrode/dye/electrode sandwich architecture, allowing for  $PCEs > 1\%$ .<sup>26</sup> Although these devices exhibited high  $V_{oc}s$  of around 1.2 V,  $EQEs$  were greatly limited because exciton dissociation (charge transfer efficiency) relied completely on thermal excitations and the built-in potential. This  $EQE$  limitation was addressed with the introduction of the PHJ, first demonstrated in 1986 utilizing copper phthalocyanine (CuPc) as the donor and 3,4,9,10 perylenetetracarboxylic bisbenzimidazole (PTCBI) as the acceptor allowing for efficient exciton dissociation due to a LUMO offset between the donor and acceptor  $> E_B$ .<sup>27</sup>  $EQE$  was further improved using the same photoactive materials in 2000 with the incorporation of the bathocuproine cathode side buffer layer, a wide bandgap n-type semiconductor which conducts electrons but blocks excitons from recombining at the cathode.<sup>28</sup>

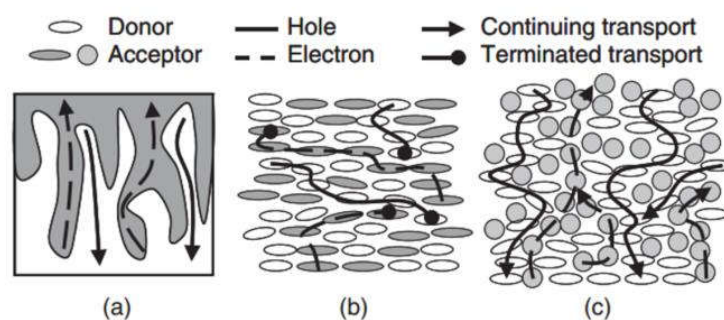


**Figure 1.12. Bulk heterojunction optimization.** Morphology scenarios for blended donor:acceptor layers in (a) the ideal case, (b) a non-optimized case, and (c) a practical optimized case. Figure reproduced from Ref. <sup>7</sup> with permission.

Bulk heterojunctions (BHJs), first demonstrated in a dye-sensitized solar cell in 1991,<sup>29</sup> offer another route toward high *EQEs* through enhanced exciton diffusion and dissociation efficiency, achieved with blended layers of donor and acceptor materials. Ideally, the blended layer consists of an interpenetrating donor-acceptor network with column widths equal to the *EDL* as shown in Figure 1.12a. This architecture was later adapted to small molecules, where CuPc was thermally co-deposited with fullerene ( $C_{60}$ ) to achieve *PCEs*  $> 3.5\%$ .<sup>30</sup> The key limitation of BHJs is the often higher series resistance (low *FF*) originating from non-ideal phase separations of the constituent materials. This results in isolated donor or acceptor domains and cul-de-sacs which prevent efficient charge carrier extraction as illustrated in Figure 1.12b. The mixed layer thickness, and therefore the absorption efficiency, must then be optimized to maximize the product of  $J_{sc}$  and *FF*. Slightly higher blended layer thicknesses are made viable through additional processing techniques such as annealing to achieve practically optimized blended layer morphologies (Figure 1.12c).<sup>31, 32</sup> A strategy to improve this structure was introduced in 2005 with the fabrication of the planar mixed heterojunction (PMHJ), a hybrid architecture that incorporates a blended donor:acceptor layer sandwiched between homogeneous layers of donor and acceptor materials.<sup>33</sup> This architecture combined high absorption efficiency from the thicker homogeneous layers with

the enhanced exciton diffusion efficiency from the optimized blended layer, resulting in CuPc:C<sub>60</sub> devices with *PCEs* > 5%.

Solution-processed small molecule *PCEs* exceeded 6% in 2012,<sup>34</sup> and 9% in 2014,<sup>35</sup> when broadly absorbing small molecule donors were blended with PCBM at optimized weight ratios in BHJ architectures. High *IQEs* near 100% at some wavelengths were achieved through 1) ordered stacking of the donor molecules and 2) PCBM percolation between donor stacks with feature sizes comparable to the exciton diffusion lengths. The current record single-junction small molecule *PCE* of 11.3% was achieved in 2016 with an analogous morphology.<sup>36</sup> This BHJ utilized a fluorinated donor molecule carefully designed to achieve highly ordered stacking along with a large interface gap (offset between donor HOMO and acceptor LUMO) and optimal miscibility with PCBM to simultaneously maximize  $J_{sc}$ ,  $V_{oc}$ , and  $FF$ .

The current record single-junction *PCE* of 13.1% was demonstrated in 2017 and utilized a newly synthesized polymer donor and small molecule acceptor in a BHJ architecture.<sup>37</sup> This fullerene-free device utilized a morphological and interfacial optimization strategy analogous to the record small molecule single-junction discussed above. A record multi-junction *PCE* of 13.8% was also demonstrated in 2017.<sup>38</sup> Because the voltages of individual sub-cells are added in series-connected multi-junctions, these architectures can eliminate some of the thermalization losses inherent to single-junction devices. This architecture utilized two complementary absorbing polymer and small molecule-based BHJ sub-cells to achieve a broad single device absorption spectrum between 300-900 nm.

In summary, the discontinuities in the densities of states within organic semiconductors yield isolated optical absorption peaks which do not occur for inorganic semiconductors. This characteristic can be exploited to design UV/NIR-selective materials that permit the transmission

of visible light, enabling highly transparent PVs. Because wavelength selective TPVs are fabricated with organic semiconductors, they face the same development challenges as OPVs, as well as unique challenges summarized in the next chapter.

## Chapter 2 – Transparent Photovoltaics

Solar energy offers a viable solution to our growing energy need. While adoption of conventional photovoltaics on rooftops and in solar farms has grown rapidly in the last decade, there is still plenty of opportunity for expansion. See-through solar technologies with partial light transmission developed over the past 30 years have initiated methods of integration not possible with conventional modules. The large-scale deployment necessary to offset global energy consumption could be further accelerated by developing fully invisible solar cells that selectively absorb ultraviolet and near-infrared light, allowing one to turn many of the surfaces of our built environment into solar harvesting arrays without impacting the function or aesthetics. In this chapter, we review recent advances in photovoltaics with varying degrees of visible light transparency. We discuss the figures of merit necessary to characterize transparent photovoltaics, and outline the requirements to enable their widespread adoption in buildings, windows, electronic device displays, and automobiles.

### 2.1 Motivation

Moving global energy consumption away from fossil fuels requires innovative and cost-effective renewable energy technologies. PVs can fulfill this need many times over if deployed over a large enough area. For example, a theoretical solar installation covering approximately 20% of Nevada could power the United States.<sup>39</sup> However, the current installed area of terrestrial PV technologies only provides approximately 1% of the worldwide energy demand.<sup>40, 41</sup> While the potential of theoretical large area PV installations in remote and sunny regions can meet this demand, maintenance and distribution costs as well as adverse environmental effects make this less practical.<sup>40</sup>

One approach to aid in this large-scale demand is through the development of building-integrated PVs (BIPVs) and building applied PVs (BAPVs) to generate electricity close to where it is utilized during peak demand, which can reduce electrical transmission losses, the need for storage capacity, and installation cost. BIPVs are integrated directly into facades or other areas of buildings as replacements for conventional building materials while BAPVs are modules retrofitted onto areas such as rooftops or awnings after initial construction. In addition to generating power, BIPVs and BAPVs can serve secondary purposes such as providing shade.<sup>42</sup> New BIPV technologies are being intimately integrated into the architectures of buildings around the world but have only modestly contributed to offset their energy consumption so far.<sup>43</sup> Considerably larger installation areas are required to achieve significant energy offset.

The total amount of rooftop area in the United States suitable for conventional PV installation is greater than 8 billion m<sup>2</sup>.<sup>44</sup> Assuming a module power efficiency of 16%, the total potential of rooftop mounted PVs is conservatively estimated as 1400 TWh per year (0.16TW), or nearly 40% of the total electricity generation of the United States. While this rooftop potential is significant, the additional surface area around buildings (siding, windows, etc.) is vastly underutilized and offers a tremendous opportunity to more than double the rooftop harvesting area<sup>45, 46</sup> and help achieve net zero energy consumption. Transparent photovoltaics (TPVs), which optimize both average visible transmission (*AVT*) and *PCE*, can tap this area without impacting underlying facades and windows.

## **2.2 Important figures of merit**

The three most important figures of merit in evaluating the applicability of TPVs are the *PCE*, *AVT*, and color rendering index (*CRI*). The recommended approach to reporting the *AVT*,

generally accepted by the window industry, is to weight the integration of the transmission spectrum against the photopic response of the human eye, as<sup>18, 47</sup>

$$AVT = \frac{\int T(\lambda)P(\lambda)AM1.5(\lambda)d\lambda}{\int P(\lambda)AM1.5(\lambda)d\lambda} \quad (2.1)$$

where  $\lambda$  is the wavelength,  $T$  is the transmission,  $P$  is the photopic response, and AM1.5 is the solar photon flux for window applications, or 1 for other applications.

For reference, the  $AVT$  for quartz glass is 92% and has ~4% reflection from the front and back surfaces. A typical clear double-paned insulated glass unit has  $AVT$  of near 80%.<sup>48</sup> With a low emissivity coating,  $AVT$ s are typically  $\leq 70\%$ . The  $AVT$  in residential windows can range from 15% for highly tinted glass up to 90% for common glass. In general, glass with  $AVT$  values above 60% look clear, and any value below 50% begins to look dark, colored, and/or reflective.<sup>49</sup> This gradual boundary also marks a transition in performance between demonstrated semitransparent and UV/NIR-selective TPV architectures.

The  $CRI$  describes quantitatively how accurately the color of a given object is rendered either from a light source or through a transparent medium with respect to an “ideal” illumination

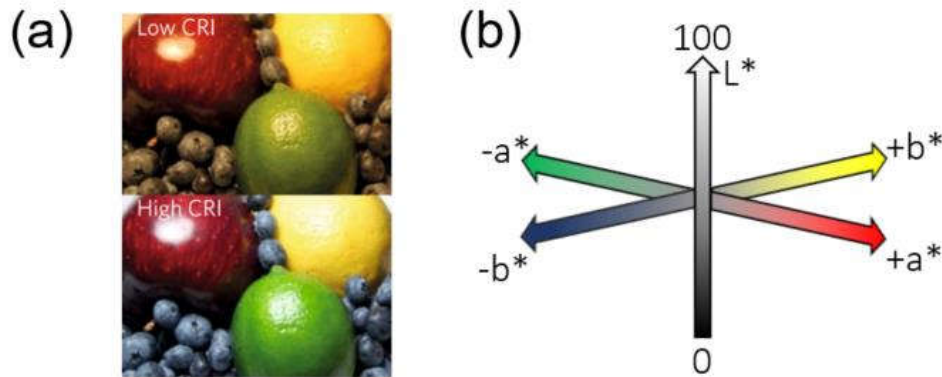


**Figure 2.1. Color rendering.** (a) Example of low (top) and high (bottom)  $CRI$ . Objects observed through a low  $CRI$  medium appear faded or improperly colored. (b) CIE Lab color space highlighting luminosity ( $L^*$ ), the converted chromaticity coordinates ( $a^*$  and  $b^*$ ), and how they determine color.

source (blackbody radiator at a certain color temperature, daylight illumination, AM1.5) and is commonly used in the lighting and window industries. A comparison of low and high *CRI* is shown in Figure 2.1a. An illumination source or transparent medium with a *CRI* of at least 70 is considered to be of good quality and >85 to be of the highest quality.<sup>18, 50</sup> For reference, a neutral or constant absorption profile through the visible spectrum will always yield a *CRI* of 100, regardless of the reference spectrum.

*CRI* is of critical importance to glass, window, and display manufacturers. These applications also necessitate reporting the chromaticity coordinates directly, typically as  $a^*$  and  $b^*$  within the CIELab color space (Figure 2.1b) as is common in the window industry. Reporting  $a^*$  and  $b^*$  for transmission and reflection gives additional information regarding the perceived color. High positive values of  $a^*$  and  $b^*$  are less common in modern window applications (yellow/red), whereas values near the origin (neutral/grey) and negative values of  $b^*$  (blue) are more typical if accompanied with high *AVT*. The lightness ( $L^*$ ) represents the human perception of contrast for given ( $a^*$ ,  $b^*$ ) coordinates, where a value of 0 is completely black and 100 is completely white. Additionally, the color difference ( $\Delta E^*$ ) between normal and off-angle reflection should be minimized to prevent color variations when viewing buildings from a distance with multiple viewing angles. Such color variation is particularly evident if the chromaticity coordinates at different angles lie on opposite sides of the origin (i.e. green to red for sign changes in  $a^*$  and blue to yellow for sign changes in  $b^*$ ). Instructions for quantitative calculations of the *CRI* and chromaticity coordinates are given elsewhere.<sup>51</sup>

*PCE* and *AVT* are often inversely related as discussed below for non-wavelength selective TPV technologies, however all TPVs have potential applications. Progressive development

warrants new compound figures of merit beyond *PCE* and *AVT* that allow for improvements to be referenced across various technologies. We propose a light utilization efficiency (*LUE*) metric as:

$$LUE = PCE \times AVT \quad (2.2)$$

This metric enables comparison between technologies against theoretical limits and also represents an overall system efficiency: for example, in a window or display application this would be the combination of generated power efficiency and overall lighting efficiency (i.e. transmitted light per incident lighting power). A device with a high *LUE* could be applied over a window to provide power without blocking natural light from entering the room to reduce the need for artificial lighting during daylight hours.<sup>52</sup> Similarly, such a device applied over an electronic display would offset energy consumption without requiring additional brightness from the display to compensate for absorbed visible light. This quantitative applicability comparison would provide greater insight into the importance of future demonstrations than *PCE* or *AVT* alone. We note that for particular applications there are often also key individual thresholds for *AVT*, *PCE*, and *CRI* that also motivate development of application-specific figures of merit that provide weighting or limits on all three metrics. For this reason, new figures of merit could be important moving forward, but should supplement and not replace independent reporting of each component metric. Ultimately the *LUE* adds to the list of important PV metrics that have emerged including, for example, the levelized cost of energy (*LCOE*) (\$/kW-hr) and specific power (W/gm).

### 2.3 Non-wavelength selective PVs

TPV technologies are grouped into variants that are either wavelength selective or non-wavelength selective in their absorption of visible light. Non-wavelength selective TPV technologies produce electricity from broad absorption of the solar spectrum (including visible

photons) and achieve some visible transmission by either segmenting opaque PV cells or using a sufficiently thin or low concentration photoactive material.

### 2.3.1 Spatially segmented PVs

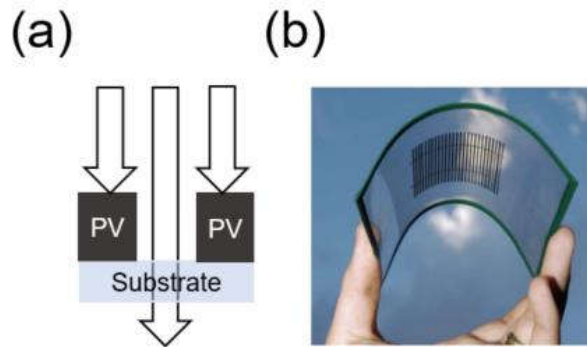


**Figure 2.2. Spatially segmented TPVs.** (a) Diagram of a spatially segmented PV and (b) an example module reproduced with permission from Ref. <sup>9</sup>. In a segmented architecture, opaque modules on a transparent substrate are spaced to permit partial transmission of all wavelengths of light (white arrows). Increasing the space between modules improves transmission at the cost of performance as this essentially reduces the active area of the combined module.

Spatial segmentation is the practice of dispersing opaque solar cells across a transparent substrate. This approach provides varied levels of neutral optical transmission through the spaces between the solar cells (Figure 2.2). Widening these spaces to increase transmission diminishes performance since this process reduces the photoactive area. While this method of achieving transparency has a low *PCE* limit at high *AVT*, it can be utilized with essentially any opaque PV material. Research on spatially segmented technologies has been focused on silicon<sup>53</sup> and copper indium gallium selenide (CIGS) (commercialized by Sharp, Solaria, Sphelar, and Sunpartner Technologies) and more recently perovskite-based<sup>54, 55</sup> materials (segmented on the microstructural level). Silicon-based segmented architectures offer simple module fabrication as Si is commonly available and readily machined. Perovskite-based architectures are usually tolerant to defects and pinholes but have yet to show high stability similar to Si.<sup>56</sup>

### 2.3.2 Non-wavelength-selective thin film PVs

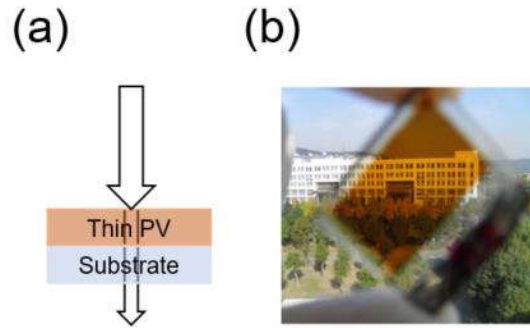


**Figure 2.3. Thin film colored TPVs.** (a) Diagram of a non-wavelength-selective thin film PV and (b) an example perovskite-based module reproduced with permission from Ref. <sup>14</sup>. In these architectures, the thickness of the optical absorbing film(s) is controlled to balance transmission and *PCE*, where increasing thickness improves *PCE* at the cost of partial transmission (narrow white arrow) and *CRI*.

Non-wavelength selective thin film PVs utilize visibly absorbing semiconductors that are thin enough<sup>57</sup> or have a large enough band gap<sup>58, 59</sup> to permit the transmission of some visible light (see Figure 2.3), and are sometimes referred to as ‘semitransparent’. Such thin film devices are currently being commercialized (e.g. by Onyx Solar and Polysolar). As is the case for spatial segmentation, broadband absorption always involves a direct trade-off between performance and visible transmission. Si,<sup>60</sup> CIGS,<sup>58</sup> metal oxide,<sup>59</sup> and perovskite-based<sup>61, 62</sup> architectures have been the focus of most inorganic, thin film TPV research. On average, these technologies feature *PCE*s between 0.1%<sup>59</sup> and 14%,<sup>62</sup> *AVT* up to 50%,<sup>59</sup> and exhibit strong color which can be an advantage for some applications. There have also been a variety of demonstrations for single junction OPVs including small molecule<sup>63, 64</sup> or polymer-based<sup>65, 66</sup> heterojunctions (commercialized by Heliateg), or dye sensitized solar cells (commercialized by Dyesol).<sup>67, 68</sup> These devices have achieved at least 0.5% *PCE*<sup>63</sup> with *AVT* between 25%<sup>65</sup> and 60%.<sup>67</sup> Non-wavelength selective multi-junction architectures have exceeded 5% *PCE*, but exhibit *AVT* below 40% due to the high incremental visible absorption produced by the individual junctions.<sup>69, 70</sup> The *CRI*s and demonstrated colors

can be greatly varied since organic materials commonly absorb various parts of the visible solar spectrum.<sup>71</sup>

### 2.3.3 Luminescent solar and scattering concentrators

Luminescent solar concentrators (LSCs) offer another promising approach to lowering the cost of photovoltaic systems and have been applicable in colorful (non-selective) devices, and more recently, in plain window glass (wavelength selective). An LSC consists of a substrate coated or embedded with an organic dye (or luminophore) that redirects incident light to the edges through photoluminescence (see Figure 2.4a and b, top).<sup>72</sup> Thin strips of conventional PVs mounted along the waveguide absorb the waveguided light and generate power with a *PCE* limit equivalent to non-selective TPVs when there is ideal light trapping.<sup>73</sup> Like other PV technologies, the *PCE* for LSCs and other concentrators is defined as the ratio of electrical power to the incident solar power on the module area, even though many studies only report the optical efficiency. These can be distinguished by the equation  $PCE = \eta_{Opt} \eta_{PV}^*$ , where  $\eta_{Opt}$  is the optical efficiency (the ratio of the photons transported out of the LSC edge to the incident photons on the active area) and  $\eta_{PV}^*$  is the

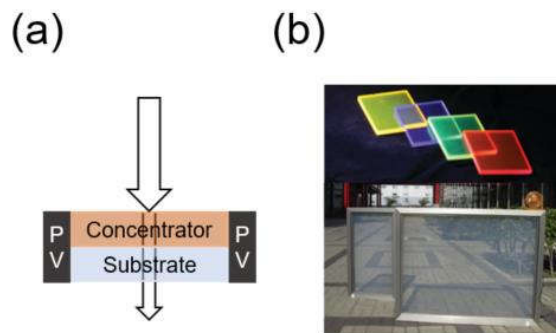


**Figure 2.4. Solar concentrators.** (a) Diagram of a non-wavelength-selective solar concentrator, (b) colored LSCs (top, reproduced with permission from Ref. <sup>8</sup>), and a scattering concentrator (bottom, reproduced with permission from Ref. <sup>19</sup>). LSCs and scattering concentrators collect light by absorbing, re-emitting, and waveguiding photons from a dye (LSCs), or by scattering incident photons (scattering concentrators) toward the edges of a substrate to be collected by edge-mounted PV strips.

*PCE* of the edge-mounted solar cell under monochromatic illumination from the luminescent emitter. Care should be taken to distinguish reports of the optical efficiency and the *PCE* as they are often different by an order of magnitude.<sup>73</sup> The optical efficiency is defined as  $\eta_{opt} = (1 - R_f) * \eta_{Abs} * \eta_{PL} * \eta_{Trap} * \eta_{RA}$ , where  $R_f$  is the front-face reflection,  $\eta_{Abs}$  is the absorption efficiency,  $\eta_{PL}$  is the luminescent efficiency,  $\eta_{Trap}$  is the waveguiding efficiency, and  $\eta_{RA}$  is the efficiency of suppressing reabsorption. Most organic-based LSCs exhibit colorful optical transmission due to the discrete visible absorption, but *PCEs* up to 7% have been reported over small LSC surface areas.<sup>74</sup> Newer quantum dot (QD)-based LSCs exhibit broader visible absorption and retain colorful transmission, but are often limited by the same performance-transmission trade-off as other inorganic thin-film technologies.<sup>75, 76</sup>

Scattering concentrators consist of light-scattering media deposited into or onto clear waveguiding substrates. Optical wavelengths shorter than the feature size are scattered, yielding a visibly hazy surface (see Figure 2.4b, bottom), with some of the scattered light waveguided to the edges of the substrate where it is harvested by thin PV cells.<sup>73, 74</sup> However, the main challenge for scattering concentrators is that optical losses are significant at area scales above a few inches due to multiple scattering events of waveguided photons that can result in significant losses via outcoupling from the device. While the intrinsic visible haziness limits adoption in many applications requiring an unobstructed view, these could become important in areas for higher privacy.

## 2.4 Wavelength selective TPVs

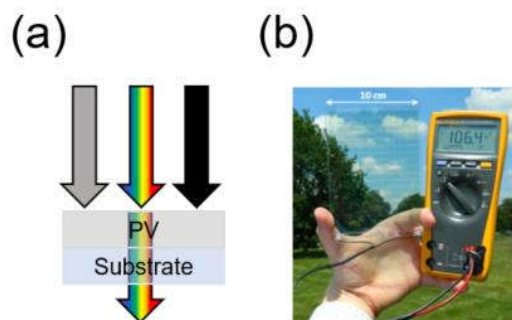


**Figure 2.5. Wavelength selective TPVs.** (a) Diagram of a wavelength-selective TPV and (b) a large-area, wavelength-selective TPV module. Wavelength-selective TPVs preferentially harvest UV (grey arrow) and NIR (black arrow) light while permitting the transmission of visible light (colored arrow).

Wavelength selective TPVs exploit the excitonic nature of nanostructured materials to achieve selective NIR/UV absorption as discussed in Chapter 1. This allows for the facile optimization of both *PCE* and *AVT* and enables solar deployment over virtually any surface without sacrificing aesthetics.

### 2.4.1 Selective thin film TPVs

Efficient NIR wavelength-selective thin film TPVs (Figure 2.5) were demonstrated in 2011 with organic small molecule planar heterojunctions consisting of chloroaluminum phthalocyanine (ClAlPc) as the donor and C<sub>60</sub> as the acceptor (Figure 2.6) sandwiched between two transparent conductive electrodes (ITO).<sup>11</sup> Through optimization of the optical interference from the top ITO thickness, a *PCE* of  $1.3 \pm 0.1\%$  and *AVT* of 65% were achieved, the highest combination achieved

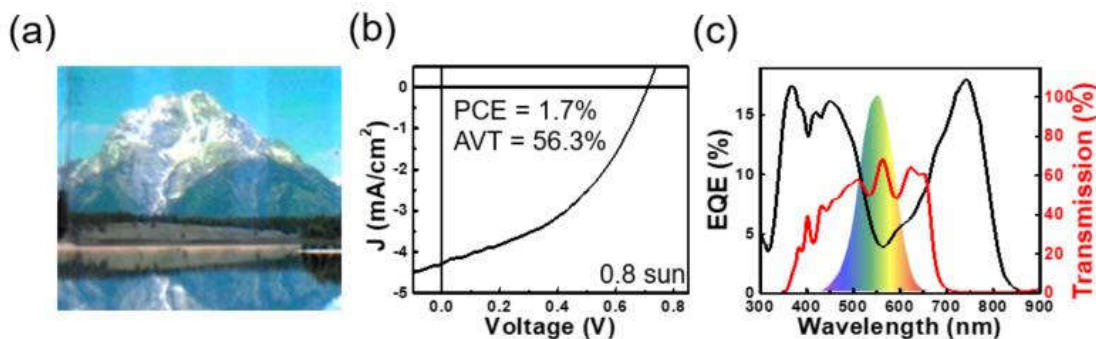


**Figure 2.6. Wavelength-selective small molecule TPVs.** (a) Photograph of the first wavelength-selective TPV device based on small molecules (12-cells, series-integrated mini-module) reproduced with permission from Ref. <sup>11</sup>, (b) the single cell  $J$ - $V$  characteristics, and (c) the  $EQE$  and optical transmission characteristics overlaid with the photopic response of the human eye.

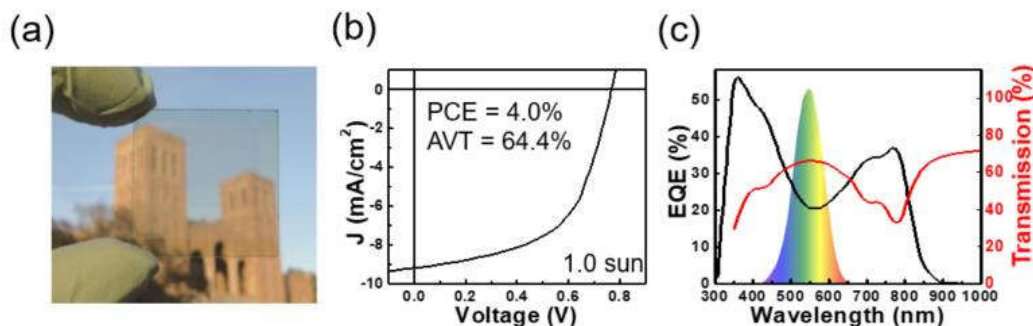


**Figure 2.7. Wavelength-selective polymer TPVs.** (a) A high efficiency single junction polymer-based wavelength-selective TPV reproduced with permission from Ref. <sup>13</sup>, with corresponding (b)  $J$ - $V$  and (c)  $EQE$  and transmission characteristics.

at the time. A  $PCE$  of  $1.7 \pm 0.1\%$  and  $AVT$  of 56% were obtained with the use of NIR-reflecting mirrors. High efficiency polymer-based selective TPVs were demonstrated in 2012 utilizing BHJ architectures of poly(2,6-bis(5-ethylhexylthienyl)benzo-[1,2-b;3,4-b]dithiophene-alt-5-dibutyl-octyl-3,6-bis(5-bromothiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4-dione) (PBDTT-DPP) and phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM).<sup>13</sup> The top electrode consisted of a combination of Ag nanowires and ITO nanoparticles that resulted in a  $PCE$  of 4% and an  $AVT$  of 64% (Figure 2.7). Wavelength selective TPVs fabricated with polymer donors and small molecule acceptors were recently demonstrated with  $PCE$ s of 7.7%<sup>77</sup> and 9.8%,<sup>78</sup> albeit with  $AVT$ s of only 26% and

32% respectively (as calculated according to Box 1). Most of the broad optical absorption exhibited by these architectures encompasses NIR wavelengths as reflected by their high NIR *EQE*. These demonstrations therefore demonstrate important molecular approaches for TPVs with lower bandgap photoactive materials, broad optical absorption, and high *EQE*.

These studies are important in not only demonstrating the feasibility of this wavelength-selective approach to TPVs, but also in highlighting the importance of photon management. Managing reflections throughout the spectrum becomes particularly important in TPVs, as reducing visible reflections and absorption are both equally key to maximizing transmission. Minimizing visible reflection requires optical interference optimization across the layers of the TPV. In contrast for NIR wavelengths, reducing frontside/contact NIR reflections and increasing backside NIR reflections can be utilized to enhance NIR photoconversion without impacting the *AVT*.

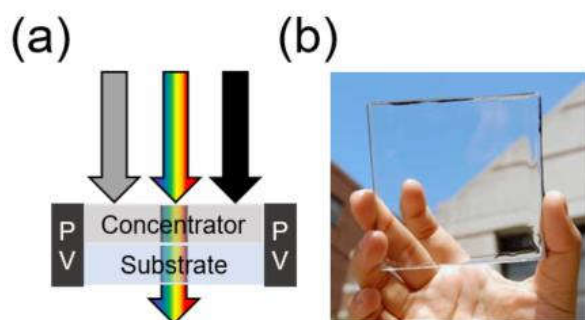


**Figure 2.8. Wavelength-selective LSCs.** (a) Diagram of a wavelength-selective LSC and (b) a wavelength-selective LSC module capable of preferentially harvesting UV and NIR light analogous to thin film wavelength-selective TPVs discussed above.

### 2.4.2 Wavelength-selective LSCs

Recently, a parallel approach to fabricate selective TPVs was demonstrated<sup>12, 79</sup> using an LSC with wavelength-selective luminophores (Figure 2.8) that could both absorb and emit outside of the visible band. This approach could simplify the manufacturing and scale-up for wavelength-selective TPVs, while also providing a route to very high transparency levels and low module costs. Wavelength selective LSCs may be designed to absorb UV and emit NIR light or absorb NIR and emit deeper NIR light. While NIR-absorbing LSCs achieve similarly high *AVT* and *CRI* to UV-absorbing LSCs, reabsorption becomes a challenge when scaling to sizes at or above square meters as the case of traditional LSCs.

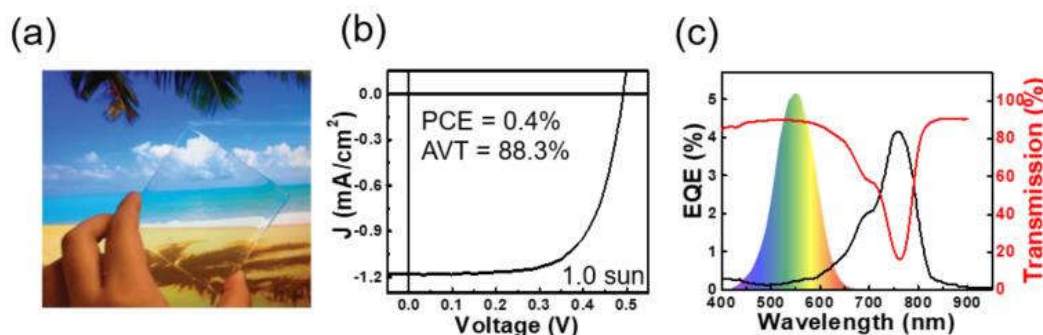


**Figure 2.9. NIR-selective LSCs.** (a) An efficient, wavelength-selective NIR-absorbing LSC reproduced with permission from Ref. <sup>12</sup> with (b)  $J$ - $V$  and (c)  $EQE$  and transmission characteristics.

The first wavelength-selective LSCs were fabricated with phosphorescent luminophores consisting of hexanuclear metal halide nanoclusters with selective harvesting in the UV and emission in the NIR. Using these materials,  $PCEs > 0.5\%$  were achieved yielding a high  $AVT (> 85\%)$  and  $CRI (> 95)$  approaching that of bare glass.<sup>79</sup> As a byproduct of the large spectral shift ( $\sim 400\text{nm}$ ), reabsorption losses in these LSCs were essentially eliminated. However, due to the lower fraction of UV photons in the AM1.5 spectrum, the maximum  $PCE$  of these devices is less than 7%.<sup>73</sup> Other demonstrations of UV-selective organic<sup>80</sup> and quantum dot<sup>81</sup> luminophores have

also been demonstrated, albeit with visible light emission that creates colorful glow. More recently, organic salt derivatives were demonstrated in NIR-selective absorbing and emitting LSCs that achieved  $PCEs > 0.4\%$  (Figure 2.9), high  $AVT$  of 88%, and  $CRI > 94$ .<sup>12</sup> Following a similar approach, silicon naphthalocyanine (SiNc) was utilized to fabricate LSCs that selectively harvest both UV and NIR light to achieve an *optical efficiency* of 1.5%.<sup>82</sup> As discussed below, most LSCs (including wavelength-selective LSCs) are limited predominately by reabsorption losses which need to be reduced before these technologies are scaled to the largest module sizes.

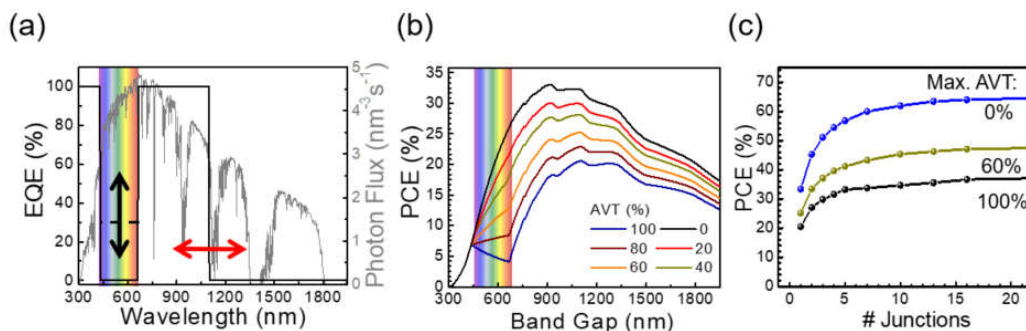


**Figure 2.10. Theoretical performance limits for single and multi-junction TPVs.** (a) Schematic showing the ideal  $EQE$  for a wavelength-selective device, adjusted as a function of wavelength (red arrow) around the visible spectrum with varying degrees (black arrow) of visible  $EQE$  (dashed line). Note that in the thermodynamic limit the  $EQE$  is assumed to be equal to the absorption efficiency. The AM1.5 photon flux spectrum (grey) indicates the large amount of NIR light available for wavelength-selective harvesting. (b)  $PCE$  plotted as a function of the absorber bandgap for various levels of visible light contribution to the  $EQE$  in a single junction. (c) Theoretical  $PCE$  limits at 1-sun intensity plotted as a function of the number of junctions in a multi-junction architecture at 0%, 60%, and 100%  $AVT$ .  $PCE$  values are calculated in Ref. <sup>18</sup>. A maximum of 3-4 junctions is typically explored for current record efficiency multi-junction devices.

## 2.5 Theoretical and practical performance limits

By selectively harvesting UV ( $< 435\text{nm}$ ) and NIR ( $> 670\text{nm}$ ) wavelengths (Figures 2.10a-b) the theoretical Shockley-Queisser (SQ)-limiting single junction  $PCE$  for a selective TPV with 100%  $AVT$  is 20.6%, compared to 33.1% for an opaque PV.<sup>18</sup> The optimal bandgap is redshifted from 1.36 eV (910 nm) to 1.12 eV (1100 nm) in going from opaque to visibly transparent cells due

to the balance in absorption and voltage given the transmission of visible light. This efficiency limit for selective TPVs stems from the large fraction of solar photon flux in the infrared. Indeed, silicon PVs generate more than half of their power from infrared photons. These thermodynamic efficiency limits are illustrated by the peaks of the 0% and 100% *AVT* curves in Figure 2.10b, where each line represents the efficiency limit with respect to bandgap for a PV with a given fraction of absorption from the visible portion of the solar spectrum. Increasing the *PCE* above the single-junction SQ limit is feasible through the use of multi-junction architectures, where losses from electron thermalization are reduced or eliminated (Figure 2.10c). The theoretical *PCE* limit for a realistic number of junctions (3-4) with 100% *AVT* is about 30%.<sup>18</sup> While this is comparable to the limit for single junction opaque architectures, it is approximately half the limit for opaque multi-junctions. Even when estimated practical limitations are considered (including resistive losses, charge recombination, diode non-idealities, parasitic electrode absorption, discussed in detail in Refs. <sup>18</sup> and <sup>83</sup>), single-junction and 3-junction TPV solar cells fabricated with UV/NIR-selective materials can achieve 13% *PCE* and 20% *PCE*, respectively, (assuming 10% loss in SQ

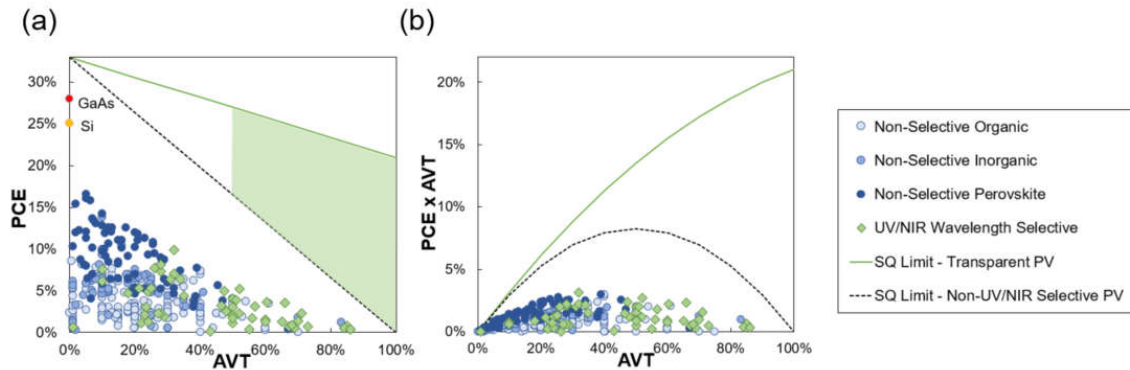


**Figure 2.11. Survey of TPVs.** (a) *PCE* versus *AVT* for wavelength-selective and non-wavelength-selective organic, inorganic, and perovskite TPV technologies. (b) Plot of the *LUE*, defined as the product of *PCE* and *AVT* in Equation 2.2, versus *AVT*. The green shaded region in (a) denotes the target *PCE* and *AVT* only achievable with UV and NIR TPV solar technologies. The red and yellow points in (a) represent the record *PCE* for GaAs and Si-based single junction PVs respectively.

photocurrent, 10% losses in the SQ fill factor and 20% loss in SQ photovoltage) approaching conventional PV technologies commercially available today with almost none of the visible absorption.

Figure 2.11 shows a representative survey of device *PCE* exhibited to date as a function of *AVT* (as calculated according to Equation 2.1) for the full range of selective and non-selective TPV device approaches. The SQ limit in broadband absorbing architectures varies sharply with *AVT* due to their inherent trade-off between performance and transmission, where *PCE* approaches zero as *AVT* approaches 100%. This is highlighted by the solid and dashed lines, which show the SQ efficiency as a function of *AVT* for wavelength selective and non-selective PVs, respectively. The shaded region between the two lines reflects the stark difference in maximum *PCE* achievable by using selective over non-selective TPVs for *AVTs* greater than 50%. Additionally, all reported UV/NIR-selective TPVs are from only the past 5-6 years, representing the rapid progress in terms of optimizing *PCE* and *AVT* simultaneously. As this field matures we expect more results to appear that approach, and eventually fall within, the shaded green region of the graph in Figure 2.11a.

## 2.6 Key challenges for wavelength selective TPVs and LSCs

Wavelength selective TPVs and LSCs face the same development challenges as their non-wavelength selective counterparts. In this section, we discuss strategies for overcoming excitonic limitations, optical losses, resistive losses, and air sensitivity to approach high *PCEs*.

### 2.6.1 TPV Exciton Diffusion Bottleneck

Reviews on excitonic and organic photovoltaics can be found elsewhere.<sup>84, 85</sup> We briefly summarize here the key points relevant for TPV research. Most excitonic materials exhibit modest exciton diffusion lengths (*EDLs*) (~10-20 nm) for both singlet and triplet excitons.<sup>23, 86</sup> In PV

configurations, this limits the active layer thicknesses to balance optical absorption efficiency and internal quantum efficiency (*IQE*, electrons collected per absorbed photon) in planar heterojunctions. BHJs are an important approach to circumvent the exciton bottleneck by introducing an interpenetrating network of donor and acceptor molecules with feature widths comparable to the *EDL*.<sup>31</sup> However, longer-term solutions could be achieved with the enhancement of the *EDL*, as recently demonstrated through molecular templating,<sup>87</sup> altering molecular packing arrangements,<sup>88, 89</sup> and tailoring crystalline order.<sup>90</sup>

### **2.6.2 Transparent Electrodes**

Scaling TPVs to sizes necessary for window integration with minimal reductions in performance requires improvements in transparent electrode conductivity, element abundance, defect tolerance, and patterning. Transparent conductive oxides (TCOs) such as ITO exhibit higher resistivity compared to metallic electrodes. While adding metallic grids can improve conductivity (often at the cost of transmission),<sup>91</sup> upscaling devices to the largest sizes without significant *PCE* loss remains a challenge. The sputtering processes required to deposit many metal oxides also potentially introduce shunting pathways which could reduce device yields.

Polycrystalline ITO often yields brittle films that can be problematic for flexible devices such as laminated window coatings, discussed below. Ideally, future oxide-based transparent electrodes will consist of amorphous, low resistivity materials which can be easily deposited. Amorphous ITO derivatives including  $\text{InZnAlO}$ ,<sup>92</sup>  $\text{InZnO}$ ,<sup>93</sup>  $\text{InZnSnO}$ ,<sup>94</sup>  $\text{ZnSnO}_3$ ,<sup>95</sup> and  $\text{InSiO}$ <sup>96</sup> retain moderate conductivity and have been demonstrated recently as potential electrodes in flexible devices. Regarding abundance, indium is sometimes considered an element that is in high demand, with potentially limited sources in the future. However, the popularity of other In-containing technologies for optoelectronics applications such as CIGS, LCDs, and touchscreens

indicate the viability of its use, where increased recycling of In can help mitigate any future availability concerns.<sup>97, 98</sup> Nonetheless, there is significant ongoing work to develop In-free electrodes and TPVs need not be constrained to only In-based electrodes. Thin metallic films, nanowires, and nanotubes are promising alternatives that offer good ductility and conductivity.<sup>99</sup> However, many architectures are subject to damage from the solution-based processes required to integrate nanowires and nanotubes. Thin metallic films can be thermally deposited but conductivity and transmission need to be balanced since discontinuous films formed at low thicknesses yield high resistivity.

### 2.6.3 Stokes shift efficiency for wavelength selective LSCs

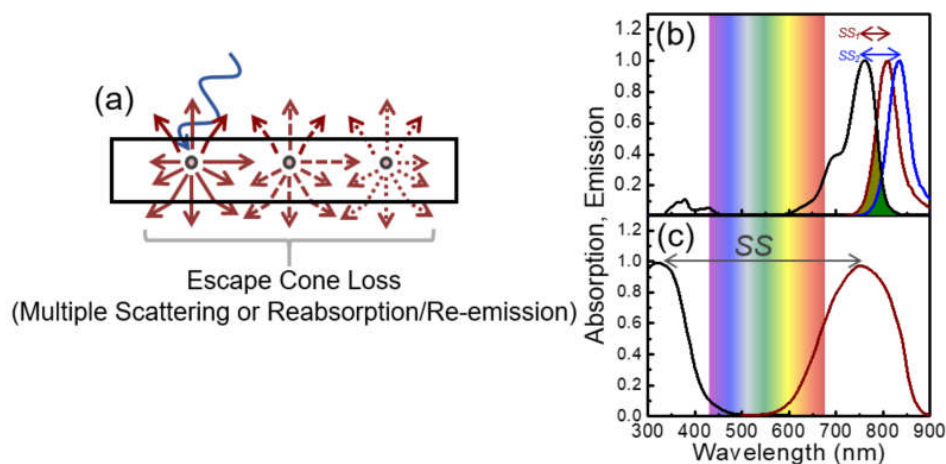


**Figure 2.12. Loss mechanisms for solar concentrators.** (a) Schematic illustrating multiple scattering or reabsorption/re-emission losses in an LSC. Following initial excitation (blue arrow), photons can be lost through scattering or re-emission through the escape cone (solid red arrows). These losses are compounded by each subsequent re-absorption/re-emission or scattering event even with a luminescence efficiency of 100% (dashed and dotted red arrows). (b) Absorption (black) and emission (red and blue) spectra for an NIR-absorbing/NIR-emitting wavelength-selective LSC with the respective Stokes shifts ( $SS_1$  and  $SS_2$ ) highlighted. Reabsorption losses are more likely to occur at small  $SS$  values ( $SS_1$ ) than larger values ( $SS_2$ ) due to greater overlap (shaded yellow region) between absorption and emission for  $SS_1$  than  $SS_2$  (shaded green region). (c) Absorption (black) and emission (red) spectrum for a UV-absorbing/NIR-emitting LSC based on down-converting nanoclusters with the Stokes shift highlighted.

Reabsorption losses, or emitted photons that are reabsorbed by luminescent dyes as shown in Figure 2.12a, are typically the dominant loss mechanisms in LSC technologies and are impacted directly by the Stokes shift (the difference between the absorption and emission peaks of the luminophore, shown in Figure 2.12b),  $\eta_{Trap}$ ,  $\eta_{PL}$ , and the device length. In the NIR-absorbing LSCs demonstrated in Ref. <sup>12</sup>, the external quantum efficiency (*EQE*, electrons generated per incident photon) of the full device including the edge-mounted solar cell decreases rapidly as plate size is increased due to reabsorption losses from a small Stokes shift. This highlights the key importance of Stokes shift in scaling any LSC to large size and is as important as the luminescent quantum yield. If the Stokes shift is increased to >100 nm (Figure 2.12c), LSC sizes could be increased to over 1 m<sup>2</sup> enabling adoptability in nearly all applications.<sup>100</sup> The key materials design challenges to achieve this goal have recently been summarized in Ref. <sup>73</sup>.

#### **2.6.4 Angle Dependence**

Losses from oblique illumination must also be considered for building integration since few surfaces (including the roof) remain at ideal incidence for long in the day. Nonetheless, there has already been significant interest in the solar research community in creating three-dimensional structures such as solar towers to enhance solar collection.<sup>101</sup> These structures can collect substantially more total sunlight than solar tracking units of an equivalent rooftop footprint. For example, the total solar flux density from all four sides of a vertical building in Boston (9.3 kWh per vertical-m<sup>2</sup>-day) is substantially more than for a solar tracking unit of equivalent footprint (6.0 kW-hr per horizontal-m<sup>2</sup>-day),<sup>102, 103</sup> and even greater if we account for the total vertical area utilized in the building; while south-facing vertical windows will give the highest solar flux and therefore highest power output and *LCOE* per installed area, east-west facing windows extend the useful power production throughout the day. Data on the orientation dependent solar flux for

various locations and an example *LCOE* calculation for window-mounted TPV modules are provided in the Appendix.

Parasitic reflections at oblique angles can be reduced or nearly eliminated by controlling various layer thicknesses.<sup>17, 104, 105</sup> For example, a selective TPV with optimized active layer and top ITO thicknesses can retain 80% of its normal-incidence performance under an illumination angle of up to 80°. <sup>104</sup> This translates into an increased yearly power output for a south-facing window by 15-40%, depending on location.<sup>17</sup> While optional NIR mirrors can also be sensitive to angle variations, more advanced designs have been demonstrated commercially that reduce or eliminate oblique angle variations in reflection.<sup>106</sup> In the case of LSCs, the nature of light absorption intrinsically reduces the impact of angle dependence to a single front side reflection, allowing for harvesting of both direct and diffuse light with little angle dependence.<sup>72</sup>

### **2.6.5 Lifetime**

An important challenge for any emerging photovoltaic technology, and particularly for nanostructured materials, is device lifetime. Organics and QD nanocrystals, for example, can react with oxygen and/or moisture. Because TPVs enable deployment in new applications, a more important question arises: what lifetime is needed? In the case of many mobile electronics, practical device lifetimes are less than 10 years. For buildings and windows, we recognize that no PV technology lasts as long as a building and this becomes a question of replaceability. TPVs applied in windows could be installed and replaced as laminates on the inside of windows, (similarly to the way overhead lighting is typically replaced every 2-3 years). The specific lifetime targets and replacement logistics for TPV laminates will ultimately be defined by both the energy and cost payback times. Considering that energy payback for many organic PV technologies can be as low as months or weeks,<sup>107</sup> organic technologies with the range of projected lifetimes already

demonstrated (1-25+ years)<sup>108, 109</sup> have great potential for use in TPVs both for added functionality and as a renewable energy source. Though nanostructured materials are reputed to being more sensitive, commercialized organic light emitting diodes (OLEDs) and quantum dot light emitting diodes (QD-LEDs) are beginning to change that perception thanks to efficient encapsulation strategies. Red fluorescent OLEDs have recently reported lifetimes in excess of 1 million hours at 1000 cd per m<sup>2</sup>. Indeed, extrapolated lifetimes for OPVs > 25 years (the accepted benchmark for traditional PVs) in an oxygen-free environment have already been reported. It is noted, however, that long lifetimes are unusual at this time; many demonstrations fall well short of this metric with extrapolated lifetimes from linear regressions (discussed in Section 3.5) of 2 years<sup>110</sup> and typical non-extrapolated lifetimes of 1.5 years or less.<sup>111, 112</sup>

While lifetimes specific to wavelength selective TPVs have yet to be reported, these demonstrations provide an indication that organic molecules are viable for long-term applications. Currently, all PV module technologies are encapsulated. Even though cavity glass encapsulation is less suitable for flexible applications, thin-film barrier layers and flexible glass could lead to comparable protection from oxygen and moisture without compromising flexibility or transmission.<sup>113</sup>

#### **2.6.6 Multi-junctions**

Multi-junctions are a route to reaching the highest *PCE* for traditional PVs and are similarly important for TPVs. These architectures consist of current-matched complementary UV and NIR-absorbing subcells connected in series. While this approach to enhance efficiencies has been demonstrated with many opaque and non-selective devices,<sup>114</sup> it has yet to be fully explored with selective TPVs and LSCs at the highest *AVTs*. Multi-junctions can be optimized for oblique illumination in the same manner as single-junctions, however this can be challenging if the

individual subcells exhibit separate angle-dependencies. In these cases, the current-limiting subcell mounted on a vertical facade would likely change over the course of a day, yielding potential reductions in device performance.

The development of multi-junction cells also requires a greater catalogue of bandgaps with selective absorption deep into the NIR. This is a significant challenge due to energy level alignment and typical exciton binding energies of 100-300 meV.<sup>115</sup> As donor and acceptor bandgaps are further reduced for deeper NIR-absorption, low interfacial gaps (the energetic offset between the donor HOMO and acceptor LUMO) could make it difficult to balance the energy offset needed to dissociate excitons while also maintaining a high  $V_{oc}$ . One approach to solve this problem utilizes organic salts,<sup>116</sup> where the frontier orbitals can be sensitively tuned via anion blending to maximize both photocurrent and photovoltage without changing the optical absorption of the cation.<sup>117</sup> At small enough bandgaps these binding energies could exceed the driving force for exciton dissociation unless the interfacial gap (and thus  $V_{oc}$ ) is reduced. Strategies to minimize the binding energy include delocalization of the HOMOs and LUMOs through molecular asymmetry to increase the exciton radius (inversely proportional to binding energy)<sup>118</sup> or condensing HOMOs and LUMOs to raise the dielectric constant.<sup>119</sup> Nonetheless, photoresponse with such organic salt molecules has been demonstrated with response as deep as 1600nm.<sup>115, 120</sup>

## 2.7 How to measure and report TPV performance

TPVs necessitate unique standardized approaches to characterization and reporting. While the *PCEs* for TPVs are defined exactly the same as any other PV technology, *PCE* measurement warrants additional consideration since TPVs are intrinsically bifacial and allow illumination from both sides. The *PCE* measurement for TPVs should therefore be standardized with a matte black background behind the cell to eliminate backside illumination from the test environment or

reflection (double pass) from a solar simulator. Testing can also be performed with a white scattering background behind the cell to simulate operation in a white painted room, but this should be in addition to the measurement with the black background.

Regarding transparency measurements, many articles on TPVs report average visible transparency based on averaging the transmission spectra over an arbitrary wavelength range and transmission spectra measured with reference samples that are not needed for the absolute transmission measurement of the entire device. The  $AVT$  should instead be reported as the integration of the transmission spectrum weighted against the photopic response of the human eye as accepted by the window industry.<sup>10, 85</sup> The  $CRI$  is equally as important to glass, window, and display manufacturers not only because of aesthetics, but due to its potential effect on the human circadian rhythm.<sup>121</sup> Photosensitive ganglion cells in the eyes of mammals, linked directly to the control of the circadian rhythm, are highly sensitive to the blue region of the visible spectrum. This sensitivity and its potential physiological effects on building inhabitants can leave PV technologies with low  $AVT$  or  $CRI$  unfit for many widespread window applications.

The last key consideration in characterizing and reporting TPVs is the photon balance at every wavelength:

$$A + R + T = 1 \quad (2.3)$$

where  $A$  is the absorption,  $R$  is the reflection, and  $T$  is the transmission of the TPV measured as discussed in Chapter 3. For spatially segmented PVs this includes both absorbing and transmitting areas. Due to difficulties in measuring  $A$  directly, this can be obtained from:

$$A = \frac{EQE}{IQE} + A_{Contact} \quad (2.4)$$

where  $IQE$  is the internal quantum efficiency,  $A_{Contact}$  is the parasitic absorption in the contact layers (close to 0 for LSCs), and the  $EQE$  can be measured directly. In the limit of  $IQE = 1$  (a reasonable approximation for some BHJ and ultra-thin planar architectures) the *minimum* absorption spectrum can then be estimated from the  $EQE$ . In this approximation, the following equation should be satisfied at every wavelength with independent measurements of  $EQE$ ,  $R$ , and  $T$ :

$$EQE + R + T \leq 1 \quad (2.5)$$

Alternatively, an estimate of  $IQE$  can be obtained from a similarly designed opaque device where  $A$  is estimated from  $R$  measurements and applied to equations 2.4 and 2.5 or obtained from optical interference simulation fitting of  $EQE$  on opaque devices.<sup>122</sup> Another approach to estimate absorption is to measure the  $EQE$  under reverse bias to extract the absorption in the active layer.<sup>123</sup> We note that the balance is still valid for multi-junction cells, where  $EQE$  is typically reduced to produce a greater voltage; in this case, the  $IQE$  of the total device is reduced (requiring multiple photons to obtain one electron at a higher potential). The minimum absorption could then be estimated by summing the reverse-biased  $EQE$  of each subcell under optical biasing of the other subcells. While in opaque cells this balance is much simpler and requires only measuring  $R$  (to obtain  $A=1-R$ ), the addition of the transmission term has created confusion in many reports that have not been shown to satisfy this balance. Thus, we encourage all reports on TPVs to provide independent  $EQE$ ,  $R$ , and  $T$  measurements for each device to allow such validation and alleviate concerns over experimental errors. This consistency check should become standard for all PVs with any visible light transmission, similar to the now standard check of integrating the  $EQE$  to confirm the measured short circuit current density ( $J_{sc}$ ) for any PV technology.

## Chapter 3 – Experimental Techniques

In this chapter, the experimental techniques required to fabricate and characterize the performance and optical properties of OPVs and TPVs are discussed. We also describe techniques specific to the characterization of thin films relevant to TPVs.

### 3.1 OPV device fabrication

Glass substrates pre-patterned with ITO are sequentially sonicated in de-ionized water, soap, and acetone for three minutes per step. Substrates are then rinsed in boiling isopropanol for three minutes and exposed to O<sub>2</sub> plasma for 90 seconds. Following the cleaning, substrates are stored in a nitrogen glove box in preparation for device fabrication.

Most steps of the OPV fabrication process are carried out in a high vacuum environment ( $10^{-6}$  Torr), with the exception of organic salt films which are solution processed in nitrogen. The pre-patterned ITO serves as the bottom electrode. A work function modifying layer, typically MoO<sub>3</sub>, is deposited over the ITO, followed by the donor (small molecule material varies), acceptor (C<sub>60</sub> or C<sub>70</sub>), and the electron transport layer (bathocuproine, BCP). These layers are deposited through a rectangular shaped “active layer” mask and patterned so that some of the bottom ITO remains exposed for device testing. Substrates are brought back into the nitrogen glove box where the mask is changed to an electrode mask without exposing the substrates to air. The electrode mask consists of holes spanning outward from the previously deposited patterned layers to the outer edges of the substrate to enable electronic connections for device testing. The electrode mask portions that allow overlap between the bottom ITO, photoactive layers, and top contact around the center determine the device active area. Substrates are then loaded back into vacuum where the top electrode is deposited. All materials except for the salts and ITO are deposited via thermal

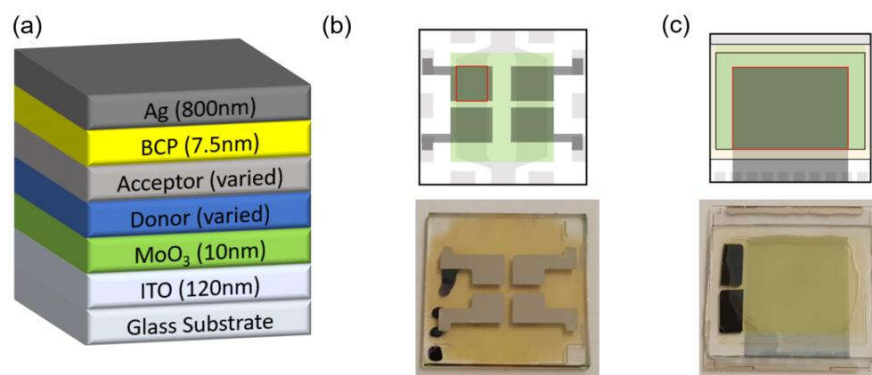


**Figure 3.1. Typical device architecture.** (a) Cross section of a full device with individual layer thicknesses. The donor and acceptor thicknesses are varied depending on materials used. (b) Illustration (top) and photograph (bottom) of a fully patterned  $1.2 \times 1.2$  cm device substrate with four  $5.2 \text{ mm}^2$  devices. (c) Illustration (top) and photograph (bottom) of a  $1.5 \times 1.5$  inch substrate with a single  $5 \text{ cm}^2$  device. The ITO pads at the bottom also allow for patterning up to 10 smaller devices. The pre-patterned ITO is shown in grey, while the photoactive materials and top contacts are shown in green and black respectively. Active areas are outlined in red. Large area devices can be packaged under cavity glass with UV-cured epoxy (yellow) in nitrogen to extend lifetime.

deposition while ITO is deposited via DC magnetron sputtering. An 80 nm Ag layer is used as the top electrode for opaque control devices, while either ITO (100 nm) or Ag (4 nm) / aluminum hydroxyquinoline (Alq<sub>3</sub>) (60 nm) are used for transparent devices. A typical device stack and patterned substrates are shown in Figure 3.1.

Thermally deposited materials (Figure 3.2) are loaded in powder form into baffled tungsten boats, and resistively heated. The material then sublimes from the boat in an outward expanding cone to the substrates where it is deposited as a film. The deposition rate is measured with a quartz crystal monitor (QCM) which resonates at a frequency depending on the volume of material deposited on it, and the rate is controlled to approximately 0.1 nm/s with a user-programmed PID controller in the deposition software.

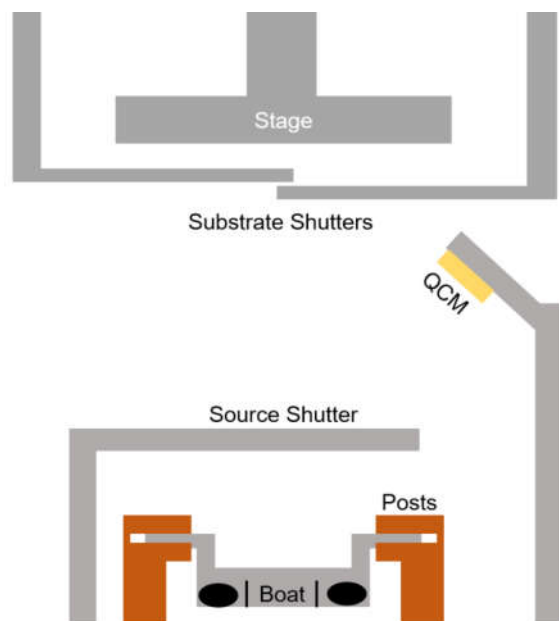


**Figure 3.2. Thermal vapor deposition.** After material (black) is loaded into a baffled tungsten boat and the deposition chamber is pumped to high vacuum, power is sourced from the posts through the boat which heats up resistively and the source shutter opens. Material sublimates upward from a hole in the center of the boat toward the substrates on the stage. Deposition rate is measured by the QCM and controlled with deposition software. Once the deposition rate reaches a user set value, the substrate shutters open and deposition proceeds until the user set thickness is reached.

Sputter deposited materials in the form of packed discs (3-inch diameter, 0.125-inch thickness) are mounted onto a magnetron sputter head and secured in place with a metallic ring serving as an anode shown in Figure 3.3a. A second ring serving as the cathode is secured and separated slightly above the anode as shown in Figure 3.3b. Under high vacuum, a small amount of inert “sputtering gas” (typically Ar) is introduced into the chamber to maintain a pressure of approximately 1.8 mTorr. A DC voltage is applied to the anode and cathode, and the electric field between the electrodes causes the sputtering gas to ionize into a plasma. Alternatively, an AC voltage can be applied such that the electrical potential across the sputtering electrodes is alternated at radio frequencies to avoid charge buildup. This allows for sputtering from any target material including insulators, as opposed to DC sputtering which requires electrically conductive targets. The ionized plasma bombards the target material with high kinetic energies, ejecting

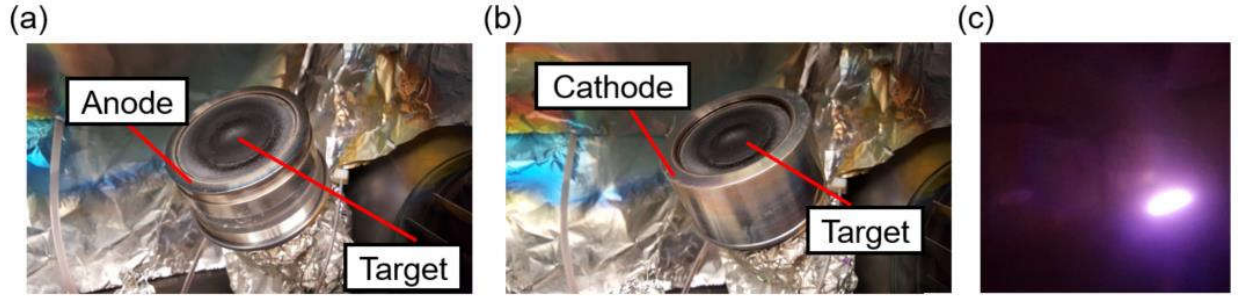


**Figure 3.3. Magnetron sputter configuration.** Magnetron sputter head showing (a) the inner anode ring holding the target material disc in place and (b) the outer cathode ring. (c) Sputter deposition of ITO using Ar plasma.

stoichiometric particles from the target toward the substrate. Deposition rate is monitored and controlled as described above for thermal vapor deposition. Due to the high kinetic energies of sputtered particles, sputter depositions over complete film stacks (e.g. the top ITO electrode for transparent devices) are limited to 0.005-0.02 nm/s to prevent the formation of electronic shorts within organic device stacks.

Thermally and sputter deposited materials are always calibrated before utilization in devices with the tooling factor ( $TF$ ), or the ratio of material deposited on the QCM to that deposited on the substrate. The  $TF$  is measured from films deposited over undoped Si substrates. The film is grown with a nominally prescribed thickness of around 10 nm, and the actual thickness is then measured using spectroscopic ellipsometry for most materials or atomic force microscopy (AFM) for opaque metals. The  $TF$  is then calculated as:

$$\frac{t_i}{TF_i} = \frac{t_f}{TF_f} \quad (3.1)$$

where  $t_i$  is the nominally measured thickness from the initial deposition,  $TF_i$  is the initial  $TF$  input during the deposition,  $t_f$  is the measured thickness from ellipsometry, and  $TF_f$  is the actual tooling factor for the given material.

Co-deposition of two or three materials can be accomplished as long as each material has a dedicated QCM. Deposition rates and nominal thicknesses are measured simultaneously. Since the *TF* for each material is calibrated according to the thickness deposited on a substrate, co-deposition allows for fine control over the volumetric concentration of the resulting blended film.

Organic salts typically exhibit sublimation temperatures higher than the decomposition temperature, and are therefore unsuitable for thermal deposition as they simply decompose in the heated boat. These materials are instead deposited via spin coating in a nitrogen environment. Solutions are made from powder dissolved in chlorobenzene, dichloromethane, or dimethylformamide according to the solubility of the given material. Powder concentration is adjusted as needed to achieve desired film thicknesses, where a higher concentration will yield a thicker film. A solution is pipetted over a substrate held in place by a vacuum chuck to cover the entire surface, and the substrate is then spun at 2000-4000 rotations per minute. The solvent is sheared off and evaporated from the substrate, leaving behind a film. Spin coated materials are always calibrated before utilization in devices. At least 3-4 solutions with varied material concentrations are spin coated over Si substrates, and the film thicknesses are measured to estimate a quantitative dependence of film thickness on concentration. Different solvents exhibit a range of vapor pressures and viscosities that impact the resulting film thicknesses. Thus, calibration is necessary for any new solvent.

### **3.2 J-V and EQE measurement**

To measure performance, devices are inserted into a test fixture shown in Figure 3.4 and illuminated by a Xe arc lamp closely matching the AM1.5 solar spectrum. The lamp is calibrated to 1-sun intensity ( $100 \text{ mW/mm}^2$ ) with a NREL-calibrated Si reference cell with KG5 filter which

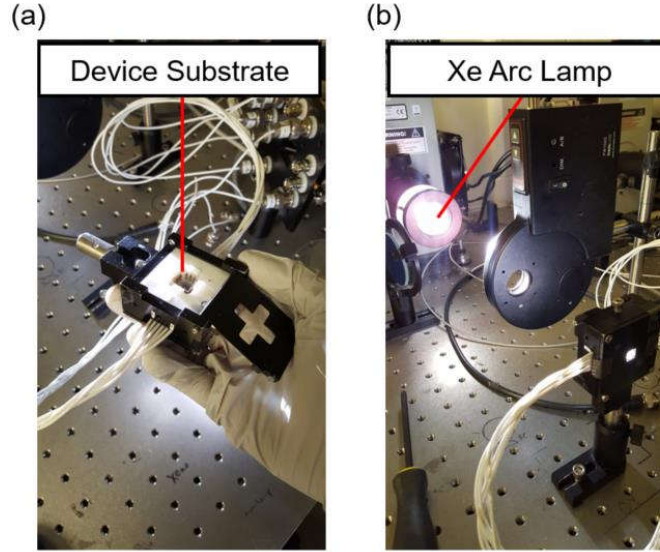


**Figure 3.4. Performance measurement.** (a) Device substrates are loaded into a testing fixture and (b) illuminated with a Xe arc lamp as  $J$ - $V$  data are acquired.

replicates the photoresponse of OPVs and improves spectral mismatch discussed below.<sup>124</sup> Voltage ( $V$ ) is scanned while current density ( $J$ ) is recorded over a high enough range to encompass the characteristic fourth quadrant diode behavior (Figure 3.5). To calculate performance, the  $J_{sc}$ ,  $V_{oc}$ , and  $FF$  are extracted from  $J$ - $V$  data. The  $J_{sc}$  is the current density at 0 V, while the  $V_{oc}$  is the voltage at 0 mA/cm<sup>2</sup>. The  $FF$  is calculated as  $FF = J_{mp} * V_{mp} / J_{sc} * V_{oc}$ , where  $J_{mp}$  and  $V_{mp}$  are the current

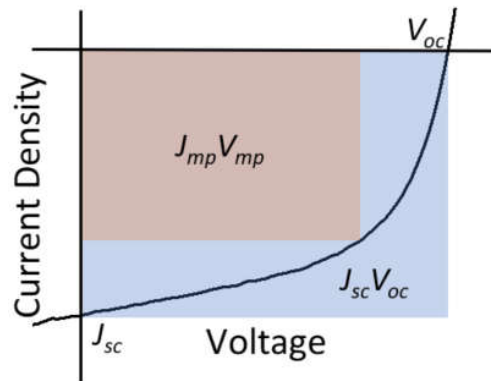


**Figure 3.5. Device performance data.** Current density ( $J$ ) response to applied voltage ( $V$ ) for an example device illuminated under 1-sun intensity with  $J_{sc}$  and  $V_{oc}$  indicated. The red and blue shaded regions show the maximum power point and  $J_{sc} * V_{oc}$  product respectively used to calculate  $FF$ .

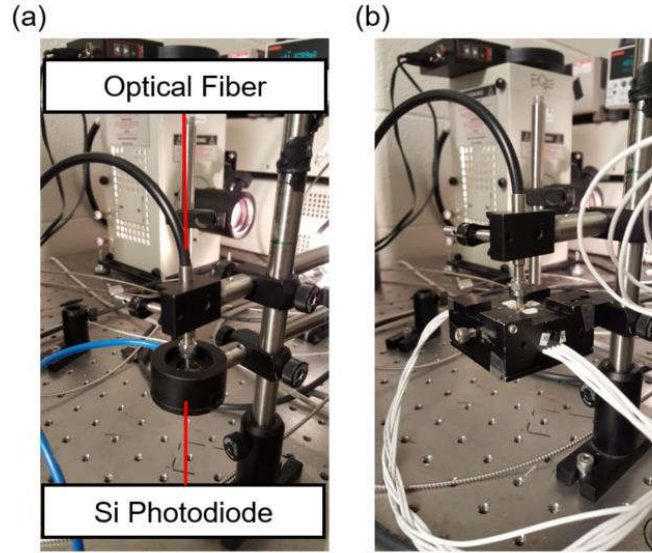


**Figure 3.6. EQE measurement.** (a) *EQE* is first calibrated with a Newport-calibrated Si photodiode before (b) devices are measured.

density and voltage respectively at the maximum power point in the fourth quadrant. The *PCE* is then calculated according to Equation 1.9 ( $J_{sc} * V_{oc} * FF / P_{in}$ ).

*EQE* is measured from monochromated light illuminated from a tungsten halogen lamp and chopped at 200 Hz to minimize interference from ambient lighting (Figure 3.6). Ideally, this is done before *J-V* data is acquired since it is required to calculate spectral mismatch (discussed below) and calibrate testing lamp intensity. Care should also be taken to ensure that the illumination spot size underfills the device area through an optical fiber to avoid underestimation of the *EQE*. Current generated from the chopped monochromated light is measured through a picoammeter and isolated from any background signal by a lock-in amplifier. *EQE* measurements are calibrated with a Newport-calibrated Si diode prior to device measurement. Measured *EQE* spectra are integrated with the AM1.5 spectrum (Equation 1.10) to calculate  $J_{sc}$  as a consistency check for the values measured from *J-V* scans.

Since the lamp intensity is measured with a Si diode with broader photoresponse than TPVs, a correction factor is needed to properly calibrate measured device performance to 1-sun illumination. This spectral mismatch factor ( $MF$ ) represents the deviation in lamp intensity from 1-sun for a device with given photoresponse compared to the reference cell, and is implemented by multiplying the nominal intensity by  $MF$ . The  $MF$  is calculated from  $EQE$  spectra measured on a given device as:

$$MF = \frac{\int E_{ref}(\lambda) S_R(\lambda) d\lambda}{\int E_{ref}(\lambda) S_T(\lambda) d\lambda} \frac{\int E_S(\lambda) S_T(\lambda) d\lambda}{\int E_S(\lambda) S_R(\lambda) d\lambda} \quad (3.2)$$

where  $E_{ref}$  is the reference spectrum solar spectrum (AM1.5G),  $E_S$  is the measurement lamp spectrum,  $S_R$  is the  $EQE$  spectrum of the Si reference diode, and  $S_T$  is the  $EQE$  spectrum of the measured device. While the  $MF$  can be used to correct previously measured  $PCEs$  as discussed above (by correcting the true incident intensity), it is ideally used to calibrate lamp intensity following  $EQE$  measurement and before  $J-V$  measurement. A  $MF$  of 1 indicates that the measurement lamp was perfectly calibrated to 1-sun intensity with the reference photodiode, while a  $MF$  of 1.1 or 0.9 indicates the need to reduce or increase the lamp intensity by 10% respectively. The KG5 filter mentioned above for the reference Si diode absorbs some infrared light, allowing for a more similar photoresponse to those of various TPVs which in turn tends to result in  $MFs$  closer to 1.<sup>124</sup>

### 3.3 Molecular salt anion exchange

Molecular salt anions are exchanged for heptamethine ( $Cy^+$ ) cations prior to salt device fabrication in Chapters 5-7. An example synthesis procedure is provided: Equimolar concentrations of  $CyI$  (American Dye Source) and a separate salt containing the desired anion are dissolved in either methanol or 5:1 methanol:dichloromethane (MeOH:DCM) depending on salt

solubilities at ~10 mg/ml and stirred together at room temperature. The reaction proceeds in under 5 minutes at room temperature and typically results in a low-polarity solid precipitate separating from the relatively polar solvent, which is then vacuum filtered and washed with MeOH. Crude products are filtered through a plug of silica using DCM as the eluent.

### 3.4 Optical characterization

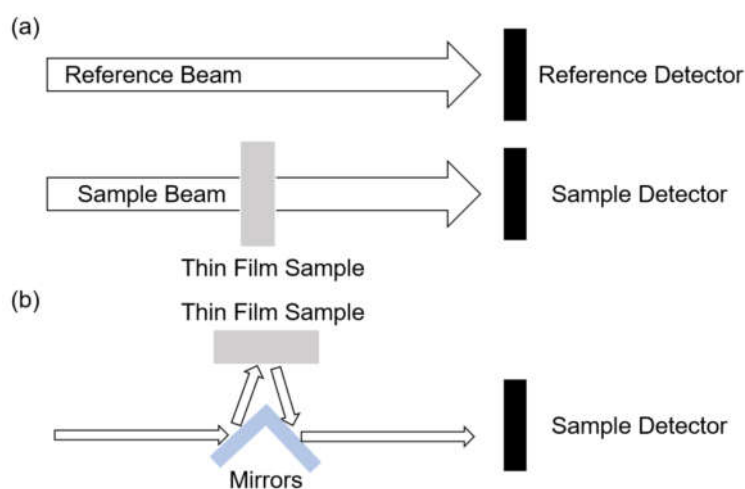


**Figure 3.7. Optical transmission measurement.** Simplified schematic of a UV/VIS spectrometer configured to measure (a) transmission and (b) reflection for a thin film sample. The reference configuration is omitted from (b) since it is identical to (a).

Transmission, reflection, and absorption are key optical properties that determine the applicability of TPVs to a given surface. These properties can be measured from complete device stacks and single films via absorption/transmission spectroscopy. In a UV/VIS/NIR spectrometer, a broad-spectrum light source is monochromated and split into two beams. One is sent through the sample to be measured and the other is directed through a reference sample to simultaneously measure the beam intensity. The two beams are then directed into separate detectors, and the intensity of the sample beam is subtracted from that of the reference beam to determine the optical transmission of the sample. Schematics of transmission and reflection measurements are shown in Figure 3.3. While solution measurements are typically performed with a reference cell consisting

of only the solvent(s) to isolate the transmission of the solute (and subtract reflections), thin films should be measured without any reference because interfacial reflections between a glass reference and air cannot be properly isolated from those between the sample glass and adjacent thin-films. Using a glass reference when measuring the transmission of a thin film sample or device would thus lead to an overestimation of the transmission. Reflection of thin-film samples and devices is measured in a similar fashion using an attachment that directs the sample beam upward to the sample where it is reflected back downward and then directed into the detector. Assuming there is no optical scattering, absorption can then be estimated using Equation 2.3 ( $A + R + T = 1$ ). Alternatively,  $A$  can be estimated as described in Section 2.7 so that Equation 2.3 becomes a consistency check on the overall energy (or population balance).

### **3.5 Lifetime measurement**

The lifetime apparatus used in Chapter 6 is configured to simultaneously test four 6 mm<sup>2</sup> devices on nine 1.5×1.5-inch substrates (expandable to 16). Prior to lifetime testing, performance is measured as described above to determine the four highest performing devices on each substrate. Substrates are then loaded into testing modules equipped with temperature sensors and photodetectors, and illuminated by a sulfur plasma lamp (Chameleon) with spectrum comparable to AM1.5 between 350-820 nm. The illumination intensity at each module position is calibrated to approximately 1 sun by adjusting the height of the lamp over the substrates and measuring intensity with a NREL-calibrated Si reference cell with KG5 filter as described in Section 3.2 and considering spectral mismatch. Module temperatures are approximately 60°C under illumination. Customized electronics are utilized to hold devices at maximum power point, short circuit, or open circuit and measure temperature, illumination intensity, and mismatch corrected  $J$ - $V$  characteristics

on each device once per hour to extract time dependent performance characteristics. A photograph of the equipment used to measure lifetime is shown in Figure 3.8.

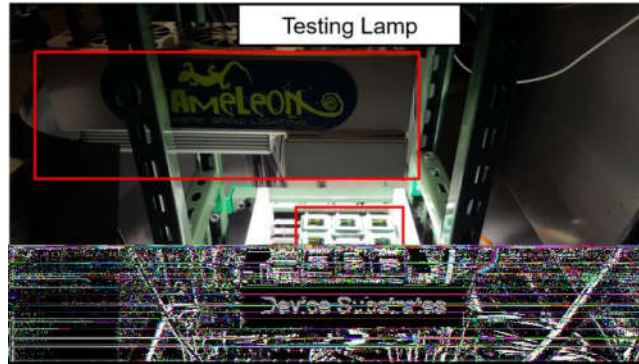


**Figure 3.8. Lifetime measurement.** A sulfur plasma testing lamp (top) is used to illuminate up to 4 devices on 9 substrates (8 pictured, bottom) while performance is measured over time.

Lifetimes are defined as the time over which the *PCE* reaches 80% or 50% of the initial value after any burn-in ( $T_{80}$  or  $T_{50}$  respectively). Lifetime tests are conducted either for 1000 hours or until all devices on a given substrate reach  $T_{50}$ . Accelerated lifetime values are multiplied by  $5.66 \times$  average hours of 1-sun illumination per day to convert from accelerated constant illumination to ambient conditions in Kansas City, MO which closely represents the average daily illumination in the United States (and peak power of  $\sim 1000\text{W/m}^2$ ). For devices that do not reach  $T_{50}$  after 1000 hours of constant illumination, a linear regression is fit to normalized performance data following any initial burn-in to extrapolate  $T_{80}$  and  $T_{50}$ .

### 3.6 Ultraviolet photoelectron spectroscopy

Ultraviolet photoelectron spectroscopy (UPS) can be used to probe valence states or work functions of semiconductors and metals. He I radiation (21.2 eV) is directed at a sample in an ultrahigh vacuum environment ( $< 10^{-7}$  Torr) resulting in the ejection of valence electrons. UPS relies on the photoelectric effect in which a photon is absorbed, resulting in the excitation of an electron from the ground state to the vacuum level. The electron is ejected from the sample surface with kinetic energy  $E_K = h\nu - E_{BE} - \Phi_S$ , where  $h\nu$  is the excitation energy,  $E_{BE}$  is the binding energy of the electron in the sample, and  $\Phi_S$  is the sample work function. Because the detector has a work function ( $\Phi_D$ ), there exists a contact potential ( $\Phi_S - \Phi_D$ ) between the sample and detector that must be accounted for when analyzing UPS spectra. Given this contact potential, the measured kinetic energy is then  $E_K = h\nu - E_{BE} - \Phi_S + \Phi_S - \Phi_D$ , or  $E_K = h\nu - E_{BE} - \Phi_D$ . For metallic samples,  $\Phi_S$  is calculated as the difference between the excitation energy and the width (secondary cutoff subtracted from primary cutoff) of the entire kinetic energy spectrum. Measuring  $\Phi_S$  for a semiconductor is less trivial because the Fermi edge ( $E_K = 21.2$  eV) in this case is aligned with the

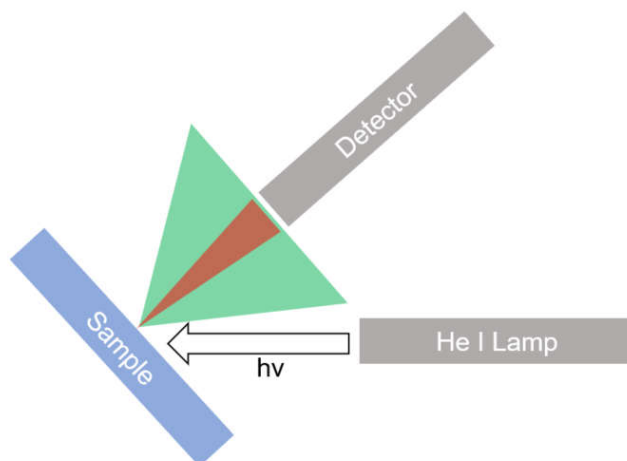


**Figure 3.9. UPS measurement.** Simplified schematic of an X-ray photoelectron spectrometer configured to measure UPS. The primary and secondary electric fields emitted from the sample are shown in red and green respectively. Primary electrons are emitted at a narrow angle, requiring the substrate to be oriented normal to the detector.

unknown HOMO. Semiconducting samples therefore require the consecutive measurement of a metallic sample with known  $\Phi_S$ . The semiconductor spectrum can then be aligned such that the lowest kinetic energy signal, corresponding to the secondary peak cutoff, matches the metallic control. The work function is still calculated as the difference between  $h\nu$  and the high binding energy cutoff, while the HOMO is then the difference between  $h\nu$  and the low binding energy cutoff.

A UPS spectrum consists of both primary and secondary electrons. The primary electrons are those that reached the detector without undergoing inelastic collisions, and therefore reflect the initial energy states of the material. The secondary signal typically consists of a single peak which varies in kinetic energy according to excitation energy and is not representative of any sample characteristics besides the work function. Because primary electrons are emitted from the sample at a narrow angle, the sample surface should be oriented normal to the detector as shown in Figure 3.9. Additionally, the sample is typically grounded to prevent charging and a voltage is biased at 15 V to shift the measured kinetic energies in the sample spectrum away from any signal

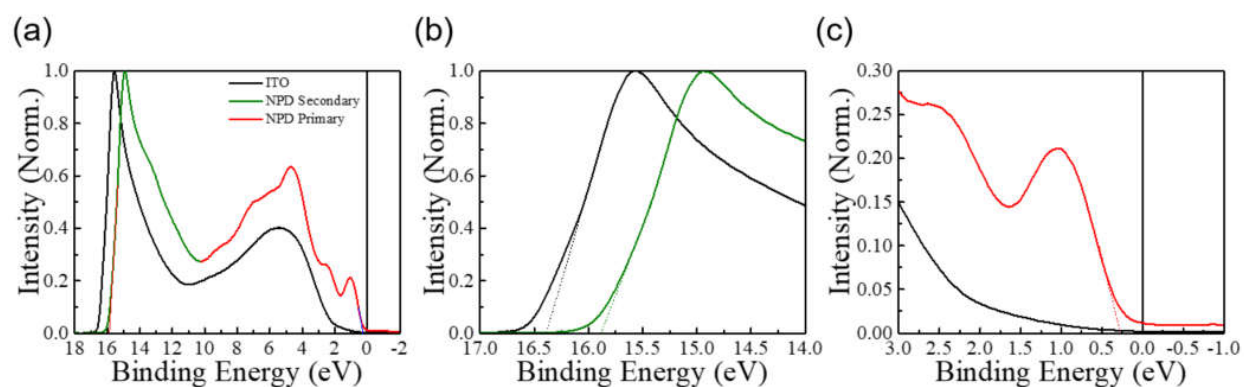


**Figure 3.10. Measuring work function and HOMO.** (a) Full, (b) high, and (c) low binding energy normalized UPS spectra for ITO (black) and N,N'-di(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPD) corrected according to the known work function of ITO. For clarity, the NPD data are separated into the secondary (green) and primary (red) signals which are used to measure work function and HOMO respectively. High and low binding energy cutoffs are indicated by the dotted lines. For ITO, the work function is  $21.2 - 16.4 = 4.8$  eV. For NPD, the work function is  $21.2 - 15.9 = 5.3$  eV and the HOMO is  $5.3 + 0.25 = 5.55$  eV.

originating from electron interactions in the detector itself. Since UPS is extremely surface sensitive with a penetration depth of  $< 10$  nm, air sensitive samples such as organics should be fabricated and loaded from nitrogen to the vacuum chamber without exposure to air. This prevents the formation of surface defects from oxygen and moisture interactions that can sensitively interfere with work function and HOMO measurements.

In practice, UPS spectra are usually automatically converted from kinetic energy to binding energy in the measurement software, simplifying the necessary corrections and calculations of  $\Phi_S$  and the HOMO. A metallic control is still required to shift all measured spectra by the same amount of energy according to its known work function, accounting for voltage bias and  $\Phi_D$ . In the corrected binding energy spectrum,  $\Phi_S$  is then the difference between  $h\nu$  and the secondary (high binding energy) cutoff, while the HOMO for a semiconductor is the sum of  $\Phi_S$  and the primary (low binding energy) cutoff. For metallic samples, the primary signal cutoff occurs at the Fermi edge ( $E_F = 0$  eV). Example binding energy UPS spectra are shown in Figure 3.10 with  $\Phi_S$  and HOMO calculations for ITO (a typical metallic control with  $\Phi_S = 4.8$  eV) and an organic semiconductor.

### 3.7 Four-point probe measurement

Sheet resistance and resistivity are important metrics that determine the viability of photoactive, buffer, and electrode materials for any PV application. These are measured with a four-point probe apparatus consisting of four linear evenly spaced electrodes placed over a thin film deposited over a non-conductive substrate such as glass as shown in Figure 3.11. The outer two electrodes apply a given current while the inner two measure the voltage drop to calculate

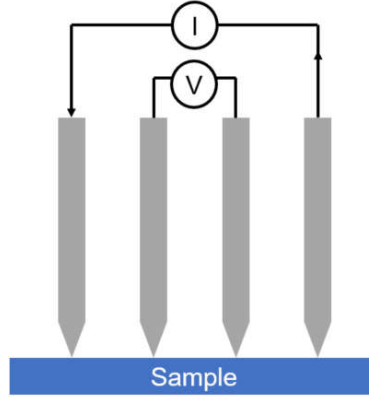


**Figure 3.11. Sheet resistance measurement.** Schematic of a typical four-point probe consisting of four evenly spaced electrodes lowered onto a sample. Current is passed between the outer two electrodes while voltage is measured from the inner electrodes.

resistance according to Ohm's law. Although resistance can be measured with only two electrodes, the four-electrode configuration eliminates any voltage drop within the current biasing electrodes from the voltage measurement yielding a more accurate resistance calculation from the sample.

The sheet resistance is calculated as

$$\rho_S = R_E \left( \frac{W}{L} \right) \quad (3.3)$$

where  $R_E$  is the measured electrical resistance,  $W$  is the sample width, and  $L$  is the sample length assuming a uniform thickness and either a square or rectangularly shaped sample. Sheet resistance is measured in Ohms, or  $\Omega$ , but given in units of  $\Omega/\square$ , where “ $\square$ ” (“square”) is a unitless placeholder used to signify the canceled sample dimension units (m) so as not to confuse  $\rho_S$  with bulk resistance. Because  $R_E$  scales with area,  $\rho_S$  can be used to compare different sized samples of a given material. Resistivity can then be calculated as

$$\rho = t_F \rho_S \quad (3.4)$$

and is given in units of  $\Omega \cdot \text{m}$  where  $t_F$  is the measured film thickness. While  $\rho_S$  gives the resistance of a sample at a given thickness,  $\rho$  is an intrinsic material property and can therefore be used to directly compare samples of both different areas and thicknesses.

### 3.8 Atomic force microscopy

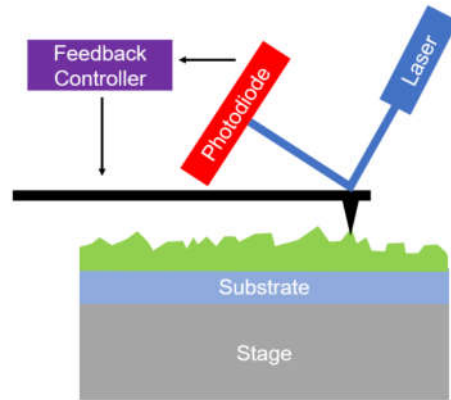


**Figure 3.12. AFM measurement.** Schematic of an atomic force microscope. The tip (black) is raster scanned across a thin film sample (green) while changes in tip deflection are measured through a feedback controller which adjusts the tip height above the sample.

Atomic force microscopy (AFM) allows the imaging of surfaces at high resolutions on the order of nanometers without the need for lenses, high vacuum, or beam irradiation incident to the sample. Images are resolved by raster scanning samples with a near-atomically sharp mechanical probe, known as the tip, and measuring changes in the tip height corresponding to a constant separation distance between the tip and the sample. As the sample is raster scanned, tip deflections are measured through changes in the intensity of light from a laser reflected off the cantilever. These deflections are measured across a pre-defined area of the sample to generate a topographic map. Since topographic changes are explicitly measured, AFM is a preferred technique used to quantitatively estimate sample roughness.

A typical AFM, schematically illustrated in Figure 3.12, consists of a sample stage, cantilever and tip, laser, photodiode, and feedback electronics. An electronic feedback loop maintains a constant force between the sample and tip by adjusting the tip height above the sample to a user-defined setpoint in response to measured deflections. The signals measured from the tip deflections are plotted by measurement software in a pseudocolor image of the sample area, where the color represents recorded topographic features.

AFM images are acquired in either contact, tapping, or non-contact mode as required for different samples. In contact mode, the tip is scanned across the sample surface and topographic features are measured directly from cantilever deflections as discussed above. Some samples such as biological materials which tend to develop liquid meniscus layers are instead measured in tapping mode, where the cantilever is oscillated up and down at its resonance frequency at a constant set amplitude maintained through adjustments in tip height. Lastly, non-contact mode is used for soft samples that would be easily deformed in the former two modes. In this case, the tip is oscillated at its resonance frequency and held a few nanometers above the sample. Van der Waals forces that extend above the sample surface interact with the tip and reduce the resonance frequency, which is recorded and used to generate images.

### **3.9 X-ray Diffraction**

X-ray diffraction (XRD) allows for the measurement of crystallinity from the elastic scattering of X-rays off atoms in a given sample. A schematic of an X-ray diffractometer in the Bragg-Brentano configuration is illustrated in Figure 3.13. XRD data is acquired by exciting the sample with X-rays using a  $\text{CuK}\alpha$  source and measuring the number of X-rays diffracted into a detector as a function of the angle between the sample and detector ( $\theta$ ). While X-rays will cancel each other out from destructive interference at most angles, they will add through constructive

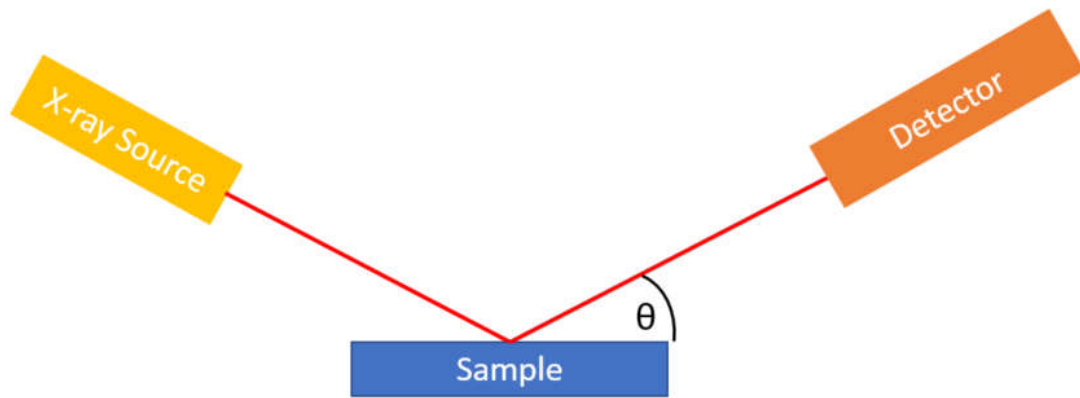


**Figure 3.13. X-ray diffractometer.** Schematic of an X-ray diffractometer configured in the Bragg-Brentano geometry.

interference at specific angles depending on the crystallographic structure of the sample. This results in isolated diffraction peaks with intensity dependent on the sample thickness and degree of crystallinity. Diffraction conditions are determined by Bragg's law, illustrated in Figure 3.14 and given as:

$$n\lambda = 2d_{hkl}\sin\theta \quad (3.5)$$

where  $n$  is an integer,  $\lambda$  is the X-ray wavelength,  $d_{hkl}$  is the interplanar spacing equal to  $a/\sqrt{h^2 + k^2 + l^2}$ ,  $a$  is the lattice constant, and  $(hkl)$  are the Miller indices of the crystallographic

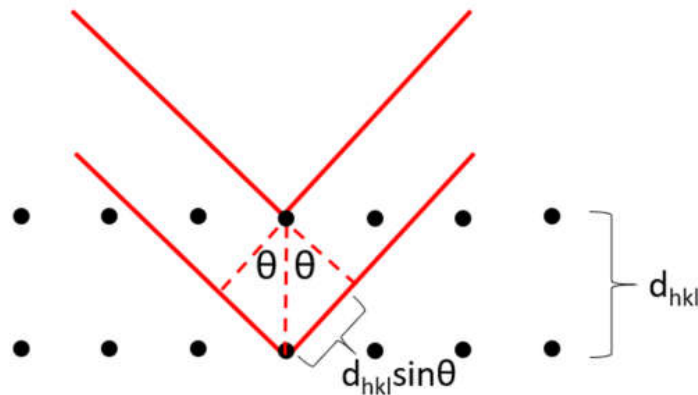


**Figure 3.14. Bragg diffraction.** Illustration of X-rays (red) diffracting off atoms (black) in a crystalline solid. Constructive interference occurs when the distance traveled by each X-ray is an integer multiple of the wavelength.

plane. XRD measurements in this dissertation were conducted with a Bruker D8 Advance diffractometer.

## Chapter 4 – Buffer Layers and TCOs for Organic Photovoltaics

Two key components in TPVs are the cathode-side buffer layer and the top electrode, typically a transparent conductive oxide (TCO). Both of these layers serve key purposes in the performance, applicability (visible light transmission), and lifetime of the device. In this chapter, we discuss alternative buffer layer materials, top electrode materials, and TCO sputtering conditions which can potentially facilitate higher device performance, lifetimes, and manufacturing yields.

### 4.1 Buffer layers and TCOs

Buffer layers are typically incorporated into OPVs to 1) prevent excitons from quenching at metal electrodes, 2) protect the active layers from damage during the electrode deposition, 3) reduce Schottky barriers for improved charge collection, and 4) extend the lifetime of the device.<sup>11,</sup>  
<sup>125</sup> Additionally, it is necessary that the cathode-side buffer layer be optically transparent to limit parasitic absorption at shorter wavelengths. Bathocuproine (BCP) is commonly used as the cathode-side buffer layer in OPVs due to its wide energy gap that enables light transmission and effectively blocks excitons.<sup>11, 125</sup> However, the low glass transition temperature and low molecular weight of BCP limit its use in long-lifetime applications due to poor thermal stability that can lead to catastrophic crystallization that results in reduced conductivity, shorting, or poor device lifetime. While cadmium-based window layers such as CdS (2.4eV band gap)<sup>1</sup> offer a potential alternative and have the best electrical performance over nearly all other known buffer layers in analogous thin-film inorganic photovoltaics,<sup>126</sup> device fabrication presents health hazards due to the high toxicity of cadmium and the small band gaps that limit blue/UV photoresponse. Because the catalog of high performance window layers in inorganic thin film photovoltaics is largely limited

to cadmium-based compounds, it is advantageous to find a greater range of alternatives that can also provide variability in energy level matching and improved transmission characteristics.

Manufacturing yield is another major challenge that must be overcome to enhance the deployment of TPVs. ITO deposited via DC magnetron sputtering often penetrates protective buffer layers and reaches the underlying organic layers, creating short circuits that shut off devices. Optimizing the conditions of this sputtering process is key to eliminating damage and thus improving manufacturing yield. Studies conducted previously show that the method of sputtering and the ionizing gas species and flow pressure utilized can potentially have significant impacts on the energy of the sputtered material and the damage dealt to organic layers.<sup>127, 128</sup>

## **4.2 ZnS buffer layer devices**

Most of these materials yielded either colored films or low efficiency devices due to high series resistance and were thus deemed unsuitable. ZnS (3.7eV band gap)<sup>1</sup> deposited via chemical bath deposition (CBD) has been used previously as a buffer layer material in CIGS-based PVs<sup>129, 130</sup> with reported power conversion efficiency of 16.9%, equaling the performance of the CdS control that yielded a power conversion efficiency of 16.8%.<sup>130</sup> Chemical bath deposited ZnS is indeed a viable alternative to Cd-based compounds for CIGS-based PVs, however the CBD process which involves chemically synthesizing the desired material(s) in a precursor solution and depositing onto a submerged substrate would dissolve existing organic layers<sup>131</sup> making this mechanism undesirable for conventional OPVs and less compatible with in-line vapor deposition of cadmium telluride (CdTe) PVs. While sputtered materials such as zinc oxide (ZnO) and Al doped ZnO (AZO) exhibit wide electrical band gaps necessary to function as window layers, the sputtering process introduces interface defects and shorting that leads to poor OPV device

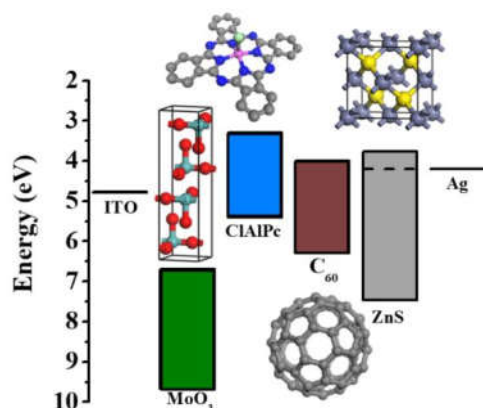


**Figure 4.1. OPV architecture incorporating ZnS.** Schematic energy diagram of the OPV device structure incorporating a ZnS cathode side buffer layer.<sup>1-4</sup> The work function (dashed line) and energy levels for intrinsic ZnS measured via UPS and calculated from the band gap<sup>1</sup> are highlighted.

performance.<sup>132</sup> Other inorganic, wide bandgap semiconductors including AlF<sub>3</sub>, AlBr<sub>3</sub>, CuI, CuS, Cu<sub>2</sub>S, V<sub>2</sub>O<sub>5</sub>, WO<sub>2</sub>, and WO<sub>3</sub> yield colored or highly resistive films, and are thus unsuitable to replace BCP.

ZnS is a more versatile alternative to sputtered or CBD materials because it may be thermally deposited in a vacuum environment suitable for both OPV and CIGS-based PV applications, analogous to MoO<sub>3</sub>, which is widely employed as the anodic buffer layer in OPVs.<sup>133, 134</sup> While the wide band gap of ZnS makes this material a potential replacement for CdS as a cathode side window layer for both PVs and OPVs, we find that high electrical resistivity from thermally deposited ZnS limits device performance to efficiencies well below those of equivalent OPV devices utilizing BCP window layers. In previous work focused on structural and conductivity characterization of isolated ZnS films, aluminum,<sup>135-137</sup> indium,<sup>137</sup> and manganese<sup>138</sup> were used as n-type dopants to improve the conductivity of ZnS. Al doping was previously reported to improve ZnS resistivity from  $2.8 \times 10^6$  to  $9.9 \times 10^4 \Omega\text{-cm}$  at 6at.% Al while increasing to  $6.5 \times 10^5 \Omega\text{-cm}$  at 10at.% due to Al atoms being unable to substitute to Zn sites at high concentrations and instead creating scattering sites rather than donating electrons.<sup>135, 139</sup>

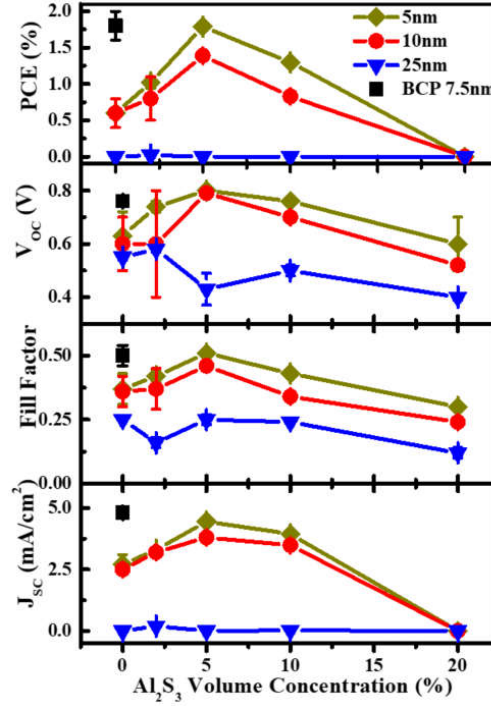


**Figure 4.2. ZnS:Al<sub>2</sub>S<sub>3</sub> optimization.** Extracted photovoltaic parameters for OPV devices utilizing various ZnS:Al<sub>2</sub>S<sub>3</sub> buffer layer thicknesses. Experimental control devices with BCP are also shown (squares).

Additionally, Ag has been used as a structural dopant to improve the crystallinity and thus the electron mobility of ZnS by sputtering ZnS:Ag targets.<sup>140</sup> However, there have been no reports of efficient devices fabricated with electrically or structurally doped ZnS by vapor deposition.

Here, we demonstrate that ZnS thermally co-deposited with aluminum sulfide (Al<sub>2</sub>S<sub>3</sub>) can act as a nearly ideal replacement for BCP as the cathode side window layer in OPV devices as shown in the energy diagram in Figure 4.1 and therefore may be added to the catalogue of window layers for other thin-film photovoltaic technologies. This is enabled by optimal doping of ZnS with Al<sub>2</sub>S<sub>3</sub>, which results in improved electrical conduction, work function, and dramatically enhanced performance over undoped ZnS.

In Figure 4.2 the  $PCE$ ,  $J_{sc}$ ,  $V_{oc}$ , and fill factor ( $FF$ ) are plotted as a function of Al<sub>2</sub>S<sub>3</sub> concentration and buffer layer thickness. Starting with a neat ZnS layer and increasing Al<sub>2</sub>S<sub>3</sub>

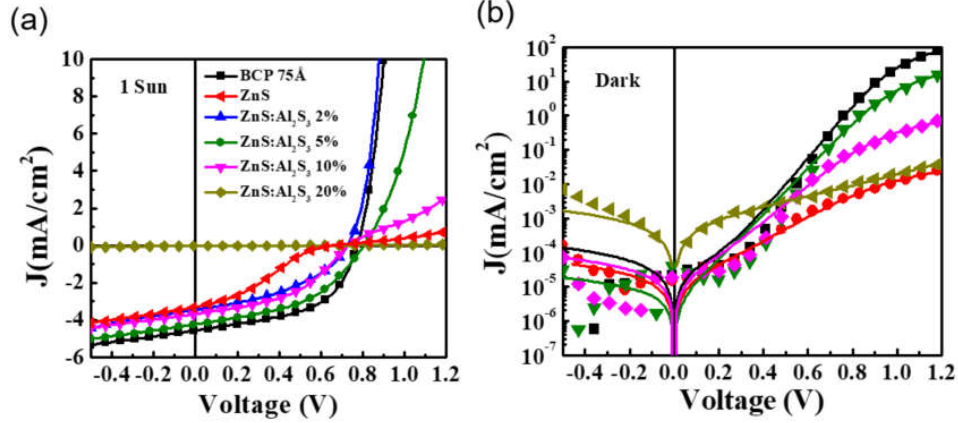


**Figure 4.3. ZnS:Al<sub>2</sub>S<sub>3</sub> J-V data.** Representative device data taken under (a) 1-sun illumination and (b) in the dark for devices with 5nm ZnS:Al<sub>2</sub>S<sub>3</sub> buffer layers as a function of the Al<sub>2</sub>S<sub>3</sub> volumetric doping plotted against a typical 7.5nm BCP control. The dark current fitting results are also shown in (b) (solid lines).

volumetric concentration, *PCE* increases from  $0.6 \pm 0.2\%$  to  $1.8 \pm 0.1\%$  at 5vol% Al<sub>2</sub>S<sub>3</sub>, identical to the control efficiency of  $1.8 \pm 0.2\%$ , and then drops to 0.0% as Al<sub>2</sub>S<sub>3</sub> concentration is increased to 20%. The  $V_{oc}$  increases from  $0.63 \pm 0.09$ V for neat ZnS to  $0.80 \pm 0.01$ V at 5vol% Al<sub>2</sub>S<sub>3</sub>, exceeding the control  $V_{oc}$  of  $0.76 \pm 0.02$ V before returning to  $0.6 \pm 0.1$ V at 20vol%. *FF* and  $J_{sc}$  follow similar trends starting at  $0.37 \pm 0.06$  and  $2.7 \pm 0.4$  mA/cm<sup>2</sup>, respectively, for neat ZnS with maxima at  $0.51 \pm 0.01$  and  $4.45 \pm 0.09$  mA/cm<sup>2</sup> at 5vol%, comparable to the control *FF* of  $0.5 \pm 0.04$  and  $J_{sc}$  of  $4.8 \pm 0.05$ , and dropping off at higher concentrations. In Figure 4.3, we plot *J-V* data from 5nm ZnS devices as a function of Al<sub>2</sub>S<sub>3</sub> concentration both under illumination and in the dark. Control data from devices with BCP layers are included in both figures. *J-V* data in the dark (Figure 4.3b) were fit to extract parallel ( $R_p$ ) and series ( $R_s$ ) resistance for ZnS and control devices using the generalized Shockley equation<sup>134, 141</sup>

$$J = \frac{R_p}{R_s + R_p} \left\{ J_s \left[ \exp \left( \frac{q(V - JR_s)}{nk_B T} \right) - 1 \right] + \frac{V}{R_p} \right\} \quad (4.1)$$

where  $J_s$  is the reverse saturation current,  $n$  is the diode ideality factor, and the  $R_p$  and  $R_s$  values are summarized in Figure 4.4.

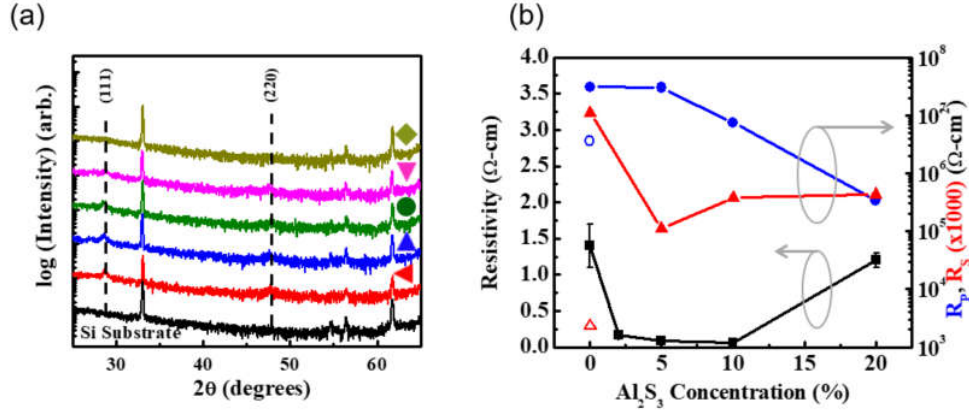


**Figure 4.4. ZnS:Al<sub>2</sub>S<sub>3</sub> characterization.** (a) XRD data, (b, left axis) measured resistivity values, and (b, right axis) calculated parallel (circles) and series (triangles) resistance values of ZnS:Al<sub>2</sub>S<sub>3</sub> 100nm films and devices. Symbols in (a) correspond to Al<sub>2</sub>S<sub>3</sub> concentrations of 0 (red triangle), 2 (blue triangle), 5 (green circle), 10 (pink triangle), and 20vol.% (yellow diamond). Open symbols in (b) correspond to fitted parameters from BCP control devices.

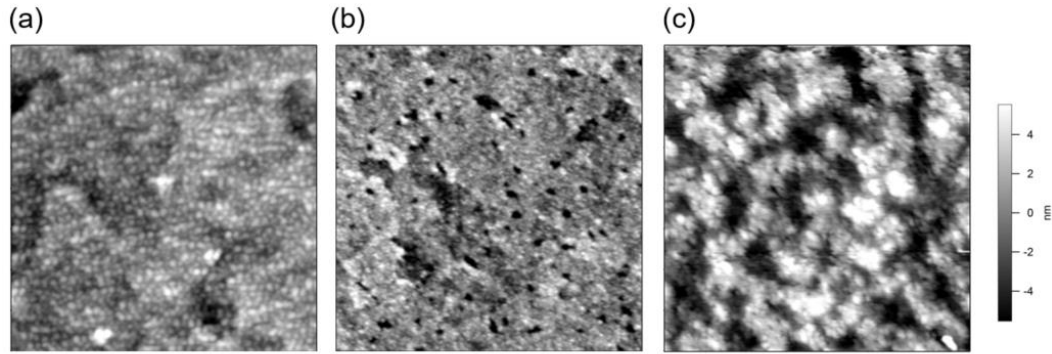


**Figure 4.5. AFM on ZnS:Al<sub>2</sub>S<sub>3</sub>.** AFM images (1.5×1.5μm) of 30nm ZnS:Al<sub>2</sub>S<sub>3</sub> films deposited over glass substrates pre-coated with 120nm of ITO and 5nm C<sub>60</sub>. Surface roughnesses are 1.6±0.1, 1.6±0.2, 1.8±0.1, 1.9±0.1, and 3.0±0.2nm at (a) 0, 2, (b) 5, 10, and (c) 20vol% Al<sub>2</sub>S<sub>3</sub> respectively. Al<sub>2</sub>S<sub>3</sub> concentrations of 2 and 10vol% were omitted due to qualitatively equivalent surface roughnesses to the 5vol% film.

### 4.3 ZnS:Al<sub>2</sub>S<sub>3</sub> thin film analysis

To understand the dramatic variation in device performance, XRD, sheet resistance, and AFM data were measured as a function of Al<sub>2</sub>S<sub>3</sub> concentration (Figures 4.4 and 4.5). Thermally deposited ZnS takes on the zincblende crystal structure ( $a = 5.403\text{\AA}$ ) as determined by the observation of the (111) and (220) ZnS diffraction peaks. The XRD data show a trend of decreasing

crystallinity at  $\text{Al}_2\text{S}_3$  concentrations  $\geq 10\text{vol}\%$  as these two peaks diminish in intensity and the film becomes rich with  $\text{Al}_2\text{S}_3$ . This correlates well with a known phase change from the zincblende crystal structure to the spinel structure as  $\text{Al}_2\text{S}_3$  exceeds  $7\text{mol}\%$  in ZnS.<sup>142</sup> Introducing  $\text{Al}_2\text{S}_3$  into ZnS dramatically decreases the resistivity of the thin films. Neat ZnS (thermally-deposited) is found to have a resistivity of  $1.4\pm0.3\Omega\text{-cm}$  while ZnS containing  $2\text{vol}\%$   $\text{Al}_2\text{S}_3$  is found to have a resistivity of  $0.17\pm0.05\Omega\text{-cm}$ . Resistivity continues to decrease to  $0.061\pm0.009\Omega\text{-cm}$  at  $10\text{vol}\%$   $\text{Al}_2\text{S}_3$  and then increases to  $1.2\pm0.1\Omega\text{-cm}$  at  $20\text{vol}\%$   $\text{Al}_2\text{S}_3$ , likely due to the saturation of ZnS with  $\text{Al}^{3+}$ .

The performance of OPV devices incorporating ZnS doped with  $\text{Al}^{3+}$  is optimized at  $5\text{vol}\%$   $\text{Al}_2\text{S}_3$  due to a combination of changes in crystallinity, work function, reduced Schottky barrier, and improved sheet resistance. The rapid improvement in performance in devices containing small concentrations of  $\text{Al}_2\text{S}_3$  over those with neat ZnS layers is explained by the decreased series resistance through the window layer, as resistivity drops nearly an order of magnitude from 0 to  $2\text{vol}\%$   $\text{Al}_2\text{S}_3$ . The XRD data, which shows diminishing crystallinity as  $\text{Al}_2\text{S}_3$  concentration exceeds  $5\text{vol}\%$ , implies that the drop-off observed in the performance of devices above  $5\text{vol}\%$   $\text{Al}_2\text{S}_3$  stems from surpassing the Al substitution solubility limit and results in increasing domains of low mobility  $\text{Al}_2\text{S}_3$ . AFM (Figure 4.5) confirms that nanoscale grains present in neat ZnS are first diminished and then replaced by larger  $\text{Al}_2\text{S}_3$  domains with increased doping of  $\text{Al}_2\text{S}_3$ . While ZnS has an upper limit crystalline mobility of  $80\text{-}230\text{ cm}^2/\text{V-s}$ ,<sup>143</sup> the mobility of  $\text{Al}_2\text{S}_3$  has not been reported, likely due to its conversion to  $\text{Al}_2\text{O}_3$  in non-doping configurations. Nonetheless, the mobility of thermally deposited nanocrystalline ZnS is likely orders of magnitude smaller than these upper limits, as evidenced by the poor performance of the undoped ZnS device.

At 0vol% and 10vol%  $\text{Al}_2\text{S}_3$ , the device  $J$ - $V$  characteristics exhibit a kink in the forward current region and a reduced slope at forward bias, while at 20vol% devices are effectively shut off. This is indicative of i) the presence of a reverse Schottky barrier known to form between undoped cubic ZnS and Ag with barrier heights reported between 1.65 and 1.81 eV<sup>144</sup> as well as ii) increased bulk resistance. In fact, a Schottky barrier likely forms across all  $\text{Al}_2\text{S}_3$  concentrations, seen in the form of increasing series resistance at forward bias and ‘kink’ formation as the overall ZnS thicknesses increases  $> 15\text{nm}$ , even for the optimally doped (i.e. lowest resistivity) films. Both the diminished crystallinity and sheet resistance trends are similar to those previously observed with Ag as a structural dopant to ZnS in a non-device demonstration.<sup>140</sup> A similar trend in device performance is observed when window layer thickness is increased across all  $\text{Al}_2\text{S}_3$  concentrations less than 20vol% likely due to the limited depletion width,  $W_D, < 10\text{nm}$ . At 5nm, the Schottky barrier is overcome by field driven tunneling while at higher ZnS thicknesses this barrier dominates the tunneling probability and diminishes device performance along with resistive losses; that is, both interface and bulk resistances play a role. Dark  $J$ - $V$  fitting indicates that changes in  $R_s$  and  $R_p$  with varying  $\text{Al}_2\text{S}_3$  concentration significantly affect ZnS device performance as  $R_p$  follows a trend similar to  $V_{oc}$  while  $R_s$  follows a trend identical to  $FF$ ,  $J_{sc}$ , and resistivity.

## 4.4 Alternative TCO devices and analysis

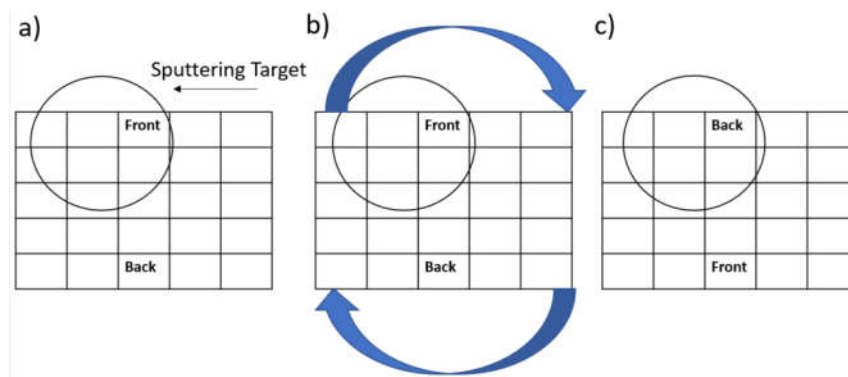


**Figure 4.6. Rotation conditions for yield optimization.** Illustrations depicting the (a) non-rotation, (b) continuous rotation, and (c) 180° rotation conditions used to optimize the yield of transparent devices with ITO top electrodes.

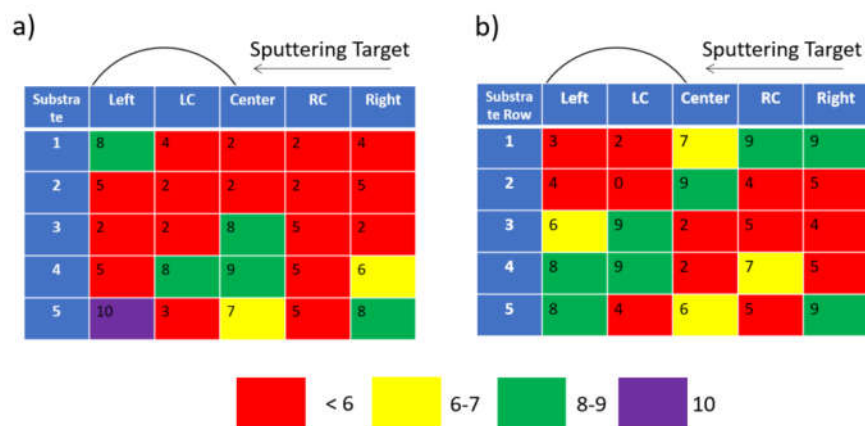


**Figure 4.7. Transparent device yield vs. rotation.** Heat maps illustrating the yields for devices with ITO top electrodes sputtered (a) without substrate rotation and (b) with a single 180° rotation. The legend at the bottom indicates the color codes for working device yields (out of 10).

Various ITO sputtering conditions have been investigated to improve transparent device yield. In the first yield optimization experiment, we fabricated 0.56mm<sup>2</sup> transparent devices with ClAlPc donors and tracked working yield (defined as number of non-shortcd devices per substrate) as a function of rotation condition (Figure 4.6) and the position of each substrate on the substrate holder. We found that depositing the first 50nm of the 100nm ITO layer without rotation, rotating 180°, and depositing the next 50nm produced the highest average yield. Heat maps illustrating the

difference in yield on each device substrate for the non-rotation and flip conditions are illustrated in Figure 4.7.

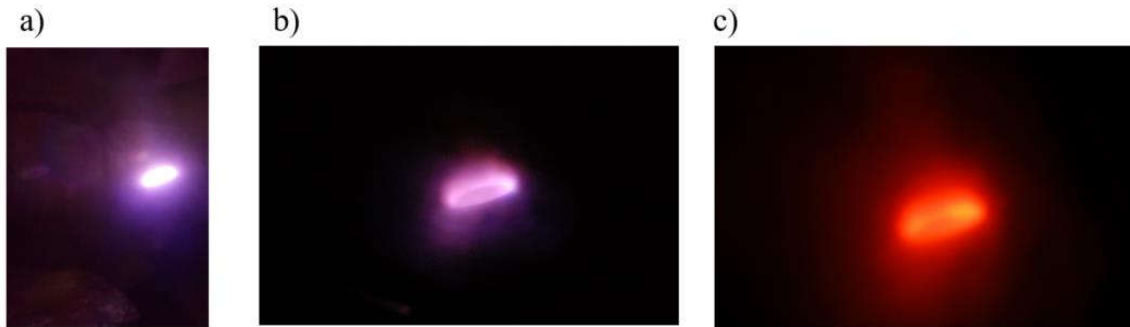


**Figure 4.8. Sputtering plasmas.** ITO sputtered with (a) Ar, (b) Kr, and (c) Ne plasma.

In addition to substrate rotation, we investigated alternative ionizing gasses for plasma sputtering including Kr, N<sub>2</sub>, and Ne for ITO deposition over organic devices (shown in Figure 4.8), as well as new transparent electrode materials including In-Al-Zn-O (IZAO) and In-Al-Zn-Sn-O (IZATO). IZAO is essentially indium oxide (In<sub>2</sub>O<sub>3</sub>) doped with zinc oxide (ZnO) and aluminum oxide (Al<sub>2</sub>O<sub>3</sub>), and consists of 90wt% In<sub>2</sub>O<sub>3</sub>, 5wt% ZnO, and 5wt% Al<sub>2</sub>O<sub>3</sub>.<sup>92</sup> IZAO is an amorphous transparent conductive oxide which may be employed in flexible panels due to its low

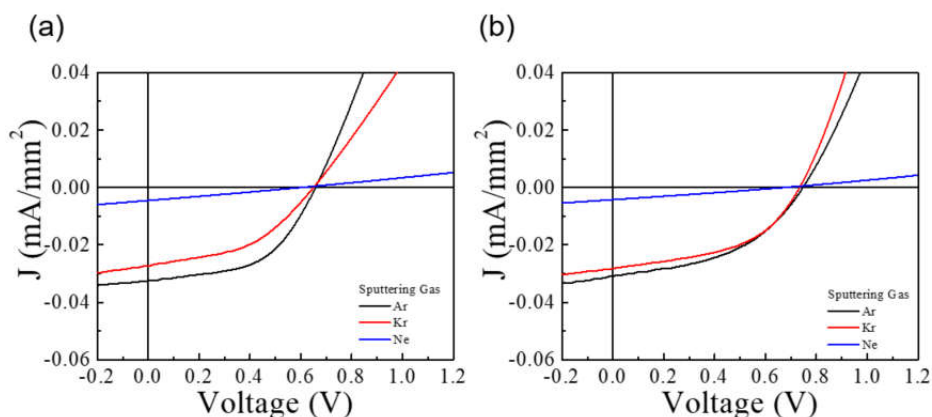


**Figure 4.9. Alternative ITO sputtering conditions.** (a) ClAlPc and (b) CyTPFB conventional planar devices with ITO top electrodes sputtered in Ar, Kr, and Ne at 0.02nm/s. The pressure used for Ar and Kr was 1.7 mTorr while that used for Ne was 6 mTorr.

content of grain boundaries, a feature not present in ITO due to the crystallinity of ITO.<sup>92</sup> For this experiment, IZATO consists of 88wt%  $\text{In}_2\text{O}_3$ , 4wt%  $\text{ZnO}$ , 4wt%  $\text{Al}_2\text{O}_3$ , and 4wt%  $\text{SnO}_2$  (prepared by Plasmaterials) We investigated IZATO specifically because we expected the presence of Sn would help to enhance the electrical conductivity similarly to ITO.

We have also performed preliminary work exploring the effects of alternative sputtering conditions on ITO, IZAO, and IZATO-coated conventional planar TPVs. Devices utilize one of two NIR-selective donors, ClAlPc and CyTPFB, the latter of which is a molecular salt with a heptamethine cation ( $\text{Cy}^+$ ) paired to the anion tetrakis(pentafluorophenyl)borate (TPFB).<sup>117</sup> To improve working yield, we deposited 2nm Ag/40nm  $\text{MoO}_3$  over the BCP for all devices. While we expected that the various kinetic energies of particles impacting the devices from different sputtering targets, gasses, flow rates, and deposition rates would affect the yield, we have also observed that performance is affected when alternative ionizing gasses are utilized with all three transparent electrode materials.

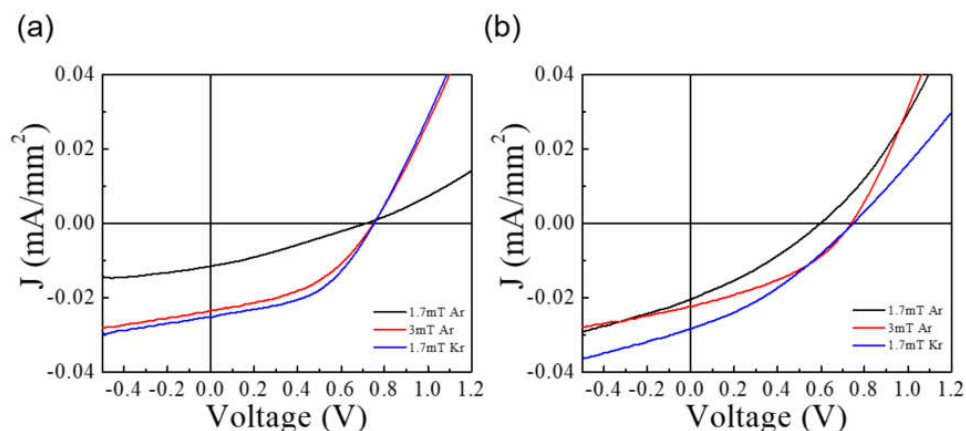


**Figure 4.10. ITO alternative electrodes.**  $J$ - $V$  data from transparent ClAlPc devices with (a) IZAO and (b) IZATO top electrodes sputtered in various ionizing gasses and flow pressures.

In the case of ITO (Figure 4.9), only insignificant change is observed in performance or yield between ClAlPc and CyTPFB devices with top electrodes sputtered in 1.7 or 3 mTorr Ar or Kr. CyTPFB devices exhibit a  $J_{sc}$ ,  $V_{oc}$ , and  $FF$  of  $0.032 \pm 0.002 \text{ mA/mm}^2$ ,  $0.65 \pm 0.01 \text{ V}$ , and  $0.48 \pm 0.03$  respectively with PCE of  $1.0 \pm 0.09\%$ . Similar performance is observed with the ClAlPc devices. However, performance is dramatically reduced when the lower atomic weight gasses Ne and  $\text{N}_2$  are used. When ITO is sputtered in Ne at 6 mTorr, the minimum pressure required to form Ne plasma,  $J_{sc}$  and  $FF$  in ClAlPc devices are reduced to  $0.003 \pm 0.001 \text{ mA/mm}^2$  and  $0.26 \pm 0.01$  respectively, however  $V_{oc}$  remains at  $0.69 \text{ V}$ , comparable to values observed with other gasses. A similar reduction in performance is observed in CyTPFB devices, where  $J_{sc}$  and  $FF$  are reduced to  $0.004 \pm 0.001 \text{ mA/mm}^2$  and  $0.26 \pm 0.01$  respectively while  $V_{oc}$  remains relatively unchanged at  $0.61 \pm 0.01 \text{ V}$ . If a working device is defined as one that exhibits a  $V_{oc}$  of at least  $0.6 \text{ V}$ , the yield is increased dramatically when ITO is sputtered in Ne from 3/16 to 8/16 for ClAlPc devices and from 6/12 to 10/12 for CyTPFB devices. These devices also exhibited similar performance and yield trends when the top ITO was sputtered in  $\text{N}_2$  at 1.7 mTorr, indicating that these results are most likely due to the atomic weight of the ionizing gas rather than the high pressure required for Ne sputtering. Given these results, it would appear that sputtering ITO in low atomic weight gasses is a considerably more gentle process than doing so in higher atomic weight gasses such as Ar or Kr, although ITO is also much more resistive in the former case.

Interestingly, IZAO and IZATO appear to yield improved device performance when deposited in Kr or high pressure Ar in the form of significantly enhanced  $J_{sc}$  and  $FF$  in the case of IZAO, and improved  $J_{sc}$  and  $V_{oc}$  in the case of IZATO across all ClAlPc and CyTPFB devices. The most dramatic changes are observed in the ClAlPc devices (Figure 4.10) with IZAO top

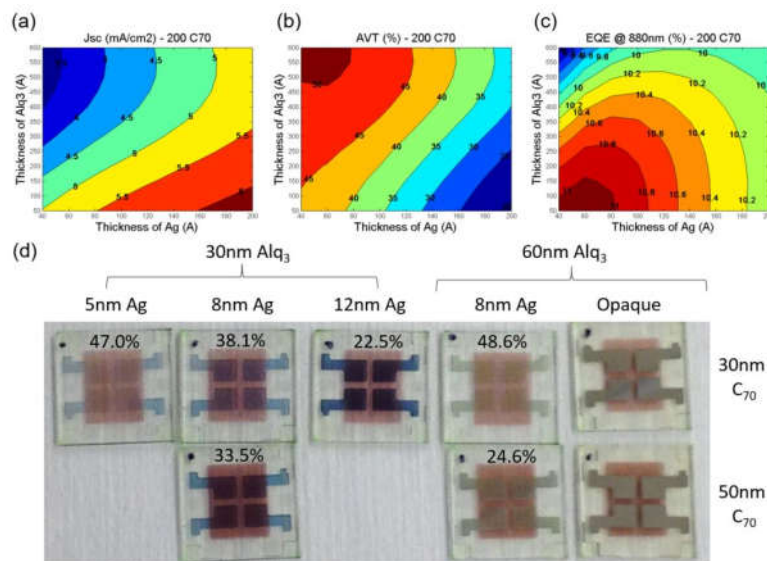


**Figure 4.11. Composite transparent electrode optimization.** (a)  $J_{sc}$ , (b)  $AVT$ , and (c)  $EQE$  for a conventional architecture with CyTPFB donor simulated according to Ag and Alq<sub>3</sub> thickness. (d) Devices with various thicknesses of Alq<sub>3</sub>, Ag, and C<sub>70</sub> with measured  $AVTs$  indicated.

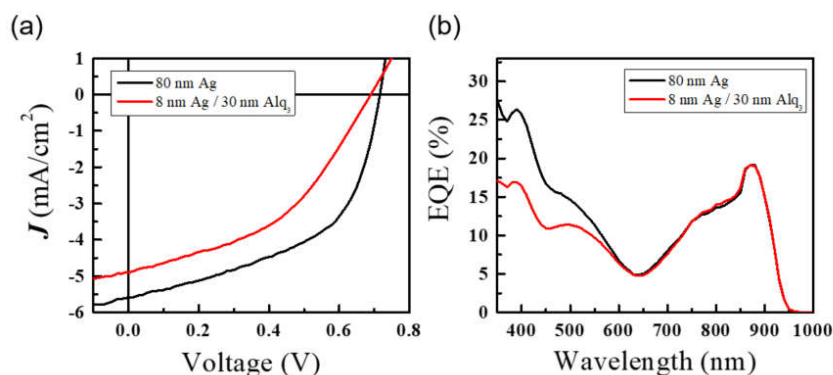


**Figure 4.12. Optimized transparent Ag/Alq<sub>3</sub> device.** (a)  $J-V$  and (b)  $EQE$  data for an opaque (black) and transparent device with an 8 nm Ag / 30 nm Alq<sub>3</sub> top electrode (red).

electrodes, where PCE is increased by 300% from  $0.21 \pm 0.03\%$  when IZAO is sputtered in Ar at 1.7mTorr to  $0.83 \pm 0.06\%$ , statistically identical to devices with ITO top electrodes ( $0.9 \pm 0.1\%$ ). This implies that reduced kinetic energy of sputtered particles colliding with high atomic weight (Kr) or high volume (high pressure Ar) gas somehow alters the conductivity of the resulting top electrode. The measured resistivity of isolated IZAO films deposited over glass is halved from 0.006 Ohm-cm when sputtered in Ar to 0.003 Ohm-cm when sputtered in Kr at the same pressure,

however the mechanism behind this reduction is yet to be fully understood. X-ray diffraction measurements and a larger range of flow pressures will be key in verifying and understanding the performance trend observed with these materials in the future.

In addition to the sputtered TCOs, we investigated thermally deposited thin Ag / Alq<sub>3</sub> composite electrodes to completely bypass the yield issues inherent to sputtering. Optimal Ag / Alq<sub>3</sub> thicknesses were determined in the following architecture: ITO (120 nm) / MoO<sub>3</sub> (10 nm) / CyTPFB (12 nm) / C<sub>70</sub> (20 nm) / BCP (7.5 nm) / Ag (*x* nm) / Alq<sub>3</sub> (*y* nm), where *x* and *y* were varied between 4-20 nm and 5-60 nm respectively. *J<sub>sc</sub>*, *AVT*, and *EQE* (880 nm) were simulated under normal illumination (Figure 4.11) using a transfer matrix model that considers layer thicknesses, refractive indices, optical absorption, and exciton diffusion lengths (CyTPFB and C<sub>60</sub>).<sup>104</sup> Alq<sub>3</sub> acts as an optical buffer which reduces electrode reflections and positions the electric field, and thus the highest population of excitons, near the donor/acceptor interface to maximize exciton dissociation efficiency.<sup>145</sup> *J-V* and *EQE* data for a representative device utilizing an optimized Ag (8 nm) / Alq<sub>3</sub> (30 nm) composite electrode are shown in Figure 4.12 alongside an opaque control. This optical layer can also simultaneously enhance the *AVT* significantly over just thin Ag alone. The transparent device matches the *EQE* of the opaque device around the absorption of CyTPFB while exhibiting an *AVT* of 40%.

In summary, we have demonstrated a route to the replacement of the cathode-side buffer layer with ZnS in TPV devices as well as investigated alternative TCOs, sputtering conditions, and thermally deposited composite electrodes to improve manufacturing yield. Co-depositing ZnS and Al<sub>2</sub>S<sub>3</sub> dramatically improves the device performance at 5 vol.% doping resulting in a *PCE* of 1.8 ± 0.1%, identical to control devices utilizing BCP. Sputtering ITO or the amorphous analogs using alternative gasses can improve device yield with modest losses in performance, while potentially

enabling mechanically flexible devices in the cases of IZAO and IZATO. Ag /Alq<sub>3</sub> could enable similar flexibility to IZAO and IZATO with the added benefit of a gentler deposition process.

## Chapter 5 – Near-Infrared Selective Organic Salt Photovoltaics

Organic molecular salts are an emerging and highly tunable class of materials for organic and transparent photovoltaics. In this chapter, we demonstrate novel phenyl borate and carborane-based anions paired with a NIR-selective heptamethine cation. We further explore the effects of anion structures and functional groups on both device performance and physical properties. Changing the functional groups on the anion significantly alters the open circuit voltage and yields a clear dependence on electron withdrawing groups. Anion exchange is also shown to selectively alter the solubility and film surface energy of the resulting molecular salt, enabling the potential fabrication of solution-deposited cascade or multi-junction devices from orthogonal solvents. This study further expands the catalog and properties of organic salts for inexpensive, and stable NIR-selective molecular salt photovoltaics.

### 5.1 Introduction to organic salts

Anion exchange with near-infrared (NIR)-selective cyanine ( $\text{Cy}^+$ ) heptamethine cations enables facile tuning of the frontier orbital energies, the interface gap (the difference in the donor highest occupied molecular orbital and the acceptor lowest unoccupied molecular orbital) between the salt donor and fullerene ( $\text{C}_{60}$ ) acceptor, and thus the  $V_{oc}$ .<sup>5, 115, 146</sup> This allows for the fabrication of Cy-based devices that approach the excitonic voltage limit. Because the  $\text{Cy}^+$  cation is primarily responsible for optical absorption, exchanging the anion does not significantly affect the spectral range or magnitude of the extinction coefficient (see Figure 5.1). Absorption is instead tuned via conjugation<sup>147</sup> of the cation molecule which can enable efficient NIR photoresponse at wavelengths of up to 1600nm,<sup>115</sup> ideal for applications in NIR-selective transparent photovoltaics (TPVs).<sup>116, 145</sup> While efficiencies have reached nearly 4% for this class of materials,<sup>148</sup> and

properties such as the HOMO and exciton diffusion have been linked to anion selection,<sup>5</sup> very little is known about the full range of tunability provided by anion pairing alone.

Here, we demonstrate alternative anions from two families, phenyl borates and carboranes, to determine the effects of the electron withdrawing groups and anion size on the performance and energy level alignment of devices utilizing the same  $\text{Cy}^+$  cation. We select anions from the family of phenyl borates because they afford large-sized anions which have previously been correlated with high *EDLs*.<sup>5</sup> Salt-based devices with tetrakis(pentafluorophenyl)borate (TPFB) anions greatly out-performed equivalent devices with smaller anions due to a high *EDL* and larger interface gap.

Carboranes are highly stable carbon-boron molecular clusters that have emerged recently for use as superacids<sup>149, 150</sup> and have been shown to serve as extremely low coordinating anions for use in organic salts, with demonstrated applications in fabricating molecular wires<sup>151</sup> and electrochemical capacitors.<sup>152</sup> They have also been employed in manipulating the band gap of emission layers to tune the emission color of phosphorescent organic light emitting diodes.<sup>115, 153</sup>

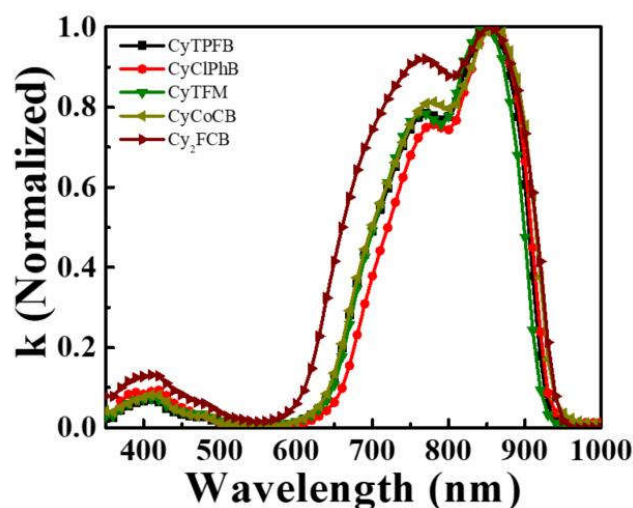


**Figure 5.1. Extinction coefficients for  $\text{Cy}^+$  cation with selected anions.** Normalized extinction coefficients representing optical absorption for CyTPFB, CyClPhB, CyTFM, CyCoCB, and  $\text{Cy}_2\text{FCB}$  salt films measured via spectroscopic ellipsometry highlighting little change in the bandgap or absorption spectra with changes in the anion.

Because of their low coordination, these anions may yield a path toward exceptionally stable organic salt PVs.

## 5.2 Anion effects on device performance

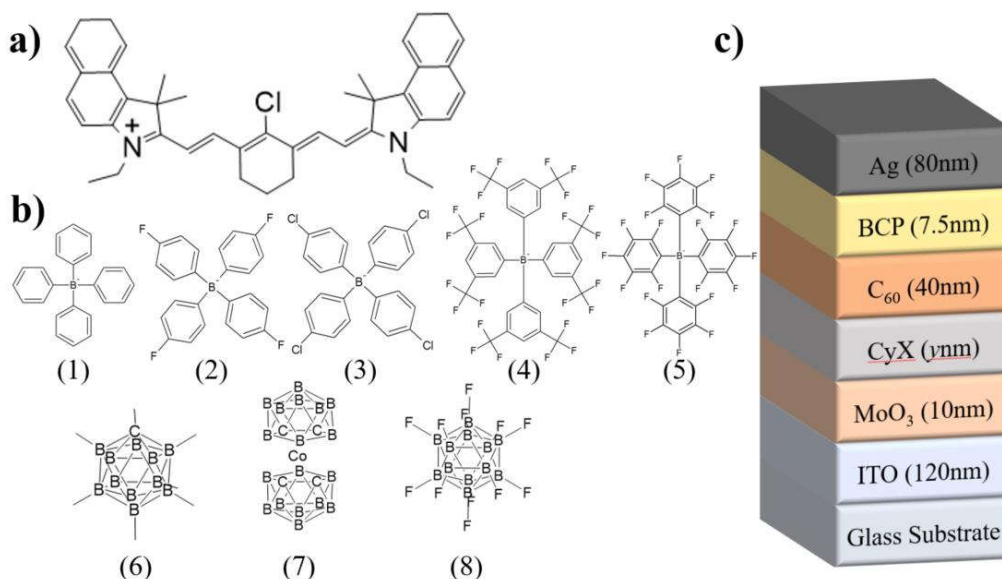


**Figure 5.2. Molecular salt structures and experimental device architecture.** (a) Chemical structure of the  $\text{Cy}^+$  heptamethine cation. (b) Chemical structures for tetraphenylborate (1) tetrakis(4-fluorophenyl)borate (FPhB) (2), tetrakis(4-chlorophenyl)borate (ClPhB) (3), tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFM) (4), tetrakis(pentafluorophenyl)borate (TPFB) (5),  $\text{CB}_{11}\text{H}_{12}$  (CBH) (6),  $\text{C}_4\text{B}_{18}\text{Co}$  (CoCB) (7), and  $\text{B}_{12}\text{F}_{12}$  (FCB) (8) anions. (c) Illustration of the photovoltaic device stack utilized in this study.

The phenyl borates investigated include tetraphenylborate (CyPhB), tetrakis(4-fluorophenyl)borate (CyFPhB), tetrakis(4-chlorophenyl)borate (CyClPhB), tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (CyTFM), and CyTPFB (control device) while the carboranes include  $\text{CB}_{11}\text{H}_{12}$  (CyCBH),  $\text{C}_4\text{B}_{18}\text{Co}$  (CyCoCB), and  $\text{B}_{12}\text{F}_{12}$  (Cy<sub>2</sub>FCB). The heptamethine cation and all anions are shown in Figures 5.2a and 5.2b, respectively. Cy salts were prepared by anion exchange of the parent CyI compound (see Chapter 3 for example exchange procedures). Mass

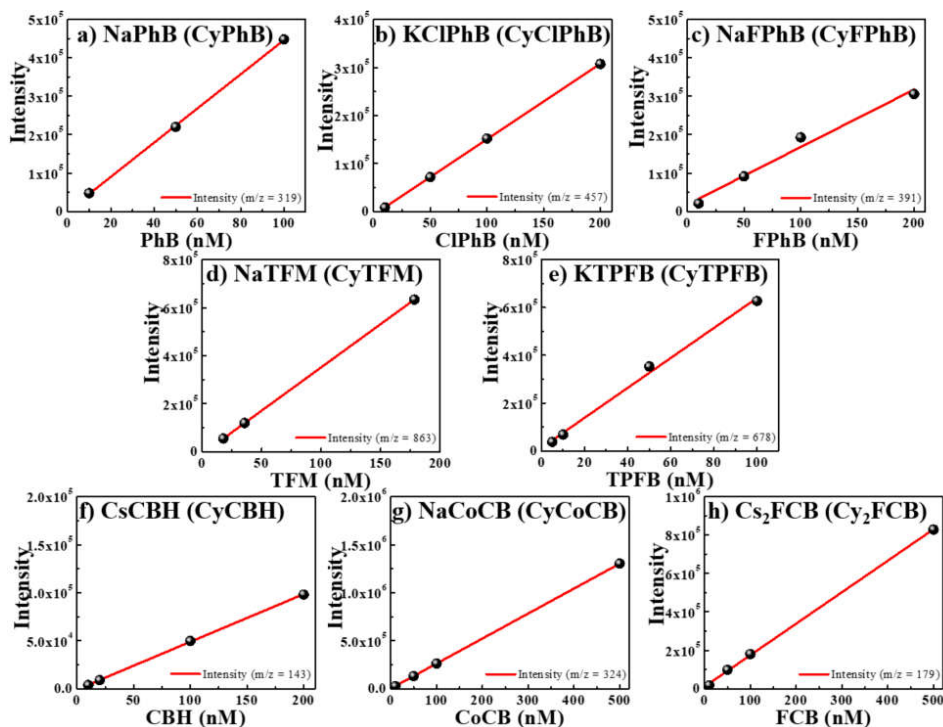


**Figure 5.3. Mass spectrometry calibration.** Calibration curves of intensity for  $m/z = 319$  (PhB) signal for NaPhB standard (a),  $m/z = 457$  (CIPhB) signal for KCIPhB standard (b),  $m/z = 391$  (FPhB) signal for NaFPhB (c),  $m/z = 863$  (TFM) signal for NaTFM standard (d),  $m/z = 678$  (TPFB) signal for KTPFB standard (e),  $m/z = 143$  (CBH) signal for CsCBH standard (f),  $m/z = 324$  (CoCB) signal for NaCoCB standard (g), and  $m/z = 179$  (FCB) signal for Cs<sub>2</sub>FCB standard (f).

spectrometry was utilized to confirm the product and determine yield for each cation-anion pairing (Figures 5.3 and 5.4). Photovoltaic devices were fabricated in the following architecture (Figure 5.2c): indium tin oxide (ITO) (120 nm) / MoO<sub>3</sub> (10 nm) / CyX ( $t_D$  nm) / C<sub>60</sub> (40 nm) / bathocuproine (BCP) (7.5 nm) / Ag (80 nm), where X is the anion paired with Cy<sup>+</sup> and  $t_D$  is the donor layer thickness. Cy donor layers were deposited from dimethylformamide (DMF) or chlorobenzene (CB) under nitrogen while all other layers were thermally deposited under vacuum. Cy layer thicknesses were controlled by varying the solution concentrations between 2-12 mg/mL to determine the effects of energy band bending on the interface gap.

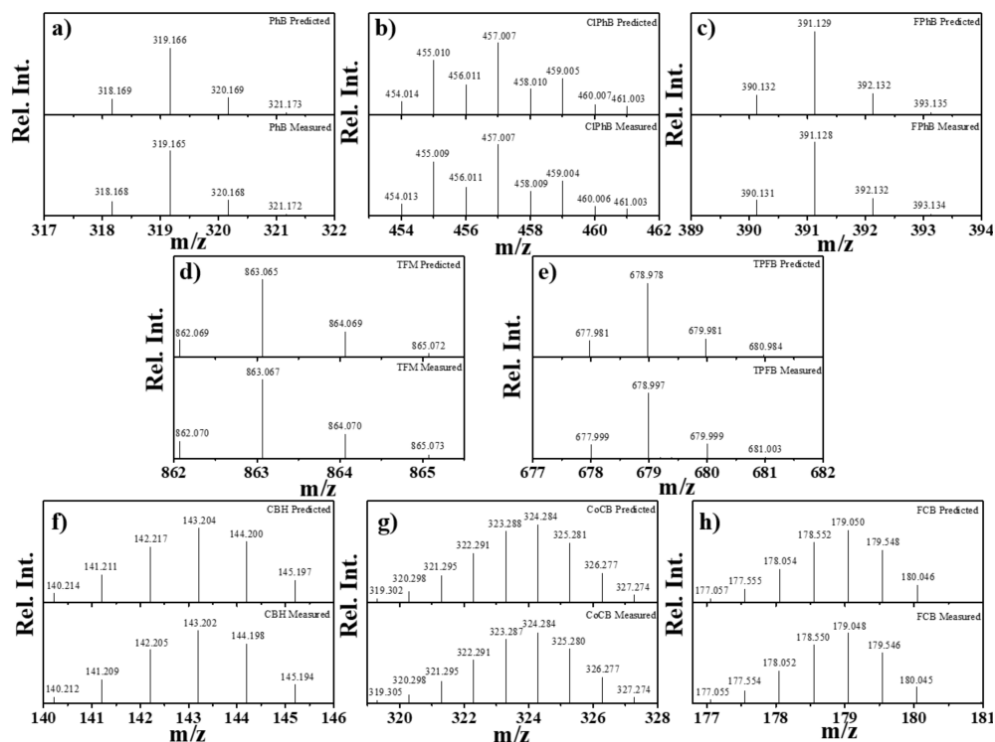


**Figure 5.4. Mass spectra.** High resolution mass spectrometry verification in negative mode electrospray ionization for CyPhB (a), CyClPhB (b), CyFPhB (c), CyTFM (d), CyTPFB (e), CyCBH (f), CyCoCB (g), and Cy<sub>2</sub>FCB (h). Predicted isotopic abundance peaks for each compound were generated using the Isotope Model tool in MassLynx software.

*J-V* and *EQE* characteristics of the devices utilizing each anion are shown in Figure 5.5, with average performance metrics for the optimum thicknesses and calculated donor *EDLs* shown in Table 5.1. *EDLs* were extracted from *EQE* data with a combined diffusion and optical interference model using least squares regression.<sup>154</sup> CyTPFB exhibits the overall highest power conversion efficiency (*PCE*) due to high combined  $J_{sc}$ ,  $V_{oc}$ , and *FF*. CyTFM exhibits similar *PCE* to CyTPFB because of high  $J_{sc}$  and  $V_{oc}$  likely due to a similar molecular size and HOMO respectively. On average, CyCoCB exhibits the best *PCE* of the carboranes due to high *FF* and  $V_{oc}$ , though CyCBH exhibits the best  $J_{sc}$  (and *EQE*) similar to that of CyTPFB. Each carborane exhibits a high *FF* indicating low series and high shunt resistance, however the  $V_{oc}$ s are considerably lower than CyTPFB and the rest of the functionalized phenyl borates. High  $J_{sc}$ s can

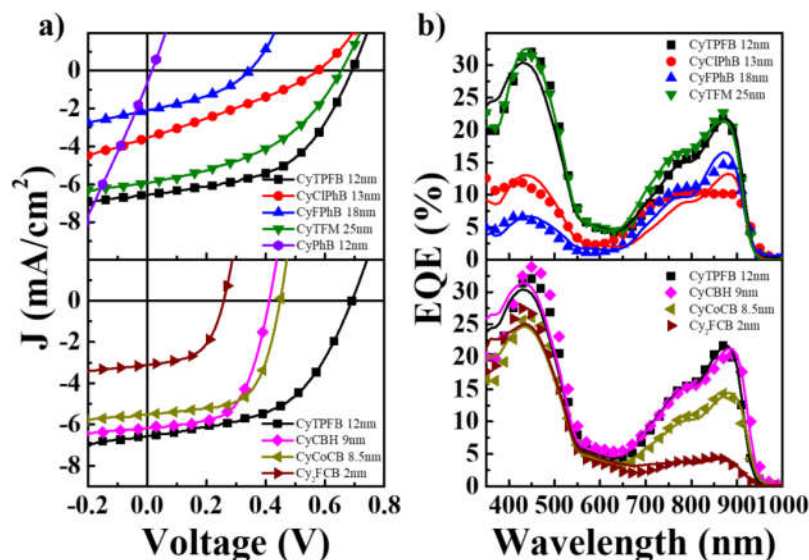


**Figure 5.5. Salt photovoltaic device data.** a) Current density-voltage ( $J$ - $V$ ) and b) external quantum efficiency ( $EQE$ ) characteristics for best devices. Symbols and lines in (b) correspond to measured and fitted  $EQE$  data respectively, the latter of which was generated when fitting spectra for exciton diffusion lengths shown in Table 5.1.

| Donor<br>(Thickness)         | $J_{sc}$<br>(mA/cm <sup>2</sup> ) | $V_{oc}$<br>(V) | FF              | PCE<br>(%)      | NIR EQE<br>(%) | EDL<br>(nm)   |
|------------------------------|-----------------------------------|-----------------|-----------------|-----------------|----------------|---------------|
| CyTPFB<br>(12nm)             | $5.6 \pm 0.6$                     | $0.66 \pm 0.03$ | $0.57 \pm 0.04$ | $2.1 \pm 0.1$   | 21.7           | $4.3 \pm 0.3$ |
| CyClPhB<br>(13nm)            | $3.5 \pm 0.3$                     | $0.59 \pm 0.05$ | $0.29 \pm 0.01$ | $0.59 \pm 0.06$ | 10.5           | $2.6 \pm 0.2$ |
| CyFPhB<br>(18nm)             | $2.1 \pm 0.2$                     | $0.36 \pm 0.01$ | $0.36 \pm 0.01$ | $0.27 \pm 0.03$ | 14.9           | $3.4 \pm 0.1$ |
| CyTFM<br>(25nm)              | $5.9 \pm 0.6$                     | $0.69 \pm 0.04$ | $0.42 \pm 0.01$ | $1.7 \pm 0.2$   | 20.7           | $7.5 \pm 0.4$ |
| CyPhB<br>(12nm)              | $0.65 \pm 0.06$                   | $0.02 \pm 0.01$ | $0.25 \pm 0.01$ | 0               | 0              | -             |
| CyCBH<br>(9nm)               | $5.7 \pm 0.3$                     | $0.42 \pm 0.01$ | $0.56 \pm 0.03$ | $1.3 \pm 0.1$   | 20.4           | $3.6 \pm 0.3$ |
| CyCoCB<br>(8.5nm)            | $5.2 \pm 0.3$                     | $0.45 \pm 0.01$ | $0.61 \pm 0.01$ | $1.4 \pm 0.1$   | 14.3           | $2.5 \pm 0.2$ |
| Cy <sub>2</sub> FCB<br>(2nm) | $3.0 \pm 0.2$                     | $0.27 \pm 0.01$ | $0.53 \pm 0.01$ | $0.42 \pm 0.04$ | 4.4            | $1.0 \pm 0.1$ |

**Table 5.1. Salt device performance parameters.** Average performance parameters for optimum donor thicknesses, donor (near-infrared) external quantum efficiency ( $EQE$ ) peak values, and exciton diffusion lengths ( $EDL$ s) calculated from  $EQE$  data in Figure 5.4.

be attributed to improved  $EDL$ s over the smaller phenyl borates, though the mechanism for this improvement is unclear.

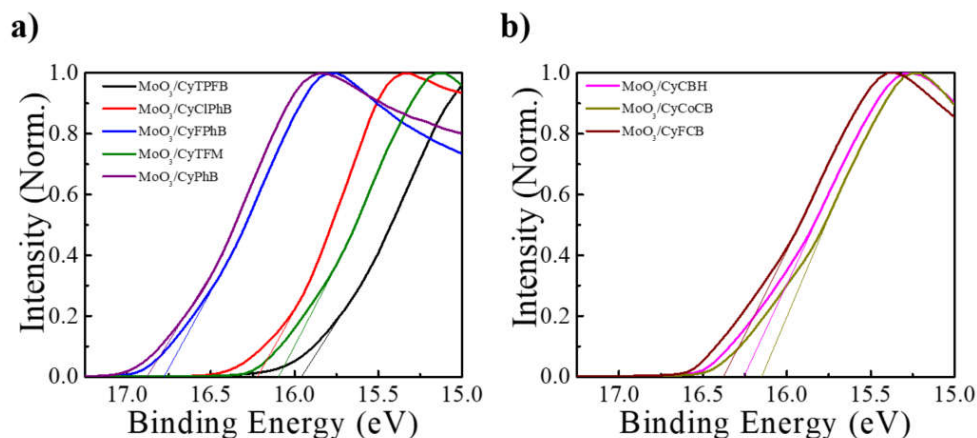


**Figure 5.6. Measured salt work functions.** Ultraviolet photoelectron spectroscopy (UPS) data for salts with (a) phenyl borate and (b) carborane anions.

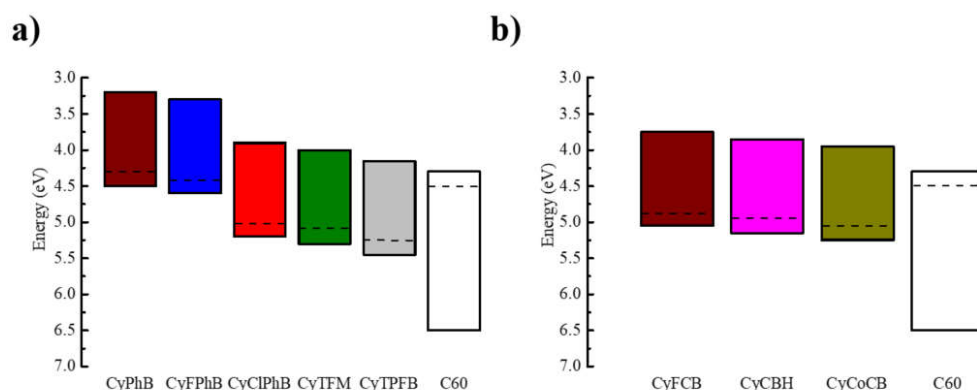


**Figure 5.7. Salt energy levels.** Energy diagrams measured for salts with phenyl borate (a) and carborane (b) anions. HOMOs are estimated as a 0.2 eV offset below the measured work functions while LUMOs are approximated as the HOMO level plus the optical excitonic gap (1.3 eV). The HOMO trends follow the observed  $V_{oc}$  trends with respect to anion.

Ultraviolet photoelectron spectroscopy (UPS) data and estimated energy levels for each salt are shown in Figures 5.6 and 5.7. A high degree of fluorination on the anion is correlated with a deepening of the HOMO and LUMO of the salt donor.<sup>5, 115</sup> Electron withdrawing groups consisting of electronegative atoms such as fluorine on the anion may induce a molecular dipole interaction (analogous to an interface dipole) between the anion and cation, shifting the HOMO and LUMO of the collective salt away from the vacuum level. The lack of fluorination on the PhB anion is more likely to yield a low ionization energy that results in a nearly negligible interface

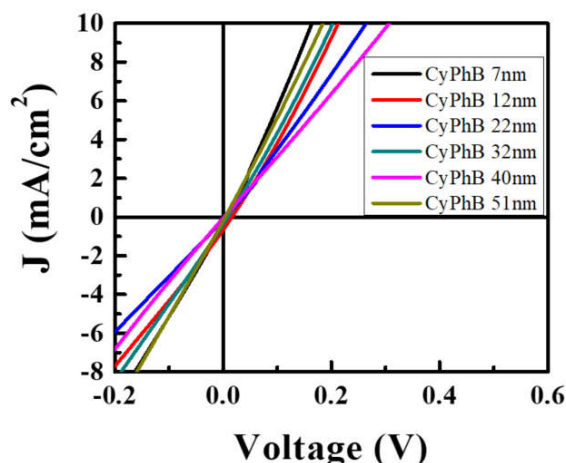


**Figure 5.8. CyPhB Thickness Dependence.** Current ( $J$ )-voltage ( $V$ ) characteristics for devices with several CyPhB donor layer thicknesses. Devices exhibit small photocurrent and photovoltage and high leakage current due to a nearly negligible interface gap between CyPhB and  $C_{60}$ .

gap with  $C_{60}$ . This explains why the CyPhB devices exhibit little  $J_{sc}$  and  $V_{oc} < 0.1$  V and high leakage current (Figure 5.8) across all donor thicknesses. The higher  $V_{oc}$ s exhibited by the other salts can then be attributed to the electronegativities of atoms in the electron withdrawing groups, with the highest  $V_{oc}$ s exhibited by CyTFM and CyTPFB owing to high degrees of distributed fluorination. This range of anions thus allows  $> 1$  eV modulation of the HOMO. Thickness dependent performance data for the phenyl borates and carboranes are shown in Figure 5.9. All anions follow a similar trend in  $J_{sc}$  with respect to thickness, where enhanced optical absorption efficiency yields a modest  $J_{sc}$  improvement as thickness is increased from 5 nm. As thickness is further increased beyond 20 nm, the optical absorption is offset by losses in exciton diffusion and carrier collection efficiencies as thickness exceeds the exciton diffusion and carrier collection lengths. Carrier collection loss is also mirrored by losses in the  $FF$ . The  $J_{sc}$  trend is correlated with the thickness dependence observed in the salt donor (NIR) portion of the  $EQE$  data (Figure 5.10).

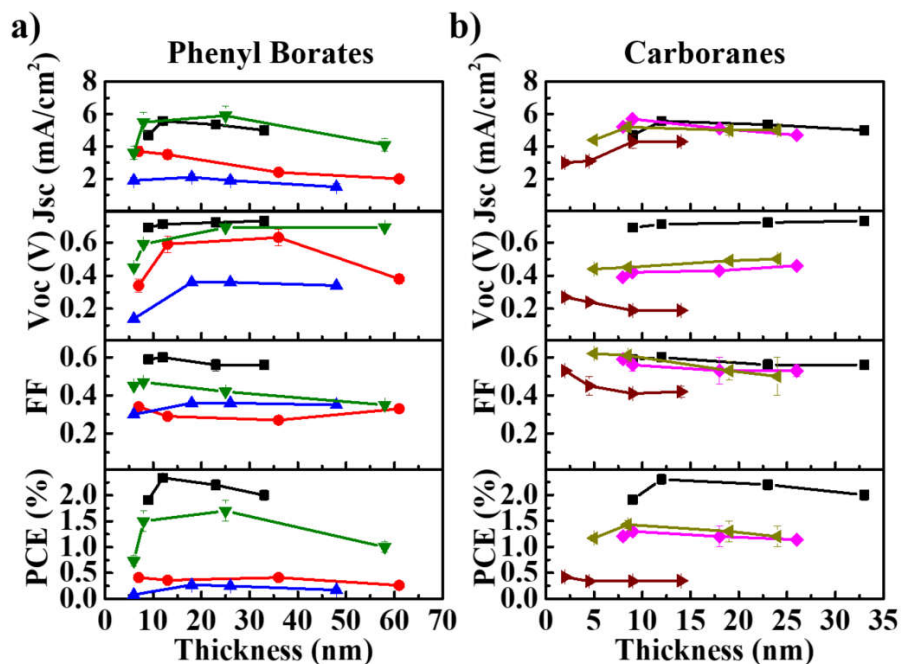


**Figure 5.9. Salt performance thickness dependence.** Thickness dependent performance data for salt devices with (a) phenyl borate and (b) carborane anions. The symbols and colors correspond to the anions in Figure 5.5.

The *EQE* roll-off is determined largely by the *EDL*, where a high *EDL* as calculated for CyTFM yields a more gradual roll-off with increasing thickness. Other anions exhibit higher rates of *EQE* loss with increasing thickness indicative of either their shorter *EDL*s or charge collection lengths.

Most anions follow a similar voltage trend in which  $V_{oc}$  improves as thickness is increased from 5 nm and levels off before recombination losses begin to dominate at high thicknesses for CyClPhB and CyFPhB. CyCBH, CyCoCB, and CyTPFB show more limited  $V_{oc}$  trends as a function of thickness, and Cy<sub>2</sub>FCB exhibits an opposing voltage trend where  $V_{oc}$  is maximized at the lowest thicknesses. AFM and cross-sectional scanning electron microscopy (SEM) data, shown in Figures 5.11 and 5.12, indicate smooth donor/acceptor interfaces. Although there may be some intermixing between the salts and C<sub>60</sub> shown in the SEM images as evidenced by charging near the interface, this appears to occur over a distance of ~2 nm and is thus not likely to impact the  $V_{oc}$

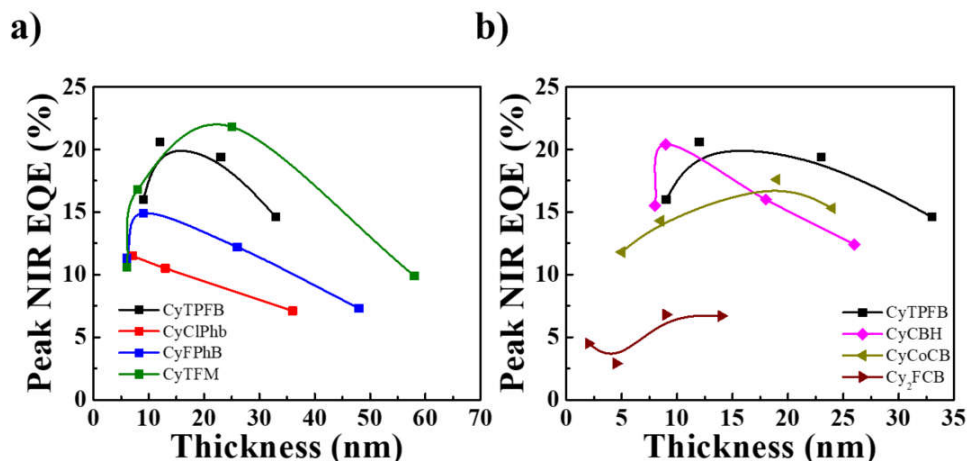


**Figure 5.10. Near-infrared EQE thickness dependence.** NIR *EQE* peaks for phenyl borate (a) and carborane (b) anion salt devices as a function of salt layer thickness. The solid lines are guides to the eye.

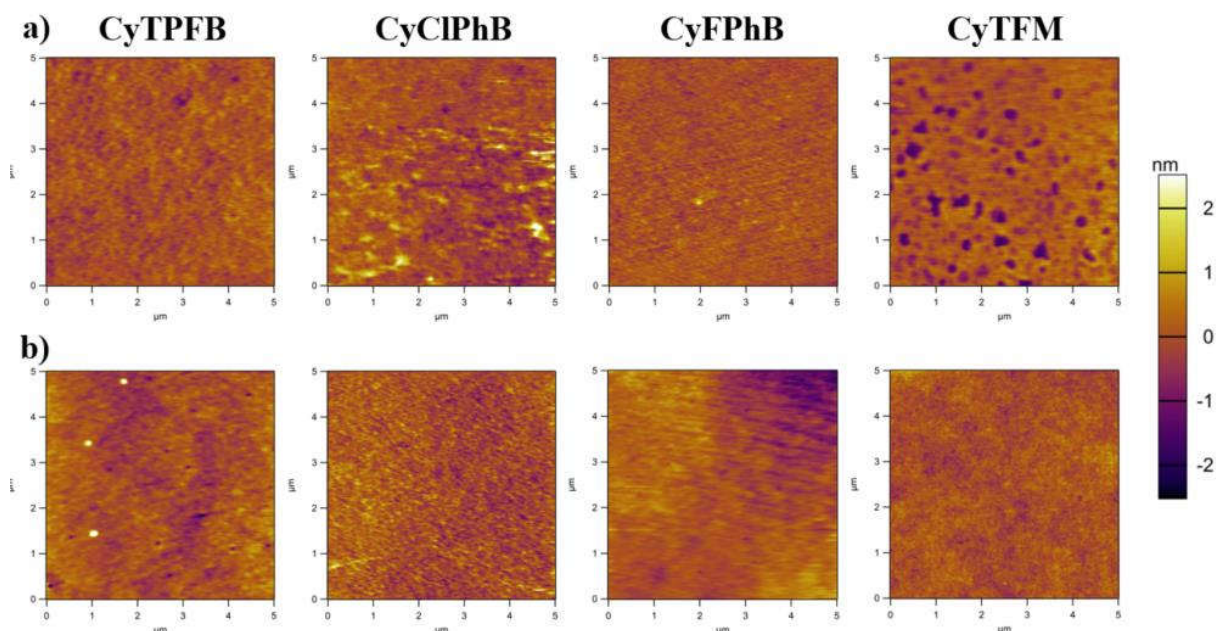


**Figure 5.11. Salt film morphologies.** Atomic force microscopy (AFM) data taken from isolated films of CyTPFB, CyClPhb, CyFPhB, and CyTFM deposited over Si from 2 mg/ml (a) and 12 mg/ml (b) solutions. The roughness scale used for all images is shown at the right. Salt films are smooth across the two thickness extremes, which suggests that roughness does not play a large role in the voltage changes observed with increasing thicknesses of CyClPhb, CyFPhB, and CyTFM.

of devices. It is important to note that anionic diffusion from other molecular salts into C<sub>60</sub> has been observed for small halide ions<sup>155</sup> and while this process could potentially affect the  $V_{oc}$

| Salt    | 2mg/ml<br>Roughness<br>(nm) | 12mg/ml<br>Roughness<br>(nm) |
|---------|-----------------------------|------------------------------|
| CyTPFB  | $0.26 \pm 0.01$             | $0.36 \pm 0.04$              |
| CyClPhB | $0.44 \pm 0.03$             | $0.40 \pm 0.03$              |
| CyFPhB  | $0.25 \pm 0.01$             | $0.4 \pm 0.1$                |
| CyTFM   | $0.41 \pm 0.03$             | $0.27 \pm 0.01$              |

**Table 5.2. Measured salt roughness.** Calculated RMS roughness values from the AFM data in Figure 5.11.

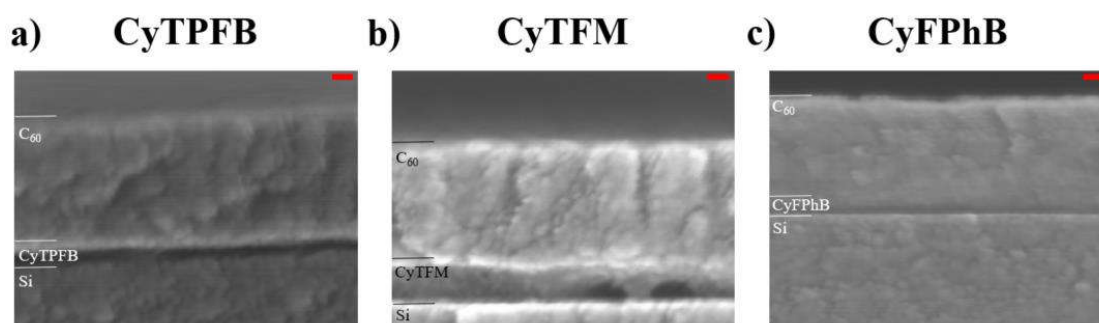


**Figure 5.12. Salt- $C_{60}$  interfacial morphologies.** Cross-sectional scanning electron microscopy (SEM) images taken from (a) CyTPFB, (b) CyTFM, and (c) CyFPhB /  $C_{60}$  bilayers deposited over Si (from bottom to top: Si / Salt /  $C_{60}$ ). The bright bands ( $\sim 2$  nm) between the salt and  $C_{60}$  layers suggests possible molecular intermixing resulting in higher resistivity and slight charging. The red scale bars at the top right corner of each image indicate a distance of 10 nm.

through changes in the interface gap, it is reported to occur over several weeks and is thus unlikely to affect newly fabricated devices with much larger counterions. The more pronounced voltage trends exhibited by CyClPhB, CyFPhB, CyTFM, and Cy<sub>2</sub>FCB are instead caused by band bending of the salt donors and concomitant changes in the interface gap as illustrated in Figure 5.13 and as seen in previous work with other anions.<sup>115</sup> Other anions show only modest changes in  $V_{oc}$  with thickness which are instead attributed to increased series resistance. Since the FCB anion carries a -2 charge, Cy<sub>2</sub>FCB layers contain higher packing densities of Cy<sup>+</sup> cations yielding lower  $J_{sc}$  and  $V_{oc}$  likely from Coulombic scattering interactions with FCB.

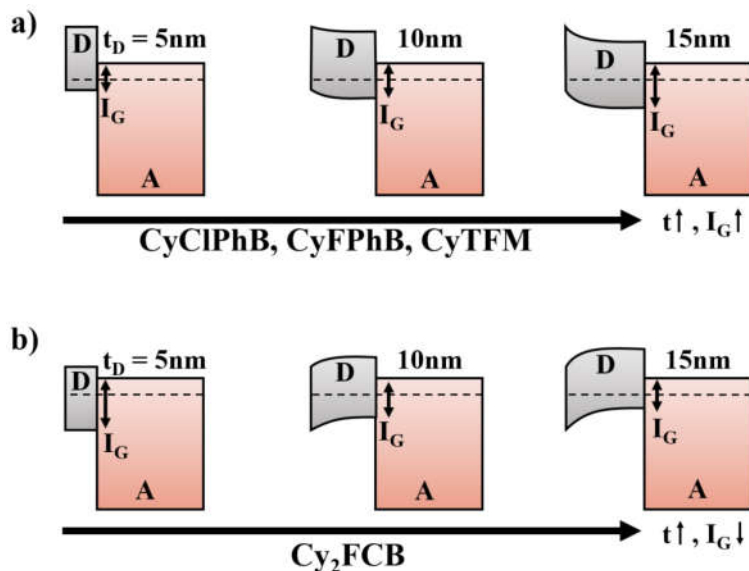


**Figure 5.13. Anion band bending.** Schematic donor-acceptor (D-A) band structures illustrating changes in interface gap ( $I_G$ ) as a function of donor thickness ( $t_D$ ). Anions given in (a) yield increasing  $I_G$  with increasing thicknesses while Cy<sub>2</sub>FCB yields the opposite trend illustrated in (b).

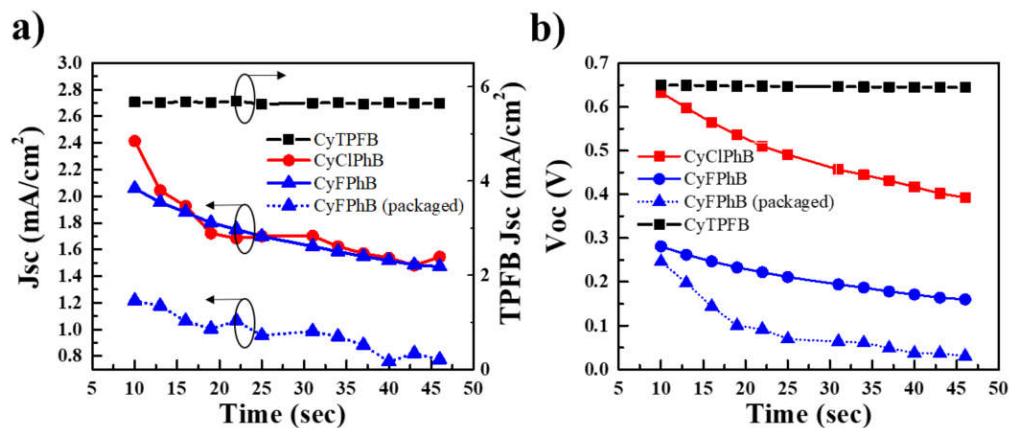


**Figure 5.14. Rapid photodegradation of CyFPhB and CyClPhB.**  $J_{sc}$  (a) and  $V_{oc}$  (b) parameters for CyClPhB, CyFPhB, and CyTPFB devices extracted from  $J$ - $V$  curves taken over 50 seconds under illumination from a Xe arc lamp. "Packaged" CyFPhB devices were sealed under UV-cured epoxy in a nitrogen environment prior to illumination and testing. While many of the salts are highly stable, the CyFPhB and CyClPhB stood out as being particularly unstable.

While CyTPFB shows no appreciable degradation, CyFPhB and CyClPhB devices show a surprising lack of photostability compared to all other anions (see Figure 5.14).  $J_{sc}$  diminishes by approximately 30% for CyFPhB and 35% for CyClPhB, while  $V_{oc}$  diminishes by around 35% for

both architectures after less than several minutes of direct illumination in air or under epoxy packaged in a nitrogen environment. This suggests that the rapid degradation is not due solely to air exposure, although parts per million of oxygen could be absorbed into the active films prior to packaging even in a nearly pure nitrogen environment.

Photoinduced reactive oxygen species, including superoxide radical and singlet oxygen (formed from intersystem crossings to adsorbed oxygen molecules)<sup>156</sup> are well-known degradation mechanisms in organic PVs due to their tendency to react with and photobleach active materials. Additionally, carbonyl groups formed from singlet oxygen interactions are known to be efficient exciton quenchers<sup>157</sup> and further compound device performance losses. Singlet oxygen formation is likely if there is a favored intersystem crossing from the singlet to triplet state of the organic material. However, because the triplet resides on the cation and the overall intersystem crossing rate is not likely to be impacted by the presence of different anions, it is more likely electron or hole injection to form superoxide species that result in degradation. The formation of superoxide species has been proposed elsewhere<sup>158</sup> as a charge transfer process in competition with exciton recombination and charge carrier extraction provided that the HOMO or LUMO of the donor or acceptor is closer to the vacuum level than the ground state of adsorbed oxygen. Large ionization energies can thus act as barriers against superoxide formation. We therefore attribute the rapid degradation of CyFPhB and CyClPhB to low ionization energies compared to the other salts due to lower concentrations of intramolecular polar bonds<sup>159</sup> and electron withdrawing groups.

### **5.3 Physical properties of organic salts and salt films**

Contact angles, calculated surface energies, and solubilities for a range of anions are listed in Table 5.3. From the water contact angle data, we observe that the anion has a pronounced effect on the hydrophobicity of the salt film, where the contact angle can be increased from  $58 \pm 4^\circ$

(weakly hydrophilic) for CyTFM to  $99.8 \pm 0.4^\circ$  (hydrophobic) for CyTPFB. Representative photographs of water droplets on various salts used to measure the water contact angles are shown in Figure 5.15. It should be reiterated that all the salts investigated here exhibit little surface roughness as shown in Figure 5.11. This ability to tune the surface energy and moisture interactions with the donor layer is also beneficial to overall device stability (see Section 6.2) and improve the flexibility in processing multi-layer devices.

In addition to the surface energy, the anion can also significantly impact the solubility in particular solvents. For example, the anion plays a significant role for dissolution in CB but very little role in water or DMF. Phenyl borate solubilities in CB are reduced from 21 mg/mL for CyFPhB to 0.45 mg/mL for CyPhB, while those of the carboranes are approximately equal ( $\leq 0.28$  mg/mL). CyI and CyPF<sub>6</sub> from previous work<sup>5</sup> also exhibit low solubilities  $\leq 2$  mg/mL in CB. The phenyl borates exhibit higher solubilities in CB than the other salts likely due to similarly

| Salt                | Water Angle (Degrees) | DIM Angle (Degrees) | Surface Energy (mN/m) | Solubility in CB (mg/mL) | Solubility in DMF (mg/mL) | Solubility in Water (mg/mL) |
|---------------------|-----------------------|---------------------|-----------------------|--------------------------|---------------------------|-----------------------------|
| CyTPFB              | $99.8 \pm 0.4$        | $52 \pm 4$          | $38 \pm 3$            | 2.4                      | 10                        | $7 \times 10^{-5}$          |
| CyClPhB             | $76 \pm 3$            | $8.7 \pm 0.6$       | $52 \pm 4$            | 7.7                      | 10                        | $3 \times 10^{-5}$          |
| CyFPhB              | $72.9 \pm 0.5$        | $6 \pm 1$           | $51 \pm 9$            | 21                       | 10                        | $2 \times 10^{-5}$          |
| CyTFM               | $58 \pm 7$            | $50 \pm 4$          | $43 \pm 5$            | 19                       | 10                        | $1 \times 10^{-4}$          |
| CyPhB               | $77 \pm 3$            | $8 \pm 2$           | $50 \pm 10$           | 0.45                     | 6.3                       | $2 \times 10^{-5}$          |
| CyCBH               | $70 \pm 2$            | $7.2 \pm 0.7$       | $51 \pm 5$            | 0.28                     | 10                        | $2 \times 10^{-5}$          |
| CyCoCB              | $80 \pm 1$            | $13 \pm 2$          | $53 \pm 8$            | 0.27                     | 10                        | $2 \times 10^{-5}$          |
| Cy <sub>2</sub> FCB | $76.3 \pm 0.4$        | $24.6 \pm 0.4$      | $47 \pm 0.8$          | 0.023                    | 10                        | $4 \times 10^{-5}$          |
| CyI                 | $71 \pm 2$            | 0                   | $55 \pm 5$            | 1                        | 12                        | $7 \times 10^{-5}$          |
| CyPF <sub>6</sub>   | $75 \pm 4$            | $25 \pm 2$          | $47 \pm 3$            | 2                        | 9                         | $5 \times 10^{-5}$          |

**Table 5.3. Salt energy and solubility data.** Water and diiodomethane (DIM) contact angles, surface energies, and solubilities in chlorobenzene (CB), dimethylformamide (DMF), and water measured for salt films utilizing selected anions from Ref. 5 and the phenyl borate and carborane anions from this study.

structured phenyl groups of the anion enabling higher miscibility. Solubility differences in CB across the phenyl borates can be explained by differences in polarity in the phenyl groups; CyFPhB is especially soluble with the single fluorine on the phenyl group compared to the non-functionalized phenyl rings on CyPhB, which are more non-polar. Solubilities in DMF are consistently about 10 mg/mL across all anions including the carboranes, while those in water are quite low ( $< 1 \times 10^{-4}$  mg/mL) for both phenyl borates and carboranes. The molecular structures of these solvents are less similar to those of the anions. The solubility differences between DMF and water might be attributed to differences in solvent molecular size, where larger DMF molecules are able to separate cation and anion molecules over greater distances, yielding more efficient ion dissociation and greater solubility. The development of solvent orthogonality with each of the salts is an enticing prospect that could allow consecutive solution depositions of salts to fabricate potential cascade (three or more active layers with HOMO-LUMO offsets favoring exciton dissociation and charge transfer at each interface)<sup>160</sup> or multi-junction<sup>161</sup> architectures with different cations for complementary NIR optical absorption.

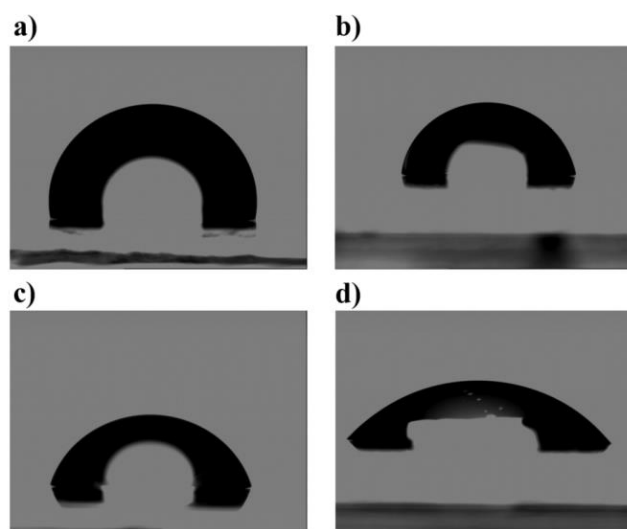


**Figure 5.15. Tuning hydrophobicity.** Photographs of water droplets on 50 nm films of a) CyTPFB, b) CyCoCB, c) CyCBH, and d) CyTFM (shown in order of decreasing contact angle) illustrate the ability to tune the hydrophobicity of the salt via anion exchange.

The anion exchange pathway provides an opportunity to compose safer and more stable chemicals by design. Approaches to reduce toxicity include avoiding toxicophores and substitutions using isosteres which have similar electronic characteristics but lower toxicity.<sup>162</sup> Design rules to hinder degradation should favor halogens, mostly chlorine and fluorine, chain branching, and nitrogen that are utilized here.<sup>163</sup>

## 5.4 Large area devices

We have fabricated transparent 5 cm<sup>2</sup> CyTPFB devices to determine the viability of scaling organic salt PVs to larger sizes than the 5.2 mm<sup>2</sup> devices discussed earlier in this chapter. *J-V* data are shown with a photograph of an example device with 67% *AVT* in Figure 5.16. A 4 nm Ag / 60 nm Alq<sub>3</sub> composite electrode was used to optimize performance and reduce optical reflections. While the *J<sub>sc</sub>* and *FF* are considerably reduced compared to the smaller scale devices likely due to poor conductivity in the top electrode, the device still outputs a photocurrent of approximately 10 mA under 1 sun. *J<sub>sc</sub>* and *FF* can both be potentially recovered through gains in carrier collection efficiency and series conductivity with the deposition of a conductive Ag microgrids over the top electrode, discussed in Chapter 8.

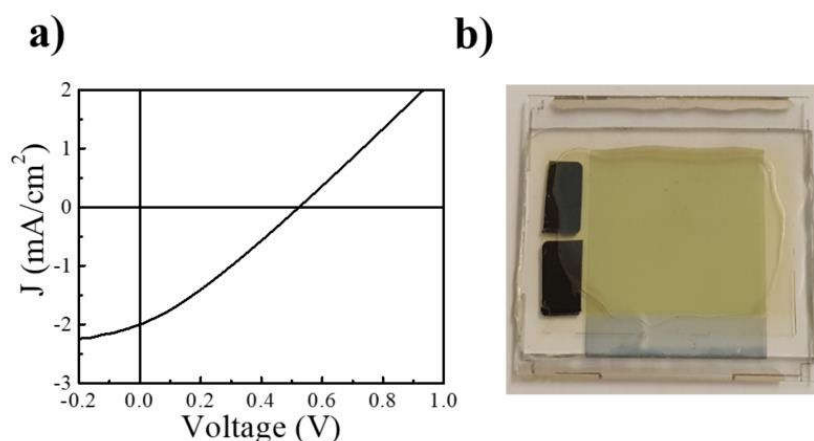


**Figure 5.16. Large area device.** (a) *J-V* and (b) a photograph of a representative 5 cm<sup>2</sup> area transparent CyTPFB device.

In summary, we have demonstrated organic molecular salts utilizing a range of phenyl borate and carborane anions for wavelength-selective photovoltaic applications. The phenyl borates demonstrate the full breadth of the effects of electron withdrawing functional groups on the density of states in a NIR-selective heptamethine salt, while the carboranes introduce a potential pathway toward highly stable organic wavelength-selective photovoltaics. This study explores the performance and physical effects of the new anions while relating the latter to previously demonstrated anions with different molecular structures. The ability to tune the interface gap, surface energy, and solubility through anion exchange offers a promising pathway toward tunable, efficient, safe, and stable NIR-selective transparent photovoltaics.

## Chapter 6 – Phthalocyanine and Organic Salt Bulk Heterojunctions

In this chapter, we discuss initial results in the optimization of BHJs and PMHJs for TPVs. This work is focused on both ClAlPc-fullerene and organic salt-fullerene architectures. ClAlPc and the molecular salts both have excellent potential for use in TPVs due to their selective NIR absorbance. Since they also feature complementary absorption regimes, they will be desirable for use in future high efficiency multi-junction TPVs. ClAlPc can be thermally evaporated with C<sub>60</sub> or C<sub>70</sub> to achieve precise control of the thickness and morphology of the mixed layer. Since molecular salts (CyTPFB and CyTRIS) decompose when before they thermally evaporate, they must be solution deposited with a soluble acceptor such as phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) or indene-C<sub>60</sub> bis-adduct (ICBA).

### 6.1 ClAlPc PMHJs

We fabricated PMHJ architectures by inserting a mixed layer of ClAlPc and C<sub>60</sub> or C<sub>70</sub> between neat layers of the same materials. The experimental device stack deposited over pre-patterned ITO substrates was: AZO (10nm)/ C<sub>60</sub> (30nm)/ ClAlPc:C<sub>60</sub> ( $x, y$ )/ ClAlPc (12.5nm)/ MoO<sub>3</sub> (100nm)/ITO (100nm). Planar, opaque devices with Ag top electrodes served as controls. Beginning with a ClAlPc:C<sub>60</sub> volumetric ratio of 1:1 deposited via thermal co-deposition, inverted devices were fabricated with mixed layer thicknesses of  $x = 2.5, 5, 7.5, 10$ , and 12.5nm. To keep the total thickness of donor/acceptor material constant, half the thickness of the mixed layer was subtracted from that of the neat ClAlPc and fullerene layers so that any enhanced performance would originate from the presence of the mixed layer and not from additional optical absorption. This experiment yielded an optimal mixed layer thickness of 10nm, which was then held static as mixed layer concentration was varied at ClAlPc:C<sub>60</sub> volumetric concentrations of  $y = 1:2, 1:1, 2:1$ ,

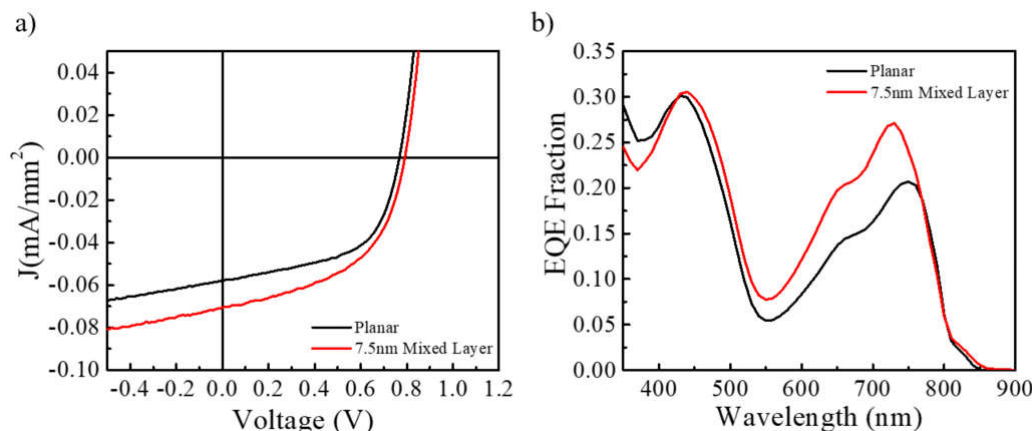


**Figure 6.1. Optimized ClAlPc:C<sub>60</sub> PMHJ.** (a)  $J$ - $V$  data and (b)  $EQE$  spectra for opaque planar and 7.5nm 1:1 mixed ClAlPc-C<sub>60</sub> devices

3:1, 4:1, and 5:1. Due to a morphology-induced change in series resistance, mixed layer thickness was varied a second time at the optimal volumetric ratio to achieve an optimized  $PCE$  for this architecture. This experiment was repeated with C<sub>70</sub> utilized as the acceptor due to enhanced optical absorption over C<sub>60</sub>. In the C<sub>70</sub> case, we reduced the thickness of the acceptor (C<sub>70</sub>) layer to 15nm to preserve visible transmission.

Figure 6.1 shows the performance enhancement brought about by a PMHJ architecture in opaque devices. In these champion conventional planar and 7.5nm 1:1 mixed layer devices,  $PCE$  is enhanced from 2.5% to 2.8% mainly due to an improvement in  $J_{sc}$  from 0.05 to 0.07mA/mm<sup>2</sup> via improved exciton dissociation efficiency.  $FF$  is reduced slightly because of increased series resistance from the non-optimized mixed layer, however this loss is more than compensated by the improvement in  $J_{sc}$ .

In the  $C_{60}$  case, we find that the initial mixed layer thickness optimization at 1:1 concentration yields a transparent  $PCE$  of  $0.9\pm0.1\%$  ( $x = 10\text{nm}$ ), with a champion  $PCE$  of 1%. Further optimization of the volumetric ratio yields a  $PCE$  of  $1.15\pm0.09\%$  at a ClAlPc: $C_{60}$  ratio of 4:1, with a champion  $PCE$  of 1.24% due to enhanced  $J_{sc}$  over the planar devices, which exhibit a  $PCE$  of  $1.08\pm0.05\%$  (Figure 6.2). As ClAlPc concentration is increased to 5:1, the  $PCE$  is reduced to approximately that of the planar devices, suggesting a mixed layer morphology similar to that of a neat ClAlPc layer with negligible amounts of  $C_{60}$ . As mixed layer thickness is increased a second time to 15 nm at 4:1 ClAlPc: $C_{60}$  volumetric concentration, the  $PCE$  remains steady at close to 1.1% and then drops to 0.7% at  $x = 17.5\text{nm}$ . When  $C_{70}$  is substituted in place of  $C_{60}$ , the planar  $PCE$  is improved to  $1.00\pm0.05\%$ . The optimal mixed layer thickness is 2.5nm at 1:1 ClAlPc: $C_{70}$  with a  $PCE$  of  $1.27\pm0.08\%$  (champion  $PCE$  of 1.4%) (Figure 6.3). While there is substantial room for performance improvement through the volumetric optimization of ClAlPc: $C_{70}$ , we are highly encouraged by the fact that the performance of the initial  $C_{70}$  devices has already eclipsed the  $C_{60}$  devices.

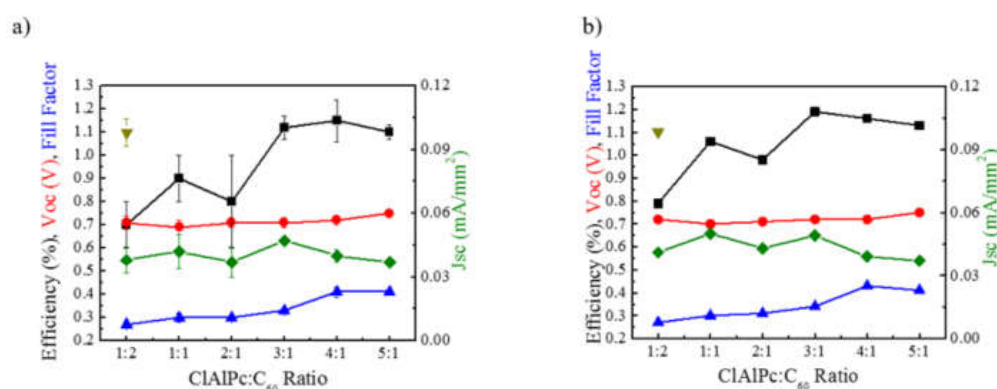


**Figure 6.2. Optimizing transparent ClAlPc: $C_{60}$  PMHJs.** Volumetric concentration optimization of the 10nm ClAlPc: $C_{60}$  mixed layer with (a) typical and (b) champion transparent device performance parameters. Planar devices are denoted by yellow triangles. This optimization was completed after optimizing the mixed layer thickness at a ClAlPc: $C_{60}$  ratio of 1:1 and prior to the thickness optimization at 4:1.

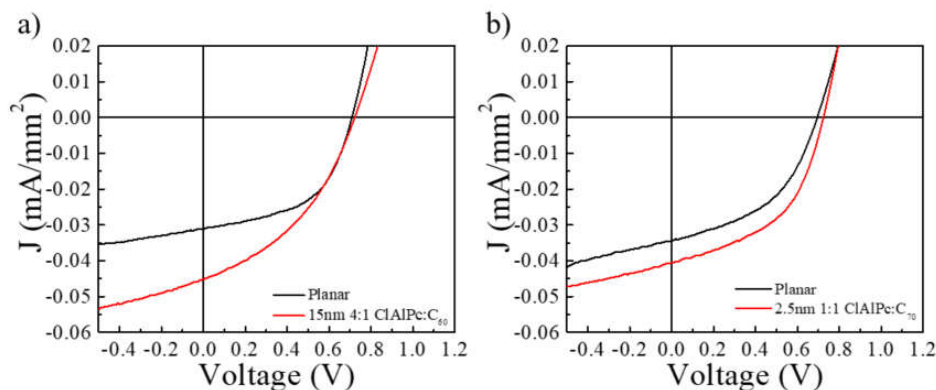


**Figure 6.3. Transparent C<sub>60</sub> and C<sub>70</sub> PMHJs.** (a) Planar and optimized PMHJ ClAlPc:C<sub>60</sub> devices. (b) Planar and preliminary PMHJ ClAlPc:C<sub>70</sub> devices.

To improve yield and performance, a 2nm interfacial Ag layer is deposited over BCP in a conventional architecture followed by a 100nm MoO<sub>3</sub> capping layer. The energy levels of MoO<sub>3</sub> are pinned by the Ag interfacial layer, allowing MoO<sub>3</sub> to be utilized as an additional electron transport layer.<sup>164</sup> While  $J_{sc}$  is reduced as compared to uncapped devices due to absorption by the interfacial Ag layer, it is expected that the PMHJ *PCE* ceiling is higher in this architecture than in an inverted architecture due to a more favorable optical arrangement. Indeed, transparent 7.5nm 1:1 ClAlPc:C<sub>60</sub> mixed layer devices in this architecture yield *PCEs* of  $1.10 \pm 0.03\%$  (champion *PCE* of 1.13%, Figure 6.4), comparable to the unoptimized inverted devices utilizing C<sub>70</sub>.

The results of these experiments followed expected performance trends with respect to mixed layer thickness and concentration.  $J_{sc}$  is increased proportionally with mixed layer thickness due to improved exciton diffusion efficiency brought about by combining donor and acceptor materials into one layer, while *FF* is diminished likely due to the formation of cul-de-sacs and domains of pure donor or acceptor material which reduce the electrical conductivity of the layer. The gain in exciton diffusion efficiency is exceeded by the loss in conductivity when the optimal

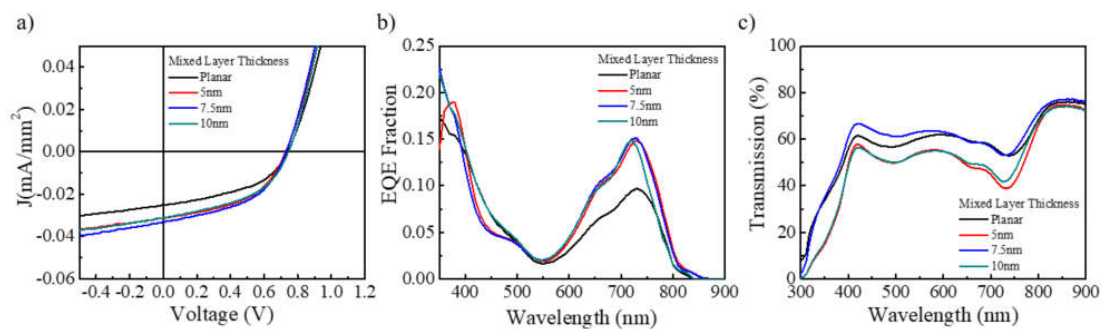


**Figure 6.4. MoO<sub>3</sub>-capped ClAlPc:C<sub>60</sub> transparent PMHJs.** (a) *J-V* data, (b) *EQE* data, and (c) optical transmission data for conventional transparent ClAlPc mixed layer devices.

mixed layer thickness is exceeded. The organization of donor and acceptor molecules in the mixed layer is altered when volumetric ratio is optimized, potentially allowing for the thickness to be increased without substantial losses in conductivity or FF. Additional volumetric ratio and C<sub>70</sub> optimization should be completed in future work to further improve the performance of transparent ClAlPc-based devices.

To measure the *AVT* of devices throughout these experiments, we simultaneously grew all layers on glass substrates pre-coated with unpatterned ITO and measured optical transmission between 300 and 900 nm in a UV/VIS spectrophotometer. The inverted C<sub>60</sub> devices exhibit *AVTs* between 60 and 65% depending on the thickness of the mixed layer, while the C<sub>70</sub> inverted and C<sub>60</sub> conventional devices (Figure 6.4c) capped with 2nm Ag/ 40nm MoO<sub>3</sub> exhibit *AVT* between 50 and 60%, similar to that of window tinting on cars and buildings (the lower limit of acceptable tinting in most cases).<sup>18</sup> Since the total thicknesses of donor/acceptor layers were kept constant throughout all experiments, variations in *AVT* observed in otherwise equivalent devices with varied mixed layer thickness are attributed to changes in optical interference which should be investigated in the future.

The *PCE* could ultimately be enhanced to over 5% by 1) optimizing the volumetric concentration of the ClAlPc:C<sub>60</sub> or ClAlPc:C<sub>70</sub> mixed layer, 2) annealing the ClAlPc:C<sub>60</sub> or ClAlPc:C<sub>70</sub> mixed layer during deposition to achieve higher molecular order and lower series resistance,<sup>165</sup> 3) depositing a mixed layer with graded concentration,<sup>166</sup> and 4) employing a distributed Bragg reflector as a NIR mirror to reflect non-absorbed NIR light within the spectral absorption range of ClAlPc back through the device to improve *EQE*.<sup>11</sup> It may also be possible to improve *FF* by employing ultrathin layers of metals deposited over the ITO to improve the sheet resistance of the anode while maintaining visible transmission.<sup>15, 167</sup>

## 6.2 Organic salt BHJs

We have previously demonstrated the ability to tune energy gaps and thus simultaneously optimize  $V_{oc}$  and  $J_{sc}$  through the molecular design of a new series of organic salts as discussed in Chapter 5.<sup>117</sup> These are highly promising candidates for donor materials in TPVs due to their efficient NIR absorption and may be potentially utilized in multijunction TPVs with ClAlPc in the future. Here, we aim to fabricate a BHJ utilizing the organic salts CyTPFB and CyTRIS solution deposited with PCBM and ICBA. Due to the possible formation of double junctions from phase separation between the salt donor and polymeric fullerenes, we employ both conventional and inverted architectures similar to those used in the ClAlPc-based BHJs.

In this experiment, we focused on optimizing BHJs in opaque devices. In the conventional architecture, the planar device stack deposited over pre-patterned ITO substrates was: MoO<sub>3</sub> (10nm)/Donor (18nm)/C<sub>60</sub> (40nm)/BCP (7.5nm)/Ag (100nm). CyTPFB and CyTRIS were both spin-coated at 3000 RPM for 30 seconds from 5mg/mL solutions consisting of chlorobenzene (CB) solvent for CyTRIS and a 1:3 volumetric mixed solvent of dichloromethane (DCM) and CB for CyTPFB due to low solubility of the latter in CB. Mixed layers with PCBM or ICBA were

deposited in place of the neat donor layer in BHJ devices and were initially optimized for thickness and volumetric concentration analogous to the ClAlPc-based BHJs.

Organic salt BHJ optimization was started in the conventional architecture employing CyTPFB as the donor with PCBM and C<sub>60</sub> as the mixed and neat acceptors, respectively. With mixed layer thickness held constant, CyTPFB:PCBM volumetric ratios of 4:1, 2:1, 1:1, 1:2, and 1:4 were analyzed alongside planar controls. As PCBM concentration is increased, *PCE* is reduced from 1.67±0.08% at 4:1 CyTPFB:PCBM to 0.15±0.01% at 1:4 due to simultaneous reductions in  $J_{sc}$ ,  $V_{oc}$ , and  $FF$  (Figure 6.5). Devices with 1:1 and 4:1 CyTPFB:PCBM mixed layers were also annealed at temperatures of 100, 150, 165, and 175C. Similar to devices with high concentrations of PCBM, annealing caused dramatic simultaneous reductions in  $J_{sc}$ ,  $V_{oc}$ , and  $FF$  so that devices were effectively shut off at 175C.

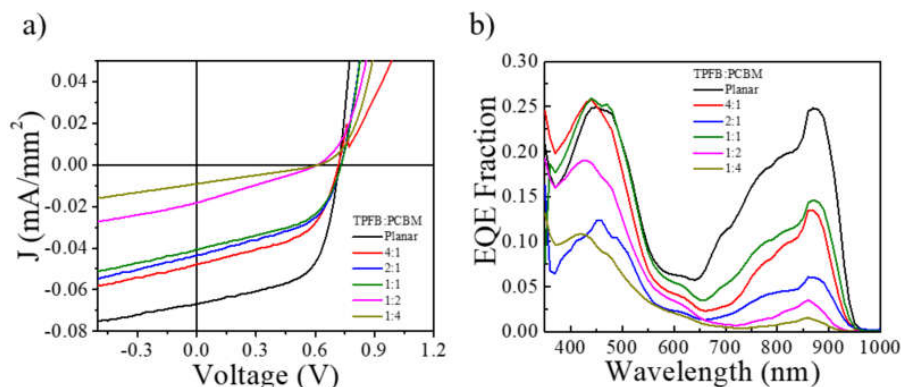


**Figure 6.5. Conventional CyTPFB:PCBM BHJs.** (a)  $J$ - $V$  curves and (b)  $EQE$  spectra for conventional planar CyTPFB and CyTPFB:PCBM mixed devices with mixed layer thicknesses of 18nm. Surprisingly we find all BHJ compositions tested thus far resulted in poorer performance unlike many other small molecule BHJs, including ClAlPc:C<sub>60</sub> BHJs.

The alternative polymeric fullerene ICBA was also utilized in the same conditions as PCBM (Figure 6.6). A similar trend of *PCE* with respect to ICBA concentration was also observed, where devices with high ICBA concentration had all performance parameters reduced, although it

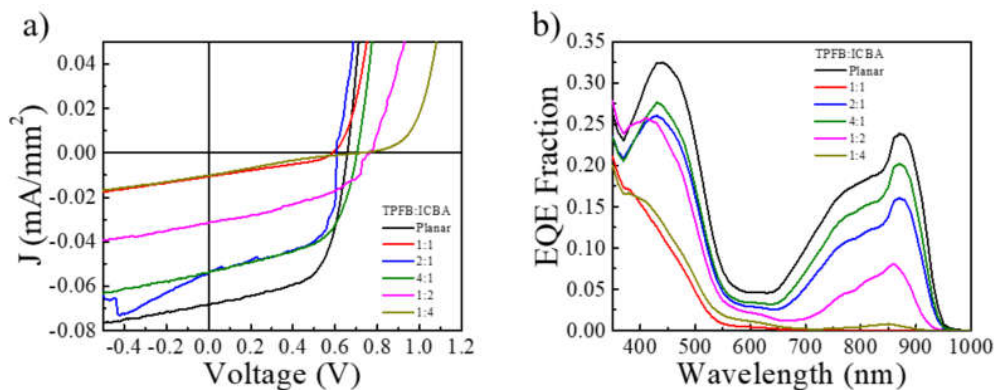


**Figure 6.6. Conventional CyTPFB:ICBA BHJs.** (a)  $J$ - $V$  data and (b)  $EQE$  spectra for conventional planar CyTPFB and CyTPFB:ICBA devices with mixed layer thickness of 18nm.

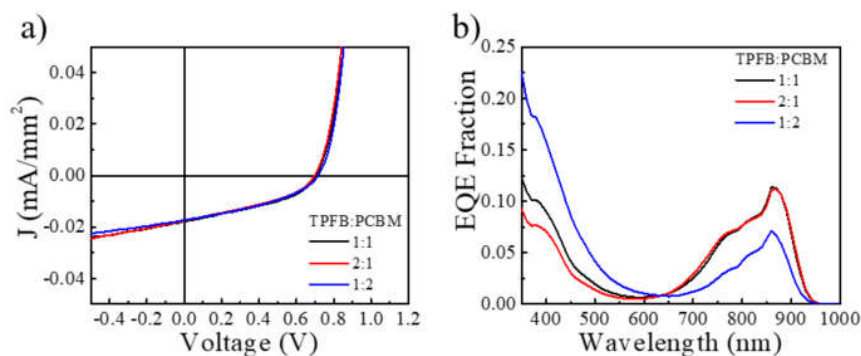


**Figure 6.7. Inverted CyTPFB:PCBM BHJs.** (a)  $J$ - $V$  data and (b)  $EQE$  spectra for CyTPFB:PCBM inverted devices

is noted that ICBA devices had improved  $J_{sc}$  and  $FF$  as compared to their PCBM counterparts.  $PCE$  appears to be optimized at 4:1 CyTPFB:ICBA ( $2.02 \pm 0.05\%$ ), however it would appear that this is only due to CyTPFB concentration in the mixed layer approaching unity so that these devices behave similarly to planar devices. As ICBA concentration was increased, aside from the 1:1 devices,  $J_{sc}$  and  $FF$  were diminished from  $0.053 \pm 0.001$  mA/mm<sup>2</sup> and  $0.54 \pm 0.01$  to  $0.01$  mA/mm<sup>2</sup> and  $0.20 \pm 0.01$  at 1:4 CyTPFB:ICBA respectively. Surprisingly, the 1:1 devices exhibited greatly diminished  $J_{sc}$  and  $FF$  ( $0.01$  mA/mm<sup>2</sup> and  $0.31$  respectively), comparable to the 1:4 devices. The  $EQE$  spectrum for a 1:1 device (Figure 7.6b) implied that CyTPFB had not been added to the solution, however an enhanced  $V_{oc}$  likely would have been observed had this been the

case due to the elimination of the interface gap. Instead,  $V_{oc}$  did not deviate significantly across any CyTPFB:ICBA concentrations including 1:1 or the planar devices. Annealing 2:1 and 4:1 CyTPFB:ICBA devices at 120, 130, and 140C for 10 minutes following the deposition of the mixed layer yielded similar trends in  $PCE$  as well, although these devices were not shut off at the highest temperature.

All the device compositions tested thus far for organic salt BHJs have resulted in poorer performance than planar controls in stark contrast to other small molecule systems (e.g. with ClAlPc). Thus, a greater understanding of the salt:fullerene mixed layer morphology is needed. Based on these results, it was hypothesized that PCBM and ICBA phase separate to the bottom of the device when deposited with CyTPFB and form a double junction when the fullerenes are used in high concentration. This suggested a need for an electrically inverted architecture to achieve a desirable phase separation, which were tested next.

Inverted devices were fabricated without neat  $C_{60}$  acceptor layers due to the susceptibility of  $C_{60}$  to be dissolved during CyTPFB deposition. The experimental device stack deposited over pre-patterned ITO was: AZO (10nm)/CyTPFB:PCBM (15nm)/MoO<sub>3</sub> (20nm)/Ag (100nm).

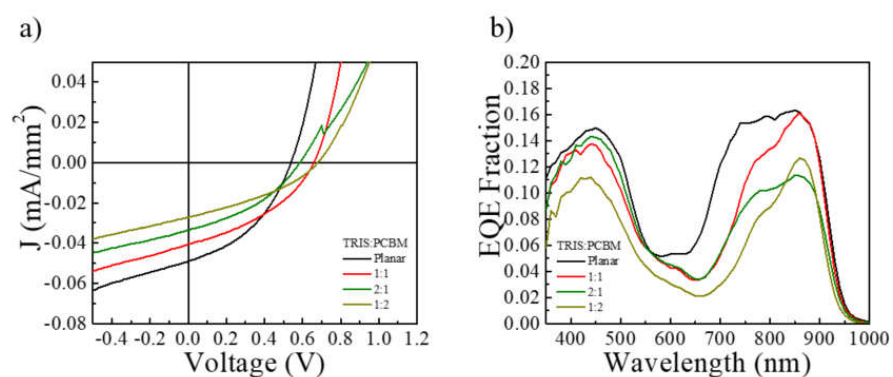


**Figure 6.8. Inverted CyTRIS:PCBM BHJs.** (a)  $J$ - $V$  data and (b)  $EQE$  spectra for CyTRIS:PCBM inverted devices

Preliminary inverted devices were fabricated with CyTPFB:PCBM concentrations of 1:1, 2:1, and 1:2 (Figure 6.7). Due to the lack of a neat acceptor layer, planar controls could not be fabricated in this experiment. While these devices were functional (*PCE* of around 0.4% across all concentrations), it is clear that a planar-mixed architecture is necessary to approach and eventually exceed the *EQE* of the planar devices. We find that chloroform is a desirable solvent to use with inverted devices due to the lack of C<sub>60</sub> solubility,<sup>168</sup> thus making it possible to deposit a 40nm neat layer of C<sub>60</sub> after AZO and prior to the solution deposition of a mixed layer.

Because CyTPFB is not soluble in chloroform, CyTRIS was utilized for the inverted planar-mixed devices (Figure 6.8). The planar-mixed device stack in the inverted architecture was: AZO (10nm)/ C<sub>60</sub> (40nm)/ CyTRIS (18nm)/ MoO<sub>3</sub> (20nm)/ Ag (100nm). While this architecture improved the *PCE* dramatically compared to the CyTPFB inverted devices, the *EQE* still did not approach that of the conventional planar devices. Additionally, the mixed devices still do not perform as well as the planar controls, indicating that the organic salts likely have not mixed with the PCBM or ICBA in these experiments and instead phase separated into two distinct layers during the mixed solution depositions. This likely occurred because of a tendency for polar and

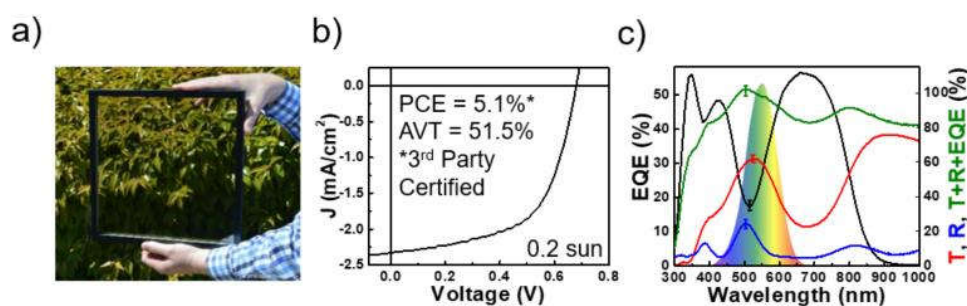


**Figure 6.9. Highest efficiency TPV to date.** (a) Photograph of series-integrated wavelength-selective TPV module. (b) A Newport-calibrated record efficiency single-junction wavelength-selective TPV cell<sup>10</sup> with (c) corresponding *T*, *R*, *EQE*, and photon balance (*T*+*R*+*EQE*) for the TPV cell.

relatively non-polar materials to phase separate. Possible strategies for overcoming the formation of ideal BHJ morphologies with organic salts are discussed in Chapter 8.

### 6.3 Highest efficiency TPVs to date

Figure 6.9 shows the highest 3<sup>rd</sup>-party certified (Newport) selective TPV *PCE* to date that we have reported and represents the motivation behind the BHJ and PMHJ optimizations discussed in this chapter. This single junction device utilizes a NIR-selective excitonic semiconductor with broad photoresponse between 650-900 nm. The *PCE* reaches 5.1% at greater than 50% *AVT*, with a  $V_{oc}$  of 0.7 V, approaching the theoretical limit for the bandgap. This TPV device architecture has also been scaled via vapor deposition into functional large area modules up to 1 sq. ft comprising monolithic series-integrated subcells.

In summary, we have made progress toward the goal of fabricating high-performance TPVs by employing BHJ and PMHJ architectures that feature complementary absorption in the NIR. Although the molecular salts do not appear to be miscible with C<sub>60</sub> analogs, new strategies to be explored in the future may allow the fabrication of efficient, salt-based BHJs.

## Chapter 7 – Long Lifetime Near-Infrared Selective Photovoltaics

Moving forward, operating lifetime is arguably the most important challenge that must be addressed to enable commercial viability of these emerging technologies. In this chapter, the lifetimes of organic PVs with near-infrared selective small molecule and molecular salt donor layers are investigated. This is the first comprehensive lifetime study on devices featuring organic salts with varied counterion. Based on the tunability afforded by anion exchange, these architectures yield champion extrapolated lifetime of  $> 7 \pm 2$  years. We compare these lifetimes with changes in external quantum efficiency, hydrophobicity, highest occupied molecular orbital, and optical absorption data to determine the stability limiting characteristics and failure mechanisms of PV devices utilizing each donor. Surprisingly, we find a significant correlation between the lifetime and the water contact angle of the donor layer. While the mechanism for this correlation is not yet clear, it still provides a targeted parameter for designing molecules and salts with exceptional lifetime and commercial viability.

### 7.1 Device lifetimes

The molecular and organic semiconductors utilized to fabricate TPVs are often considered to have inherently low stability compared to inorganic technologies due to a tendency to react with oxygen and moisture. However, encapsulation alone can alleviate many of the stability issues with OPVs and organic light emitting diodes so that devices retain high performance for many years; recent organic demonstrations with reported extrapolated device lifetimes  $> 20$  years<sup>109</sup> provide a clear indication that OPV technologies can be just as viable for long-term applications as inorganic technologies even though most reports demonstrate extrapolated and non-extrapolated lifetimes of approximately 2 years<sup>110</sup> and  $< 1.5$  years<sup>111, 112</sup> respectively.

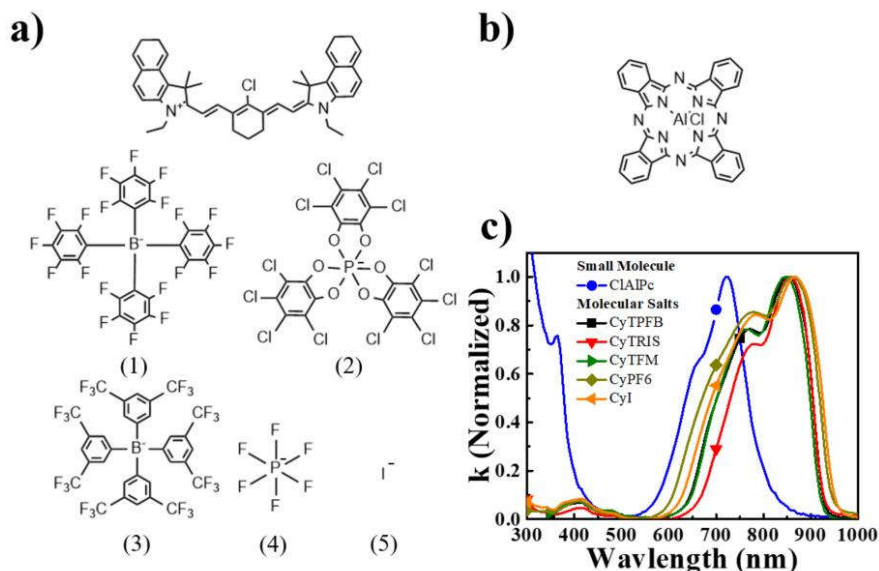


**Figure 7.1. Optical absorption for NIR donors.** (a) Molecular structures for the heptamethine (Cy<sup>+</sup>) cation (top) and the anions paired with it: (1) TPFB<sup>-</sup>, (2) TRIS<sup>-</sup>, (3) TFM<sup>-</sup>, (4) PF<sub>6</sub><sup>-</sup>, and (5) I<sup>-</sup>. (b) Molecular structure for ClAlPc. (c) Normalized extinction coefficients for each donor.

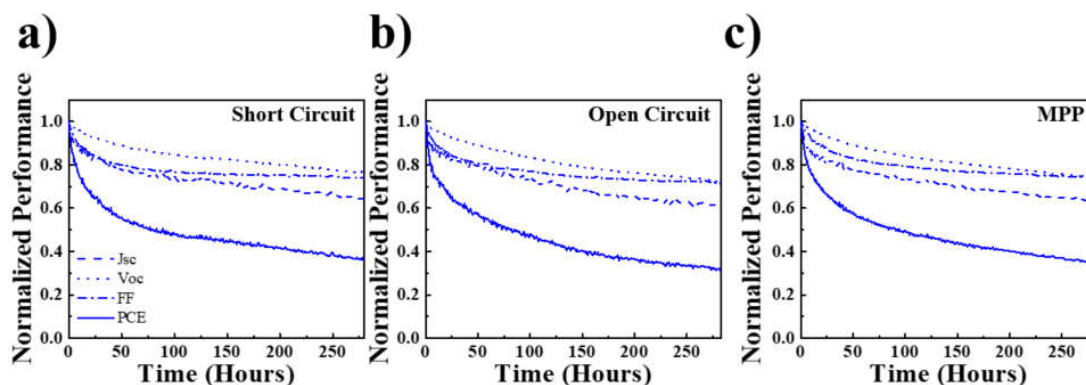


**Figure 7.2. Lifetime load conditions.** Representative ClAlPc PHJ devices held at (a) short circuit, (b) open circuit, and (c) maximum power point (MPP). We do not observe a significant difference in stability across these three loading conditions for any architecture.

Although the properties of photoactive layers,<sup>169-171</sup> transport layers,<sup>111, 172-174</sup> and electrodes,<sup>175, 176</sup> have previously been correlated to OPV lifetime, little work has focused explicitly on NIR wavelength selective photoactive materials with bandgaps applicable to TPVs. In this work, we report the operating lifetimes of OPV architectures utilizing two classes of NIR-selective donors, solution-deposited molecular salts and vacuum-deposited small molecules, to

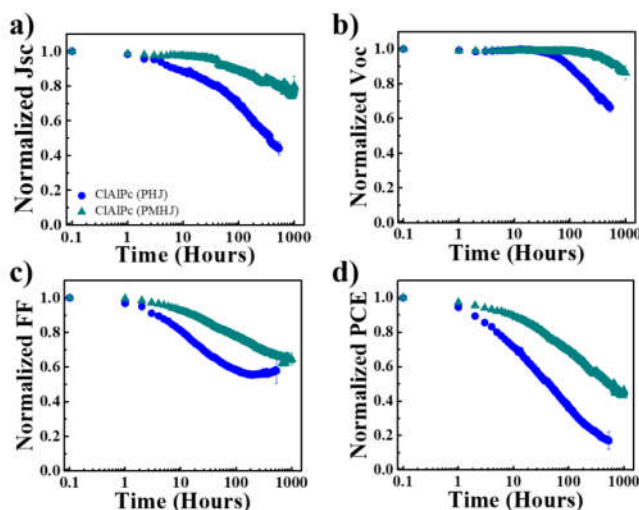


**Figure 7.3. CIAIPc lifetime.** Normalized lifetime data for CyTPFB, CIAIPc PHJ, and CIAIPc PMHJ devices.  $J_{sc}$ ,  $V_{oc}$ ,  $FF$ , and  $PCE$  are shown in panels a-d respectively. Representative error bars denote the maximum standard deviations across all devices for each performance parameter.

determine the effects of donor molecular structure, morphology, molecular orbitals, and surface properties on device stability. For the molecular salts, a NIR selective heptamethine cation ( $Cy^+$ ) is paired with various anions including tetrakis(pentafluorophenyl)borate (CyTPFB),  $\Delta$ -tris(tetrachloro-1,2-benzendiolo)phosphate(V) (CyTRIS), tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (CyTFM),  $PF_6$  (Cy $PF_6$ ), and I (CyI).  $Cy^+$  and the various anions are illustrated in Figure 7.1a. Cy salts were prepared by anion exchange of the parent CyI

compound, detailed elsewhere.<sup>5</sup> Planar and planar-mixed heterojunctions (PHJs and PMHJs) were investigated utilizing chloroaluminum phthalocyanine (ClAlPc, Figure 7.1b), a NIR-selective vacuum-deposited small molecule previously demonstrated in wavelength-selective TPVs.<sup>11</sup> The absorption spectra for all donors are shown in Figure 7.1c.

PHJ and PMHJ devices were fabricated as described in Section 3.1 and encapsulated under nitrogen. Four devices across at least two substrates per architecture were then tested under constant 1-sun illumination while held at maximum power point (MPP) for 1000hrs. We focus on MPP here because it represents a realistic load placed on devices in practical applications. Moreover, we surprisingly do not observe significant differences in stability for the various architectures tested at short circuit, open circuit, and MPP as illustrated in Figure 7.2. Current-voltage characteristics were measured once per hour to extract time dependent performance parameters. External quantum efficiencies (*EQEs*) and transmission measurements were collected periodically on representative devices. Lifetimes are defined as the time over which the power

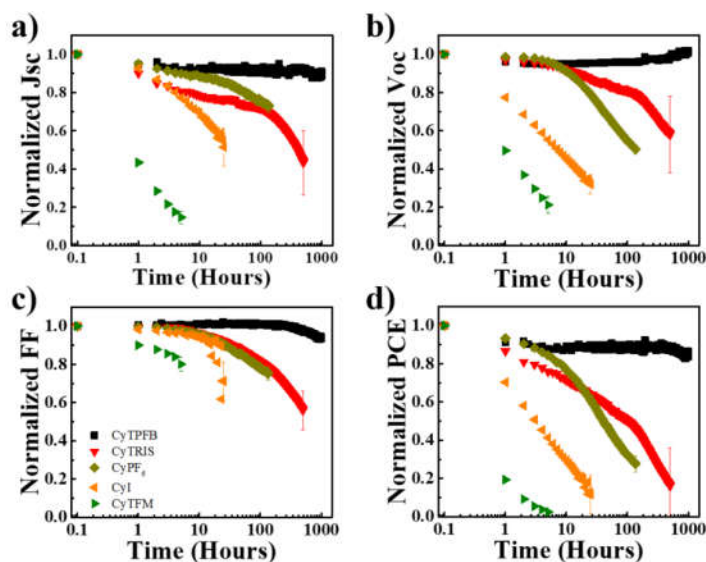


**Figure 7.4. Salt lifetime.** Normalized lifetime data for CyTPFB, CyTRIS, CyPF<sub>6</sub>, CyI, and CyTFM devices.  $J_{sc}$ ,  $V_{oc}$ ,  $FF$ , and  $PCE$  are shown in panels a-d respectively. Representative error bars denote maximum standard deviations across all devices for each performance parameter.

conversion efficiency (*PCE*) reaches 80% or 50% of the initial value following any burn-in ( $T_{80}$  and  $T_{50}$  respectively). Accelerated lifetime values were then extrapolated by multiplying by  $5.66 \times$  average hours of 1-sun illumination per day to convert from accelerated constant illumination to ambient conditions in Kansas City, MO which closely represents the average daily illumination in the United States (and peak power of  $\sim 1000 \text{ W/m}^2$ ). Other studies have reported greatly enhanced measured lifetimes from seasons to years in some cases for devices tested under constant illumination and outdoors respectively.<sup>111, 177</sup> These demonstrations suggest that this extrapolation can be an accurate representation of lifetime under ambient illumination.

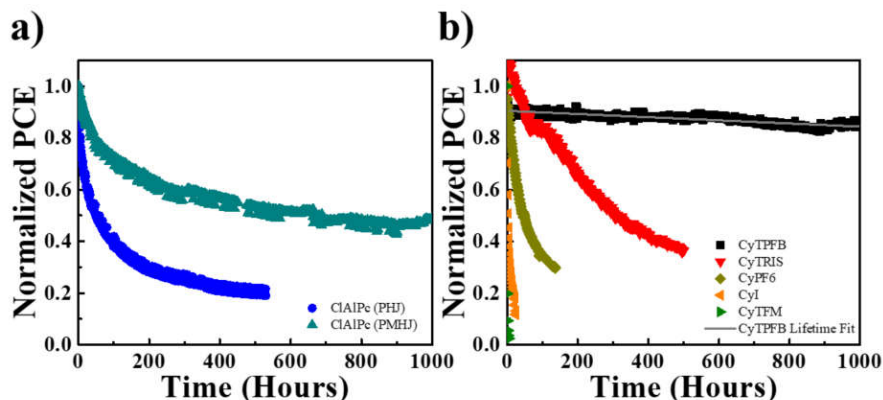


**Figure 7.5. Champion small molecule and molecular salt device lifetimes.**

Normalized short circuit current density ( $J_{sc}$ ),  $V_{oc}$ , fill factor ( $FF$ ), and *PCE* characteristics are shown as a function of time in Figure 7.3 for small molecule donors and Figure 7.4 for molecular salt donors. Representative best lifetime data are shown in Figure 7.5 for all architectures. We find a wide range of device lifetimes among the architectures tested. For example, the CIAIPc PMHJs exhibited significantly higher stability than the CIAIPc PHJs, with a champion  $T_{50}$  of 4380 hours compared to 270 hours, respectively. In the CIAIPc architectures,  $J_{sc}$  and  $FF$  losses dominated the performance roll-off for approximately the first 30 hours of each test, after which  $V_{oc}$  began to decline first in the PHJs and then in the PMHJs. Surprisingly, a larger

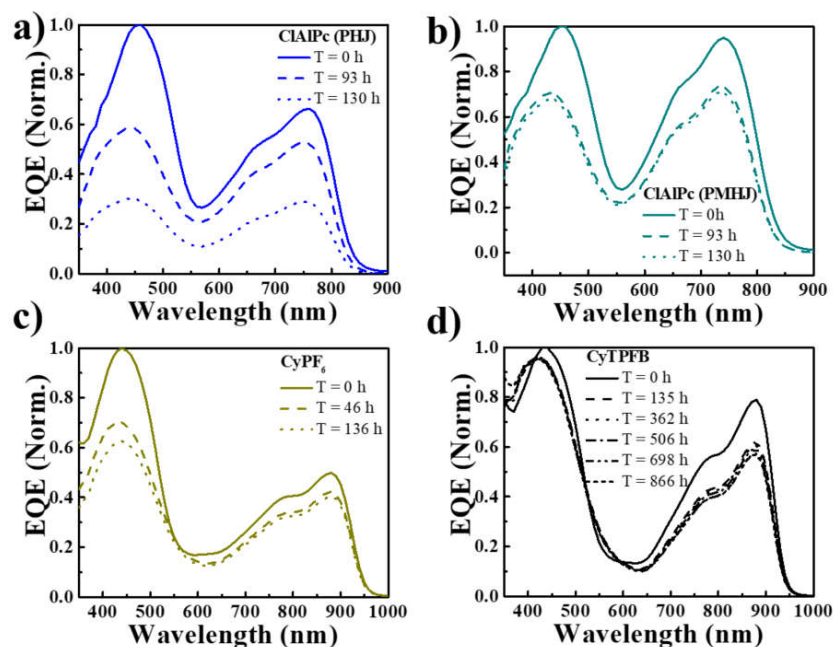


**Figure 7.6. EQE for selected devices.** Normalized *EQE* data measured from representative (a) ClAlPc PHJ, (b) ClAlPc PMHJ, (c) CyPF<sub>6</sub>, and (d) CyTPFB devices during lifetime testing.

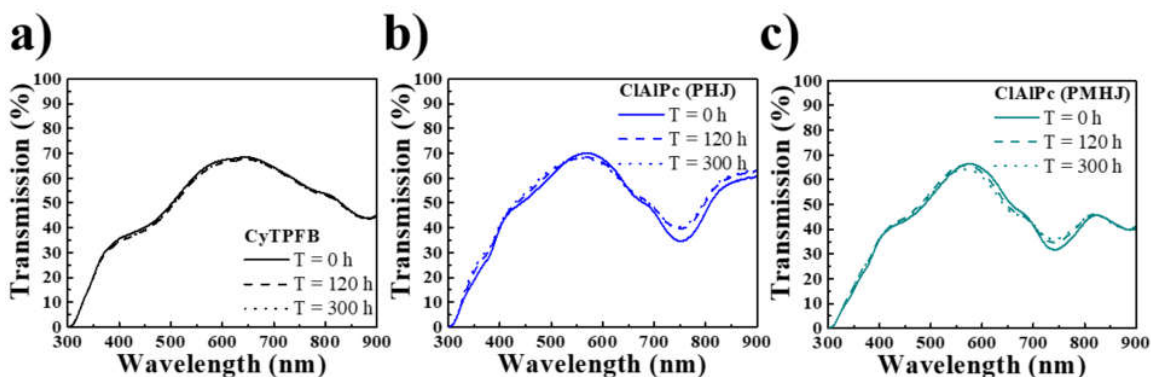


**Figure 7.7. Optical transmission for selected devices.** Transmission spectra for (a) CyTPFB, (b) ClAlPc (PHJ), and (c) ClAlPc (PMHJ) devices without top Ag electrodes measured before and after illumination.

range of lifetimes was observed throughout the organic salts even though they all contain the same photoactive cation. CyTPFB devices showed dramatically enhanced stability compared to the ClAlPc devices as well as the rest of the salt devices with the best  $T_{50}$  of  $7 \pm 2$  years. Salt devices with other anions exhibited comparable lifetimes to the ClAlPc PHJs with the exception of CyTRIS ( $T_{50} = 1740$  hours). CyPF<sub>6</sub> devices had a  $T_{50}$  of 280 hours while CyI devices exhibited a

| Donor             | T <sub>80</sub>       | T <sub>50</sub>       | Water Contact Angle [Degrees] | HOMO (eV) |
|-------------------|-----------------------|-----------------------|-------------------------------|-----------|
| CyTPFB            | 3 years <sup>a)</sup> | 7 years <sup>a)</sup> | 99.8 ± 0.4                    | 5.45      |
| CyTRIS            | 340 hours             | 1740 hours            | 80 ± 1                        | 4.9       |
| CyPF <sub>6</sub> | 60 hours              | 280 hours             | 75 ± 4                        | 4.8       |
| CyI               | 4 hours               | 18 hours              | 71 ± 2                        | 4.6       |
| CyTFM             | 1.4 hours             | 4 hours               | 58 ± 4                        | 5.3       |
| ClAlPc (PHJ)      | 30 hours              | 270 hours             | 62 ± 1                        | 5.5       |
| ClAlPc (PMHJ)     | 270 hours             | 4380 hours            | 69 ± 2                        | 5.5       |

<sup>a)</sup>Values calculated from linear extrapolation.

**Table 7.1. Champion lifetimes and physical properties.**

$T_{50}$  of 18 hours. CyTFM devices exhibited the lowest stabilities, with a best  $T_{50}$  of only 4 hours, despite similar initial performance to CyTPFB. For the salt devices,  $J_{sc}$ ,  $V_{oc}$ , and  $FF$  values simultaneously rolled off within 100 hours and largely determined the overall losses in  $PCE$  with the exception of CyTPFB. For CyTPFB devices,  $J_{sc}$  underwent a slight burn-in over the first 10 hours of the tests before stabilizing,  $FF$  slightly rolled off after 200 hours, and  $V_{oc}$  remained essentially unchanged.  $EQE$  data measured for individual devices from selected architectures during lifetime testing are shown in Figure 7.6 while optical transmission data are shown in Figure 7.7. The  $EQE$  is immediately diminished across the full spectrum for all architectures including the absorption wavelengths of C<sub>60</sub>. While the ClAlPc PHJ  $EQE$  rolls off significantly as time approaches  $T_{50}$ , the  $EQE$ s for other architectures stabilize shortly after lifetime tests are started.

Optical transmission is increased slightly over time around ClAlPc absorption wavelengths indicating slight photobleaching, however all architectures retain apparent absorption well beyond observed NIR  $EQE$  losses. The losses in C<sub>60</sub>  $EQE$  suggest that the uniform losses in  $EQE$  likely indicate that these defects originate on the donor and act as recombination sites for all hole collection.

Physical properties including the HOMO and water contact angles for isolated donor and mixed ClAlPc:C<sub>60</sub> films are shown in Table 7.1. Co-depositing ClAlPc and C<sub>60</sub> together in a mixed layer increases the contact angle from  $62 \pm 1^\circ$  for neat ClAlPc to  $69 \pm 2^\circ$ , which might be attributed to changes in surface roughness. Interestingly, CyTPFB exhibits a contact angle of  $99.8 \pm 0.4^\circ$  (hydrophobic) while CyTFM has a contact angle of  $58 \pm 4^\circ$  (hydrophilic). CyTRIS, CyPF<sub>6</sub>, and CyI exhibit contact angles of  $80 \pm 1^\circ$ ,  $75 \pm 4^\circ$ , and  $71 \pm 2^\circ$  respectively. It should be noted that the salt films are amorphous, each exhibit RMS roughness  $< 1$  nm, and none exhibit any significant solubility in water.<sup>178</sup> AFM data shown for CyTPFB and CyTFM in Figure 7.8 demonstrate no significant change in surface roughness, indicating this variation in hydrophobicity is due primarily to the structure of the anion.

## 7.2 Lifetime analysis

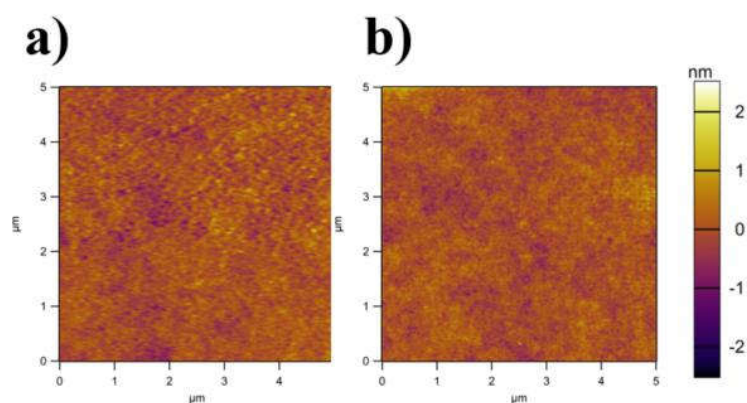


**Figure 7.8. AFM on CyTPFB and CyTFM.** AFM images collected on 50 nm (a) CyTPFB and (b) CyTFM films deposited over Si. The RMS roughnesses are  $0.36 \pm 0.04$  nm and  $0.27 \pm 0.01$  nm respectively.

The deviation between ClAlPc PHJ and PMHJ stabilities is largely attributed to the morphology of the photoactive layers. In PMHJs, photocurrent generation is significantly enhanced and confirmed by increases in *EQE*. This enhancement primarily stems from a shorter length over which excitons need to diffuse before dissociation, resulting in an overall shorter

exciton lifetime. Excitons in the PMHJ are therefore less likely to interact or annihilate with polarons or other excitons to form defects which act as charge traps in the bulk donor and acceptor layers.<sup>179</sup> The longer exciton lifetimes in the PHJs increase the probability of these defect generating events, causing more immediate roll-offs in  $J_{sc}$  and  $FF$ . The losses in  $V_{oc}$  across both architectures can be attributed to the gradual formation of photo-activated interfacial states which also further degrade  $J_{sc}$ . Because the donor-acceptor interfacial area is considerably larger in the PMHJs than in the PHJs, longer periods of illumination may be required to form a significant concentration of interfacial states to affect the  $V_{oc}$ . As demonstrated elsewhere in bulk heterojunction architectures,<sup>180</sup> PMHJ stabilities can potentially be further improved with the incorporation of additional donor and acceptor materials in the mixed layer to prevent phase separation.

It is reiterated that the donor is the only unique material in each architecture. Changes in device stability are therefore unlikely to originate from electrode, transport, or acceptor layer degradation. Although all the devices are encapsulated in a nitrogen environment, oxygen and moisture can still be present in ppm quantities during encapsulation or leak through the seal and penetrate top electrodes<sup>176</sup> to damage photoactive materials. Thus, one possible explanation for the large lifetime variation could be the deepening of the donor HOMO level which could alter the generation efficiency of reactive oxygen species. Superoxides, formed in a charge transfer process if the HOMO is closer to the vacuum level than the oxygen ground state,<sup>158</sup> can photobleach the donor material, severely limiting the lifetime of the collective device. Such a mechanism would be expected to degrade absorption with time. However, we surprisingly see little correlation between HOMO and lifetime as shown in Table 7.1 and little reduction in the absorption efficiency in Figure 7.7. In particular, the key comparison between CyTPFB and CyTFM shows that while

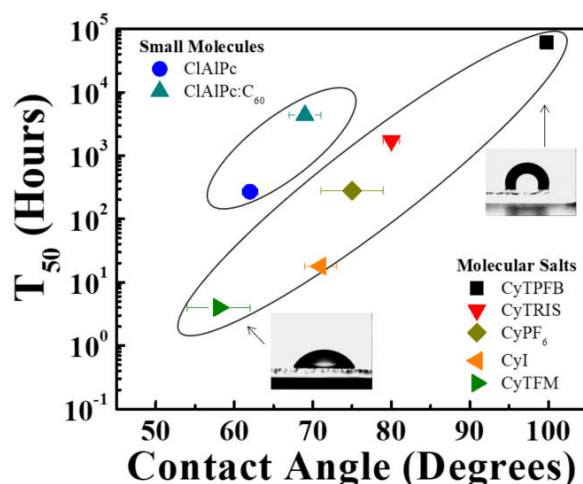


**Figure 7.9. Correlation between lifetime and hydrophobicity.** Champion lifetimes ( $T_{50}$ ) plotted as a function of isolated donor film water contact angle for all devices. Lifetime is directly correlated to water contact angle for both vacuum deposited small molecule donor and solution deposited molecular salt devices.

these two compounds have similar HOMO,<sup>5, 178</sup> similar voltage, and even similar fluorinated chemical structures, they have vastly different lifetimes. Though reactive oxygen species may still play a role in lifetime, this indicates the presence of a separate degradation mechanism.

An alternative explanation could stem from the degree of hydrophobicity (as measured by water contact angle). Indeed, in Figure 7.9, we plot lifetime versus the water contact angle for the respective donor types. The salt lifetimes are correlated exponentially (linearly on a semilog plot) to water contact angle, where contact angle increases from  $58 \pm 4^\circ$  for CyTFM to  $99.8 \pm 0.4^\circ$  for CyTPFB while lifetime increases from 4 hours to  $7 \pm 2$  years respectively. Additionally, the order of magnitude difference in lifetime between the CIAIPc PHJ and PMHJ, while largely attributed to exciton lifetime reductions, is also seemingly correlated with the difference in contact angle which could imply additional degradation mechanisms similar to the salts that are reduced as the layer becomes more hydrophobic.

The most striking variation observed is the 40° difference in water contact angle between CyTPFB and CyTFM. This is explained by the degree of functionalization of the respective anions. As demonstrated previously,<sup>178</sup> polar functional groups can significantly alter the solubility of the collective salt in a given solvent. The phenyl groups present on the TFM anion are made slightly more polar by the trifluoromethyl functionalization as compared to the more symmetric distribution of fluorine atoms around the phenyl groups on the TPFB anion. Although both CyTPFB and CyTFM exhibit low water solubilities, the structure of the TFM anion may still permit chemical interactions (particularly at the C-H bonds in the anion) with water resulting in a lower contact angle. The stark differences in lifetime are then likely explained by ppm or sub-ppm levels of moisture interaction still present even in packaged devices. Differences in hydrophobicity can potentially also represent prevention of other sources of degradation such as physical repulsion of reactive species (oxygen, hydroxyl, water, and nitrogen based radical species)<sup>181</sup> or an inertness to interaction at the C<sub>60</sub> interface where donor-acceptor(C<sub>60</sub>) adducts can be formed<sup>182</sup> under favorable interactions. The hydrophobicities of buffer<sup>183, 184</sup> and encapsulation<sup>185, 186</sup> layers have previously been correlated to lifetime, however lifetime has not been connected to the active layer hydrophobicity. For compounds that have higher degree of water solubility, water contact angle could be made with dynamic wetting measurements or correlated to other representative solvent contact angles. The design of hydrophobic photoactive materials could therefore provide a key metric to identify highly stable molecular salt and non-salt devices.

In summary, we have demonstrated the impact of chemical structure and morphology of NIR wavelength-selective donor materials on the lifetime of OPV devices. We systematically investigate a series of organic small molecules and molecular salts containing a common photoactive cation with varied counterion. The range of donor materials studied in otherwise

identical architectures shows that most changes in stability are intrinsically related to the donor material and not products of acceptor, transport, or electrode layer degradation. We evaluate the impact of HOMO, water contact angle, and anion structure in the case of the molecular salts, and find a strong correlation between stability and hydrophobicity. Devices utilizing a hydrophobic donor layer (CyTPFB) exhibited a champion lifetime (CyTPFB) of  $7 \pm 2$  years. This is the first demonstrated improvement in lifetime related specifically to donor hydrophobicity. While the hydrophobicity could be an indicator of other interactions it can nonetheless serve as a rapid indicator/screening-metric for longer lifetimes. This work presents an important roadmap toward the fabrication of stable, NIR selective donor materials that can be utilized in visibly transparent PVs.

## Chapter 8 – Conclusions and Outlook

In this chapter, we summarize potential applications and the challenges that must be addressed to enable large scale commercial deployment. We also discuss new approaches for achieving high performance TPVs with bulk heterojunction architectures and alternative indium-free electrodes.

### 8.1 TPV applications

Achieving widespread adoption requires the compound optimization of the *PCE*, *AVT*, and *CRI*. Ultimately, wavelength-selective and non-wavelength-selective TPV technologies are unlikely to be direct competitors but will likely find complementary applications and markets, based on their unique performance space. While electronic displays require *AVT* greater than 80%, tinted architectural glass requirements typically start closer to 50%. *PCE*s between 5-10% will be required to achieve competitive LCOE in BIPV applications, however, 2-5% *PCE* is sufficient to self-power low power mobile electronic devices. TPVs with similar *PCE* but lower *AVT* can self-power smart windows or complement passive window coatings (e.g. low-emissivity) or smart window technologies (e.g. electrochromic). TPVs have already demonstrated the ability to achieve beyond these entry application thresholds.

Building windows coated with TPVs enable electricity generation to offset building electricity consumption, to autonomously power electronic smart window technologies, and reduce incident heat load. TPVs can be designed to selectively absorb UV<sup>79, 187</sup> or deep NIR<sup>115</sup> light to work in concert with visible or NIR-selective smart window technologies.<sup>188, 189</sup> A window enhanced with a TPV coating can also replace or be combined with low-emissivity coatings, which reflect NIR light. In terms of the overall electricity potential, we estimate that there is approximately 5-7 billion m<sup>2</sup> of glass surface in the US. Equipping this area with 15% *PCE* TPVs

(with average flux of approximately  $2.7 \text{ kWh/m}^2\text{-day}$  across all faces in vertical configurations and skylights in a horizontal configuration) this would approximately output an additional 100 GW that approaches the rooftop potential and which could be substantially augmented if also integrated in the non-glass siding of buildings.

TPVs have also caught the attention of the automotive industry.<sup>190, 191</sup> Well in advance of the 10-15% *PCEs* that a TPV-coated electric vehicle would need to extend its range by 10-20 miles a day with only solar energy, auto makers are now looking at incorporating TPVs on a smaller scale. A TPV-coated sunroof, for example, could power fans or maintain the tinted state of an electronic tinting (i.e., in a smart window) to cool a car parked in the sun.

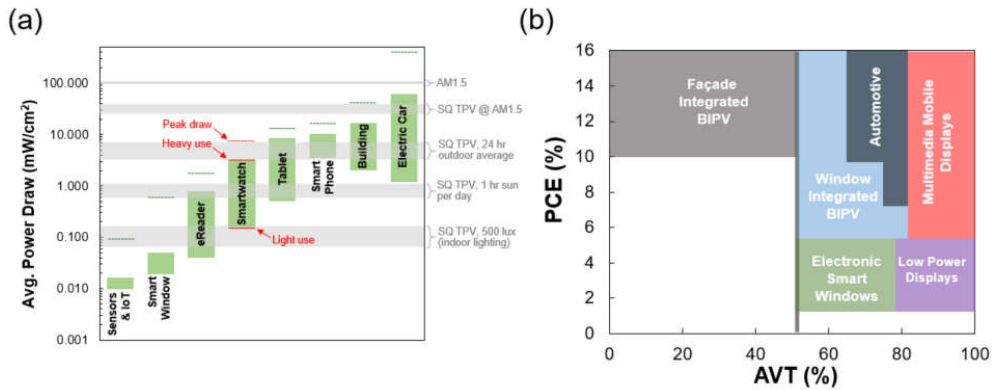


**Figure 8.1. Integration requirements.** (a) Average power draw per device surface area applicable to TPV for various applications ranging in power draw from the Internet of Things (IoT) to electric cars. The shaded green bars correspond to the average power draw of a device (total energy consumption averaged over the full use profile, including representative periods of use and non-use), with the range capturing differences between user types and brands. An average TPV power output that is higher than the average power draw results in a completely autonomous device (infinite battery life), whereas a lower power output results in battery life extension. For comparison, the shaded grey bars show the power output of an SQ TPV under various illumination conditions. Dashed lines are also included for reference to show a representative peak power draw for each device type during full use (for example, when the display is on). (b) Application requirements for TPV as a function of *PCE* and *AVT*. Tinted architectural glass is typically at least 50% transparent, whereas electronic displays require an *AVT* of at least 80%. *PCE* values of 2–5% are sufficient to autonomously power smart windows and low-power displays, whereas *PCE* values of at least 5–10% are required to power mobile displays or achieve competitive LCOE to match semitransparent modules in automotive and building-integrated applications.

Integrating TPVs across the surface of electronic displays can enable extended use by charging the batteries of the device while maintaining a view of the display. In low-power wearables and e-readers, TPVs could eliminate the need for ever connecting to a charger. The impact of TPVs on battery life is assessed by comparing the average power draw of the electronic device to the average power output produced by the PV across use conditions as illustrated in Figure 8.1a.

The estimated performance requirements for TPVs are mapped in Figure 8.1b across various applications. Wide-scale deployment will require further improvements in long-term durability and electrode conductivity. However, the path toward large-area commercialized wavelength selective TPVs is feasible given that many glass manufacturers already currently employ in-line deposition systems for a range of multilayer glass coatings. With preliminary TPV demonstrations already exceeding the *PCE*, *AVT*, and *LUE* metrics for architectural glass and low-power mobile electronic applications, wavelength selective TPVs offer a promising route to inexpensive, widespread solar adoption on both small and large surfaces that were previously inaccessible.

## 8.2 New approaches to organic salt bulk heterojunctions

The optimization of molecular salt-based BHJs is a challenging endeavor as discussed in Chapter 7 because of phase separation between the polar salts and relatively non-polar acceptors PCBM and ICBA. One method of addressing this may be to utilize a  $C_{60}$ -based salt acceptor which would match the polarity of the salts and theoretically yield a blended layer morphology conducive to efficient BHJs and PMHJs. Because the anion and cation form a molecular interfacial dipole resulting in tunable frontier orbital energies, it follows that the interface gap can also be tuned through acceptor anion exchange analogous to the donor anion exchanges discussed in Chapter 5.

This is an exciting prospect that would therefore enable further tuning of the interface gap by exchanging the iodide with another anion on the acceptor. Exchanging to a similar anion as the donor may also enable higher miscibility in a blended layer between donors and acceptors with similar anions.

Another strategy to utilize salts in an efficient BHJ architecture may be to incorporate compounds within a ternary blended layer with a polymer and PCBM, as accomplished previously with visibly absorbing photoactive materials (Figure 8.2).<sup>16, 192</sup> In this type of architecture, for example, a molecular salt could be added to a PBDTT-DPP:PCBM template<sup>13</sup> in as a NIR sensitizer, allowing optical absorption to be expanded to deeper NIR wavelengths than the existing PBDTT-DPP donor. The ability to fine tune frontier orbital energies through anion exchange and salt alloying would once again be advantageous here as this architecture would require an efficient energetic cascade across both donors and the acceptor.

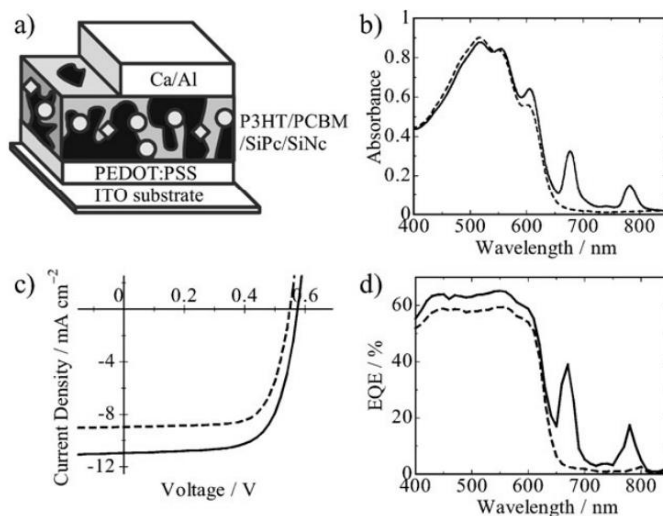


**Figure 8.2. BHJ NIR dye sensitization.** (a) Configuration of a quaternary BHJ utilizing PEDOT:PSS as the hole transport layer, P3HT:PCBM as the initial donor/acceptor materials, and silicon phthalocyanine (SiPc) and silicon naphthalocyanine (SiNc) as the NIR sensitizers. (b) Absorption spectra, (c)  $J$ - $V$  data, and (d)  $EQE$  spectra for non-sensitized (dotted lines) and quaternary sensitized (solid lines) devices. Figure reproduced with permission from Ref. <sup>16</sup>.

### 8.3 New approaches to alternative transparent electrodes

Indium-free electrodes could provide an ideal route toward commercializing TPVs on a wide scale. Many of these alternatives currently result in reduced transmission and conductivity, and some alternatives such as metallic nanowires require solution deposition. Nonetheless, significant work has been done to develop these electrodes as mentioned in Section 2.6.2 as well as formulate strategies to address low visible transmission.

Silver films with thicknesses less than 12 nm can be rendered non-conductive due to incomplete layer formation.<sup>15</sup> However, ultrathin metallic<sup>15, 167, 193</sup> seed layers can serve as nucleation sites, allowing silver electrodes to be deposited at lower thicknesses without significant losses in conductivity as shown in Figure 8.3. These strategies can also potentially enable improved optical transmission compared to equally conductive electrodes without seed layers.

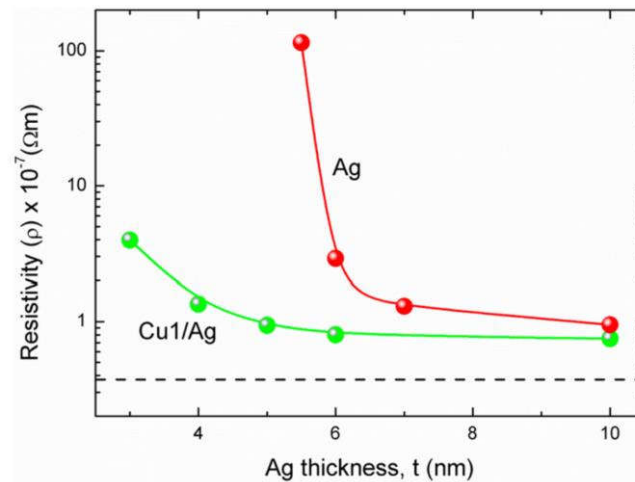


**Figure 8.3. Improved Ag conductivity from seeding.** Resistivity comparison of isolated and Cu-seeded Ag films. The dashed line denotes the measured resistivity of a 300 nm Ag film. Figure reproduced with permission from Ref. <sup>15</sup>.

Another route toward alleviating the transmission issues inherent to thin metallic electrodes is through the use of metal-semiconductor composite electrodes. These can consist of semiconductor/metal/semiconductor<sup>194</sup> trilayers or metal/semiconductor<sup>195</sup> bilayers and serve to reduce reflections off the metallic electrode as well as alter the optical fields within devices analogous to the thickness control of ITO electrodes.<sup>11</sup> By controlling the thickness of the semiconducting top capping layer, the optical field can be shifted so that exciton generation is maximized around the donor/acceptor interface, yielding significant performance enhancements in transparent architectures.

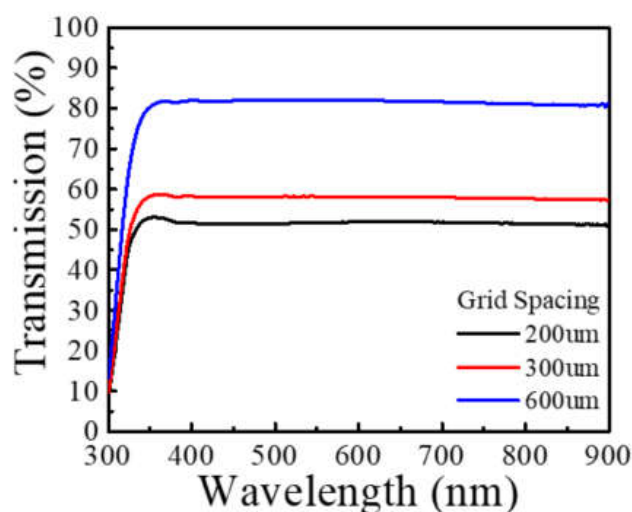


**Figure 8.4. Ag microgrid transmission.** Transmission scans of Ag microgrids printed over glass substrates. Grids were printed with a line width of 10  $\mu\text{m}$ , thickness of 5  $\mu\text{m}$ , and varied spacings.

Aerosol-printed Ag microgrids deposited over thin-film metallic electrodes may also offer a way to improve conductivity without significantly sacrificing transmission and enable device scaling to practical sizes. Highly conductive and transparent indium-free electrodes can then be achieved through careful optimization of the line width, thickness, and grid spacing (Figure 8.4). While inks used to print microgrids currently require annealing treatments to reach high

conductivity shown in Table 8.1, rapid annealing could be a viable alternative process that would preserve underlying organic TPV devices.

#### 8.4 Organic salts for luminescent solar concentrators

| Grid Spacing      | Initial Sheet Resistance ( $\Omega/\text{sq}$ ) | 160° 1 Hour Anneal Sheet Resistance ( $\Omega/\text{sq}$ ) |
|-------------------|-------------------------------------------------|------------------------------------------------------------|
| 200 $\mu\text{m}$ | $11 \pm 3$                                      | $0.43 \pm 0.06$                                            |
| 300 $\mu\text{m}$ | $10.5 \pm 0.3$                                  | $0.32 \pm 0.02$                                            |
| 600 $\mu\text{m}$ | $10.8 \pm 0.4$                                  | -*                                                         |
| No Grid           | $11 \pm 1$                                      | $11 \pm 2$                                                 |

\*Electrical connection could not be established on the 600  $\mu\text{m}$  sample after annealing.

**Table 8.1. Ag microgrid sheet resistance.** Measured sheet resistance values for Ag microgrids printed over BCP (7.5 nm) / Ag (4 nm) / Alq<sub>3</sub> (60 nm) composite electrodes.

Wavelength-selective luminescent solar concentrators (LSCs) can benefit greatly from the optical tunability of organic salts. As discussed in Section 2.6.3, low Stokes shifts are a key reabsorption loss mechanism for LSCs and are particularly important for wavelength-selective LSCs that absorb and emit within a narrow band of NIR wavelengths. Matching NIR photoemission to the absorption of the PV strips placed at the edge of the LSC is also highly important for preventing optical losses. Both challenges can be addressed by controlling the conjugation of photoactive cations to finely tune absorption and emission. This can allow photoactive waveguiding films to be optimized and tailored for any given edge-mounted PV material, enabling highly efficient transparent LSCs.

#### 8.5 Organic salts for cancer treatment

Organic molecular salts also offer exciting opportunities outside photovoltaics. One novel application where absorption and frontier molecular orbital tunability could be particularly useful

is in photodynamic therapy (PDT) for cancer treatment. PDT relies on excitonic interactions with molecular oxygen to create reactive oxygen species (ROS) such as singlet oxygen discussed in Chapter 5. The generation of a range of ROS can result in damage to DNA, cell membranes, and mitochondria, ultimately leading to cell death. Because anion exchange alters the HOMO of the collective salt, it can be used to control the favorability of ROS generation, allowing the same molecule ( $\text{Cy}^+$ ) to be used for both imaging and treatment since phototoxicity can be activated or de-activated at will.

## 8.6 Final summary

Organic and excitonic photovoltaics that selectively absorb UV and NIR light offer the highest possible combinations of *PCE* and visible transmission. This enables deployment over previously unavailable areas such as building and automobile windows, electronic displays, and virtually any other surface to complement conventional PVs. While the current highest performance TPVs can already be integrated onto architectural windows, considerably higher *PCEs*  $> 10\%$  with high *AVT* are practically achievable and therefore represent a strong motivation to continue investigations into various component material design and morphological optimization strategies. This work has presented important strategies for circumventing short exciton diffusion lengths, achieving efficient and broad NIR harvesting, as well as preventing degradation in ambient environments. Incorporating these design strategies will enable highly efficient TPV solar deployment to offset a significant fraction of global energy consumption.

## **APPENDICES**

## APPENDIX A Levelized cost of energy

To calculate the levelized cost of energy (*LCOE*) for the proposed PV window films we utilized the System Advisor Model (SAM) developed by the National Renewable Energy Laboratory (NREL). For a 12 story fully glazed building in a given set of locations (Baltimore, Phoenix, and Chicago), we can combine (1) the capacity factor and (2) the estimated first costs described above with (3) the energy generation potential and (4) the energy savings potential to plot the impact of each on the *LCOE*. This analysis includes: generation-based operating and maintenance (O&M) expenses of \$15/MWh; 20 years of energy generation; 5.2% real discount rate; multiple capacity factors (6%, 10%, and 14%) representative of various U.S. climates zones based on an extensive study of locations and building geometries (aspect ratios and orientations); 165 kW inverter capacity (downsized due to the capacity factor impact of the vertical orientation); system degradation factor of 0.5% year-over-year; AC derate factor of 90% due to various losses in the system; and financial considerations for depreciation, debt financing, and tax benefits. Given the performance range in Figure A1, competitive *LCOEs* are within reach for TPVs, driven by annual energy savings and reduced module and balance of systems (BOS) costs by leveraging sunk costs in the existing window glass infrastructure and supply chain.

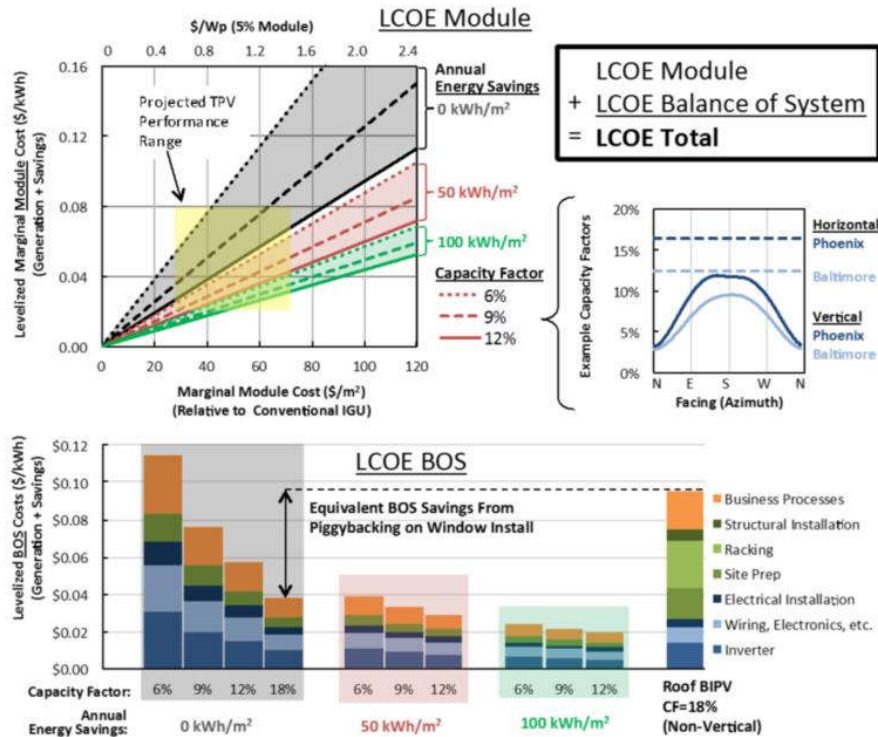


**Figure A.1. Levelized cost of energy estimation.** Component breakdown of LCOE incorporating energy savings and generation for TPV window coatings. The module component of the LCOE are shown as a function of marginal module cost relative to conventional IGU for representative capacity factors and annual energy savings. Note that the entry level module efficiency of 5% was utilized in this analysis – approaching efficiencies > 10% further reduces this estimated LCOE considerably. for each device type during full use (for example, when the display is on). (b) Application requirements for TPV as a function of *PCE* and *AVT*. Tinted architectural glass is typically at least 50% transparent, whereas electronic displays require an *AVT* of at least 80%. *PCE* values of 2–5% are sufficient to autonomously power smart windows and low-power displays, whereas *PCE* values of at least 5–10% are required to power mobile displays or achieve competitive LCOE to match semitransparent modules in automotive and building-integrated applications.

## APPENDIX B Directional solar flux variation

Directional changes in solar flux (Figure A.2) were used to calculate the *LCOEs* for vertically mounted TPVs in Section A.1. As discussed in Section 2.6.4, the total surface area on all four sides of a building is exposed to significantly higher solar flux density than a solar tracking unit of equivalent footprint, providing strong motivation for building-integrated TPVs.

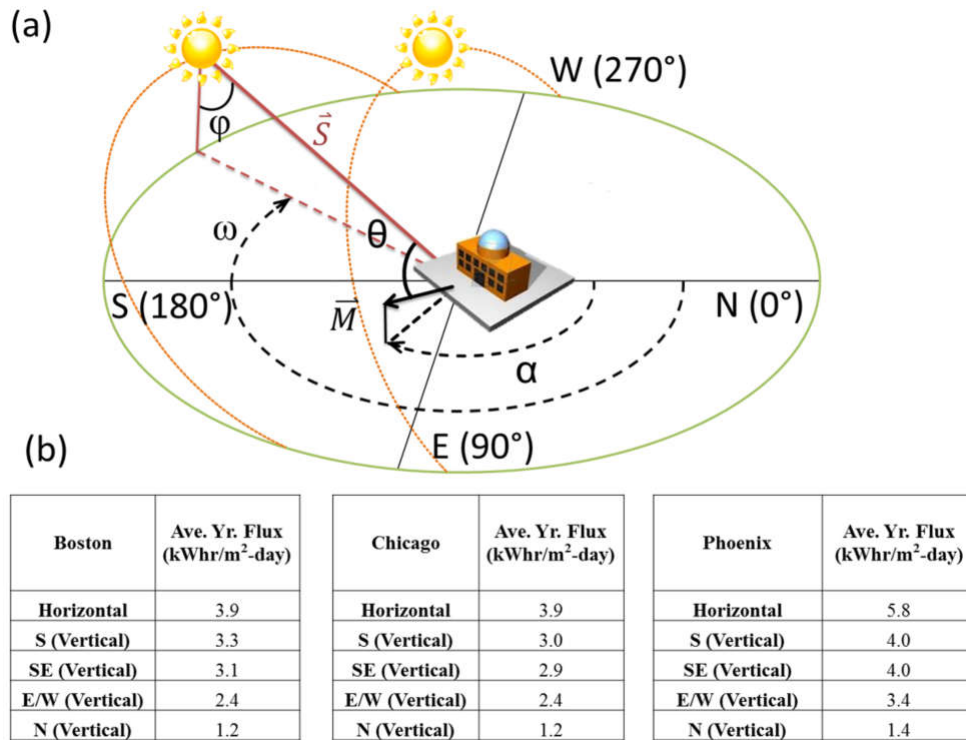


**Figure A.2. Directional solar flux.** (a) Representative schematic of the solar position relative to a building in the northern hemisphere adapted from Ref. <sup>17</sup>, Copyright 2015, with permission from Elsevier, where  $\theta$  is the incident angle of direct solar irradiance with respect to a given photovoltaic module,  $\phi$  is the zenith angle of the sun with respect to the horizon,  $\omega$  is the azimuth angle of the sun with respect to north,  $\alpha$  is the azimuth angle of the PV module,  $\vec{M}$  is the normal vector of the PV module, and  $\vec{S}$  is the unit vector of incident radiation. (b) Yearly average estimated solar flux densities in Boston (MA), Chicago (IL), and Phoenix (AZ) as a function of orientation (Ref. <sup>20</sup>).

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