

Reliability of Small Molecule Organic Photovoltaics with Electron-Filtering Compound Buffer Layers

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Abstract

Electron-filtering compound buffer layers (EF-CBLs) improve charge extraction by blending an electron-conducting fullerene with a wide energy gap exciton-blocking molecule. Here we explore the impact of EF-CBLs on the operational lifetime of planar-mixed heterojunction tetraphenyl-dibenzoperiflanthene (DBP):C₇₀ organic photovoltaic (OPV) cells. We find that devices with EF-CBLs have substantially longer lifetimes than those with a neat bathophenanthroline (BPhen) buffer due to the enhanced morphological stability of the blends. High glass transition temperature (T_G) exciton-blocking thin films with a low crystallization rate are found to produce stable morphologies and devices. The most stable

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OPVs employ 1:1 2,2',2''-(1,3,5-benzenetriyl tris-[1-phenyl-1*H*-benzimidazole] TPBi:C₇₀ buffers that lose <20% of their initial power conversion efficiency of $PCE = (6.6 \pm 0.6\%)$ after 2700 hr under continuous simulated AM1.5G illumination, and show no significant PCE degradation after 100 days of outdoor aging. When exposed to 100-sun (100kW/m²) concentrated solar illumination for 5 hr, their power conversion efficiencies decrease by < 8%. Moreover, we find that the reliability of the devices employing stable EF-CBLs has either reduced or no dependence on operating temperature up to 130°C compared with BPhen:C₆₀ devices whose fill factors show thermally activated degradation. The robustness of TPBi:C₇₀ devices under extreme aging conditions including outdoor exposure, high temperature, and concentrated illumination is promising for the future of OPV as a stable solar cell technology.

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I. Introduction

Advances in materials, deposition technologies, and device architectures continue to drive improvements in the power conversion efficiencies (*PCE*) of organic photovoltaic (OPV) cells.^[1-4] Due to the large variety of materials and structures explored, a general understanding of the factors leading to high reliability is needed to make a significant impact on their successful, widespread deployment.^[5-7] One important component influencing the lifetime of OPVs is the buffer layer located between the cathode and the photoactive layer. Buffer layers are used to confine excitons within the charge generation region, tune the optical field intensity within the active region, protect the active layer from damage during metal cathode deposition,^[8] and transport charge to the appropriate electrode.^[9,10] Recently, a class of electron-filtering compound buffer layers (EF-CBLs) has been introduced that simultaneously achieve high conductivity and efficient exciton blocking by blending a wide energy gap and electrically insulating exciton blocking molecule with a conductive fullerene.^[3,8] These improvements result in high fill factors (*FF*) and *PCE* even at light intensities exceeding one sun (1 kW/m^2).^[8] The impact of such buffers on device operational lifetime has shown promise,^[11] but has yet to be explored in conjunction with stable, blended active-layer OPVs.

Accelerated aging can provide valuable insights into the processes underlying device degradation.^[12-15] The longest-lived OPV cells now take more than a year to degrade to 80% of their initial *PCE* under one sun illumination, making conventional lifetime testing increasingly impractical.^[16-18] In complex OPVs, optimization must occur across a large device architectural and materials space, thereby highlighting the importance of developing accurate methodologies for accelerating and understanding degradation. Exposure to elevated temperature, concentrated sunlight, continuous illumination, thermal or light cycling, and

exposure to reactive atmospheres have been employed as potential acceleration techniques.^[14,19–21] An effective method should only speed up one of perhaps several mechanisms responsible for degradation, and should not promote new failure modes that are different than those experienced by the device under normal operating conditions.

Thermally accelerated aging methods assume that the degradation of a parameter, p , proceeds at a thermally activated rate, $k_{deg}(T)$:

$$k_{deg}(T) = A \exp\left(\frac{-E_A}{k_B T}\right), \quad (1)$$

where A is a constant, E_A is the activation energy leading to degradation, k_B is Boltzmann's constant, and T is the temperature. The rate at each temperature is found by fitting the value of p over time, t , to:

$$p(t) = \alpha \exp(-k_{deg}(T)t) + \beta \quad (2)$$

where α and β are constants. If more than one mechanism is active, a multi-exponential fit similar to Eq. 2 can be used to extract additional failure rates.

Here we explore the impact of using various EF-CBLs on the stability of archetype tetraphenyldibenzoperiflanthene (DBP):C₇₀ planar-mixed heterojunction OPV cells at elevated temperatures and high intensity illumination to accelerate and identify the most active performance failure mechanisms.^[22] X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, and differential scanning calorimetry (DSC) measurements are used to evaluate the changes induced in exciton blocking compounds employed in efficient EF-CBLs. We find that devices with EF-CBLs have longer operational lifetimes than those with a neat bathophenanthroline (BPhen) buffer, which is attributed to the improved morphological stability of the blends. While all devices have relatively stable open-circuit

voltages (V_{OC}) and exhibit a linear decrease in short-circuit current density (J_{SC}) under continuous illumination, changes in FF are functions of EF-CBL composition and morphological stability.

We find that DBP:C₇₀-based OPVs with BPhen:C₆₀ EF-CBLs are the least stable among those studied. These buffer layers experience a thermally activated FF degradation due to morphological changes in BPhen with $T_G = 61^\circ\text{C}$. In contrast, devices employing 2,2',2''-(1,3,5-benzenetriyl tris-[1-phenyl-1*H*-benzimidazole] (TPBi, $T_G=120^\circ\text{C}$):C₇₀ EF-CBLs have stable FF s with little evidence of degradation at temperatures up to 130°C . Finally, we study the performance of devices employing TPBi:C₇₀ EF-CBLs both outdoors and under concentrated sunlight. Following a 5 hr dose of 100-sun ($100\text{kW}/\text{m}^2$) illumination, the active layer shows no changes in absorption while losing just 7% in PCE and 2% in external quantum efficiency (EQE). Finally, after >100 days of outdoor operation, no degradation was apparent, suggesting that continuous illumination aging may underestimate OPV lifetime under real-world conditions.

This paper is organized as follows: In Sec. II we outline methods used to fabricate and test EF-CBLs and devices, and in Sec. III we report experimental results. In Sec. IV, we discuss the theory of small molecule crystal growth and relate the thermal properties of various EF-CBLs to their morphological and OPV stability. Analysis of degraded devices following accelerated aging is also discussed in Sec. IV, and compared with state-of-the-art OPV devices from the literature based on the total energy generated before failure. Conclusions are presented in Sec V.

II. Experimental

The materials Al, MoO₃, C₆₀, C₇₀, DBP, BPhen, TPBi, tris[2,4,6-trimethyl-3-(pyridine-3-yl)phenyl]borane (3TPYMB), and 3,3',5,5'-tetra[(m-pyridyl)-phen-3-yl]biphenyl (BP4mPy) were obtained from commercial sources. The chemical structural formulae for the exciton blocking materials and the electron conducting fullerenes are shown in Figs. 1 and 3. Devices were fabricated on pre-patterned indium tin oxide (ITO)-coated glass substrates. Prior to use, the substrates were cleaned by sequential sonication in tergitol/deionised (DI) water solution, DI water, acetone, and isopropyl alcohol, followed by drying with ultrapure N₂. Substrates were subsequently cleaned with a stream of supercooled CO₂ gas for 1 min, followed by a 10 min exposure to ultraviolet (UV)-ozone.^[23] Sapphire windows used for XRD measurements were similarly cleaned, omitting the UV-ozone treatment. The XRD diffraction patterns were obtained by illumination from a rotating anode, Cu K α source in the Bragg-Brentano configuration. The KBr windows for FTIR measurements were used without cleaning.

All layers were deposited by thermal evaporation in high vacuum ($< 2 \times 10^{-7}$ torr) at rates between 0.2 and 1.6 Å/s. Layer thicknesses and optical constants were measured using a variable angle spectroscopic ellipsometer. Device areas of 11.3 mm² were defined by the intersection of the pre-patterned ITO anode and a patterned Al cathode deposited through a shadow mask. Aging experiments were conducted without an optical aperture mask that confines illumination within the device active area so as to realistically simulate actual exposure conditions. Following fabrication, devices and thin films for XRD measurements were encapsulated by a cover glass in a glovebox filled with ultrahigh purity N₂ (< 1 ppm O₂ and H₂O) and sealed to the substrate with a UV-curable epoxy bead applied around its periphery. The packages contained a BaO_x/SrO_x desiccant to remove residual O₂ and H₂O incorporated during packaging, or from small package leaks. The active layer used for

absorbance measurements was deposited on quartz and packaged with a desiccant similar to the OPVs.

Substrates containing six OPV cells each were fabricated with the structure: 150nm ITO/10nm MoO_x/54nm 1:8 DBP:C₇₀/9nm C₇₀/EF-CBL/100nm Al. The EF-CBL consisted of either 10nm 1:1 BPhen:C₆₀/5nm BPhen (henceforth called BP60), 10nm 1:1 3TPYMB:C₆₀/5nm 3TPYMB (3T60), 10nm 1:1 TPBi:C₇₀/3nm TPBi (TP70), 10nm 1:1 TPBi:C₆₀/3nm TPBi (TP60), or 10nm 1:1 BP4mPy:C₆₀/3nm BP4mPy (BPPy60). Temperature dependent lifetime data were collected from devices fabricated in the same batch. All lifetime data shown are from a representative device on each substrate, where the device-to-device lifetime variation is included in the error bars along with the measurement error.

Fourier transform infrared spectra (Nicolet 6700) of 100nm thick organic films on KBr were measured immediately following growth, while a companion film was aged under 1kW/m² xenon arc lamp illumination inside a glovebox filled with high purity N₂ for 1 week prior to measurement. The FTIR spectrometer was purged with purified N₂ for >10 min prior to measurement to remove ambient H₂O and CO₂, and spectra were corrected for atmospheric interference and to establish a signal baseline. Each spectrum from 400 cm⁻¹ to 4000 cm⁻¹ consisted of averaging 32 scans with a resolution of 4 cm⁻¹.

Differential scanning calorimetry (Perkin Elmer DSC-7) was performed on 0.1-2 mg powder samples contained in a hermetically sealed Al pan. A heat-cool-heat cycle at 10°C/min was performed from 25°C to the subject material vacuum evaporation temperature to avoid decomposition.

Devices were aged under continuous illumination from a class AAA Xe arc lamp solar simulator at an intensity of 1kW/m^2 . Packaged devices were mounted on printed circuit boards and connected to a current-voltage source meter through a relay multiplexer. During aging, each device was connected to a resistor to fix its current and voltage near the maximum power operating point. A resistive heater was placed on a Cu plate beneath each device to independently control temperature which was monitored using an integrated thermocouple. The current density vs. voltage (J - V) characteristics were measured twice per hour. One film prepared for XRD analysis was measured immediately following growth, while a separate sample from the same batch was aged in N_2 under simulated solar illumination and then analyzed.

Devices for outdoor aging were fabricated and packaged as above, then mounted on a fixed-angle (30°) platform located at Sede Boqer ($30^\circ 51'$ N, $34^\circ 46'$ E) in the Negev Desert, Israel, where they remained under open-circuit conditions for 120 days. Cell temperature was measured using a thermistor mounted directly on the device substrate, and solar irradiance was monitored with a calibrated Si photodetector. During periods when the solar irradiance was $>300\text{ W/m}^2$, 4th quadrant J - V characteristics were measured twice per hour.

High light intensity (100 suns) device aging was also performed outdoors in Sede Boqer. Sunlight was collected, concentrated, and focused into a transmissive, 1 mm diameter quartz-core optical fiber coupled onto the OPV that operated at open circuit.^[24,25] Flux uniformity was achieved by placing a multimode, $3\text{ cm} \times 1\text{ cm} \times 1\text{ cm}$ quartz block between the cell and the fiber. Intensity was controlled with an iris, and measured using a spectrally blind calibrated pyranometer.^[19] The temperature of the illuminated area was estimated to be approximately 100°C .^[19,26] Experiments were limited to clear-sky periods, 2.5 hr around solar noon. The spectrum during this period was nearly invariant, and close to AM1.5G.^[27]

III. Results

X-ray diffraction measurements of 200 nm thick films of 1:1 exciton blocker:fullerene (C_{60} or C_{70}) on sapphire were taken both before and after aging for one week under simulated one sun AM1.5G illumination. After aging, a diffraction peak in the 1:1 BPhen: C_{60} film appears at an angle, $2\theta = 13.7^\circ$ (Fig. 1a), which is also observed in BPhen powder XRD patterns. The background intensity at $2\theta < 10^\circ$ of the 3TPYMB: C_{60} film (Fig. 1b) decreased to reveal a broad feature extending from $2\theta = 9^\circ$ to 12° . The 1:1 TPBi: C_{70} spectrum was featureless both before and after aging, as were the BP4mPy: C_{60} and TPBi: C_{60} spectra (not shown).

The glass transition temperature (T_G) of the wide energy gap exciton blockers BPhen, BP4mPy, 3TPYMB, and TPBi obtained by DSC are 61°C , 105°C , 106°C , and 120°C , respectively, and are listed in Table 1. Liquid-solid transitions were observed in BPhen and TPBi at 218°C and 274°C , while BP4mPy and 3TPYMB did not melt under atmospheric pressure. From the DSC melting peaks, we calculate an enthalpy of fusion of 79.9kJ/mol for BPhen, and 46.6kJ/mol for TPBi, indicating that BPhen has a larger intermolecular cohesive binding energy.^[28] The vaporization temperatures in vacuum (1×10^{-6} Torr) of the materials follow a similar trend, where TPBi evaporates at 320°C , BP4mPy at 350°C , 3TPYMB at 240°C , and BPhen at 230°C .

Figure 2 shows the FTIR absorption spectra for C_{60} , C_{70} , DBP, 3TPYMB, BP4mPy, TPBi, and BPhen both before (as-grown) and after aging for 1 week under one sun, AM1.5G simulated solar illumination in N_2 . No changes are observed in the C_{70} , DBP, 3TPYMB, BP4mPy, or TPBi spectra. In contrast, peaks at wavenumbers of 1612, 1382, 921, 842, and

809 cm^{-1} become more pronounced in the BPhen spectrum, while the changes in C_{60} are consistent with photo-oligomerization.^[29,30] The CO_2 absorption band from 640-700 cm^{-1} is omitted for clarity.

The device structures used in lifetime tests are shown in the inset of Fig. 3a. The performance of as-grown devices at $t = 0$ with the five EF-CBLs are listed in Table 1. The normalized J_{SC} , FF , V_{OC} , and PCE under simulated AM 1.5G illumination (at ambient temperature 50-60°C) are plotted in Fig. 3 as functions of time for TP60, BPPy60, and 3T60 cells. Figures 4 and 5 show the normalized J_{SC} , FF , V_{OC} , and PCE for BP60 devices between 50°C and 80°C, and for TP70 devices between 55°C and 130°C. A biexponential in Eq. 2 was used to fit the $FF(t)$ of BP60 with two rates, $k_{fast}(T)$ and $k_{slow}(T)$, as shown in Fig. 4b (solid lines). All data are normalized to the point at which the equilibrium temperature is reached.

From Figs. 3, 4, and 5, we observe that the J_{SC} of all devices decreases approximately linearly with time (5% to 10% per 1000 hr) under continuous, simulated AM 1.5G illumination. In contrast, V_{OC} is stable for BPPy60, TP60, and TP70. A decrease in V_{OC} is observed for 3T60 cells (by 4% after 320 hr) and BP60 cells (by 9% at 80°C and by 2% after 800 hr at all other temperatures). A similar trend is observed for FF where TP70, TP60, and BPPy60 cells are stable, while BP60 loses 11% to 23% after 800 hr depending on temperature, and 3T60 decreases by 6% over 300 hr of operation. The time for PCE to decrease by 20% from its starting value at ambient temperature (known as T_{80})^[14] is 800 hr for BP60, 2700 hr for TP70, 2200 hr for TP60, 1100 hr for 3T60, and 1700 hr for BPPy60 (the last three lifetimes are extrapolated).

Dark J - V characteristics were measured for all devices both before and after aging under continuous, simulated AM1.5G illumination. Results for BP60 and TP70 cells are shown in Fig. 6. The dark current at $<0.8\text{V}$ in the as-grown BP60 devices was considerably smaller than for the aged devices (Fig. 6a). After 800 hr, devices aged at higher temperatures exhibit higher dark currents. To characterize losses due to the dark current increase, we separate the illuminated J - V characteristics obtained under 1 sun into two parts: a shunt current that is linear with voltage (J_{SH}), and a non-linear component due to recombination, (J_{REC}). We extract J_{SH} by linearly extrapolating the current near 0V, and J_{REC} by taking the difference between the measured current and J_{SH} at the maximum power point. These components are plotted as functions of time and normalized to J_{SC} in Figs. 7a and 7b. In contrast, the most stable devices (TP70) show almost no change after aging (Fig. 6b), and exhibited no systematic dependence on temperature. The J - V characteristics of the TP70 devices aged at intermediate temperatures are omitted for clarity.

The degradation rates, $k_{fast}(T)$ and $k_{slow}(T)$, extracted from the biexponential fits to $FF(t)$ are plotted vs. $1/k_B T$ at each aging temperature for BP60 (Fig. 8). Using Eq. 1, we find that the two activation energies are equal to within the error of the measurement: 0.56 ± 0.06 eV for $k_{fast}(T)$ and 0.53 ± 0.13 eV for $k_{slow}(T)$.

To understand the performance of OPVs in an actual operating environment, four identical TP70 devices were placed outdoors from November 8th, 2015 to February 21st, 2016. The responsivity (which equals the ratio of J_{SC} to the solar irradiance), FF , V_{OC} , and PCE as functions of time are plotted in Fig. 9. Prior to catastrophic package failure resulting from a leak in the epoxy seal at Day 104, no discernable degradation was observed. After package failure, the J_{SC} and responsivity degraded rapidly due to oxidation and water ingress, highlighting the importance of robust encapsulation.

Since the degradation rates of some devices were not increased by thermal stress, we exposed the most stable TP70 devices and a 54 nm thick 1:8 DBP:C₇₀ thin film to 100-sun concentrated sunlight (100kW/m²) for 5 hr. Figure 10a shows the *J-V* characteristics under one sun illumination both before and after aging. The V_{OC} is stable, while a decrease of 2% in J_{SC} and 5% in FF are observed. No change in the optical absorbance of the DBP:C₇₀ active layer blend was observed after high intensity exposure (left axis of Fig. 10b). The integrated photocurrent calculated from the *EQE* (right axis of Fig. 10b) decreases by 2%, which is comparable in magnitude to the decrease in J_{SC} measured at one sun.

IV. Discussion

Blending organic materials can result in a morphology that is more stable than either of the constituents comprising the mixture.^[31,32] The compounds act to stabilize each other by breaking up the interactions between similar molecules, which prevents the formation of aggregates and growth of crystallites. Here, we find that T_G of the blocking molecule in the EF-CBL can be predictive of morphological and device stability. Nevertheless, we caution that molecular diffusion and crystallite domain growth can still occur at $T < T_G$.^[33] Materials with a low enthalpy of fusion, high T_G and high melting point produce lower crystallization rates, leading to more stable amorphous states that are required for reliable OPVs.^[33,34]

In Fig. 1a we find that including C₆₀ in the EF-CBL mixture significantly impedes, but does not completely eliminate BPhen crystallization, an effect that can induce interfacial charge build up and low resistance shunts through organic heterojunctions (HJs).^[31,35,36] The improved lifetime of blended cathode buffers was also shown for the bathocuproine:C₆₀ system in planar OPVs.^[11] As a result of the stabilized morphology, the lifetime of the BP60

EF-CBL devices ($T_{80} = 800$ hr) under continuous one sun simulated illumination is two orders of magnitude longer than devices with neat BPhen buffers reported by Song, et al.^[35] TPBi has a significantly higher $T_G = 120^\circ\text{C}$, melting point of 274°C , and lower enthalpy of fusion of 46.46kJ/mol than BPhen; thus the XRD spectra of aged TPBi blends with either C_{60} or C_{70} (Fig. 1c) show no evidence of morphological changes. The T_G 's of 3TPYMB and BP4mPy are 105°C and 106°C , respectively, but neither material melted at temperatures up to 400°C , and their XRD patterns did not show evidence of crystallization. Their large size compared to BPhen and increased degrees of intramolecular rotational freedom likely limits their tendency to form crystalline domains.^[37] No change was observed in the BP4mPy: C_{60} XRD spectra after aging, although a broad amorphous feature appeared in the 3TPYMB: C_{60} spectra, suggesting that the morphology has changed over time. The detailed nanomorphology (i.e. packing density, cluster size, and molecular orientation) within the EF-CBL blends was not revealed in the XRD spectra, although such information may be accessible with the use of more specialized characterization techniques that are beyond the scope of this work.^[38]

The trends in FF and V_{OC} follow those observed in XRD, where TP70 (Fig. 5), TP60 (Fig. 3a), and BPPy60 (Fig. 3b) are stable under continuous illumination, while BP60 (Fig. 4) and 3T60 (Fig. 3c) show decreases in these operating parameters. The J_{SC} of all devices decreases approximately linearly under continuous illumination, and has a comparatively weak dependence on EF-CBL composition or aging temperature. The origin of the decrease in J_{SC} was not apparent from the thin film analysis methods employed here. However, the optically generated polaron density in neat films is low compared with the density in the illuminated device since the films lack a junction to dissociate excitons. Therefore, polaron-

induced degradation such as exciton annihilation may be underrepresented in the thin film analyses such as in the FTIR spectra.

The FTIR spectra in Fig. 2 suggest that C₇₀, DBP, 3TPYMB, BP4mPy, and TPBi are photochemically stable under illumination in a non-reactive gas atmosphere. The largest changes are observed in C₆₀ that oligomerizes under illumination, which has been shown to result in a decrease in the exciton diffusion length and broadened optical absorption.^[30] Here, C₆₀ is used as an electron conductor in some EF-CBLs, and its effect on lifetime compared with C₇₀ is a likely the result of increased absorption in the EF-CBL. The discrepancy in J_{SC} degradation rate between the various C₆₀ EF-CBLs may be due to small changes in charge extraction as the morphologies of the buffers change with aging; an effect that should be largest for buffers with the lowest T_G . The relative changes in BPhen peak height are due to crystallization.

As noted, the EF-CBL controls charge extraction and exciton recombination, and hence its composition impacts the PCE .^[3,8] Previously, Xiao, et al. demonstrated that the $PCEs$ of devices with a BPhen:C₆₀/BPhen EF-CBL are >25% higher than those with a neat BPhen exciton blocking buffer, primarily resulting from increases in FF .^[8] Excitons at the acceptor-buffer interface are efficiently blocked due to a large difference in both the LUMO and HOMO energies between BPhen and the fullerenes, while the high conductivity and the alignment of the C₆₀ EF-CBL and the C₇₀ acceptor orbital energies leads to efficient electron extraction. The energy gaps of TPBi, BP4mPy, and 3TPYMB are sufficiently large to block excitons and have stable morphologies compared with BPhen, leading to more stable OPV operation (see Table 1).

After aging the BP60 devices, we observe a temperature dependent increase in dark current (Fig. 6a). Accordingly, the dark current subtracts from the photocurrent, shifting the

maximum power point toward the origin, thus reducing both FF and PCE .^[23] From the biexponential fits to $FF(t)$, two degradation rates are extracted, $k_{fast}(T)$ and $k_{slow}(T)$. We find that J_{SH}/J_{SC} can be fit at each temperature by a single exponential (Eq. 2) with the rate $k_{slow}(T)$ from the fit to $FF(t)$, shown in Fig. 7a. The effect of J_{SH} on FF is relatively small, accounting for only 1% to 3% of the loss, depending on temperature. Crystallization of BPhen has been shown to penetrate from the metal cathode into the device active region^[35], and is likely responsible for J_{SH} in the devices studied here. In contrast, changes in J_{REC} result in a 7% to 13% decrease of FF depending on aging temperature, as shown in Fig. 7b. The solid line shows the result of a biexponential fit to J_{REC}/J_{SC} using $k_{slow}(T)$ and $k_{fast}(T)$, where $\alpha < 0$ in Eq. 2. This asymmetric increase in forward-biased dark current is suggestive of an increase in recombination that may result from an increased defect density or decreased electron extraction efficiency at the buffer interface over time.^[39,40] The remaining FF loss in BP60 that is not accounted for by the increased dark current (5% to 9%, depending on aging temperature) results from a reduction in voltage at the maximum power point. As seen in Fig. 6b, the dark current of TP70 is stable compared with BP60, and consequently no change in FF is observed. Due to the relative stability of the EF-CBL devices that do not contain BPhen, both J_{SH} and J_{REC} likely result from the same process of BPhen crystallization. Thus, we expect that E_A of both $k_{fast}(T)$ and $k_{slow}(T)$ should be equal, and indeed this is the case to within experimental error, as shown in Fig. 8.

The performance of a population of four TP70 devices aged under sunlight shows no degradation after >100 days (see Fig. 9). This is in contrast to the cells with the same TP70 device architecture but aged under continuous simulated illumination, which show a linear decrease in J_{SC} over time (Fig. 5a). The results suggest that the lifetime of the devices under real-world operating conditions may be longer than they appear under simulated conditions.

For example, the operational lifetime under real conditions consists of alternating illumination and dark exposure, and may therefore allow for recovery in the dark if the degradation is partially reversible.^[21,41] However, this conclusion remains to be proven by additional experiments since the outdoor exposure carried out under open circuit conditions is significantly less (<500 hr of one sun equivalent radiation) than the 2500 hr maximum power operating point continuous illumination measurement using a solar simulator light source.

No change in absorption in the DBP:C₇₀ active layer film was observed after illumination for 5 hr under 100-sun intensity (Fig. 10b left-axis). Under these conditions, the *EQE* of the TP70 device was slightly reduced between $\lambda = 350\text{nm}$ and 600nm (Fig. 10b right-axis). The 2% loss in J_{SC} obtained from integration of the *EQE* spectrum after aging is comparable to the $4\pm 2\%$ decrease in J_{SC} observed after a similar dose of photons under continuous simulated illumination (500 hr). A 6% decrease in *FF* is also observed in Fig. 10a, resulting from a significant increase in dark current that was not observed during continuous illumination (c.f. Fig. 5b). Exciton-exciton or exciton-polaron annihilation may be responsible for the degradation, as their rates would be approximately four orders of magnitude higher at 100kW/m^2 than 1kW/m^2 .^{[42],[43]} Such processes are responsible for the degradation of blue phosphorescent organic light emitting diodes, but have not been similarly reported in OPVs.

In practical applications, solar cells must simultaneously achieve high efficiency and long term reliability. It is useful, therefore, to define a figure of merit that is equal to the total energy generated by a device prior to falling below an acceptable level of performance. For this we assume that cell failure occurs at T_{80} . Then the total energy generated prior to failure is:

$$E_{80} = \int_0^{T_{80}} PCE(t) \cdot P_{inc}(t) dt. \quad (5)$$

where $P_{inc}(t)$ is the solar irradiance as a function of time, t .

In Fig. 11 we plot E_{80} for the previously reported OPVs summarized in Table 2, including the TP70 devices studied here.^[7,17,18,44–53] Apparently, both lifetime and PCE have improved over the last several years, producing dramatic increases in E_{80} from $<10^6$ J/m² in 2005 to 5.9×10^8 J/m² in this work. Some polymer and small molecule cells experience a significant decrease in initial efficiency (known as burn in), presumably due to morphological rearrangement following deposition, or chemical instabilities, although that is not observed in several cells investigated here.^[14,16,18,51] Among devices with $E_{80} > 10^8$, only two have $PCE > 5\%$, and only three were aged using lamps with AM1.5G UV content. In all cases, the E_{80} for organic solar cells still fall >10 times short of those attained by inorganic solar cells where $E_{80} > 10^{10}$ J/m² for Si, CdTe, and CuInGaSe₂ devices, with initial $PCE = 13.4\%$ to 20.5% and degradation rates $<1.2\%/yr$.^[54]

V. Conclusions

The operational lifetimes of small-molecular weight, planar-mixed HJ OPVs with different EF-CBLs were determined using a range of test conditions, and were related to their morphological and photochemical stabilities based on the analysis of XRD, FTIR, and DSC data. Compared to OPVs with neat BPhen cathode buffer layers; BP60, 3T60, TP60, TP70, and BPPy60 EF-CBLs were found to be more morphologically stable, leading to reduced degradation in their long-term performance characteristics. High T_G exciton blocking molecules with a reduced tendency to crystallize produce the most stable EF-CBLs and

longest-lived OPVs. For example, BP60 has the shortest operational lifetime among the EF-CBL devices with a thermally activated loss in FF due to BPhen crystallization that leads to junction shunts and increased recombination. This is in contrast to TP70 devices which were stable at temperatures as high as 130°C , leading to an operational lifetime of $T_{80} = 2700$ hr and $E_{80} = 5.9 \times 10^8$ J/m^2 under continuous illumination. Under 5 hr exposure to concentrated sunlight (100-suns), TP70 devices experienced a 2% loss in J_{SC} , which is comparable to that observed under continuous one sun intensity illumination of the same dose (500 hr). However, during aging under sunlight, no performance loss was observed in a population of TP70 devices for >100 days.

Our results suggest that the morphological and photochemical stabilities of constituent layers are predictive of long term device stability, and form a useful basis for the design and selection of OPV materials. The robustness of TP70 devices under extreme aging conditions including outdoor exposure, high temperature, and concentrated illumination is promising for the future of OPVs as a highly stable solar cell technology.

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Table 1: Principal photovoltaic parameters of organic photovoltaic cells comprising electron filtering-charge blocking layer (EF-CBL) with various glass transition temperatures (T_G)

EF-CBL	Blocker	T_G (°C)	J_{SC} (mA/cm ²)	FF (%)	V_{OC} (V)	PCE (%)	T_{80} (hr)
BP60		61	12.1±1	62±1	0.93±0.01	6.9±0.5	800
TP70		120	11.7±1	61±1	0.93±0.01	6.6±0.6	2700
TP60		120	11.8±1	62±1	0.91±0.01	6.7±0.5	2200*
3T60		106	12.2±1	59±1	0.93±0.01	6.7±0.5	1100*
BPPy60		105	11.8±1	57±1	0.91±0.01	6.1±0.5	1700*

* T_{80} extrapolated

Table 2: Power conversion efficiency (*PCE*) and device lifetime (T_{80}), and E_{80} for several organic photovoltaic cells.

Cell Type	<i>PCE</i> (%)	T_{80} (hr)	E_{80} (J/m ²)	Illumination Source*	Reference
Polymer	2.7	12,000	8.9×10^8	S Plasma	[53]
Small Molecule	6.6±0.6	2700	5.9×10^8	Xe Arc	This Work
Polymer	5.5±0.15	1200	2×10^8	S Plasma	[16]
Small Molecule (tandem)	4.1	1600	1.9×10^8	Halogen	[17]
Small Molecule	3.2±0.05	1700	1.5×10^8	Xe Arc	[18]
Small Molecule	2.1	1800	1.2×10^8	Metal Halide	[49]
Polymer	5.1	250	4.2×10^7	Metal Halide	[50]
Polymer	2.59	300	2.6×10^7	N/A	[51]
Polymer	3.1	200	2.1×10^7	S Plasma	[52]
Polymer	3.54	50	5.9×10^6	N/A (50mW/cm ²)	[48]

Small	2.1	20	9.4×10^5	Xe Arc (75mW/cm ²)	[44]
Molecule					
Polymer	1.4	1	4.6×10^4	Xe Arc	[47]
Polymer	0.2	<1	450	N/A	[46]

* N/A = information not available

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Figure Captions

Figure 1 X-ray diffraction patterns of 200 nm thick films before (Fresh) and after aging (Aged) for one week under $1\text{kW}/\text{m}^2$ (one sun) illumination in N_2 : (a) 200nm BPhen: C_{60} 1:1, (b) 3TPYMB: C_{60} 1:1, (c) TPBi: C_{70} 1:1 Molecular structural formulae are shown as insets: (a) C_{60} (left) and BPhen (right), (c) C_{70} (left) and TPBi (right). The spectra are offset along the y-axis for clarity.

Figure 2 Fourier transform infrared absorbance spectra of 100 nm thick films of C_{60} , C_{70} , DBP, 3TPYMB, BP4mPy, TPBi, and BPhen films on KBr before (Fresh) and after aging (Aged) for one week under simulated $1\text{kW}/\text{m}^2$ (one sun) AM1.5G illumination in N_2 .

Figure 3 Normalized short circuit current (J_{SC}), fill factor (FF), open circuit voltage (V_{OC}), and power conversion efficiency (PCE) vs. time under continuous simulated AM1.5G illumination for (a) TP60, (b) BPPy60, and (c) 3T60 OPV cells, with the device structure shown in the inset of (a). Molecular structural formulae for BP4mPy and 3TPYMB are shown in the insets of (b) and (c), respectively.

Figure 4 Normalized (a) J_{SC} , (b) FF with biexponential fits (dashed lines), (c) V_{OC} , and (d) PCE vs. time at aging temperatures of 50°C , 60°C , 70°C , and 80°C for BP60 cells under continuous simulated AM1.5G illumination (one sun intensity).

Figure 5 Normalized (a) J_{SC} , (b) FF , (c) V_{OC} , and (d) PCE vs. time at 55°C , 80°C , 105°C , and 130°C for TP70 cells under continuous simulated AM1.5G illumination (one sun

intensity). The discontinuity in the data at 1200 hr comes from replacement of the light source.

Figure 6 Dark current density vs. voltage for **(a)** BP60 devices before (Fresh) and after aging for 800 hr at aging temperatures of 50, 60, 70, and 80°C; and **(b)** TP70 before (Fresh) and after aging for 2700 hr at 130°C.

Figure 7 **(a)** J_{SH} and **(b)** J_{REC} normalized to J_{SC} as a function of time for BP60 devices aged at 50, 60, 70, and 80°C, with exponential or biexponential fits (lines) using the degradation rates extracted from $FF(t)$.

Figure 8 Natural logarithm of degradation rates (k_{fast} and k_{slow}) vs. $1/k_B T$ obtained from biexponential fits to FF for BP60, where T is the aging temperature. Linear fits used to extract the activation energy (E_A) from each exponential are shown by the lines in the plot.

Figure 9 Normalized **(a)** J_{SC} , **(b)** FF , **(c)** V_{OC} , and **(d)** PCE vs. time for 4 different TP70 cells aged outdoors. The sharp decrease in performance after 100 days is due to a failure of the epoxy-sealed package.

Figure 10 (a) Current density vs. voltage for TP70 cells before (Fresh) and after aging (Aged) under concentrated 100-sun illumination for 5 hr. **(b)** Left axis: Optical absorbance vs. wavelength for a 54nm thick 1:8 DBP:C₇₀ film, and right axis: *EQE* of TP70 aged under the same conditions as **(a)**.

Figure 11 Energy produced prior to a loss of 20% in the power conversion efficiency (E_{80}) vs. publication year for the TP70 devices reported here, and previously reported OPV cells with literature references indicated. Device lifetime measured using light sources which include little or no UV light are noted with an asterisk (*). Some cells experience a “burn-in” for the first several hundred hours, during which 20-40% of the initial *PCE* is lost, and are noted by a dagger (†). The E_{80} calculated considers T_{80} measured from $t=0$ for all devices.