Organic solar cells are promising for low-cost energy conversion, and while their power-conversion efficiencies have steadily climbed, recently reaching 11%, there still remains a wide efficiency gap between OPVs and conventional inorganic solar cells. This discrepancy is due in large part to differences in the way that charges are generated in OPVs compared with their inorganic counterparts. Whereas photon absorption in an inorganic semiconductor leads directly to free charge formation, optical excitation in organic semiconductors results in a tightly bound electron–hole pair, known as an exciton, owing to a low dielectric constant and weak intermolecular electronic coupling. A heterojunction between donor (D) and acceptor (A) molecules is therefore needed to drive exciton dissociation and yield separated charges. However, even after electron transfer occurs across the D/A interface, the electron and hole are still Coulombically bound to one another, forming an intermediate charge transfer (CT) state. Overcoming the CT state binding energy, typically on the order of 0.1–0.5 eV results in energy losses that fundamentally reduce the thermodynamic limiting efficiency of OPVs below the Shockley–Queisser limit. Despite the seemingly large differences between organic and inorganic optoelectronic properties, similarities have been shown, particularly when structural order of the molecules is enhanced. Charge transport in disordered organic semiconductors relies on a phonon-assisted organic photovoltaic cells possess desirable practical characteristics, such as the potential for low-cost fabrication on flexible substrates, but they lag behind their inorganic counterparts in performance due in part to fundamental energy loss mechanisms, such as overcoming the charge transfer (CT) state binding energy when photogenerated charge is transferred across the donor/acceptor interface. However, recent work has suggested that crystalline interfaces can reduce this binding energy due to enhanced CT state delocalization. Solar cells based on rubrene and C₆₀ are investigated as an archetypal system because it allows the degree of crystallinity to be well controlled from a highly disordered to highly ordered system. Using a postdeposition annealing method to transform as-deposited amorphous rubrene thin films into ones that are highly crystalline, it is shown that the CT state of a highly crystalline rubrene/C₆₀ heterojunction undergoes extreme delocalization parallel to the interface leading to a band-like state that exhibits a linear Stark effect. This state parallels the direct charge formation of inorganic solar cells and reduces energetic losses by 220 meV compared with 12 other archetypal heterojunctions reported in the literature.

1. Introduction
Organic photovoltaic cells (OPVs) are promising for low-cost energy conversion, and while their power-conversion efficiencies have steadily climbed, recently reaching 11%, there still remains a wide efficiency gap between OPVs and conventional inorganic solar cells. This discrepancy is due in large part to differences in the way that charges are generated in OPVs compared with their inorganic counterparts. Whereas photon absorption in an inorganic semiconductor leads directly to free charge formation, optical excitation in organic semiconductors results in a tightly bound electron–hole pair, known as an exciton, owing to a low dielectric constant and weak intermolecular electronic coupling. A heterojunction between donor (D) and acceptor (A) molecules is therefore needed to drive exciton dissociation and yield separated charges. However, even after electron transfer occurs across the D/A interface, the electron and hole are still Coulombically bound to one another, forming an intermediate charge transfer (CT) state. Overcoming the CT state binding energy, typically on the order of 0.1–0.5 eV results in energy losses that fundamentally reduce the thermodynamic limiting efficiency of OPVs below the Shockley–Queisser limit. Despite the seemingly large differences between organic and inorganic optoelectronic properties, similarities have been shown, particularly when structural order of the molecules is enhanced. Charge transport in disordered organic semiconductors relies on a phonon-assisted...
hopping mechanism. However, studies conducted on certain highly ordered organic single crystals show band transport of both holes\cite{9} and electrons,\cite{10} mimicking the transport mechanisms in inorganic materials. Further, extremely long exciton diffusion lengths of up to 8 \( \mu \)m have been measured in rubrene single crystals.\cite{11} These results suggest that highly ordered organic systems can be key to unlocking other advantages typically only seen with inorganics, such as the absence of CT state energy losses.

Further, it has recently been shown that enhancing the degree of crystallinity in certain organic systems can enable CT states to delocalize over multiple molecules.\cite{12} Much debate exists about the role of CT state delocalization in charge generation and whether or not higher-order “hot” CT states—believed to be more delocalized—are necessary precursors to the separated charge state.\cite{13-15} In this work, we investigate a highly crystalline system of rubrene and \( \text{C}_{60} \) and observe for the first time the presence of a dense distribution of long-range CT states that is band-like in nature, yielding a binding energy low enough to parallel the process of direct charge formation in inorganic materials and lead to lower energetic losses at the heterojunction.

2. Results and Discussion
Rubrene thin films deposited via thermal evaporation are amorphous. We have reported previously\cite{16} a simple heat treatment to induce crystallization of these amorphous films. Incorporation of a thin (5 nm) layer of tris[4-(5-phenylthiophen-2-yl) phenyl]amine (TPTPA) prior to rubrene deposition further improves the crystallization process\cite{17} and allows access to pinhole-free films with crystalline domains exceeding 1 mm in size, as seen in the polarized optical microscope image in Figure 1a. The uniform coloring of the grains indicates a single molecular orientation within the domain. The atomic force microscope image in Figure 1b shows that growing \( \text{C}_{60} \) atop this crystalline rubrene template layer results in plate-like
crystalline C{sub 60} domains with lateral dimensions on the order of 200 nm that adopt the crystal structure of bulk C{sub 60} (ref. [18]). The grazing-incidence X-ray diffraction (GIXD) pattern in Figure 1c of C{sub 60} grown atop the crystalline rubrene template shows that rubrene (reflections identified in white) adopts its orthorhombic crystal structure with its (h00) planes preferentially organized parallel to the substrate while C{sub 60} (reflections identified in red) adopts a highly oriented face-centered cubic crystal structure with its (111) plane parallel to the substrate. [19,20] These data provide ensemble-averaged structural information for each of the heterojunction materials; to ascertain how rubrene and C{sub 60} orient at the molecular scale at the D/A interface, we carried out molecular mechanics simulations whose calculated lowest-energy configuration of this interface is shown in Figure 1d (additional simulation results can be found in Figures S1–S4 in the Supporting Information).

External quantum efficiency (EQE) measurements allow us to visualize photocurrent generation from the CT state at energies less than that of the Frenkel molecular absorption. Since C{sub 60} defines the low-energy absorption edge in this heterojunction pair, the measured EQE of a single-layer C{sub 60} device (Figure 2a) shows that the photocurrent produced below 1.6 eV is a result of direct excitation of the CT state (EQE and absorption spectra for single-layer amorphous and crystalline rubrene control devices are shown in Figure S5 in the Supporting Information). Amorphous rubrene planar heterojunction (PHJ) and bulk heterojunction (BHJ) devices with C{sub 60} show a single CT state with a typical Gaussian lineshape centered at \( \approx 1.6 \) eV. Data fitting yields a CT state energy (\( E_{\text{CT}} \)) of 1.48 eV and reorganization energy (\( \lambda \)) of 0.11 eV for the amorphous PHJ device, in agreement with previous work on amorphous rubrene/C{sub 60} solar cells. [21] However, the CT state photocurrent from a crystalline rubrene/C{sub 60} PHJ (“crystal PHJ”) device is much broader and does not resemble the Gaussian lineshape observed in many previous studies [21,22] that characterizes a local CT excitation between neighboring D and A molecules.

To study the impact of local structural order on CT state behavior, we investigate a method by which to modulate the degree of crystallinity of the heterojunction between these extreme cases of order (crystalline C{sub 60} atop crystalline rubrene)
and disorder (C$_{60}$ atop amorphous rubrene). Despite the fact that pristine rubrene adlayers will propagate the crystallinity of the crystalline rubrene template, Bragg–Brentano X-ray diffraction reveals that a 1:1 blend of rubrene-C$_{60}$ grown on top of the crystalline rubrene template is largely disordered (Figure S6a, Supporting Information). Therefore, the interfacial disorder will increase with increasing thickness of this disordered blend until any remaining exposed areas of the ordered crystal PHJ interface are covered.

A schematic of the device stack is shown in Figure 2b. The thickness of this disordered blend, $X$, is swept from 0 to 100 nm and the resulting EQE measurements of the CT state behavior are shown in Figure 2c (a finer thickness sweep is shown in Figure S6b in the Supporting Information). As $X$ increases, we see a distinctly parabolic shape centered at 1.6 eV rise in prominence. Remarkably, for the thickest values of $X$, the peak EQE for this CT state exceeds 1.5%, which, to our knowledge, is the highest-ever reported EQE for a CT state. Even when $X = 2$ nm, the high-energy feature ($\approx 1.6$ eV, Figure 2c dashed arrow) has greatly enhanced prominence, producing nearly two orders of magnitude higher photocurrent, but the low-energy tail ($\approx 1.1$ eV, Figure 2c, solid arrow) remains largely unchanged, indicating that these features possess a different origin. Since the CT states in the amorphous rubrene devices are energetically aligned with the higher-energy (Figure 2c, dashed arrow) CT feature that appears for $X > 0$ nm, it suggests that the higher-energy feature is a result of disorder at the heterojunction. The interfacial disorder (and hence prominence of the higher-energy feature) saturates when $X = 4$ nm devices, the absorption at $\approx 1.55$ eV (corresponding to the disordered CT state in the blend) is isotropic, with slight deviations due to optical interference effects, thereby confirming the disordered origin of this CT feature. Crucially, however, the low-energy CT state at $\approx 1.1$ eV in the crystalline PHJ and the $X = 4$ nm devices must be of different origin because it is strongly anisotropic, with a nearly cos$^2\theta$ polarization pattern indicative of well-aligned transition dipoles.

The anisotropic optical response of the low-energy CT state provides a way to explicitly isolate its photocurrent contribution by eliminating common-mode isotropic absorption via the difference, EQE$_{TM}$–EQE$_{TE}$ (ref. [26]). The result plotted in Figure 3d reveals a step function-like CT state absorption spectrum in the range 1–1.6 eV that is clearly different from the Gaussian lineshape observed for other localized CT excitations using this same method. Instead, the shape of the absorption spectrum in Figure 3d is reminiscent of that observed for 2D electronic systems such as inorganic quantum wells and 2D transition metal dichalcogenides [27–30] that have step function-like density of states (DOS) functions, which is the same dimensionality expected for an extended CT state that is Coulombically confined to the interface. In this context, we applied a 2D DOS direct bandgap model [31] to the EL and polarized EQE subtraction data of the crystal PHJ device (see the Supporting Information for model details). Using this reciprocity approach, we simultaneously fit these two data sets to yield a shared set of parameters (see inset of Figure 3d) and found that such a model provides a consistent description of the data. Compared with a CuZnSnSSe solar cell, the crystal PHJ device has a $\gamma = 1.55$ eV, which underscores the narrowing of its emission peak as a result of the highly ordered system.

To further investigate the CT state delocalization and bandlike characteristics, we applied quantum chemical calculations to the ordered and disordered systems under investigation. Due to random molecular orientations in the disordered system, we model the disordered CT state by considering single rubrene and C$_{60}$ molecules in solution. We take the minimum energy geometry to be the most likely dimer configuration (Figure 4a) and compute a calculated CT state energy of 1.61 ± 0.2 eV in good agreement with the Marcus fit value of $E_C = 1.48$ eV. Although this simple single-solvated dimer model does not account for the configurational broadening of the CT state
peak, and does not include structural orientation effects of the surrounding disordered interface beyond a mean-field level, it still provides a useful comparison between theory and experiment; we see that localization of the CT state on a single representative rubrene/C₆₀ dimer is sufficient to explain the energy of the center of the disordered CT state peak. Upon incorporating additional rubrene molecules with the interfacial alignment shown in Figure 1d based on the experimental molecular orientation of the crystalline rubrene and crystalline C₆₀ films, we calculate that the lowest-energy crystalline CT state is characterized by a hole wavefunction that is delocalized over several rubrene molecules along the interface and is limited mainly by the binding electron in C₆₀. While the hole-only system is fully delocalized, the presence of the electron on C₆₀ breaks translational symmetry, localizing the hole wavefunction. Further, the C₆₀ molecule reduces the rubrene–rubrene hole-hopping coupling along the c-axis from 0.14 to 0.09 eV. However, we note that it has been shown in the literature that crystallization can lead to delocalization on either the donor[13] or acceptor[12,15] side, with varying effects on CT state behavior.

The spatial character of the crystalline CT state is also evident from electroabsorption (EA) measurements in the CT energy range with an electric field applied normal to the heterojunction in reverse biased devices (EA measurements on single-layer control devices can be found in Figure S7 in the Supporting Information). The data in Figure 5a show that the X = 100 nm device exhibits a single CT feature at ≈1.55 eV, while the crystal PHJ (X = 0 nm) device exhibits a single CT feature at ≈1.1 eV, confirming that the high-energy (disordered) CT state is not present in this device. The X = 4 nm device displays both...
high- and low-energy CT features in accord with our interpretation of the EQE in Figure 2c. Similar to the EQE, the low-energy CT EA response is strongly TM-polarized, whereas the higher-energy disordered CT EA feature is largely independent of polarization. Figure 5b shows that, in contrast to the usual quadratic Stark effect exhibited by the disordered CT state, the crystal PHJ EA arises from the linear Stark effect due to its highly oriented net CT dipole moment.\[32\] In this case, a uniform electric field, \( F \), applied in reverse bias couples to the orientation-averaged net CT dipole moment and leads to a decrease in its energy given by \( \Delta E_{CT} = -\langle F \cdot \mu_{CT} \rangle \), which leads to a red-shift of the CT absorption spectrum\[32\] and thus to the first derivative differential absorption lineshape shown in Figure 5a. This red-shift is directly evident in the crystal PHJ EQE spectra recorded for different reverse bias fields shown in Figure S8 in the Supporting Information. Normalizing the EQE spectra to account for improved charge collection in reverse bias reveals a \( \approx 10 \) meV red-shift of the crystal PHJ CT absorption edge in Figure 5c that is absent from the disordered CT absorption in Figure 5d. This red-shift enables the crystal PHJ CT dipole moment normal to the interface to be determined\[32\] as 31.8 ± 12.6 D, which is consistent with the calculated value of 56.0 D that is determined from the calculated CT state charge density distribution in Figure 4b. Meanwhile, the dipole moment for the \( X = 100 \) nm device, as determined via EA measurements\[32\] yields a smaller value of 8.4 ± 2.4 D, thereby indicating that the average electron–hole separation in the crystal PHJ CT state is significantly larger than that of the disordered CT state. EA carried out with the electric field applied in-plane should alternatively probe the substantial CT delocalization predicted along the D/A interface; however, it has so far proven challenging to isolate signal from noise in this measurement configuration, preventing a direct comparison with the simulated results.

Our computational models provide important implications for material selection and reducing energy losses in OPV devices. To begin, we compute a CT exciton binding energy of \( \approx 0.1 \) eV in the crystal PHJ device, substantially lower than the \( \approx 0.6 \) eV CT exciton binding energy computed for the amorphous devices. The CT state binding energy is computed as the difference between the lowest energy (bound) state and the lowest energy unbound state of the lattice model. This analysis suggests a substantially reduced energy loss mechanism for the crystal PHJ device compared with the amorphous devices, which is confirmed via temperature-dependent \( V_{OC} \) measurements (Figure 6). In the amorphous PHJ device, we find that \( V_{OC} \) increases linearly with decreasing temperature until \( \approx 225 \) K where it saturates at 1.08 V. In the crystal PHJ device, however, there is no \( V_{OC} \) saturation down to 125 K at which
point, the $V_{OC}$ is 0.81 V. The saturation of $V_{OC}$ at low temperature has previously been interpreted as a result of decreased CT state dissociation efficiency and therefore suggests that charge separation proceeds more easily at the crystal PHJ than at the amorphous PHJ$^{[33]}$ due to a smaller CT state binding energy in the former. This smaller binding energy manifests directly as a reduced loss in potential relative to the CT-defined optical absorption energy gap. To make this comparison, we consider the difference between the highest measured $V_{OC}$ for each device (at low temperature) relative to its CT state energy (1.48 eV, amorphous PHJ) or CT band gap (1.07 eV, crystal PHJ) measured at room temperature. These calculations yield differences of 0.40 eV for the amorphous PHJ and 0.26 eV for the crystal PHJ, proving that the crystal PHJ has a reduced energy loss of at least 140 meV compared with the amorphous device. We emphasize that this number represents a lower bound to the amount of energy loss reduction since the crystal PHJ $V_{OC}$ still has not saturated even at the lowest temperatures we can probe.

It has been suggested$^{[4,6,22]}$ that energy losses for a D/A interface can be quantified by the difference between the room temperature $qV_{OC}(T)$ and $E_{CT}(T)$ converge at 0 K. Indeed, using this method, the D/A systems, both polymer and small molecule, listed in Table 1 have an average energy loss of 0.57 eV, with a standard deviation of 38 meV. Remarkably, the crystal PHJ device presents a difference $qV_{OC}(0 K) - qV_{OC}(295 K) = 0.35$ eV, thereby exhibiting a reduced energy loss of 220 meV. The crystal PHJ energy loss is significantly smaller than it is for the amorphous control device (0.54 eV) and represents an energy loss nearly six standard deviations below the mean of the material systems in Table 1. While the $V_{OC}$ of the crystalline rubrene/C$_{60}$ device is lower than that of the amorphous device, the reduced energy loss indicates that an alternative acceptor with a shallower lowest unoccupied molecular orbital level than C$_{60}$ could be used to reduce the gap between $V_{OC}$ and the Frenkel absorption edge even further to realize higher power conversion efficiency. These exceptional results confirm that structural order is an important design principle to reduce energy loss and allow for more efficient OPVs.

Finally, we consider alternative crystalline interfaces between rubrene and C$_{60}$ (Figure S4, Supporting Information) in order to understand the role of molecular interfacial orientation in these
charge transport is a prerequisite to band-like charge photogeneration. Though we are not yet able to fully answer this question, we have found that pentacene, which also possesses band-like charge transport,[34] does not exhibit band-like charge photogeneration of the CT state when paired with C_{60} (ref. [26]).

3. Conclusion

In summary, we have found a domain where OPVs not only work in a delocalized fashion but also, through the existence of a band-like CT state, can dissociate interfacial CT excitons into free charges in a process that parallels inorganic semiconductors where formation of charge is a direct process. The results presented here distinguish the CT state of the crystal PHJ device from previous reports in that the delocalization is so great that the CT state exhibits band-like properties, such as narrow band-edge emission, a consistent description of emission and absorption via a band model, and reduced energy loss in solar cell devices. Using the design guidelines presented here, future high-efficiency OPVs should utilize molecules with high degrees of structural order and interfacial orientations that maximize charge delocalization. This opens the door for organic solar cells to operate in a new regime in which energy losses are reduced by avoiding the need to overcome large CT state binding energies in order to produce free charges. Further, this report underscores the importance of the local environment at the D/A interface on charge photogeneration in organic solar cells.

4. Experimental Section

Glass substrates prepatterned with indium tin oxide (ITO) were cleaned via ultrasonication in deionized water, acetone, and isopropanol before undergoing an O$_2$ plasma treatment. All organic materials were sourced from commercial vendors and purified via thermal gradient sublimation prior to use: TTPA (Lumtec), rubrene (Nichem), C$_{60}$ (Nano-C), and bathocuproine (BCP, Nichem). All layers were deposited via thermal evaporation with a base pressure of $\approx 3 \times 10^{-7}$ Torr. The following evaporation rates were used: TTPA (0.5 Å s$^{-1}$), rubrene (1 Å s$^{-1}$), rubrene:C$_{60}$ (0.3:0.3 Å s$^{-1}$), C$_{60}$ (1 Å s$^{-1}$), BCP (1 Å s$^{-1}$), and Al (1.5 Å s$^{-1}$). To fabricate the crystalline samples, after the initial 22 nm of rubrene deposition, the samples were removed from vacuum and heated at 141 °C for 7 min in a clean, dry N$_2$ environment to facilitate rubrene crystallization. The samples were then reintroduced into the vacuum chamber where the subsequent layers were deposited. The structure of the amorphous PHJ device was: ITO/rubrene(20 nm)/C$_{60}$(20 nm)/BCP(10 nm)/Al(100 nm). The structure of the amorphous BHJ device was: ITO/rubrene:C$_{60}$(1:1)(40 nm)/BCP(10 nm)/Al(100 nm). For polarized EQE and EL measurements, samples were encapsulated with a N$_2$ atmosphere using a solvent-free epoxy and a glass cap.

Polarized optical microscope images were taken with an Olympus BX60FS, and atomic force microscopy images were taken with a Veeco Innova, model 840-012-711. GIXD was collected at the G1 station at the Cornell High Energy Synchrotron Source. The X-ray beam (9.95 ± 0.05 keV) was selected to be 0.05 mm tall and 1 mm wide. The beam was aligned above the critical angle of the film but below that of the substrate, at a 0.18° incident angle. GIXD images were collected on a 2D charge coupled device (CCD) detector positioned 111.6 mm from the sample. Due to the short sample-to-detector distance, the width of the samples was kept at 5 mm to reduce geometric smearing. 2D GIXD images

---

**Figure 6.** Temperature-dependent open-circuit voltage for the crystal and amorphous PHJ devices. Open-circuit voltage linearly increases (solid lines are guides to the eye) as temperature decreases, but the amorphous PHJ saturates below 225 K whereas the crystal PHJ does not, even down to 125 K, indicating that charge separation occurs more easily in this device due to increased delocalization and reduced binding energy.

**Table 1.** Energy losses from the CT state to $V_{OC}$.

<table>
<thead>
<tr>
<th>Material system</th>
<th>$E_{CT-qV_{OC}}$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline rubrene/C$_{60}$</td>
<td>0.35</td>
</tr>
<tr>
<td>Amorphous rubrene/C$_{60}$</td>
<td>0.54</td>
</tr>
<tr>
<td>6T/DIP (ref. [4])</td>
<td>0.62</td>
</tr>
<tr>
<td>Pentacene/C$_{60}$ (ref. [4])</td>
<td>0.60</td>
</tr>
<tr>
<td>DIP/C$_{60}$ (ref. [4])</td>
<td>0.51</td>
</tr>
<tr>
<td>CuPc/C$_{60}$ (ref. [4])</td>
<td>0.57</td>
</tr>
<tr>
<td>6T/C$_{60}$ (ref. [4])</td>
<td>0.52</td>
</tr>
<tr>
<td>APFO3:PCBM 1:4 (ref. [6])</td>
<td>0.59</td>
</tr>
<tr>
<td>APFO3:PCBM 1:1 (ref. [6])</td>
<td>0.59</td>
</tr>
<tr>
<td>P3HT:PCBM 1:1 (ref. [6])</td>
<td>0.53</td>
</tr>
<tr>
<td>RRA P3HT:PCBM 1:4 (ref. [6])</td>
<td>0.61</td>
</tr>
<tr>
<td>MDMO-PPV:PCBM 1:4 (ref. [6])</td>
<td>0.58</td>
</tr>
</tbody>
</table>

DIP = diindenoperylene, CuPc = copper phthalocyanine, APFO3 = poly(2,7-(9-di-octyl-fluorene)-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole), PCBM = [6,6]-phenyl-C$_{61}$-butyric acid methyl ester, P3HT = poly[3-hexylthiophene], MDMO-PPV = poly[2-methoxy-5-(30,70-dimethyloctyloxy)-1,4-phenylene vinylene].
have been background subtracted, and polarization and absorption corrections were applied. EQE measurements were taken using a Newport TLS-300X tunable light source pass system. Measurements were performed under short-circuit conditions using a Stanford Research Systems SR30 lock-in amplifier and SR570 current preamplifier to detect the photocurrent produced by the device from the incident (110 Hz) light. Calibrated Si and Ge photodetectors (Newport) served as reference cells.

Steady-state EL measurements were collected under constant current bias of 250 mA cm\(^{-2}\) for the X = 100 nm device and 1 A cm\(^{-2}\) for the crystal (PHJ) device using a Horiba iHR fiber-coupled spectrometer with an air-cooled Si CCD array and a N\(_2\)-cooled InGaAs array. All figures present EL data with units of normalized photons/area \(\times\) time \(\times\) bandwidth.

Polarized EQE measurements were performed using an Energetic laser-driven Xe light source passed through a Princeton Instruments SP2150 monochromator and chopped at a frequency of 400 Hz. Synchronous photocurrent was detected using an Amtek 7230 lock-in amplifier and SR570 current preamplifier. Monochromatic light was passed through a broadband wire grid polarizer (Edmund Optics) fixed to a precision rotation mount to define the polarization of the beam, which was then incident on the device at an angle of 30°. Calibrated Newport Si and Ge photodetectors were used as reference cells. Biased EQE measurements were similarly obtained using TM-polarized light and the current preamplifier to hold the devices in reverse bias. EA measurements were performed using the same system. TM-polarized light was incident on the device and the reflection off the Al cathode (i.e., incident light passed through the active layer twice) was collected with calibrated Si and Ge photodetectors. Spectra were obtained by depleting all devices with a \(-1.5\) V reverse bias and a 3 V peak-to-peak, \(f = 400\) Hz sinusoidal voltage to measure the change in reflected light. EA as a function of reverse DC bias was collected using a constant AC voltage of 3 V peak-to-peak.

Bragg–Brentano X-ray diffraction measurements were performed on a Bruker D8 Discover diffractometer with CuK\(_x\) source, parallel mirror optics, 0.6 mm divergence slit, and a point scintillation detector. For low-temperature \(V_{\text{OC}}\) measurements, devices were mounted in a Janis ST-100 liquid–nitrogen cryostat. Cold finger and device temperatures were controlled and monitored with a LakeShore 335 Cryogenic Temperature Controller. A Si diode mounted directly on to the device substrate was used to carefully monitor device temperature throughout all measurements. \(V_{\text{OC}}\) was measured using a Keithley 2400 SourceMeter at cold finger temperatures ranging from 77 K to room temperature. A 405 nm laser diode was used as the light source, and incident intensity was tuned using a continuous neutral density filter to yield a \(V_{\text{OC}}\) similar to one-sun conditions at room temperature for each device. Intensity was monitored during measurements with a calibrated Si Photodiode and ThorLabs digital power meter.

Density functional theory calculations were performed using the Q-Chem 4.3 package\(^{[31]}\) with the 31G, 31G*, and 6-31G* basis sets.\(^{[32]}\) Charge transfer state energies, couplings, and transition dipole moments were computed using constrained density functional theory configuration interaction (C-DFT-CI).\(^{[33]}\) CT state energies computed with C-DFT-CI were expected to be accurate to within 0.2 eV. Dielectric effects were simulated using the conducting polarizable continuum model.\(^{[34]}\)

Molecular dynamics calculations were performed using the GROMACS package.\(^{[35]}\) The Lennard-Jones parameters for carbon were \(r = 0.3431\) nm and \(\epsilon = 0.4196\) kJ mol\(^{-1}\). The Lennard-Jones parameters for hydrogen were \(r = 0.2571\) nm and \(\epsilon = 0.1842\) kJ mol\(^{-1}\). The Lennard-Jones parameters were taken from the OPLS-aa force field for aromatic carbon and for hydrogen bond to an aromatic carbon.\(^{[36]}\) Further computational details can be found in the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors thank R. A. Kerner for assistance with Bragg–Brentano X-ray diffraction measurements. The authors acknowledge support for this work from the U.S. Department of Energy, Office of Basic Energy Sciences, and Division of Materials Sciences and Engineering under award numbers DE-SC0012458 and DE-SC0012365. The theory work on this project was supported as part of the Center for Excitronics, an Energy Frontier Research Center funded by the US Department of Energy, Office of Science, and Office of Basic Energy Sciences (award no. DE-SC0001088, MIT). G.E.P. was supported by the Department of Defense (DoD) through the National Defense Science and Engineering Graduate Fellowship (NDSEG) Program. CHESS is supported by the NSF & NIH/NIHMS via NSF award DMR-1332208. Y.-L.L. acknowledges support by the National Science Foundation (NSF) Materials Research Science and Engineering Center program through the Princeton Center for Complex Materials (DMR-1420541). This work was performed, in part, at the Center for Nanoscale Materials, a U.S. Department of Energy Office of Science User Facility, and supported by the U.S. Department of Energy, Office of Science, under Contract No. DE-AC02-06CH11357.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

charge transfer state, crystal, delocalized, rubrene, solar cells

Received: May 31, 2017
Revised: August 7, 2017
Published online: