Today’s most prevalent information display technology is the liquid crystal display (LCD). Unfortunately, LCDs are energy inefficient, as most of the backlight energy (around 75%) is lost to the orthogonal polarizers. Here, we demonstrate a novel energy recycling concept called polarizing organic photovoltaics (ZOPVs), which can potentially boost the function of an LCD by working simultaneously as a polarizer, a photovoltaic device and an ambient light or sunlight photovoltaic panel. The ZOPV film was created by the uniaxial orientation of an organic conjugated polymer. A novel inverted quasi-bilayer structure was used to produce ZOPV devices. Significant anisotropic optical and photovoltaic effects were obtained, indicating the great potential of ZOPV as a promising green technology.

As an electromagnetic wave (EM), light can be divided into two linear oscillation components: the parallel (||) and perpendicular (⊥) polarizations. They can be separated by a linear polarizer to provide linear polarized light, and have vast applications. One of the most prevalent applications is for LCD technology. Figure 1a shows schematically the construction of LCD panels. The fundamental principle underpinning LCD operation is the modulation of light using a combination of two orthogonal polarizers with liquid crystal molecules between these two polarizers to form light valves. Currently, the most commonly used linear polarizer is the absorptive polarizer, which absorbs and wastes the unwanted polarization component while allowing the other component to be transmitted. From an energy point of view, these absorptive polarizers in LCDs are rather inefficient as far as the usage of the backlight photons is concerned. The power consumption of the backlight units takes up approximately 80–90% of the total power consumption in LCD modules. Unfortunately, most of the backlight energy is lost to these absorptive polarizers (75%). This loss is at a maximum when the pixel displays the color black (this is when the polarizers are completely crossed), since the backlight is still fully on.

In this work, we innovate on the biggest energy loss component, the polarizers, by turning the polarizer into an energy-generating photovoltaic (PV) unit, creating a polarizing organic photovoltaic device (we use the acronym ZOPV in this manuscript rather than POPV, which is often used to refer to polymer organic photovoltaics). A unique advantage of the organic conjugated materials is that the molecular chains can be easily oriented, leading to anisotropic response to polarized incident light. This feature makes organic PV systems superior to inorganic PV or organic-hybrid PV systems for the purpose of polarizing PV. ZOPV devices integrated into an LCD panel (Figure 1b) have three potential benefits: i) polarization, whereby the EM wave component with an electric field perpendicular to the oriented molecular chain (s-mode polarized light) propagates through the film without absorption, serving its conventional role in LCDs; ii) as a PV device, the ZOPV film harvests the EM wave component parallel to the molecular chain orientation (p-mode polarized light, which is absorbed and wasted in a conventional LCD), converting it into electricity; and iii) ambient light or sunlight PV panel, when the ZOPV device is integrated into the LCD panel, its photovoltaic function remains even when the LCD panel is not in use, producing electricity through conversion of photons from ambient light or sunlight.

ZOPV films can be realized by the uniaxial orientation of polymer conjugated molecules. Here, the polymer used is poly(3-ethylthiophene) (P3HT), which is the most popular p-type polymer in organic photovoltaic (OPV) technology. By rubbing P3HT film with a velvet cloth at 150 °C, polymer chains were oriented along the rubbing direction, resulting in a polarizing P3HT (z-P3HT) film with anisotropic optical properties. Figure 1c,d compare the anisotropic appearance of z-P3HT film. The pictures were taken by placing a traditional linear polarizer in front of a digital camera as an analyzer. In Figure 1c, the z-P3HT (behaving as a polarizer) and the analyzer had parallel molecular orientation; therefore, the polarized light could pass through both of them, resulting in a transparent appearance. In Figure 1d, the z-P3HT film and analyzer were placed with perpendicular molecular orientation. This resulted in a dark view due to the crossed-polarization by the two polarizers. Subsequent spin-drop-coating of phenyl-C_{61}-butyric acid methyl ester (PC_{60}BM) on the z-P3HT film created a structure, which we term a quasi-bilayer structure. As has been reported earlier, in spite of the sequential spin coating, PC_{60}BM molecules will diffuse into the oriented P3HT matrix forming an interpenetrating layer and giving the P3HT-PC_{60}BM quasi-bilayer ZOPV films. This is not a true bilayer structure but closer to the bulk-heterojunction (BHJ) structure required for efficient operation of an OPV device.

Figure 2 shows the results of an optical study of the films. In Figure 2a, the absorption of regular (non-rubbed) P3HT film was studied to monitor changes in the film as a result of subsequent processing steps to fabricate a complete PV device. Dichloromethane (DCM) is a poor solvent for P3HT. When spin-coating pure DCM onto the P3HT film, no significant difference is observed (see Figure 2a, series 1 and 2), indicating the resistance of P3HT film against DCM solvent. When PC_{60}BM was coated onto P3HT from its DCM solution
annealing at 150 °C for 5 min, PC_{60}BM molecules diffused into the aligned P3HT matrix. From the polarized absorption spectra in Figure 2d, we note that the final ZOPV film still have the high DR value of approximately 11.3 at 604 nm, indicating that the aligned P3HT molecular chains maintain high orientation after thermal annealing. From these spectra, it can be concluded that PC_{60}BM molecules do not affect the P3HT molecular orientation and packing of P3HT when they are diffusing into the aligned P3HT matrix to form the quasi-bilayer ZOPV films.

Rubbing of P3HT films might create scratches on the surface. This will lead to the short circuits in the film, resulting in failure of the regular bilayer structure.\(^5\, 6\, 24\text{--}26\) Although by introducing a quasi-bilayer structure (wherein we spin coat PC_{60}BM on top of P3HT) we fill most of the cracks, still a thick buffer layer between the active layer and the electrode is required to prevent shorts in the device. An ideal buffer layer would be thick enough to prevent the evaporated metal electrode from penetrating the active layer and also be electrically conductive to facilitate OPV operation. One such candidate is the conductive polymer poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS). However, it is a p-type polymer, which necessitates that an inverted architecture is utilized for device fabrication.\(^{29}\) Moreover, PC_{60}BM spin-coated after P3HT would form a Schottky contact with PEDOT:PSS.

**Figure 1.** Schematic constructions of LCD (a) and the potential LCD system integrated with ZOPV devices (b). Z-P3HT film with the rubbing direction parallel (c) or perpendicular (d) to the molecular orientation in the analyzer.
To fabricate a working PV device, we introduce another novel structure where we introduce optimum annealing of PC$_{60}$BM so that PC$_{60}$BM penetrates to the bottom of the P3HT layer to contact the ITO electrode forming optimum electron extraction morphology through the Bulk active layer.$^{[26,27,30]}$ This will also expose some of the P3HT on the top layer to form ohmic contact (for holes) with the PEDOT:PSS anode. Figure 2 shows the inverted quasi-bilayer device structure based on the non-rubbed P3HT film. In this device, the P3HT-PC$_{60}$BM quasi-bilayer PV film was prepared on the cathode modification layer (TiO$_2$:Cs$_2$CO$_3$).$^{[31]}$ The anode modification layer, PEDOT:PSS, was coated onto the P3HT-PC$_{60}$BM quasi-bilayer film. Figure 3b gives the current density versus voltage (J–V) characterization of the inverted quasi-bilayer devices based on the non-rubbed P3HT film (control device). The measurement was performed under regular AM 1.5G 1 sun irradiation. A power conversion efficiency ($\eta_e$) of 2.62% was obtained with a short-circuit current density ($J_{sc}$) of 6.45 mA cm$^{-2}$, an open-circuit voltage ($V_{oc}$) of 0.61 V and fill factor (FF) of 66.6%. The high device efficiency is evident that the PC$_{60}$BM diffuses through the P3HT matrix to the bottom TiO$_2$:Cs$_2$CO$_3$ to form a continuous transport route for efficient electron collection.$^{[30]}$

Based on the inverted quasi-bilayer device architecture, we fabricated ZOPV devices using the aligned P3HT film. Both reflective electrodes (Al, 100 nm, Figure 4a) and semitransparent electrodes (Au, 10 nm, Figure 4b) have been used for the devices. Table 1 summarizes the device performance. The devices were tested under both unpolarized and polarized AM1.5G illumination. When tested under unpolarized AM1.5G 1 sun condition, the ZOPV devices with reflective Al electrode reached a power conversion efficiency ($\eta_e$) of 1.38%, with $J_{sc}$ = 3.69 mA cm$^{-2}$, $V_{oc}$ = 0.60 V, and FF = 62.2%. Compared with control device using regular P3HT film (Table 1), the low $J_{sc}$ in the ZOPV device is because only the $p$-portion of the incident light can be efficiently absorbed and transferred into electricity. The ZOPV device with semitransparent Au electrode gave a $\eta_e$ = 0.69%, with $J_{sc}$ = 2.74 mA cm$^{-2}$, $V_{oc}$ = 0.60 V, and FF = 42.2%. These results confirm that the PEDOT:PSS layer provides an effective sealing layer and prevents the short circuit. The low FF for the semitransparent ZOPV device is primarily because of the high series resistant of the 10 nm Au electrodes on the PEDOT:PSS film.
1. For the polarizing PV performance characterization of ZOPV devices, a polarizer was placed between devices and light source to provide polarized incident light. The polarized light intensity was approximately 33 mW cm$^{-2}$. Figure 4c shows the dichroic photovoltaic effect of ZOPV device with reflective electrode. The reflective ZOPV device generated a $J_{sc}$ of 1.92 mA cm$^{-2}$ under $p$-mode polarized light, with $\eta_e = 2.00\%$, $V_{oc} = 0.57$ V, and $FF = 62.2\%$. In contrast, when tested under $s$-mode polarized light, the $J_{sc}$ was only 0.68 mA cm$^{-2}$, with $\eta_s = 0.64\%$, $V_{oc} = 0.528$ V, and $FF = 58.53\%$. The ratio of $J_{sc}(p)$ to $J_{sc}(s)$ is 2.76. Polarized incident photon-to-current conversion efficiency (IPCE) was also utilized to identify the polarized $J_{sc}$, which gave $J_{sc}(p) = 1.92$ mA cm$^{-2}$, $J_{sc}(s) = 0.71$ mA cm$^{-2}$ and a $J_{sc}$ ratio of 2.70.

2. Figure 4d shows the polarized $J-V$ characterization of the semitransparent ZOPV device. A higher $J_{sc}$ ratio of up to 3.54 was achieved with $J_{sc}(p) = 1.45$ mA cm$^{-2}$, and $J_{sc}(s) = 0.41$ mA cm$^{-2}$. Compared to the ratio in the reflective electrode, this is a little higher. This is because the incident light in the reflective ZOPV is reflected by the electrode, causing the incident light to propagate through the active layer twice and be absorbed twice. For the transparent ZOPV, the incident light is not reflected and only absorbed once. Further investigation is under way to provide a much higher $J_{sc}$ ratio. Large scale quasi-bilayer device can be fabricated using spray-coating deposition.[42] Moreover, higher ZOPV performance can be expected if a better transparent electrode is used and this is also important for its future application in LCD panels.

3. To conclude, we have developed polarizing organic photovoltaic technology, a novel concept for energy harvesting and recycling technology. We have successfully achieved highly oriented P3HT films with high DR values of up to 14.3 through a surface rubbing method. To realize the ZOPV device, we also introduce novel inverted quasi-bilayer device architecture. The structure gives the flexibility to process P3HT and PC$_{60}$BM separately. This provides the feasibility to fabricate polymer donor films with additional functions, such as the anisotropic optical property shown here. Good device performance has proved that the PC$_{60}$BM molecules will penetrate through the highly aligned P3HT matrix and reach the bottom electrode while keeping the orientation of P3HT chains. Dichroic photovoltaic effect characterization has given a high $J_{sc}$ ratio of 3.54. We also calculated the ideal energy recycling efficiency for the ZOPV devices (see the Supporting Information); at a value greater than 10%, this shows great promise for revolutionizing the architecture of the traditional LCD display. This method of both recycling otherwise wasted energy and harvesting the ambient light energy represents significant progress towards the development of another promising green technology.

**Experimental Section**

Materials: Poly(3-hexylthiophene) (P3HT) was purchased from Rieke Metals, Inc. [6,6]-phenyl C$_{61}$-butyric acid methyl ester (PC$_{60}$BM) was purchased from Nano-C. Poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS, CLEVIOS P VP Al 4083) was purchased from H. C. Starck. All materials were used as received.

Polarizing P3HT ($p$-P3HT) Film Fabrication: The solution of P3HT in chlorobenzene (2 wt%) was spin-drop-cast onto substrate at a speed of 2500 rpm for 5 s. The film was then annealed at 150 °C for 10 min. The P3HT film was rubbed gently with a velvet cloth 80 times at 150 °C. See the Supporting Information for a video of the rubbing process for P3HT in detail; Figure S2 and Table ST1 (Supporting Information) show the increase in DR as a function of the rubbing time. We believe that the rubbing process induces orientation of the P3HT molecules. This orientation probably arises from two effects: i) the shear of the surface during rubbing and ii) the compression of the surface by the loading force. The resultant process propagates the orientation obtained at the surface to the bulk. Furthermore, the detailed physical mechanism behind orientation of the bulk film is under investigation.

Inverted Quasi-Bilayer Device Fabrication: The devices were fabricated on indium tin oxide (ITO)-coated glass substrates with a sheet resistance of 15 Ω square$^{-1}$. TiO$_2$:CsCO$_3$ solution, prepared by blending 0.4 wt% TiO$_2$ and 0.4 wt% Cs$_2$CO$_3$ in a 1:1 volume ratio, was spin-coated at 2500 rpm for 30 s, and the thermal annealing was performed at 150 °C for 15 min. The P3HT films (regular or polarizing films) were fabricated over the TiO$_2$:CsCO$_3$ layer. A 0.5 wt% solution of PC$_{60}$BM in DCM was spin-drop-coated onto the P3HT film while the substrate was spinning at 4500 rpm. The films were then annealed at 150 °C for 1 to 5 min to form a quasi-bilayer structure. Then, PEDOT:PSS with surfactants was spin-coated at 4000 rpm for 60 s and annealed at 80 °C for 2 min. The device fabrication was completed by thermal evaporation of Al (100 nm) as the reflective electrode or Au (10 nm) as the semitransparent electrode under vacuum at a base pressure of 2 × 10$^{-4}$ Torr.
Electrical, Optical, and Microscopic Characterization: Absorption spectra were taken using a Hitachi ultraviolet–visible spectrophotometer (U-4100). For the polarized absorption characterization, a prism polarizer accessory was placed between the light source and the samples to provide the polarized incident light. J–V characteristics of photovoltaic cells were taken using a Keithley 2400 source unit under a simulated AM1.5G spectrum with an Oriel 91191 solar simulator. For the polarizing PV measurement, a polarizer was placed between the light source and the sample.

Table 1. Device performance summary.

<table>
<thead>
<tr>
<th>Anode Type</th>
<th>Device Type</th>
<th>Test Condition</th>
<th>( J_{sc} ) [mA cm(^{-2})]</th>
<th>( V_{oc} ) [V]</th>
<th>FF [%]</th>
<th>( \eta_e ) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reflective electrode, PEDOT:PSS/Al (100 nm)</td>
<td>Control</td>
<td>AM1.5G, 1 sun, unpolarized light</td>
<td>6.45</td>
<td>0.61</td>
<td>66.6</td>
<td>2.62</td>
</tr>
<tr>
<td></td>
<td>ZOPV</td>
<td>AM1.5G, 1 sun, unpolarized light</td>
<td>3.69</td>
<td>0.60</td>
<td>62.2</td>
<td>1.38</td>
</tr>
<tr>
<td></td>
<td>ZOPV</td>
<td>s-mode polarized light, 0.33 sun, ( \perp )</td>
<td>0.68</td>
<td>0.53</td>
<td>58.5</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td>ZOPV</td>
<td>p-mode polarized light, 0.33 sun, ( \parallel )</td>
<td>1.88</td>
<td>0.57</td>
<td>62.2</td>
<td>2.00</td>
</tr>
<tr>
<td>Semitransparent electrode, PEDOT:PSS/Au (10 nm)</td>
<td>ZOPV</td>
<td>AM1.5G, 1 sun, unpolarized light</td>
<td>2.74</td>
<td>0.60</td>
<td>42.2</td>
<td>0.69</td>
</tr>
<tr>
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<td>ZOPV</td>
<td>s-mode polarized light, 0.33 sun, ( \perp )</td>
<td>0.41</td>
<td>0.51</td>
<td>53.1</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>ZOPV</td>
<td>p-mode polarized light, 0.33 sun, ( \parallel )</td>
<td>1.45</td>
<td>0.57</td>
<td>50.3</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Figure 4. Inverted quasi-bilayer ZOPV device architecture using reflective Al electrode (a) or semitransparent Au electrode (b). Dichroic J–V characterization of the inverted quasi-bilayer ZOPV devices with reflective (c) and semitransparent (d) electrodes; inset: polarizing IPCE spectra.
source and device to provide the polarized incident light. The intensity of the polarized light was approximately 33 mW cm\(^{-2}\), as calculated using a Si photodiode.

**Supporting Information**

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

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[2] The parallel and perpendicular polarizations are defined using the oriented polymer backbone axis as the reference. If the optical polarization is parallel to the polymer backbone, it is parallel polarization (defined as \( p \)-mode), it will be absorbed by the polymer film; if it is perpendicular polarization (defined as \( s \)-mode), the light will have minimum absorption in the polymer film.