FULLY VACUUM-FREE SEMITRANSPARENT POLYMER SOLAR CELLS FOR POWER-GENERATING WINDOW WITH PURE ACHROMATIC APPEALING

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Abstract
Among the existing renewable independent energy sources, semitransparent (ST) solar cells have attracted attention owing to their ability to be integrated into the windows of buildings or vehicles. To realize not only practical electricity production but also esthetic appearance, we fabricated PTB7:PC71BM-based ST polymer solar cells via fully vacuum-free and low-cost manufacturing methods. Fully vacuum-free manufacturing could be achieved from a silver nanowire and conductive polymer-based transparent lamination top electrode, thereby achieving complete and concrete electrical contact with the underlying polymer bulk-heterojunction layer through a simple hot-press lamination step. In addition, for the insertion of an appropriate hole-extracting interlayer between the lamination electrode and polymer layer, ST solar cells with a lamination electrode provided the best power conversion efficiency (PCE) of 4.36% with a fill factor (FF) of 53.9%. For comparison, opaque solar cells with a metal top electrode were also fabricated, providing the best PCE of 9.07% with an FF of 65.4%. However, the inferior electricity production of these ST solar cells can be compensated for by its pure achromatic appeal owing to its superior optical properties. Detailed optical analysis was performed to evaluate the compatibility of the lamination electrode-based ST solar cells for power-generating window applications. ST solar cells did not exhibit a noticeable optical cavity resonance effect, resulting in an extremely good visual appearance with achromatic sensation and a window illumination source with luminosity of 38.1%, CCT of 6480 K, and general CRI of 95.5 under D65, which is a standard daylight illuminant.

KEYWORDS
enhanced achromatic sensation, high color rendering index, lamination electrode, polymer solar cell, semitransparent solar cell, vacuum-free manufacturing
1 INTRODUCTION

Photovoltaic (PV) systems have been regarded as one of the most promising renewable energy sources that can be used to curb global warming and carbon emissions issues. This is because PV has no fuel costs (economical) and can be installed where needed (standalone). In addition, if PV can be integrated into buildings or vehicles, further cost reductions can be achieved by reducing the land cost. Therefore, recent PV research has focused more on widespread deployment by integrating solar cell modules with existing infrastructures such as building-integrated PVs and solar-powered vehicles. In this respect, semitransparent (ST) solar cells have attracted much attention because they can be seamlessly employed in windows, thereby considerably reducing the land cost without hurting the esthetic appearance. Although most commercially viable ST solar cell modules at the current stage are partially opened crystalline silicon solar cells, there are still critical challenges for the various form factors of underutilized substances owing to their brittle nature.

For the widespread adoption of ST-PV systems, several researchers have investigated alternative solar cell technology with increased feasibility and cost-effectiveness. In particular, polymer solar cells based on a bulk-heterojunction (BHJ) architecture have been widely studied owing to their compatibility with the solution process and mechanical flexibility. Through the development of low-bandgap polymeric semiconducting materials, BHJ polymer solar cells have begun emerging as promising semitransparent energy-harvesting devices, showing higher optical transparency in the visible light and more neutral coloring under ambient sunlight than any other PV device. In addition, the more enhanced device performance has been reported by adjusting the active layer thickness and the weight ratios of donor to acceptor or by selecting the combination of a broad bandgap polymer as donor and two narrow bandgap materials as an alloyed acceptor. The layer-by-layer structured polymer PV device has been reported, where the thickness of donor layer was adjusted to improve the optical transmittance of semitransparent polymer solar cells by harvesting near-IR light. To enhance the optical properties and ensure high harvesting efficiency, an ultrathin layer with a highly conductive metal (e.g., silver, copper, or gold) has been generally utilized as the top electrode of solar polymer cells by using the highly vacuumed thermal evaporation method. However, there are two imperative drawbacks for the ST polymer devices from this ultrathin metal layer: (i) the elaborated manufacturing process increases the PV module cost, and (ii) the device characteristic is highly influenced by the thickness of ultrathin top metal electrode of the solar cells; the slight variation in thickness results in a significant change in the energy-harvesting efficiency and the optical characteristics.

The most straightforward strategy to implement semitransparent optoelectronic devices is to use an alternative electrode with increased optical properties. With respect to this approach, instead of the thin metal layer, a conductive polymer material can be used to implement a top electrode with the benefit of low-cost solution processing and high flexibility. Generally, an aqueous poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) solution with additives (e.g., ethylene glycol or dimethyl sulfoxide), which can be simply coated or sprayed on top of the BHJ polymer layer, has been widely studied as a top electrode in ST polymer solar cell devices. The silver nanowire (AgNW) dispersed solution is another promising material for transparent top electrodes with enhanced sheet resistance. By introducing AgNW-based composite transparent conductors, Yang's group demonstrated an ST polymer solar cell with a power conversion efficiency (PCE) of 4.02% and an average light transmission of 61% over the 400–650-nm range. Although the top electrodes using solution processing can become a promising low-cost method for the fabrication of semitransparent devices, critical issues remain regarding the shunting problem due to the electrical contact between the top and bottom electrodes; this is due to the wet deposition of these highly conductive materials, causing physical damage to the underlying organic semiconducting layer. Therefore, another simple but promising method can be a vacuum-free lamination process, wherein the pre-made electrode is physically transferred to the top of the polymer solar cell with the help of a supporting film (e.g., PDMS or PET). Liu et al reported a polymer solar cell with all-graphene electrodes, which had a PCE of 3.4% and a transmittance of ~40% in the visible region. In our previous work, we reported a fully vacuum-free and solution-processed polymer solar cell device with a PCE of 2.61% by laminating the AgNW-PEDOT:PSS hybrid electrode. However, both the proper work function of the lamination electrode and the concrete electrical contact at the interface without an adhesion-promoting additive remain challenging owing to the high harvesting efficiency.

In this paper, we report on fully vacuum-free and solution-processed ST polymer solar cells with increased optical transparency and neutral coloring for built-in window applications. For solution-processed visibly transparent polymer solar cells, a BHJ layer with poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:5,6-b’]dithiophene-2,6-diyl][3-fluoro-2-{(2-ethylhexyl)carbonyl]thieno[3,4-b] thiophenediyl]} (PTB7) and (6,6)-phenyl C71 butyric acid methyl ester (PC71BM) was selected as the low-band-gap donor polymer for near-IR absorption and the acceptor material for UV absorption, respectively. The proposed lamination electrode comprised a coated AgNW as a transparent conductor and PEDOT:PSS as a conductive...
adhesion layer on a polyethylene terephthalate (PET) supporting film with an ethylene vinyl acetate (EVA) layer that can assist in void-free contact between the top electrode and the underlying BHJ active layer during a conventional thermal laminating process in ambient air. To evaluate our lamination electrode, we adopted a fabricated lamination electrode as the top anode electrode of an inverted structured polymer solar cell. We tested three types of lamination transparent electrodes with different additional hole-extracting interlayers to ensure high extraction efficiency of the generated charge carriers from PTB7. Therefore, the fabricated ST polymer solar cells with three types of laminated transparent electrodes exhibited a concrete electrical connection inside the device and a stable PV characteristic. In particular, the prepared ST-PV devices showed enhanced optical assessment such as a high optical transmittance, a slight change in the corresponding color temperature (CCT), and a high value of the general color rendering index (CRI), which meets the general requirements for a power-generating window. The optical and electrical characteristics of the polymer solar cells with the proposed lamination electrodes were carefully analyzed. Furthermore, the conventional opaque reference device from the vacuum thermal evaporation method was characterized to compare the final device performance. In addition, the influence of the additional hole-extracting buffer layer on the photo-voltaic performance and the optical properties was investigated by introducing the optical simulation results.

2 EXPERIMENTAL SECTION

The pre-cleaned glass substrate was prepared using acetone and isopropanol in an ultrasonic bath, followed by 10 min of plasma treatment. After cleaning, the hole-transporting layer was first spin-coated at 2000 rpm for 1 min. To prepare lamination transparent electrodes (TEs) that facilitate the efficient extraction of charges generated in the active layer, we tested three types of TEs: (i) without a hole-extracting interlayer for TE A; (ii) with PEDOT:PSS HTL Solar (Clevios™) for TE B; and (iii) with PEDOT:PSS P VP A1 4083 (Clevios™) for TE C. After complete drying in a convection oven at 100°C, the plasma treatment was followed to make the surface of the coated hole-extracting layer hydrophilic. Subsequently, a silver nanowire (AgNW) solution, which was 20 nm in diameter and 20 µm in length (0.5 wt% silver in deionized water, Flexioxwire2020a, Flexio Co.), was spin-coated at 1000 rpm, followed by annealing at 80°C on a hot plate for 30 min. After additional plasma treatment for 10 min, highly conductive PEDOT:PSS (PH-1000, CLEVIOS™) mixed with 6 vol% ethylene glycol (EG, Alfa Aesar) and 0.5 wt% fluorosurfactant (FS-31, DuPont™) was spin-coated onto the AgNW layer at 1500 rpm and annealed in an 80°C convection oven for 30 min. To fabricate a free-standing lamination TE film, a commercially available 100-µm-thick PET film with an EVA layer (A4-100 mic; HyundaiOffice, Inc.) was applied as the supporting film, and a UV-curable optical adhesive (NOA-63; Norland Products, Inc.) was utilized to peel off the prepared TEs from the glass substrate. After the UV curing process, the TEs with the PET film could be easily removed using only a small amount of mechanical force. To trace the change in electrical conductivity depending on the cumulated stacks of TEs, the sheet resistance value was measured using a noncontact sheet resistance meter (2014; Delcom Instrument, Inc.) with a sample size of 3 × 3 cm².

To fabricate inverted polymer solar cells, we started with cleaning indium tin oxide (ITO; 140 nm, 15 Ω/sq; Geomatec Co.) glass substrates with a 2 × 2 mm² active area in an ultrasonic bath with acetone and isopropanol alcohol in sequence. After 10 min of plasma treatment, a 20-nm ZnO layer was prepared on the ITO layer by spin-coating the ZnO sol-gel solution. Successively, polyethylacrylate ethoxylated (PEIE; 80% ethoxylated solution, Sigma-Aldrich) dissolved in 2-methoxy ethanol (99%, Sigma-Aldrich) was spin-coated at 4000 rpm for efficient electron extraction on a bottom electrode. For the active layer of the solution-processed polymer PVs, a mixture of 8-mg PTB7 (OS0007, 1-material) and 12-mg PC71BM (99%, OSM) was dissolved in 970 µl of chlorobenzene (ACS, 99.5%, Alfa Aesar) and 30 µl of 1,8-Diiodooctane (98%, Sigma-Aldrich) solution by stirring at 60°C for 1 day. The PTB7:PC71BM solution was filtered using a 0.20-µm PTFE syringe filter just before use. The 80-µm-thick BHJ active layer was prepared inside a N₂-filled glovebox after spin-coating at 1000 rpm, followed by annealing at room temperature for 30 min. Subsequently, the annealed active layer was treated with anhydrous methanol (99.8%, Sigma-Aldrich) to increase the PV properties. For the reference opaque device, the stacked active layer was transferred into a UHV chamber (~10⁻⁷ Torr, CETUS OL 100, Selcos) without breaking the N₂ ambient, and molybdenum trioxide (MoO₃, 1 nm) and aluminum (150 nm) were evaporated in sequence. For the semitransparent devices, the delaminated TE film was cut into the shape of the top electrode and placed onto the prepared BHJ PTB7:PC71BM layer. We utilized a conventional thermal laminator (Photolami-A504; HyundaiOffice, Inc.) for the hot-pressing process in ambient air at a speed of 70 cm/ min at 100°C, which resulted in complete electrical contact between the lamination TE and the underlying active layer. Finally, all devices fabricated via vacuum-free lamination and vacuum evaporation processes were encapsulated with glass lids in an N₂-filled glove box.
The level of work function for the three types of TEs was measured using an advanced scanning Kelvin probe system (ASKP200200, Kp technology) after peel-off from the glass substrate. The photovoltaic characteristics of the fabricated devices were measured using a solar simulator system comprising a digital source meter (Keithley 2410) and a Class-A solar simulator (WXS-155S-L2; Wacom Co.) for 100 mW/cm² AM 1.5G illumination. The external quantum efficiency (EQE) spectra were recorded using a spectral response measurement system (CEP-25BX; Bunkoukeiki Co.) with an irradiation intensity of 50 W/m². Optical transmittance measurements were performed using a calibrated transmittance measurement setup with a fiber-optic spectrometer (BLUE-Wave VIS2-50; StellarNet, Inc.) with a measuring spot size of 10-mm diameter and a light source (LS-BA, OrO Photonics). The CCT and color rendering qualities were analyzed by plugging the spectra into a simulation software (LightTools™, Optical Research Associates).

3 | RESULTS AND DISCUSSION

To realize energy-harvesting windows based on semitransparent photovoltaics (ST-PVs), considering not only electrical power production but also optical aspects to ensure visual comfort is necessary. For the universal deployment of ST-PVs, their optical performance has to meet the general preference with negligible chromatic alternation of the light through ST solar cells, wherein one can watch outside scenes with natural colors and can see inside objects without any color distortion during the daytime. The schematic in Figure 1A represents the device structure of the fully vacuum-free semitransparent polymer solar cell used herein. Our approach to the ST polymer solar cell is based on the bulk heterojunction (BHJ) of the PTB7:PC71BM layer, which is a widely adopted active material with high transparency in the visible regime. As the transparent top electrode, AgNW and EG-doped PEDOT:PSS were selected owing to their low refractive index value and low visible light absorption properties, resulting in high optical transparency. However, a low-bandgap donor polymer, such as PTB7, requires a compatible hole-extracting layer with a high work function to facilitate a high PCE. For this reason, we tested lamination TEs embedded with an interlayer such as PEDOT:PSS HTL Solar (TE B) and PEDOT:PSS VP AI 4083 (TE C). A lamination TE without an additional interlayer was also prepared to compare the resultant device performance (TE A). As shown in the inset of Figure 1A, each TE can be distinguished from its optical transparency and coating.
conditions. The slight difference between TE A and TE C mainly originated from the additional interlayer of PEDOT:PSS HTL Solar and P VP AI 4083 (20 nm). However, TE B with PEDOT:PSS HTL Solar (20 nm) does not have a uniform AgNW layer owing to the poor wettability of the aqueous AgNW solution even after hydrophilic surface treatment.

The optical transmittance is shown in Figure 1B. Although TE B was not uniformly coated, all TEs had similar transmittance values. This is because the measured transmittance is an averaged value over the measuring spot size of 10 mm in diameter. Figure S1 shows the cumulative transmittances measured after the deposition of each stack layer for the TEs. The transmittance at 550 nm began from the glass substrate (100%) and slightly decreased by 96.1% and 96.6% after the deposition of PEDOT:PSS HTL Solar and P VP AI 4083, respectively. The stack of TE without the supporting film has a high optical transparency of over 90% in the visible range because the utilized 100-µm supporting film has a transmittance of 82.5% at 550 nm. However, the EVA/PET supporting film is the key element over 90% in the visible range because the utilized 100-µm supporting film has a transmittance of 82.5% at 550 nm. The optical transmittance is shown in Figure 1B. After the hot-press laminating process under ambient pressure, the prepared TE electrode can make a complete attachment and good electrical contact with the underlying polymer BHJ active layer. The TE A, TE B, and TE C films can now be cut for the top electrode and be transferred to the stack of polymer solar cell device by the pick-and-place method (Figure 2A). As discussed in our previous work, the TE film with EVA-coated PET supporting film introduced a concrete and complete electrical contact with low contact resistance on top of ~1-µm-thick patterned PR layer.28 The fabricated ST-Devices with an area of 2 × 2 mm were measured under illumination from a solar simulator (AM 1.5G spectrum calibrated at 100-mW/cm² intensity) onto the ITO side. To compare the photovoltaic performance of the ST solar cells, an opaque reference PTB7:PC71BM solar cell from a vacuum-evaporated metal top electrode was fabricated. The measurement results for the eight tested samples of ST solar cell devices with TE A (ST-Device A), with TE B (ST-Device B), and with TE C (ST-Device C) are listed in Tables S2–S4, respectively, while the opaque devices are listed in Table S5. For convenience, the PV characteristic parameter is summarized in Table 1, and the J–V curve of the best device is shown in Figure 2B. From the shunt resistance values in Table 1, the developed lamination process did not cause an electrical shunt as the shunt resistance value was over 30 Ω. ST-Devices provided uniform short-circuit current (Isc) values in the range of 10.43–10.74 mA/cm², although the reference device had a Isc of 19.00 mA/cm². The higher Isc of the opaque solar cell is accounted for by the metal-induced back reflection, which re-sends the light back to the polymer active layer. The FF value of the reference device (63.8%) was higher than that of the ST-Device (50.0%–53.5%), which can be attributed to the higher Rsh value of the laminated TE compared to that of the thermally evaporated Al electrode (~1 Ω/sq). The reverse saturation current density and ideality factor were extracted from the dark I–V fitting and are listed in supporting information (Figure S9 and Table S6).28 In this respect, the best achieved PCE for the ST-Device was 4.36%, while that for the opaque device was 9.07%.

However, special attention must be paid to the difference in PCE between ST-Devices. Depending on the hole-extracting layer, the PCE increased from 3.59% (ST-Device A) to 4.32% (ST-Device C), and this result mainly originated from the difference in the open-circuit voltage (Voc).
KANG et al. ST- Device C, which showed the highest work function level in Figure 1F, had the highest $V_{oc}$ of 756 mV, which was even higher than the $V_{oc}$ of the reference device with the vacuum-evaporated MoO$_3$/Al electrode. The energy barrier between the work function of an anode electrode and the HOMO level of the donor polymer in the BHJ active layer influences the $V_{oc}$ of the polymer solar cell.\textsuperscript{32,33} Based on the energy level diagram for the proposed inverted PTB7:PC$_{71}$BM solar cell in Figure S4, one can expect that TE C with a high work function level (>5.0 eV) can have a higher hole-extracting ability than the other electrodes. To investigate the dependence of the energy barrier on the TEs, we tested a hole-only device where only a positive charge carrier can be injected from the top laminated anode into the PTB7:PC$_{71}$BM layer, and the negative charge carrier can be blocked from the bottom cathode (Figure 2C). From the $J$–$V$ curves in the dark state, TE C with highest work function had the pronounced high hole-injection property. From this, we stress that the TE film integrated with the proper interlayer can diminish the energy barrier between the electrode and the polymer active layer and can facilitate the increased PCE of ST polymer solar cell devices.

To analyze the spectral influence of each TE on the light-harvesting ability, we measured the EQE in the absorption range from 300 to 850 nm. As shown in Figure 3A, the opaque device with a vacuum-evaporated metal electrode exhibits EQE values almost two times higher than those of the ST-Devices, and the EQE values of the three ST-Devices were comparable. This result is in good agreement with the measured $J_{sc}$ values in Table 1. With the same active polymer layer, the shape of the EQE curves mainly follows the extinction coefficient spectrum of the BHJ PTB7:PC$_{71}$BM active layer (Figure S5). However, the opaque device showed an outstanding EQE peak at approximately 400 nm, whereas ST-Devices did not have this EQE peak. To explain this phenomenon, we performed an optical simulation based on the transfer matrix method (TMM) for both the ST-Device and opaque device. The profile images in Figure 3B represent the calculated exciton generation rate within the 80-nm PTB7:PC$_{71}$BM layer by assuming sunlight illumination with AM1.5G onto the ITO side. The TMM optical model accounts for the increase in the EQE using the localized position of the generated excitons inside the active layer. In particular, the profile of the interference effect ($f_{int}$) due to the distribution of the optical electric field intensity can explain the peak of EQE at a 400-nm wavelength depending on the device structure (Figure S6). In an opaque device, a $f_{int}$ due to the back-reflected light contributes to the additional enhancement in the conversion efficiency. As the cavity resonance effect from a $f_{int}$ also helps ST-Devices to approach the performance of their opaque counterparts, many researchers have utilized the thin metal layer as the top electrode, partially reflecting the transmitted light back to the active layer.\textsuperscript{6,19,20} However, the use of the cavity resonance

FIGURE 2 (A) Image of the fabricated semitransparent photovoltaic (ST-PV) cell based on the corresponding lamination electrode (upper) and the remaining TE on glass substrate after cutting and floating off the lamination electrode (lower). (B) Current density vs. applied voltage ($J$–$V$) curves of the tested ST-PV devices with lamination TEs as well as the opaque reference PV device with thermally evaporated MoO$_3$/Al electrode. The PV characteristics were measured under 100-mW/cm$^2$ AM 1.5G illumination onto ITO glass side. (C) The $J$–$V$ curves for the hole-only devices at dark state depending on the selection of the lamination TE. The structure of the tested hole-only device is schematically depicted in the inset image

ST-Device C, which showed the highest work function level in Figure 1F, had the highest $V_{oc}$ of 756 mV, which was even higher than the $V_{oc}$ of the reference device with the vacuum-evaporated MoO$_3$/Al electrode. The energy barrier between the work function of an anode electrode and the HOMO level of the donor polymer in the BHJ active layer influences the $V_{oc}$ of the polymer solar cell.\textsuperscript{32,33} Based on the energy level diagram for the proposed inverted PTB7:PC$_{71}$BM solar cell in Figure S4, one can expect that TE C with a high work function level (>5.0 eV) can have a higher hole-extracting ability than the other electrodes. To investigate the dependence of the energy barrier on the TEs, we tested a hole-only device where only a positive charge carrier can be injected from the top laminated anode into the PTB7:PC$_{71}$BM layer, and the negative charge carrier can be blocked from the bottom cathode (Figure 2C). From the $J$–$V$ curves in the dark state, TE C with highest work function had the pronounced high hole-injection property. From this, we stress that the TE film integrated with the proper interlayer can diminish the energy barrier between the electrode and the polymer active layer and can facilitate the increased PCE of ST polymer solar cell devices.

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effect results in a remarkable chromatic alternation of the light through ST-Devices, which are not favorable for a power-generating window. In Figure 3B, a $f_{\text{int}}$ does not exist in the ST-Device using the lamination TE with AgNW and EG-doped PEDOT:PSS. Nevertheless, it cannot be overemphasized that ST-Device showed the higher $J_{\text{sc}}$ (10.68 mA/cm$^2$) than the simulated $J_{\text{sc}}$ (8.86 mA/cm$^2$) using TMM optical model, whereas the opaque reference device showed the similar simulated $J_{\text{sc}}$ (18.45 mA/cm$^2$) to the measured $J_{\text{sc}}$ (19.00 mA/cm$^2$). We attribute this increase in $J_{\text{sc}}$ to the enhanced absorption in the polymer active layer, which correlated with the light-scattering effect induced by AgNWs. Wang et al. reported a 17% increase in $J_{\text{sc}}$ in a PTB7:PC71BM BHJ solar cell by replacing the ITO electrode with the AgNW and PEDOT:PSS electrodes. 34 In their publication, the light scattering from an AgNW film has a flat distribution in the visible range from 400 to 750 nm. From this result, we emphasize that the lamination TE with AgNW and EG-doped PEDOT:PSS is a promising candidate for the top electrode of an efficient power window without the cavity resonance effect.

To evaluate the compatibility of the proposed lamination TE with the ST solar cells, the visual appearance of the fabricated ST-Devices was evaluated by measuring their optical assessments. Figure 4A shows the optical transmission spectrum for the PTB7:PC71BM BHJ layer of both opaque and ST-Device C obtained via the transfer matrix method optical model.

**TABLE 1** Solar cell characteristic parameters of fabricated polymer PVs with various top electrodes

| Devices | $V_{\text{oc}}$ (mV) | $J_{\text{sc}}$ (mA/cm$^2$) | FF (%) | Eff. (%) | $R_{\text{se}}$ ($\Omega$-cm$^2$) | $R_{\text{shunt}}$ ($\Omega$-cm$^2$) |
|---------|-------------------|-----------------|-------|---------|-----------------|-----------------|
| Ref. device – VTE (Avg.)$^{a,b}$ | 715 ± 2 | 19.00 ± 0.81 | 63.8 ± 1.5 | 8.67 ± 0.40 | 2.24 ± 0.73 | 721 ± 77 |
| Ref. device – VTE (Best) | 724 | 19.13 | 65.4 | 9.07 | 1.65 | 778 |
| ST-Device A (Avg.)$^{a,b}$ | 688 ± 5 | 10.43 ± 0.62 | 50.0 ± 1.2 | 3.59 ± 0.28 | 17.85 ± 1.76 | 562 ± 107 |
| ST-Device B (Avg.)$^{a,b}$ | 698 ± 5 | 10.74 ± 0.14 | 51.7 ± 0.6 | 3.87 ± 0.09 | 14.83 ± 0.59 | 556 ± 100 |
| ST-Device C (Avg.) | 756 ± 4 | 10.68 ± 0.06 | 53.5 ± 0.6 | 4.32 ± 0.03 | 15.52 ± 0.69 | 872 ± 277 |
| ST-Device C (Best) | 757 | 10.70 | 53.9 | 4.36 | 15.64 | 817 |

*aAveraged values for eight different samples.

b“±number” corresponds to the standard deviation.
average transmittance (the luminosity) decreased from 84.3% (86.4%) to 36.9% (38.1%) as the cumulative stack of the ST polymer solar cell is increased, where the analysis also shows <1% difference of the luminosity and the average transmittance between ST-Device A, B, and C. For the further investigation of energy-harvesting property and optical transmittance of the prepared ST-Devices, quantum utilization efficiency (QUE) spectra, defined as the sum of the optical transmittance and the measured external quantum efficiency, were calculated and depicted in Figure S7. The QUE values of ST-Devices were less than 85% in the visible light range from 400 to 750 nm of wavelength, resulting from the inevitable photon and charge loss.\textsuperscript{35} Based on the QUE results, one can also notice that the proposed laminated transparent electrodes and the hot-press lamination processes can make the ST-devices form good electrical contacts without severe degradation of light-harvesting performance such as exciton dissociation efficiency.\textsuperscript{35} From the photographs in Figure 4B, one can easily notice the different drop of luminosity between samples. An outstanding decrease in luminosity occurred through the PTB7:PC\textsubscript{71}BM active layer, and the image

FIGURE 4  (A) Optical transmission of the 80-nm PTB7:PC\textsubscript{71}BM BHJ layer on ZnO-coated ITO glass and fabricated semitransparent (ST) PV devices with various lamination TEs. The plot of circles corresponds to the simulation result by using thin film-based optical simulation. (B) Photograph containing natural red, green, and blue colors was captured through lamination TE C, coated PTB7:PC\textsubscript{71}BM layer, and ST-Device C. (C) Representation of the color coordinates (x, y in CIE1931). (D) Representation of the UCS coordinates (CIE 1960) of ITO glass, coated PTB7:PC\textsubscript{71}BM layer, and fabricated ST-Devices under standard daylight illuminant D65. The white line in (D) is the Planckian locus for a black body radiation, and the numbers in the enlarged image in (D) denote the correlated color temperature (CCT) for each sample.
through ST-Device C appeared slightly darker. However, the perception of color was quite distinguishable between the samples. In particular, the image through the polymer active layer appears blueish, whereas ST-Device C looks achromatic. In Figure 4C, the transparency color perceptions of the samples are depicted using the CIE 1931 chromaticity diagram, which is specially designed to represent the colors perceptible to the human eye. As summarized in Table 2, the coordinates of illuminant D65 (0.3127, 0.3290) shifted to blue (0.3007, 0.3276) through the BHJ active layer. After laminating the TE films, the color coordinates of the ST-Devices recovered near the original D65 position. This result corresponds to the fact that the proposed ST-Device can provide extremely high-quality illumination with achromatic sensation, acting as a neutral density filter.4

Another key optical assessment for an ST-PV device is related to the color constancy that corrects for the color deviation caused by varying illumination conditions. To further investigate the quality of the white light source, we evaluated the color coordinates in the CIE 1960 UCS (uniform color space) and compared the correlated color temperature (CCT) of the transmitted light through ST-Devices (Figure 4D). The standard daylight illuminant D65 is known to have a CCT of 6504 K and is close to the Planckian black body radiation. After passing through the PTB7:PC71BM layer, the CCT increased to 7219 K, and the UCS color coordinates also shifted away from the corresponding Planckian locus. However, the final ST-Devices showed CCT similar to that of the original D65 illuminant in the range of 6480–6823 K. The conservation of the CCT of the sunlight through the ST-PV device can be favorable for the power-generating window. The proposed architecture based on AgNW and PEDOT:PSS TE can be more compatible with an indoor illumination source, whereas the previously reported ST solar cells with thin metal top electrodes normally showed a higher CCT than ambient sunlight.4,19 The color rendering capacities were also analyzed using the test sample method (TSM) module in LightTools™ software, where the tested white light incident in the normal direction onto eight standard color samples (TCS01-08).31 The change in the CRI is plotted in Figure S8, and the general CRI (the averaged value for eight TCs) is shown in Table 2. One can recognize that ST-Devices exhibited a high CRI of over 95.5, which is comparable to the conventional window film.

Upon optimizing the lamination TE, ST-Device C, which showed the highest PCE of 4.36%, can become a promising element for an energy-harvesting device as well as a perfect achromatic illumination window with 38.1% of luminosity, 6480 K of CCT, and 95.5 of general CRI. Although the fabricated ST-devices in this work were prepared through the low-cost vacuum-free conditions, the PCE and optical transmittance can be comparable with the previously reported results based on vacuum-evaporated top electrodes (Table S7).36,37 Of course, the proposed lamination TE can be adopted not only for polymer BHJ solar cells with other low-bandgap polymer materials but also for flexible polymer solar cells. Especially, our strategy using the proposed lamination electrode with the insertion of an appropriate hole-extracting interlayer between the lamination electrode and polymer layer can be compatible with the ST solar cells with emerging low-bandgap polymeric semiconducting materials, such as PM6:Y6.15–18 Further studies regarding large-area solar cell modules and low-cost encapsulation techniques using lamination electrodes will be conducted.

4 | CONCLUSIONS

In this study, we demonstrated fully vacuum-free semi-transparent polymer solar cells with a PCE of 4.36% and luminosity of 38.1% for power-generating window applications. Semi-transparency with a low-bandgap polymer materials but also for flexible polymer solar cells. Especially, our strategy using the proposed lamination electrode with the insertion of an appropriate hole-extracting interlayer between the lamination electrode and polymer layer can be compatible with the ST solar cells with emerging low-bandgap polymeric semiconducting materials, such as PM6:Y6.15–18 Further studies regarding large-area solar cell modules and low-cost encapsulation techniques using lamination electrodes will be conducted.

### Table 2: Optical characteristics of standard illuminant D65 through the ITO glass, the coated PTB7:PC71BM BHJ on ZnO/ITO glass before laminating TEs and the fabricated ST-devices

| Samples                        | AVT (%) | Luminosity (%) | CIE 1931 (x, y) | CCT (K) | General CRI |
|-------------------------------|---------|----------------|-----------------|--------|-------------|
| Illuminant D65                | 100     | 100            | 0.3127, 0.3290  | 6504   | 100         |
| D65 + ITO glass              | 84.3    | 86.4           | 0.3179, 0.3411  | 6181   | 97.5        |
| D65 + BHJ on ZnO/ITO         | 41.8    | 42.8           | 0.3007, 0.3276  | 7219   | 95.9        |
| D65 + ST-Device A            | 37.0    | 38.4           | 0.3084, 0.3377  | 6678   | 95.7        |
| D65 + ST-Device B            | 36.2    | 37.4           | 0.3062, 0.3345  | 6823   | 95.7        |
| D65 + ST-Device C            | 36.9    | 38.1           | 0.3118, 0.3409  | 6480   | 95.5        |

*The whole optical characteristics were obtained over the whole visible range of 400–750 nm in wavelength.*
complete attachment and concrete electrical contact to the underneath PB7:PC$_{71}$BM active layer without electrical shunting. Optimization was performed by inserting different hole-extracting interlayers, and the lamination electrode with PEDOT:PSS PV P AI 4083 hole-extracting interlayer provided the best solar cell performance with a $V_{oc}$ of 757 mV owing to its work function of 5.08 eV. Through the analysis of the EQE measurement and optical simulation with the TMM, the proposed ST solar cell did not exhibit a noticeable optical cavity resonance effect, and a higher $J_{sc}$ than the simulated value with a low interference effect can be explained by the light-scattering effect of the AgNWs. In addition, under the standard illuminant of D65, the developed ST solar cell exhibited an extremely high-quality visual appearance with achromatic sensation and a window illumination source with a color rendering index close to 100 for power-generating windows with enhanced visual comfort.

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