High-performance semi-transparent polymer solar cells possessing tandem structures†

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In this study we employed tandem device architectures to tune the external appearance and light-conversion properties of polymer solar cells (PSCs) from visibly transparent to semi-transparent, making them more versatile for integrated photovoltaic applications and more efficient under solar illumination. Our best transparent solar cell was a tandem PSC exhibiting an efficiency of 6.4% and a maximum transmission of 51% at 550 nm; in contrast, a semi-transparent tandem PSC having an average transmission of 30% in the visible range exhibited an efficiency greater than 7%.

Broader context
Polymer solar cell (PSC) technology is an efficient and cost-effective solution for the utilization of solar energy. Transparent PSCs, in particular, have great potential for building-integrated photovoltaics, where the photovoltaic elements can simultaneously serve as building materials and power generators while maintaining an attractive building exterior. In this study, a novel tandem structure was used to improve the light absorption for better energy conversion and provide controllability of exterior color in a transparent PSC. Refining our control of the optical and electronic properties of transparent and semi-transparent PSC devices will allow for their implementation in a diverse range of optical applications from windows to privacy screens to structural accents in future architectural designs.

1 Introduction
Polymer solar cells (PSCs) are extremely attractive candidates for use in next-generation solar cell technologies because of their mechanical flexibility, light weight, and cost-effective production through solution-based manufacturing processes. To reach commercialization and mass production, PSCs must exhibit high performance and unique applications. A great effort is currently being exerted across a variety of research fields in the quest to achieve high-efficiency devices.1–2 For example, morphological control, interfacial engineering, and multi-junction tandem structures have been developed to increase the degree of light absorption and improve the generation and transport of charge carriers within PSCs.3–7 Tandem PSC structures in particular can provide power conversion efficiencies (PCEs) greater than 10%.8–10 The enhancement in performance arises from more comprehensive coverage of the solar spectrum through the effects of multiple organic materials possessing carefully chosen band gap energies.11–13 Transparent-type PSCs represent an extension of common PSCs with special and value-added applications.14–18 Unlike traditional bulk solar cells prepared from silicon or polysilicon, organic absorbing materials with confined absorption band can selectively be either transparent or semi-transparent in different regions of the solar spectrum.19 Accordingly, transparent PSCs with various degrees of visible transmission have been identified as key components for building-integrated photovoltaics that can be fabricated into power-generating windows, roof covers, and exterior wall materials, all while maintaining an attractive building exterior.20 These unique applications of transparent PSCs assist in distancing PSC technology from other competing new solar cell technologies.

Although many transparent organic solar cells have been reported previously, a lack of suitable materials for use in the absorbing layer and the transparent top electrode has meant that these devices have exhibited either low efficiency (<4%) or low visible transmission (<30%).21–25 Recently, we attempted to simultaneously optimize both of these parameters through the fabrication of an infrared (IR)-absorbing solar cell featuring a silver nanowire (Ag NW) composite electrode.26 We obtained high visible transmission and a PCE of 4% in a single-junction device. However, the photocurrents of these transparent PSCs remained poor as a result of the optical loss through the transparent electrodes that only allowed polymer films to capture the incident light in a single pass. Ideally, we wish to increase the degree of absorption by escalating the thickness of
polymer films; however, thin polymer films are often required for the active layer to suppress charge recombination. To reach a balance between maximum absorption and sufficient charge extraction, it was necessary for the photoactive layer in our previously reported transparent OPV to have a thickness less than 120 nm. One way to further enhance the effective absorption is to stack polymer films in serial connection in a tandem architecture. Accordingly, multiple photoactive materials can readily be introduced into a PSC, allowing fine adjustment of its absorption and, thus, its external color. Therefore, in this study we employed IR-absorbing single-junction solar cells as subcells in tandem structures to absorb IR solar energy more efficiently and, thereby, obtain transparent solar cells exhibiting greater photovoltaic performance.

Herein, we report a transparent PSC possessing a tandem structure featuring a new low band gap polymer, PBDTT-FDPP-C12, and PBDTT-SeDPP that sensitize well in different regions of the IR spectrum. Through the variation of chemical structures, we could differentiate the photoresponse of the IR-sensitive polymer from 900 to 950 nm thus improving the current gain in the tandem solar cell. Furthermore, to realize highly efficient tandem PSCs, interconnecting layers (ICLs) between the two subcells are the keys to minimize the contact loss in between. In our solution-processed, low-temperature-derived ICLs, we found that the conjugated polyelectrolyte as the interfacial dipole layer could lead to electrical connection of the two subcells with the lowest degree of ohmic loss. A resulting transparent tandem PSC optimized for high transparency achieved a PCE of 6.4%; a semi-transparent tandem PSC exhibiting slightly lower transmission achieved a higher PCE of 7.3%.

2 Experimental

2.1 Single-junction device fabrication

Pre-cleaned indium tin oxide (ITO) substrates (sheet resistance of 15 Ω ▪□⁻¹) were first treated with UV-ozone for 15 min. A poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS; Clevios AI 4083) layer was spin-coated (4000 rpm, 60 s) and then annealed (120 °C, 15 min) in air. A solution of the polymer (PBDTT-FDPP-C12, PBDTT-SeDPP):fullerene (PC₆₀BM, PC₇₁BM) blend (weight ratio, 1:2) in dichlorobenzene (0.7 wt%) was spin-coated (2500 rpm, 80 s) on top of the PEDOT:PSS layer to form the active layer (thickness: ca. 100 nm). A TiO₂ sol-gel solution was spin-coated (2500 rpm, 30 s) onto the active layer and then it was annealed (100 °C, 30 s) to form the n-type interfacial layer. A dispersion of Ag NWs in isopropyl alcohol (IPA; Blue Nano) was diluted to 2 mg mL⁻¹ and dropped onto the TiO₂ layer rotating at 2500 rpm to form a 100 nm thick conducting network of Ag NWs. A diluted ITO nanoparticle (NP) dispersion (10 wt% in IPA; Sigma-Aldrich) was dropped onto the Ag NW matrix rotating at 4000 rpm to form the composite electrode. Each device was formed by cutting the films with a razor blade and blowing N₂ onto the devices to avoid short circuits between the top Ag NW network and the bottom ITO substrate. The active area, defined by the overlap between the bottom ITO substrate and the top fingers, was 10 mm²; it was calibrated using an optical microscope.

2.2 Tandem device fabrication

The fabrication of the front subcell followed the procedure for the preparation of the single-junction device until the active layer was deposited, at which point the diluted PFN solution (0.02 wt% ADS180BE in methanol; American Dye Source Inc.) was spin-coated at 4000 rpm. The thickness of the PFN interlayer was approximately 10 nm. A TiO₂ sol-gel solution was spin-coated (2500 rpm, 30 s) onto the PFN layer and then it was annealed (100 °C, 10 s) to form the n-type dual interfacial layer. A conductive PEDOT:PSS (85 vol% Clevios PH1000, 10 vol% IPA, 5 vol% DMF) was spin-coated onto the TiO₂ surface at 4000 rpm. The second resistive PEDOT:PSS (100 vol% Clevios AI 4083) was spin-coated at 4000 rpm to form a double PEDOT:PSS layer structure. The back subcell was fabricated in the same manner as the front subcell, with the rate of spin coating ranging from 200 to 3500 rpm. Finally, the remaining TiO₂ buffer layer, Ag NW electrode, and ITO NPs as conductive fillers were deposited using the same procedures as those described for the preparation of the single-junction cells.

2.3 Device characterization

The current density–voltage (J–V) characteristics of the photovoltaic cells were recorded with a 0.1 cm² mask using a Keithley 2400 source-measurement unit under a simulated AM1.5G illumination from an Orion 9600 solar simulator. A KG-5 filter silicon photodiode (traceable to NREL calibration) was used as the reference cell to calibrate the light intensity to 1 sun (100 mW cm⁻²). To avoid parasitic current during measurement, each device (finger) was isolated completely by scratching the surrounding films around the device. The transmission and absorption of the devices were measured using a Hitachi U-4100 UV-Vis-NIR double beam spectrophotometer. External quantum efficiencies (EQEs) were measured using an Enlitech QE-R spectral response measurement system to calibrate the current density of devices.

3 Results and discussion

3.1 Device architecture with IR absorbers

In this study, we employed the high-performance IR-sensitive polymers PBDTT-FDPP-C12 and PBDTT-SeDPP as electron donor materials in the subcells of the tandem structure; Fig. 1a and b display their chemical structures and absorption spectra. Unlike conventional tandem solar cells that usually incorporate one visible-sensitive polymer and one IR-sensitive polymer, in our present approach we used two IR-sensitive polymers to minimize optical absorption in the visible spectrum. To avoid complete overlap of the absorption spectra of the two polymers in the IR range, PBDTT-FDPP-C12, a new IR-sensitive polymer, was synthesized. In Fig. 1b we observe a 50 nm blue-shift of the spectral signal of PBDTT-FDPP-C12, together with a narrower absorption band. The optical energy band gaps of PBDTT-FDPP-C12 and PBDTT-SeDPP were 1.49 and 1.38 eV, respectively. The relatively wide band gap of PBDTT-FDPP-C12 was critical for improving the current gain in the tandem structure. Fig. 1a also displays the structures of the
fullerene derivatives PC$_61$BM and PC$_{71}$BM, which we used as electron acceptor materials in the active layer. In Fig. 1b we observe that the absorbance spectrum of PC$_61$BM exhibits very limited photo-response in the visible range, whereas that of PC$_{71}$BM displays a broad, strong signal from 400 to 700 nm. As a result, we chose to combine the IR-sensitive polymer and PC$_61$BM as the transparent absorber for the solar cell devices (to allow visible photons to pass through), while PC$_{71}$BM in the semi-transparent absorber can be used to tune the visible transmittance for semi-transparent devices.

### 3.2 Performance of single-junction solar cells

Prior to preparing tandem solar cells, we first evaluated the transparent and semi-transparent absorbers in single-junction devices. Fig. 1c presents the structure of a single-junction device. Using a Ag NW composite as the top transparent electrode, we sandwiched three different absorbers between the TiO$_2$ NPs and the PEDOT:PSS buffer layer. Table 1 summarizes the PCEs; Fig. 2a displays the corresponding current density–voltage ($J$–$V$) curves. First, the transparent absorber prepared from PBDTT-FDPP-C$_{12}$ (optical band gap: 1.49 eV) and PC$_{61}$BM provided a single-junction device with an optimized PCE of 4.2%. The transparent absorber prepared from PBDTT-SeDPP, which had a smaller optical band gap of 1.38 eV, resulted in a device exhibiting a similar PCE of 4.5%, but with an improved short-circuit current density ($J_{sc}$) of 10.9 mA cm$^{-2}$. Hence, by decreasing the band gap of the IR-sensitive polymers, we might, in turn, expect a higher photocurrent through the harvesting of energy farther into the IR range. When combining PBDTT-SeDPP as the donor with PC$_{71}$BM as the acceptor in the semi-transparent absorber, we improved the PCE further to 5.6%, with a value of $J_{sc}$ as high as 13.4 mA cm$^{-2}$; this enhancement in $J_{sc}$ arose from the absorption of visible photons by PC$_{71}$BM.$^{34,35}$

Fig. 2b and c present the EQEs and internal quantum efficiencies (IQEs), respectively, of the single-junction devices. In tandem solar cells, an absorber with high quantum efficiency is required to ensure complete conversion of the absorbed photons. Here, the relatively low EQE peaks presumably resulted from either limited absorption or a poor rate of charge extraction. The relatively high and constant efficiency in the IQE spectrum suggests that the limiting factor was insufficient absorption, due to its low thickness.$^{27}$ Based on this observation, the stacking of multiple IR-sensitive polymers with thin thickness in a tandem device should increase the absorption of the whole device while maintaining high IQE for each subcell.$^{36}$ Fig. 1d displays the design of such a tandem structure.

### 3.3 Optical properties of a transparent solar cell

When building a transparent PSC having a tandem structure, a major concern is the degree to which visible transparency is compensated to ensure effective IR absorption, and vice versa. In Fig. 2d, the front subcell incorporating the transparent absorber PBDTT-FDPP-C$_{12}$:PC$_{61}$BM exhibits an average visible transmission ($T_{\text{average}}$) from 400 to 650 nm of approximately 60% and an IR transmission ($T_{\text{IR}}$) of 52% from 650 to 800 nm. Therefore, approximately half of the IR energy was not fully captured for energy conversion in the single-junction cell, in a good agreement with the quantum efficiency measurements. The back subcell featuring PBDTT-SeDPP:PC$_{61}$BM as the absorber exhibits a similar $T_{\text{IR}}$ of 53% with extended IR response from 650 to 900 nm. By stacking these two transparent absorbers in a tandem structure, $T_{\text{IR}}$ dropped to 26%. In other words, the photon absorption efficiency in the IR range...
increased nearly twofold. The value of $T_{\text{average}}$ for the transparent tandem PSC decreased to 43% with a high maximum transparency of 51% at 550 nm—still very competitive with previously reported systems.14–18,21–25 In terms of visual effect, the transparent tandem PSC was highly transmissive in the range 500–550 nm, giving a green color slightly darker than that of the transparent single-junction device (Fig. 2f). Thus, through the use of the tandem structure, the IR energy was harnessed more completely, while transmitting half of the visible photons. These optical properties make such structures viable candidates for a variety of applications requiring high efficiency and outstanding visible transmission.

### 3.4 Optical properties of a semi-transparent solar cell

As mentioned above, replacing PC$_{61}$BM with PC$_{71}$BM as the electron acceptor in the active layer allowed us to further increase the photocurrent of the single-junction device. Fig. 2e presents the transmission spectrum of PC$_{71}$BM based polymer-fullerene blend films denoted as the back subcell. The presence of PC$_{71}$BM in the semi-transparent absorber tuned the color of the exterior of the solar cell to a semi-transparent gray because of increasing optical absorption in the range 450–600 nm. These devices exhibited a neutral brownish color as a result of the maximal transmission band being flatter and having red-shifted to 600–650 nm. The value of $T_{\text{average}}$ (48%) was 12% lower than that of its corresponding transparent absorber. In the design of the semi-transparent tandem PSC, we connected, in series, one transparent absorber as the front subcell and one semi-transparent absorber as the back subcell. This design provided us with the ability to obtain a balanced photocurrent between the two subcells, because the semi-transparent back subcell, which captured only the remaining light that passed...
through the front subcell, now had additional visible sensitivity to deliver a higher photocurrent matching that of the front subcell. In Fig. 2e, we observe that the transmission spectrum of the semi-transparent tandem PSC was simply the superposition of the transmission spectra of the two subcells, providing a value of $T_{\text{average}}$ of 30%.

Fig. 2f displays a photograph of the single-junction and tandem devices incorporating different absorbers with the Ag NW composite. The simple method we adopted to prepare the tandem structure allowed us to control the visible transparency and thus the color of the solar cell. In terms of their visible transparency, we obtained devices ranging from highly transparent ($T_{\text{average}} = 63\%$ for the transparent single-junction device), to mildly transparent ($T_{\text{average}} = 48\%$ for the semi-transparent single-junction device and 43% for the transparent tandem device), and finally to semi-transparent ($T_{\text{average}} = 30\%$ for the semi-transparent tandem device). In terms of color-tunability, the maximal transmission band could also be shifted, from 500–550 nm (greenish) to 600–650 nm (brownish). The corresponding CIE diagram is also provided in the ESI.†

Thus, the preparation of tandem structures is an effective approach toward adjusting the optical properties of organic solar cells.

### 3.5 All-solution-processed interconnecting layers

Next, we employed a new design of robust interconnecting layers (ICLs), consisting of multiple interlayers of poly[(9,9-di(3,3′-N,N′-trimethylammonium)propylfluorenyl-2,7-diyl)-alt-(9,9-di-ctylfluorenyl-2,7-diyl)] diiodide salt (PFN)/TiO2/PEDOT:PSS, for low-temperature, solution processing of organic tandem solar cells. Earlier examples of ICLs have typically involved one n-type layer (e.g., TiO$_2$) serving as an electron injection interlayer and one p-type layer (e.g., PEDOT:PSS) serving as a hole injection interlayer.8–10 In previous studies we have found, however, that TiO$_2$ requires UV light excitation for a certain period of time to form ohmic contact at the interface with the photoactive layer, due to a relatively low carrier density.37,38 Here, we used PFN, a solution-processed conjugated polyelectrolyte, to form dual electron injection layers with TiO$_2$ in the ICLs. PFN as an electron-transporting layer can outperform those prepared from low-work-function metals (e.g., Ca) in single-junction devices.31 In our ICLs, we sandwiched PFN between the polymer and TiO$_2$. The positively charged amino groups of PFN led to the formation of a positive interface dipole and lower the energy barrier for electron injection, thereby improving the degree of electron extraction from the front subcell (Fig. S1, ESI†). In addition, the presence of PFN can passivate the hydroxyl-terminated surfaces of metal oxides and minimize charge trapping at the interface.40 Similarly, the hole injection layer in our ICLs comprised two layers of distinct PEDOT:PSS formulations. For the first PEDOT:PSS layer, which came into contact with TiO$_2$, we chose Clevios PH1000, which has the metal-like conductivity required to form an ohmic contact with TiO$_2$.37 For the second layer of PEDOT:PSS, we employed the highly resistive formulation Clevios AI 4083 to provide a deeper work function and to minimize the energy level offset with the IR-sensitive polymer of the back subcell.32 The high ratio of PSS in the Clevios AI 4083 formulation also reduced the dark leakage current contributing

![Fig. 3](a) Proposed energy level landscape within the tandem structure. $J$–$V$ curves of the (b) transparent and (c) semi-transparent tandem PSCs, measured using incident light coming either from the Ag NW top electrode or from the ITO/glass substrate.
to an improved device performance in the back subcell (Fig. S2, ESI†). Fig. 3a displays the energy level landscape for our present ICLs design, which we prepared through all-solution processing at low temperature requirement (ca. 100 °C).

### 3.6 Performance evaluation of tandem solar cells

To fabricate the tandem devices, we deposited the front subcell, the ICLs, and the back subcell sequentially. Afterward, similar to the single-junction devices, we completed the tandem structure through the deposition of TiO₂ and the Ag NW composite electrode on the top. The Ag NW composite electrode, which comprised Ag NWs as the mesh network and ITO NPs as the conductive filler, had an average transmittance of approximately 89% from 400 to 1000 nm, with a sheet resistance of approximately 30 Ω sq⁻¹. Fig. 3b and c present the J–V curves of the transparent/semi-transparent tandem PSC under AM1.5G illumination (100 mW cm⁻²) entering from the bottom ITO electrode. For a light beam to pass through our tandem solar cell in a single journey without any interference, the optimal design to achieve high visible transparency would be a transparent tandem PSC featuring two transparent absorbers in the subcells. Our transparent tandem PSC provided a PCE of 6.4% with a value of $J_{sc}$ of 7.22 mA cm⁻², a value of $V_{oc}$ of 1.46 V, and a fill factor (FF) of 61.2%. When we replaced the back subcell with PBDTT-SeDPP:PC₇₁BM, the PCE of the newly formed semi-transparent tandem PSC reached 7.3% with values of $J_{sc}$, $V_{oc}$ and FF of 8.41 mA cm⁻², 1.47 V, and 59.1%, respectively. Clearly, the improvement in PCE arose from the enhancement in the value of $J_{sc}$. The back subcell incorporating PC₇₁BM provided a higher current density to better match that of the front subcell incorporating PC₆₀BM. The FF (59–61%) of the tandem cell is comparable with those of its corresponding single-junction subcells, indicating that an efficient series connection existed between the subcells—presumably a result of our robust polyelectrolyte-containing ICLs. In addition, the value of $V_{oc}$ of each of our tandem cells was consistent with the sum of the values of $V_{oc}$ of its two subcells, indicating that nearly no parasitic loss occurred as a result of the presence of the ICLs. Compared with the single-junction subcells, the tandem solar cells produced twice the voltage output at a similar current density—a potentially very useful property for low-power electronics applications.⁴¹ Overall, the PCEs of 4.5 and 5.6% for the transparent and semi-transparent single-junction devices, respectively, were greatly enhanced in the transparent and semi-transparent tandem structures, reaching 6.4 and 7.3%, respectively—the mark of high-performance PSCs.

We measured the EQEs of the subcells in the tandem structure to ensure the accuracy of our measurements of device performance. Here, we simulated the EQE of only the back subcell, assuming that the performance of the front subcell was almost identical to that of its analogous single-junction device. The details of the experimental setup and results are provided in the ESI (Fig. S3†). For the transparent tandem PSC, we simulated the back subcell absorber (PBDTT-SeDPP:PC₆₀BM) and calculated a value of $J_{sc}$ of 7.0 mA cm⁻² from the EQE curve; this result is close to the value of 7.2 mA cm⁻² that we measured from the $J$–$V$ curve. Using the same method to analyze the semi-transparent tandem cell featuring PBDTT-SeDPP:PC₇₁BM in the back subcell, we calculated a value of $J_{sc}$ (ca. 8.1 mA cm⁻²) from the EQE curve, in good agreement with that (8.3 mA cm⁻²) measured from the $J$–$V$ curve. These results reveal that the back subcell was the factor limiting the performance of the tandem solar cells when illuminated from the bottom ITO.

Likewise, we recorded the $J$–$V$ curves of the tandem solar cells when illuminating from the top (from the Ag NW electrode). For the semi-transparent tandem PSC that exhibited a PCE of 7.3% when illuminated from the bottom (from the ITO/glass), we measured a PCE of 6.1% with a value of $J_{sc}$ of 6.65 mA cm⁻² when illuminated from the top. Similarly, the transparent tandem cell that provided a PCE of 6.4% when illuminated from the bottom exhibited a PCE of up to 5.7% when illuminated from the top. We ascribe the loss of output current to unbalanced current generated from the subcells. In the top-illumination setup, light was first harnessed by the back subcell, leaving the unharnessed energy for the front subcell to utilize. Because we originally designed the front subcell absorber to exhibit a lower photocurrent output, the performance of the tandem PSC, limited by the front subcell, would result in a lower photocurrent. From the EQE measurements in Fig. S3,† we confirmed that the front subcell was the factor limiting the photocurrent in the top-illumination setup. We also found that the tolerance (insensitivity) toward the illumination direction of the transparent tandem PSC was better than that of the semi-transparent tandem PSC. Despite the differences in photocurrent upon changing the illumination direction, our results suggest that these tandem solar cells have great potential for use with top illumination, bottom illumination, or both.

### 4 Conclusions

We have constructed high-performance transparent and semi-transparent PSCs possessing effective tandem architectures. The two subcells in tandem devices are connected by a new solution-processed, low-temperature processed ICL featuring low ohmic loss achieved by embedded interface dipoles between PFN/TiO₂/PEDOT:PSS. By synthesizing a new polymer of PBDTT-FDPP-C12, we could narrow the absorption band of the front subcell, thereby improving the current output of the tandem PSC. Given two transparent absorbers (IR-sensitive polymers:PC₆₀BM) in the subcells, we obtained a transparent tandem PSC optimized for visible transparency, along with improved efficiency: an average PCE of 6.4% under AM1.5G illumination with a maximum transmission of 51% at 550 nm and a value of $T_{average}$ of 43%. A semi-transparent tandem PSC optimized for efficiency achieved a PCE of 7.3% with a $T_{average}$ of 30%. Furthermore, we have also demonstrated that these tandem solar cells can be used in either top- or bottom-illumination modes without any major differences in their device performances. Finally, with judicious choice of the donor and acceptor materials, the preparation of tandem structures can also be used to adjust the external appearance of PSCs from greenish (transmission maxima at 500–550 nm) to a shade of gray (transmission maxima at 600–650 nm). These results suggest that the tandem structure can refine the optical and...
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