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Molecular design of cost-effective donor polymers with high visible transmission for eco-friendly and efficient semitransparent organic solar cells

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ABSTRACT

Photoactive laver materials that overcome the trade-off between power conversion efficiency (PCE) and average visible transmittance (AVT) are required to prepare successful high-performance semitransparent organic solar cells (ST-OSCs). Among 12 novel cost-effective $D-\pi=A$ polymers with high visible light transmission, P(3IN = 12)0.3)(3IN2F = 0.5)(BDD = 0.2) achieved a PCE of 14.0% and high stability in an eco-friendly solvent-processed OSC with BTP-eC9. This blend film exhibited an AVT of 62.1% and a color rendering index of 95.0, demonstrating the high potential for ST-OSCs. The ternary OSC with PM6 greatly enhances the PCE to 17.3%. Binary and ternary ST-OSCs achieve light utilization efficiencies (LUEs) of 4.38% and 4.04%, respectively, demonstrating the potential of the D- π =A structure. Under a 3000 K light-emitting diode light at 958 lx low illuminance, PCEs of 12.4% and 15.7% are obtained for binary and ternary ST-OSCs, respectively, and the indoor LUEs (LUIEs) of ST-OSCs are greatly enhanced to 5.52% and 5.48%, respectively. Air-processed eco-friendly ternary ST-OSC module (4.7 cm²) achieves not only a PCE of 12.1% and LUIE of 3.90% under 958 lx, but also color coordinates of (0.290, 0.323) and an infrared radiation rejection rate of 87.5%, meeting the civil engineering specifications for windows. This ST-OSC module can be a substitute power source of the thermo-hygrometer in real time, even operate at 195 lx, which paved the way towards zero-energy indoor and outdoor electrical devices as well as windows for buildings and vehicles.

1. Introduction

Semitransparent solar cells can generate electricity from sunlight and thereby replace the outer walls or windows of existing buildings, cars, greenhouses, and self-generation facilities [1–10]. This technology offers significant potential for new markets and value creation in the near future because sustainable energy sources have recently attracted much attention owing to the increase in the global energy consumption. The Si-based solar cells have been greatly studied because of their extensive light absorption in the visible (Vis) to near infrared (NIR) regions and the efficiency that exceeds over 20%. However, this technology may not satisfy the requirements for semitransparent solar cell applications because of the intrinsic limitations in its band gap tunability. Therefore, the focus has been shifted to the development of next-generation solar cell technologies, such as organic solar cells (OSCs) and perovskite solar cells, which can effectively modify the optical characteristics of photoactive materials [11]. In particular, organic materials used in OSC technology are light, highly flexible, and amenable to relatively lowtemperature firing. Therefore, after printing OSC films on plastic substrates using a high-speed and high-throughput solution manufacturing process, they can be incorporated into solar window applications to achieve a high economic efficiency and an excellent form factor

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[1,2,5,8,12]. More importantly, because of the rapid development of non-fullerene acceptors (NFAs) and the discovery of structurally superior materials such as Y6 derivatives [13,14], the power conversion efficiencies (PCEs) have significantly improved to over 19% in single-junction devices [15–20] and over 20% in tandem devices [21]. These findings demonstrate that OSCs have comparable efficiency to other solar cells.

In contrast to the current research trend, which focuses primarily on high efficiency, semitransparent OSC (ST-OSC) technology has been evaluated from various perspectives, including efficiency versus transmittance and color features, for practical solar window applications [2,3,7,9,11,22]. However, efforts to enhance the PCE usually lowers the average visible transmittance (AVT) and color rendering index (CRI) because enhancing the PCE necessitates the maximal utilization of the incident sunlight [23,24]. Therefore, the light utilization efficiency (LUE = PCE \times AVT), which reflects the properties of both the window and solar cell, is a critical parameter for evaluating ST-OSCs. Furthermore, the AVT must be evaluated in the full Vis light range of 380–780 nm as well as the photopic response region, which is directly associated with the capacity of the human eye to distinguish objects and colors [24]. Generally, an AVT of >40% is recommended for use in windows for buildings, vehicles, and other consumer products [11]. The CRI is a performance indicator for the transmitted color that provides a quantitative measurement of the correct rendering of color. For high-quality window applications, a CRI of 85 or higher is recommended [24]. Many studies on ST-OSCs have focused on the development of transparent electrodes [22,25-27], design of beneficial optical structures [5,7–10,23], and introduction of efficient OSC systems [4,6,8]. Particularly, most photoactive layer combinations for achieving efficient ST-OSCs have limited ability to improve the transmittance of ST-OSCs because they are primarily matched with wide-band-gap donor and acceptor materials that have complementary absorption in Vis and NIR regions [7-10,22,23,25,27-32]. Consequently, to create highly transparent ST-OSCs, it is necessary to change the molecular structure of the core photoactive layer, particularly the donor, which primarily absorbs the Vis light.

The NIR region accounts for 51% of solar energy in the AM 1.5G standard solar spectrum, whereas Vis and ultraviolet (UV) regions contribute 47% and 2%, respectively. Therefore, ST-OSCs that efficiently utilize the NIR region have significant potential for power production similar to that of conventional solar cells [3,11]. Therefore, the ideal donor-acceptor (D-A) polymer for ST-OSCs typically consists of a strong donor coupled with a stronger acceptor to significantly improve the intramolecular charge transfer (ICT) and absorb light mainly in the NIR region [3]. Theoretical calculations have shown that single-junction ST-OSCs with AVTs of 60% and 100% can achieve high PCEs of 14.6% and 11%, respectively, using an active layer that selectively absorbs UV and NIR light [33]. To the best of our knowledge, very few studies have developed low-band-gap donor polymers that matched the low-bandgap NFAs, resulting in PCEs of 5-6% and AVTs of 40-50% in ST-OSCs [33–37]. To explore the potential of this strategy, the band gaps and frontier energy levels of PTB7-Th, a well-known low-band-gap D-A polymer, were fine-tuned by introducing halogenation and copolymer strategies. As a result, the best polymer matched well with Y6 was developed and thus achieved a high LUE over 4% in ST-OSC [38]. This finding demonstrated that developing an all-low-band-gap photoactive layer combination that transmits the Vis light and selectively utilizes the NIR region is a feasible strategy for realizing transparent and efficient ST-OSCs. However, challenges such as a low open-circuit voltage (V_{oc}) due to a high energy loss [3,5,6,26,33-36,38], high synthetic complexity (SC) [3-10,22,23,25-27,29-34,36-38], and use of toxic solvents [3,5-7,9,10,22,23,25-27,33-38] still hinder the industrial applications of ST-OSCs.

Considering the aforementioned challenges to the commercialization of ST-OSCs, this study describes donor polymer synthesis strategies based on a novel $D-\pi=A$ structure that can be provided relatively

transparent and efficient devices compared to the typical D-A building block. Low-band-gap polymers based on the D- π =A structure, in which pendant side chains are introduced into π -conjugated spacers in fullerene-based OSCs, have been developed in several previous studies; however, they have received limited attention owing to the difficulty in controlling the molecular structure orientation and morphology [39–42]. In contrast, we rationally designed highly oriented D– π =A donor polymers with low extinction coefficients in the Vis region based on BTP-eC9, which is an NFA that absorbs mainly in the NIR region. Furthermore, the D– π =A polymers were optimized by continuous and systematic research on various structural changes, such as the introduction of halogenation effects and expansion of terpolymer and quaterpolymer systems, and the consequent photovoltaic characteristics. Significantly, the materials can be scaled up at relatively low cost by considering the SC from the molecular structure design perspective (which will be discussed in detail later). Further, for polymers with ternary and quaternary building blocks, the number of possible conformations increases and they can be processed using eco-friendly solvents owing to the improved solubility, meeting the requirements for ST-OSCs

Herein, 12 donor polymers with high visible light transmission were newly synthesized using the molecular design of the D- π =A structure. Among them, the best material P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2)exhibited high transparent properties with an AVT of 62.1% and a CRI of 95.0 in the blend film with BTP-eC9. This blend achieved the highest PCE of 14.0% with a dominant face-on structure in an eco-friendly solvent o-xylene (XY)-processed OSC. Moreover, it was demonstrated that P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2):BTP-eC9-based OSCs has superior tolerance in comparison with PM6:BTP-eC9-based OSCs through various stability assessments, such as the long-term stability [26,43,44], thermal stability [45], and photostability [45–48], based on the International Summit on Hybrid and Organic Photovoltaic Stability (ISOS) protocols. Notably, ternary OSCs containing an edge-on dominant PM6 polymer yielded the optimal PCE of 17.3% owing to the enhanced crystallinity and orientation characteristics. The ST-OSCs, which were produced using WO3 as a distributed Bragg reflector (DBR) [28], showed 9.8% PCE and 44.5% AVT (LUE = 4.38%) for the binary blend and 11.6% PCE and 34.9% AVT (LUE = 4.04%) for the ternary blend. These results show the high potential of the D– π =A donor polymer for use in efficient ST-OSCs.

Furthermore, considering that actual ST-OSC devices, such as those used in windows, smart sensors, and wearable electronic devices, are exposed to diverse indoor conditions, the solar cell properties were evaluated under the illumination of a 3000 K white light-emitting diode (LED) [6,49-53]. The binary and ternary ST-OSCs showed significantly high PCEs of 12.4% and 15.7% under a low illumination of 958 lx, respectively, despite having a relatively high energy loss and poor spectral matching with the LED spectrum because NIR acceptors were used. Therefore, the indoor LUE (LUIE) values of binary and ternary ST-OSCs are greatly enhanced to 5.52% and 5.48%. It is noteworthy because ST-OSCs with both high transparency and low-light performance have been rarely reported so far [6,50,53]. Additionally, this result is highly significant because it may further enhance the performance of indoor solar cells by lowering their energy loss with a structural modification simpler than that of the typical D-A structure and efficient acceptor matching.

From an industrialization perspective, an air-processed eco-friendly ternary ST-OSC module with an active area of 4.7 cm² was fabricated and was demonstrated to replace the power supply of an electronic thermo-hygrometer and work reliably under a low illumination up to 195 lx. Finally, we present the potential of utilizing molecular structure design strategies to further improve the performance of the device by extensively investigating the structure–property–performance relationship in terms of energy loss, miscibility, photoluminescence quenching rate (PLQ), and scalability factor (SF). We believe that commercial products of ST-OSCs could be successfully implemented in the near future by integrating the efficient, inexpensive, and eco-friendly $D-\pi=A$ polymer design strategies, with various state-of-the-art transparent technologies.

2. Experimental section

2.1. Materials synthesis and characterization

Detailed synthetic procedures of monomers (Scheme S1 and Figs. S1–25) and polymers/terpolymers (Schemes S2–4 and Figs. S26–38) for D– π =A donor materials are described in the Supporting Information (SI).

3. Results and discussion

3.1. Part I: Novel $D-\pi=A$ polymers enabling high visible transmission

A typical D–A donor polymer has two absorption bands derived from the π – π * transition and ICT effect, and the absorption band in the longwavelength region is relatively broad and intense [15,16,18,28,29,43,44,46,54,55]. In this case, intensifying the electron push–pull effect by modifying the chemical structure shifts the ICT absorption to the NIR region, substantially increasing transmittance in the Vis region [6,33-38]. However, this design strategy occasionally raises the highest-occupied molecular orbital (HOMO) energy level when the band gap narrows, resulting in a substantial energy loss when matching with low-band-gap NFAs and, in certain cases, a poor Voc and PCE [33–37]. Therefore, we proposed a new donor polymer design strategy based on the D- π =A structure that compensates for the deficiencies of conventional building blocks for realizing efficient ST-OSCs. The building blocks of the D- π =A polymer were composed of 2-ethylhexvl thiophene-substituted two-dimensional benzodithiophene (2DBDT) as a donor, thiophene as a π -spacer (π), and the oxygen of carboxaldehyde (CHO), barbituric acid (BA), indanedione (IN), and thiophenecyclopentadione (TC) as acceptors. The synthesized polymers are labeled P(3CHO), P(3BA), P(3IN), and P(3TC), respectively (Fig. 1a). Owing to the asymmetry of the π =A substituents in the backbone (Fig. S39), all polymers exhibit high structural regio-randomness, resulting in an adequately high degree of polymerization despite the restricted side chains. In particular, the molecular weight increased in the order of P(3BA), P(3IN), and P(3TC). This result is attributed to a reduction in the total dihedral angle between moieties or an increase in the number of possible conformations (which will be discussed in detail later) [43,56,57].



Fig. 1. (a) Molecular structures and photographs (50 nm-thick films) of P(3CHO), P(3BA), P(3IN), and P(3TC). (b) Normalized potential energy scans as a function of the dihedral angle between D and π =A (inward A) units of model compounds for polymers at n = 1 (red arrows: increasing steric hindrance). (c) Simulated UV–Vis spectra and oscillator strength (sold lines and hole bars) of model compounds for P(3CHO)-in and P(3IN)-in with a stable form. (d) Molar extinction coefficient and normalized absorption spectra (solid and dotted lines) of neat D– π =A polymers and P(3CHO) in solution and film states (yellow area: photopic response). (e) Absorption coefficient and transmittance spectra (solid and dotted lines) for optimized polymer films blended with BTP-eC9 (yellow area: Vis region at 380–780 nm). (f) EQE curves and integrated current densities (solid and dotted lines) of optimized OSCs. (g) 2D-GIWAXS diffraction patterns of neat polymer films (yellow dot–dashed lines: indicating π – π stacking distances; optimized PCEs of OSCs). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

As illustrated in Fig. S40, transparent properties of $D-\pi=A$ polymers exhibited visibly distinct difference with P(3CHO). The average AVT and CRI values of three polymers were unexpectedly enhanced by 20.5% and 25.5, respectively, compared to those of P(3CHO) (Table S1). To explain this phenomenon from the perspective of the molecular structure, potential energy dihedral scan calculations were performed on the corresponding model compounds at one repeating unit (n = 1) [58]. Consequently, the potential energy environments of model compounds for polymers were distinct according to the electron withdrawing groups (EWGs) (Fig. 1b and Figs. S41-44). A significant steric hindrance was observed in P(3BA), P(3IN), and P(3TC) compared to that in P(3CHO) because the substituents inserted into A unit were the relatively bulky EWGs. The one-dimensional BDT-based P(3IN)-1D also showed a similar trend with P(3IN) (Fig. S45). Therefore, the two thermodynamically preferred stable and metastable structures were more twisted up to 30° and 20°, respectively. Based on stable forms, time-dependent density functional theory (TD-DFT) calculations of model compounds for P (3CHO) and P(3IN) were performed and compared. As shown in Fig. 1c, d, the theoretical absorption waveform was comparable to the experimentally obtained absorption waveform. Particularly, considering Fig. S46, S47 and Table S2, P(3IN) exhibited approximately two times lower oscillator strength than that of P(3CHO) in the HOMO to LUMO transition corresponding the ICT effect. This difference is caused by relatively delocalized π -electron clouds at the LUMO level derived from the highly twisted backbone [41,59] and explains the significant transmittance difference in the photopic response region between the two actual polymers. The calculated DFT parameters of all model compounds are presented in Fig. S48-53 and Table S3. Furthermore, the physical and thermal properties of all polymers are summarized in Fig. S54 and Table S4.

As shown in Fig. 1d, the absorption spectra were measured in chloroform (CF), and molar extinction coefficients of the solution were calculated using the Beer-Lambert equation by averaging four different concentrations ($\approx 10^{-5}$ M) [28,43,44,54–56,58]. In particular, the extinction coefficient of P(3IN) was 2.2 times less than that of P(3CHO), at 555 nm which was the maximum absorption wavelength of the photopic response. This result was in excellent agreement with the theoretical calculations. In addition, P(3BA) and P(3TC) exhibited tendencies similar to that of (3IN), which demonstrates that the excellent transparent properties of the polymer is owing to its $D-\pi=A$ structure. In contrast to P(3CHO), which has two absorption bands based on typical D-A structure, the other three polymers possess three prominent absorption bands. Therefore, the light-harvesting properties of $D-\pi=A$ polymers were anticipated to be similar or higher to those of P(3CHO) owing to a relatively broader absorption region despite the high transmittance in the photopic response region. Moreover, the optical band gap (E_g^{opt}) values decreased in the order of P(3CHO), P(3TC), P(3IN), and P(3BA) in accordance with the varying electron withdrawing strength of the EWGs. The frontier energy levels of polymers were calculated using cyclic voltammetry (CV) measurements (Fig. S55). The results revealed that the HOMO energy levels decreased in the order of P(3CHO), P(3IN), P(3TC), and P(3BA), which could be anticipated that V_{oc} s exhibited a similar trend in devices [43,44,54-56]. The detailed optical and electrochemical properties are presented in Table S5.

As shown in Fig. S56 and Table S6, all the OSCs were optimized by blending with BTP-eC9. P(3CHO), P(3BA), P(3IN), and P(3TC) exhibited adequate PCEs of 10.5%, 2.8%, 10.6%, and 11.7%, respectively. Notably, as shown in Fig. 1e, the polymer blend films with the same conditions as those of optimized devices indicated that P(3IN) and P (3TC) reached high efficiencies despite having lower extinction coefficients in the Vis region than P(3CHO). The AVTs and CRIs of P (3CHO), P(3BA), P(3IN), and P(3TC) were calculated to be 45.3%, 56.0%, 65.5%, and 57.8% and 81.7, 90.7, 92.0, and 90.3, respectively. These results suggest the high potential of P(3IN) and P(3TC) as donor polymers for ST-OSCs (Fig. S57 and Table S7). As demonstrated in the results for OSCs of P(3BA), P(3IN), and P(3TC), the short circuit current

density (J_{sc}) values dramatically increased to 9.0, 20.09, and 24.27 mA/ cm⁻², which is attributed to the photo-response gradually improving across the whole absorption range depending on the EWG structure as seen in the external quantum efficiency (EQE) curves (Fig. 1f).

To further investigate the relationship between the photovoltaic performance and structure, neat and blend films were analyzed using two-dimensional grazing incidence wide-angle X-ray scattering (2D-GIWAXS) (Fig. S58-61 and Tables S8 and S9). As shown in Fig. 1g, P (3CHO) exhibited the strongest face-on structure compared to other polymers owing to the lowest steric hindrance. The strength of the faceon structures of D- π =A polymers increased in the order of P(3BA), P (3IN), and P(3TC), and even the π - π stacking distance became shorter. These changes are due to an increase in the intra/inter-molecular π - π stacking interactions of the polymer, as the conjugated planarity of EWG enhances in the order of BA, IN, and TC [60]. These trends were also observed for the blend films and were in excellent agreement with A_{xy} A_z values which are the (100) to (010) ratio, as well as the J_{sc} s, that is, the efficiency trends. The photovoltaic results also agreed well with the morphological and charge carrier transport results, obtained using atomic force microscopy (AFM) (Fig. S62), space charge-limited current (SCLC) (Fig. S63 and Table S10), photoluminescence (PL) analyses (which will be discussed in detail later).

Furthermore, as shown in Fig. S64, temperature-dependent aggregation (TDA) behaviors in the solution state were investigated for polymers. With an increase in the temperature, the twisted structures loosened in the order of P(3CHO), P(3TC), P(3IN), P(3BA), and P(3IN)-1D. This result supports the structure–performance relationship because polymers with appropriate aggregation in solution tend to form fine domains, whereas those with poor aggregation behavior tend to generate indistinguishable phase-separated morphologies [61]. Comprehensively, it was established that D– π =A polymers based on high planar 2DBDT and EWGs not only reached high visible-transparent films derived from strong steric hindrances in their structure, but also achieved efficient photovoltaic performance owing to high π – π stacking effects when blending with BTP-eC9.

3.2. Part II: Halogenation effects of $D-\pi=A$ polymers/terpolymers

Next, the promising D– π =A polymers were halogenated to fine-tune the frontier energy levels and increase the crystallinity to further improve the photovoltaic performance. In particular, F and Cl were rationally introduced into IN and TC acceptors, respectively, considering the steric hindrance and SC [62,63]. Furthermore, a terpolymer design strategy was introduced to address the issue of polymer solubility and molecular weight, both of which decreased after halogenation [44,55]. The detailed design strategy of D– π =A halogenated polymers/terpolymers can be founded in the SI. As shown in Fig. 2a, P(3IN2F), P(3IN) (3IN2F = 0.5), P(3IN)(3TC1Cl = 0.4), and P(3TC1Cl) polymers were successfully synthesized. The detailed theoretical, physical, optical, and electrochemical properties are presented in the SI (Fig. S65–71 and Tables S11–14).

All halogenated polymers and terpolymers with appropriate molecular weights retained high transparent properties similar to those of P (3IN) and P(3TC). As a relatively electron-deficiency increased by the halogenation effect, the polymers show narrow E_g^{opt} values of approximately 1.64 eV on average. Therefore, the devices were expected to possess improved J_{sc} values based on light harvesting in a broader region. Furthermore, as demonstrated in Fig. 2b, as the HOMO energy levels down-shifted by the halogenation effect, HOMO offset between the polymer donor and BTP-eC9 acceptor was reduced to a maximum of 0.02–0.15 eV, which can decrease the energy loss and enhance V_{oc} [44,55,62,63]. As shown in Fig. 2c,d, the optimized OSCs of P(3IN2F), P (3IN)(3IN2F = 0.5), P(3IN)(3TC1Cl = 0.4), and P(3TC1Cl) showed reasonable PCEs of 10.1%, 12.6%, 12.3%, and 10.0%, respectively, based on higher V_{oc} values of 0.878 V, 0.841 V, 0.846 V, and 0.838 V than those of P(3IN) and P(3TC) (Fig. S72 and Table S15). It is



Fig. 2. (a) Molecular structures, photographs (50 nm-thick films), and optimized PCEs of P(3IN2F), P(3IN)(3IN2F = 0.5), P(3IN)(3TC1Cl = 0.4), and P(3TC1Cl). (b) Energy diagrams of halogenated $D-\pi=A$ polymers/terpolymers with BTP-eC9. (c) *J*–*V* curves and (d) EQE curves and integrated current densities (solid and dotted lines) of optimized OSCs based on halogenated $D-\pi=A$ polymers/terpolymers.

highlighted that P(3IN)(3IN2F = 0.5) and P(3IN)(3TC1Cl = 0.4) terpolymers are even higher performance by processing an eco-friendly solvent, XY. The polymer blend films reveal an average AVT of 56.8% and a CRI of 88.3, which are similar to those for P(3TC) (Fig. S73 and Table S16). Among the polymers, P(3TC1Cl) has poor efficiency with the lowest J_{sc} . It is due to the introduction of relatively large Cl atoms into the polymer backbone, resulting in the longest π - π stacking distance and a small crystal coherence length (CCL) (Fig. S74, S75 and Table S17) [63]. In contrast, P(3IN)(3IN2F = 0.5) exhibited the closest π - π stacking distance derived from non-covalent intra/inter-molecular interactions such as hydrogen bond interactions owing to the appropriately fluorination effects [62]. In particular, after blending with BTP-eC9, its crystal and orientation characteristics were further improved at (010), reaching the optimal efficiency based on the highest J_{sc} of 24.14 mA cm⁻² (Fig. S76, S77 and Table S18). All photovoltaic results agreed well with the morphological and mobility results (Fig. S78, S79 and Table S19) [64.65].

3.3. Part III: Highly crystalline unit-incorporation of $D-\pi=A$ terpolymer/quaterpolymer

The synergistic strategy of halogenation and terpolymer building blocks effectively decreased the HOMO level of the D- π =A polymers and provided them with high solubility in environmentally friendly solvents. However, these polymers still show lower J_{sc} and FF values than the typical D-A donor polymers. Therefore, to further improve the efficiency, the high-performance 2DBDT-based polymer, PM6 as a motif, a highly crystalline acceptor unit, benzodithiophenedione (BDD), which induces a strong edge-on structure and long-range order, was incorporated into the D- π =A backbone with type of the terpolymer or quaterpolymer [55]. The detailed design strategy of BDD-incorporated D- π =A terpolymer/quaterpolymer can be founded in the SI. As shown in Fig. 3a, P(3IN2F)(BDD = 0.5) and P(3IN = 0.3)(3IN2F = 0.5)(BDD =0.2) were synthesized using the P(3IN)(3IN2F = 0.5) as the main backbone which exhibited the highest efficiency in the Part II. Consequently, as presented in Fig. S80 and Table S20, P(3IN2F)(BDD = 0.5)and P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2), with 50% and 20% BDD units, respectively, when introduced into the D- π =A structure, reduced

the AVT by only 2–3% and induced negligible changes in the CRI, compared to those of P(3IN)(3IN2F = 0.5). Therefore, both polymers exhibited higher AVT and CRI values compared to PM6. This result suggests that excellent transparent properties can be maintained when the polymer has a dominant D– π =A backbone. The detailed theoretical, physical, optical, and electrochemical properties of the polymer are presented in the SI (Fig. S81–86 and Tables S21–23).

Specifically, the solubility and molecular weight enhanced simultaneously when BDD was incorporated into the D– π =A polymer backbone. Interestingly, P(3IN2F)(BDD = 0.5), in which 50% BDD, exhibited a band gap comparable to that of P(3IN)(3IN2F = 0.5), whereas P(3IN =0.3)(3IN2F = 0.5)(BDD = 0.2), which contained a relatively small amount of BDD (20%), exhibited the lowest E_g^{opt} of 1.57 eV, indicating that substantial light harvesting in the long-wavelength region could be expected. In Fig. 3b, the molar extinction coefficient in the photopic response region decreased in the order of PM6, P(3IN2F)(BDD = 0.5), and P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2). The same trend was observed for blend films with BTP-eC9. In other words, both terpolymers and quaterpolymers incorporating BDD exhibited higher visibletransparent films than PM6. As shown in Fig. 3c, toluene (TL) and XYprocessed P(3IN2F)(BDD = 0.5) and P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2) exhibited high PCEs of 13% and 14%, respectively, which were improved compared to that of P(3IN)(3IN2F = 0.5) (Fig. S87 and Table S24). As shown in Fig. 3d, photo-responses of both polymers are comparable to that of PM6 in the whole EQE region and even higher at 400–450 nm. Therefore, the polymers yielded high $J_{sc}s$ of over 25 mA cm⁻², which were approximately the same as that of PM6. Notably, P (3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2), which showed the highest performance, exhibited transparent properties with an AVT of 62.1% and a CRI of 95.0 in the blend film, which is sufficient for application to ST-OSCs (Fig. S88 and Table S25). In addition, as shown by the 2D-GIWAXS, AFM, SCLC, and TDA analysis results, the shortest d-spacing distance among the polymers showed, the twisted structures loosen at temperatures comparable to that of PM6, the RMS is the lowest, and the charge mobilities are balanced. These results explain the relatively high FF of P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2) (Fig. S89–95 and Tables S26-28) [60,61,64-66].

To achieve the ultimate objective of commercializing the OSC



Fig. 3. (a) Molecular structures, photographs (50-nm-thick films), and optimized PCEs of P(3IN2F)(BDD = 0.5), P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2), and PM6. (b) Molar extinction coefficients and absorption coefficient spectra (solid and dotted lines) of D– π =A terpolymer/quaterpolymer and PM6 in solutions and blend films (yellow area: photopic response). (c) *J*–*V* curves and (d) EQE curves and integrated current densities (solid and dotted lines) of optimized OSCs based on BDD-incorporated D– π =A terpolymer/quaterpolymer and PM6. Stability test curves according to (e) ISOS-D-1, (f) ISOS-D-2, and (g) ISOS-L-1 for optimized OSCs based on (3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2) and PM6 (dotted lines: linear fitting plots). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

technology, the material reliability of P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2) was tested from various perspectives and compared with that of PM6. As shown in Fig. 3e–g, two photoactive layer combinations were extensively investigated in terms of the shelf-lifetime (ISOS-D-1) [26,43,44], thermal (ISOS-D-2) [45], and photo (ISOS-L-1) [45–48] stabilities in accordance with the ISOS protocols. All OSCs were encapsulated to reduce the possibility of delamination and electrode oxidation between the photoactive and upper/lower layers over time. The characterization methodologies and specifics of the stability evaluations are presented in the SI.

First, in terms of the shelf-life stability, both P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2) and PM6 demonstrated continuous reduction in efficiency over approximately 1000 h. The devices also exhibited good atmospheric stability, with PCEs of 89.4% and 90.0%, respectively, when compared with the initial efficiency (Fig. S96). Next, the trend in the efficiency reduction owing to continued degradation at 85 °C was examined. P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2) showed a slightly faster reduction in efficiency than that of PM6 until 700 h; afterwards, an opposite trend was observed. After 922 h, the device efficiency of P (3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2) remained at 68.5% of its initial efficiency and showed a higher heat tolerance than that of PM6 (65.9%) (Fig. S97).

Finally, the photostability of the material was assessed. Briefly, after continuous irradiation with an LED light source, the PM6-based device

showed burn-in loss and rapidly photo-degraded for the first 40 h. It lost 20% of its initial efficiency after 158 h, which was recorded as the T_{80} (the time required to reach 80% of initial performance). Subsequently, the device maintained 71.9% of its initial efficiency after 1023 h. In contrast, the devices based on P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2) showed exceptional photostability without burn-in-loss by maintaining an efficiency of 91.4% of the initial efficiency over the same time period. Therefore, the T_{80} is anticipated to be recorded after approximately 3000 h based on the trend line (Fig. S98).

The substantial disparity in photostability between two OSCs is probably because of the differences in the donor polymer structure. In general, UV light with a wavelength less than 400 nm contains more energy than NIR and Vis light, triggering a critical breakdown of organic conjugated materials. As discussed earlier, P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2) with the D- π =A structure has a relatively strong π - π * transition effect than PM6, which has a D-A structure. Therefore, it can utilize a relatively large amount of light in the 315–400 nm region corresponding to UVA. This finding implies that P(3IN = 0.3)(3IN2F =0.5)(BDD = 0.2) may absorb a significant amount of UV light. Furthermore, by protecting the organic electron transport layer (ETL) which is relatively thinner than the other layers and hence more unstable, from UV irradiation might be prevent the photoaging of the entire device. The outstanding photostability of P(3IN = 0.3)(3IN2F =0.5)(BDD = 0.2) was confirmed by comparing the change in the absorbance of neat polymer films over time measured under UV irradiation (365 and 254 nm) (Fig. S99) [67]. Consequently, the strategy of inserting highly crystalline BDD units into the D– π =A polymer backbone can help achieving a high efficiency by simultaneously increasing J_{sc} and FF. Notably, the significant stability of P(3IN = 0.3)(3IN2F = 0.5) (BDD = 0.2) was established, emphasizing the prospect of industrial applications of OSCs.

3.4. Part IV: Realization of high-performance and eco-friendly ternary ST-OSCs compatible with both outdoor and indoor illumination

The ternary blend strategy which is convenient and effective method to improve the PCEs of OSCs, was studied to further enhanced the efficiency of P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2). Generally, enhancing light absorption and energy transfer properties by introducing a third material with well-matched frontier energy levels and band gaps with those of the photoactive materials is preferred when fabricating efficient ternary OSCs [4–7,9,10,15–17,19,20,22,28,30,50,68,69]. Herein, PM6, a well-known long-range-order crystalline polymer, was introduced as a third component to promote the charge transport in the vertical direction and induce a high-quality crystalline donor phase to improve the PCE. The P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2) polymer processed with TL has a face-on dominant structure, with an A_{xy}/A_z ratio of 0.93, as illustrated in Fig. 4a–c, S100, S101 and Table S29. In contrast, PM6

ratio of 0.24. Notably, when processed with TL instead of CF, the PM6 film exhibited a higher crystalline order with increase in CCL, particularly at (100) and (300), and A_{xy}/A_z ratio decreased to 0.16. This may facilitate an efficient flow of charge carriers along the vertical transport route inside the device, eventually improving the FF by shortening the charge extraction distance [9,18,28,69]. Furthermore, compared to CF, the BTP-eC9 acceptor in the TL-processed films increased the crystallinity in both (100) and (010) and the molecular order developed beyond the boundaries of the crystalline clusters, enabling multiple charge transfers [60]. Considering the balance between the efficiency and transparency, ternary OSCs were designed by precisely adjusting the component ratios of the two donors (D1 and D2) while keeping the quantity of BTP-eC9 constant.

As shown in Fig. 4d, transparent properties of the ternary blends were compared and analyzed based on D1:D2 ratios. Both AVT and CRI tended to decrease when PM6, which exhibits significant absorption properties in the photopic response region, was added to the P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2):BTP-eC9 combination. However, because of the P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2) polymer, which has excellent transparent properties, ternary OSCs maintained AVT values that were approximately 10% higher than those of PM6:BTP-eC9 up to a ratio of D1:D2:A = 0.4:0.6:1.2 (Fig. S102 and Table S30). As a result of optimizing the ternary OSCs processed with TL, J_{sc} and FF improved simultaneously with the increase in the proportion of PM6, as shown in Fig. 4e,f, S103 and Table S31. At a ratio of D1:D2 = 0.4:0.6, the highest



Fig. 4. (a) 2D-GIWAXS diffraction patterns, (b) 1D line-cut profiles (solid lines: OOP; dotted lines: IP), and (c) azimuthal pole figures (extracted from the $0-90^{\circ}$ of (100) lamellar diffraction) of neat P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2) and PM6 films. (d) Transmittance spectra of ternary blend films with P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2):PM6:BTP-eC9 = x:y:1.2. (e) *J*–V curves and (f) EQE curves and integrated current densities (solid and dotted lines) of optimized P(3IN = 0.3) (3IN2F = 0.2)(BDD = 0.2):PM6:BTP-eC9 = x:y:1.2. (e) *J*–V curves and (f) EQE curves and integrated current densities (solid and dotted lines) of optimized P(3IN = 0.3) (3IN2F = 0.2)(BDD = 0.2):Dased ternary OSCs. (g) 2D-GIWAXS diffraction patterns of all ternary OSCs (yellow dotted–dashed lines: indicating π – π stacking distances; dashed circles: excessive crystalline peaks). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

PCE of 16.5% was achieved with a V_{oc} of 0.827 V, a J_{sc} of 26.25 mA cm⁻², and an FF of 75.8%. The PCE was further enhanced to be 17.3% ($V_{oc} = 0.845$ V, $J_{sc} = 26.29$ mA cm⁻², and FF = 77.9%) by employing 1,4-diiodobenzene which is known to assist tighter molecular stacking with acceptor molecules (Fig. S104) [20]. Surprisingly, the optimized ternary PCE increased by 3.5% compared to that of the device without PM6. This improvement is highly significant and indicates that the efficiency is improved by approximately 25% using the ternary blend strategy with two donors. In contrast, when PM6 was introduced at a proportion of 80% or more instead of P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2), both V_{oc} and J_{sc} decreased, resulting in a reduction of the PCE to 13.9% at 100% of PM6.

These results could be directly related to crystallinity and orientation changes as well as optical and electrochemical properties between photoactive layer materials. As shown in Fig. 4g, as PM6 was gradually introduced into the mixed phase of P(3IN = 0.3)(3IN2F = 0.5)(BDD =0.2):BTP-eC9, the distances in both the (100) and (010) planes decreased, and the overall orientation of the ternary blend simultaneously changed from face-on to edge-on dominant one. Particularly at 0.4:0.6:1.2, the d-spacing was the shortest (21.45 Å), which was smaller than that of CF-processed PM6:BTP-eC9 (21.63 Å), which exhibited the highest FF of 76.8%. When the ratio of PM6 exceeded 80% of the donor phase, the π - π stacking distance decreased to 3.53–3.54 Å, whereas the d-spacing increased to 22.78-22.89 Å. In addition, the (100) CCL unexpectedly increased to 193.33-252.22 Å and polycrystalline peaks were observed at approximately 0.45–0.50 and 1.45 \AA^{-1} which had been detected for the neat BTP-eC9 film. It is presumed that this phenomenon causes excessive phase separation, resulting in an imbalance of the mixed domains between photoactive layer materials (Fig. S105, S106 and Table S32) [60,66]. The photovoltaic performance of the ternary OSCs agreed well with the AFM and SCLC analysis results (Fig. S107 and S108 and Table S33) [64,65]. Comprehensively, by

appropriately mixing edge-on dominant PM6 with face-on dominant P (3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2) can produce high photovoltaic performance by manipulating the material crystallization and forming a high-quality crystalline donor phase.

To successfully fabricate high-performance ST-OSCs, the optical potentials of P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2) and PM6 were compared and analyzed by performing finite-difference time-domainbased optical simulations [9,22,32,35,46]. Herein, we employed the measured optical parameters (refractive index and extinction coefficient) for fabricating mixed films with the same thickness to minimize the effects of the thickness of the photoactive layer on the optical transparency and electricity-generation of the device (Fig. S109). The optical simulation model (transfer matrix method, which was used here) calculates the electric field intensity $(|E|^2)$ at each position of the overall multilayer structure considering the effects of the light wave characteristics, reflection, and transmission at the interface between the media. As observed in Fig. 5a, P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2):BTP-eC9 formed a strong optical field with a strength of >1 N²C⁻² at 400–500 nm when compared to PM6:BTP-eC9, whereas it showed a relatively weak field of strength less than 1 at 500–650 nm. This finding suggests that the absorbance of P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2) increases in the former region compared to that of PM6, whereas it relatively decreases in the latter region, resulting in relatively high transmittance. This tendency was also observed for the optical simulation results calculated in multiple layers, identical to the actual device structure. In particular, an electric field >1.7 N^2C^{-2} at 400–500 nm observed for the P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2):BTP-eC9-based device indicates that an exciton significantly stronger than that of PM6:BTP-eC9 can be formed, which contributes to high EQE and J_{sc} values similar to those of the PM6based device. Significantly, the difference in the $|E|^2$ distribution in the region in which the human eye is the most sensitive (500-650 nm, as illustrated in Fig. 5b) shows that the P(3IN = 0.5)(3IN2F = 0.5)(BDD =



Fig. 5. (a) Simulated optical electric-field $(|E|^2)$ distributions of polymer blend films and optimized OSCs based on P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2) and PM6. (b) Simulated optical 1D line-cut profiles for P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2) and PM6-based OSCs in different regions (500–650 nm). (c) Photographs of P (3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2) and PM6 films with similar thickness. (d) *J*–*V* curves, (e) EQE curves and integrated current densities (solid and dotted lines), and (f) transmittance spectra of optimized eco-friendly binary/ternary ST-OSCs and the CF-processed PM6:BTP-eC9-based OSC.

0.2)-based device has a lower intensity than that of PM6 in all wavelength ranges except at 500 and 510 nm, resulting in high transmittance in the photopic response region. Moreover, both OSCs exhibit similar high $|E|^2$ values in the NIR region, which has a higher photon energy than that of the Vis region. This explains the absence of a large J_{sc} loss for the P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2):BTP-eC9 device compared to that of PM6:BTP-eC9.

Next, as shown in Fig. 5c, the transparency of the two donor polymers exhibited a more distinct difference depending on the film thickness. The thicker the film, the easier it was to distinguish the texts and colors using the P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2) film than with the PM6 film. This is because of the higher AVT and CRI values of the material (Fig. S110, S111 and Tables S34, S35). These results suggest that more efficient ST-OSCs can be fabricated by selectively transmitting Vis light and absorbing UV and NIR light when using the P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2):BTP-eC9 device instead of the PM6:BTP-eC9 device.

Encouraged by the aforementioned findings, we fabricated efficient ST-OSCs using P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2)-based binary and ternary blends, which showed the highest transparent and photovoltaic properties, respectively. The efficiency and transparency of the ST-OSCs were optimized by adjusting the thickness of the Ag top electrode to 10 and 15 nm, respectively. In particular, a 30 nm-thick WO₃ layer as a DBR was introduced into all ST-OSCs to prevent the decrease in stability in the device due to the introduction of thinner electrodes than those in the opaque device and to further enhance the transparency [28]. The results were compared with those of the PM6:BTP-eC9 device.

As shown in Fig. 5d,e, first, the P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2)-based binary ST-OSC with 15 nm-thick Ag showed an adequate PCE of 10.5% based on a high J_{sc} of 19.8 mA cm⁻². Next, the optimized ternary ST-OSC exhibited the highest PCE of 12.7% as FF increased rapidly by 10% or more owing to the introduction of PM6. This achievement is significant because the obtained efficiency differs by only 0.5% when compared with that of PM6:BTP-eC9-based ST-OSC with poor transmittance. The ST-OSCs in which 10 nm-thick Ag was introduced, showed efficiency reductions of only 0.7% and 1.1% in the binary and ternary blend devices, respectively, because of the reduced

 J_{sc} s compared to those of ST-OSCs (15 nm-thick Ag). Conversely, as shown in Fig. 5f, as the AVT was increased from 37.6% to 44.5% in the binary blend and from 26.1% to 34.9% in the ternary blend, high LUE values of 4.38% and 4.04%, respectively, were observed. In particular, the binary ST-OSC showed the maximum transmittance of 47.9% at 555 nm, which was the most sensitive wavelength in the photopic response region, further emphasizing its potential as a donor polymer for highly transparent ST-OSCs (Table S36). The values obtained for binary and ternary ST-OSCs are comparable to the LUEs of efficient ST-OSCs reported to date, and belong to the top level among the eco-friendly processed ST-OSCs (Table S37) [2,4,5,7,9,23,25,26,28,32,37,38]. The photovoltaic performances for all ST-OSCs agreed well with the tendencies of the relevant parameters associated with opaque OSCs. The high reliability of ST-OSCs was ensured as the J_{sc} values obtained using EQE and J-V curves had discrepancies of less than 5% (Fig. S112). Moreover, the optimized ST-OSCs were validated via checks of EQE + T + R < 100% (Fig. S113).

Thanks to the advantages of easy adjustment of the molecular structure and band gap of photoactive laver materials, the OSC technology has recently been established as a highly promising methodology for achieving efficient indoor light harvesting devices [49–52]. Therefore, it is essential to assess the indoor photovoltaic performance of the P (3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2)-based binary and ternary OSCs/ ST-OSCs. As shown in Fig. 6a, 3000 K LED warm white light was selected as an indoor light source, and the input power density of the emission spectrum for each illuminance was obtained accurately using a calibrated spectrometer in a dark room. The results were utilized for efficiency calculations. Moreover, the illumination, photon flux, and integrated current density for each illuminance were determined using the same method (Figs. S114-116) [49-51,70]. As discussed earlier, P (3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2) has a relatively low extinction coefficient in the photopic response region; however, it showed a J_{sc} similar to that of PM6 at 1 sun illumination and demonstrated a higher J_{sc} in the ternary blend. Additionally, P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2) can absorb light below 500 nm with an extinction coefficient higher than that of PM6 as well as in the 650-750 nm region, which cannot be absorbed by PM6. Therefore, it was expected that a relatively large



Fig. 6. (a) Emission power and integrated power spectra (solid and dotted lines) of warm white LED (3000 K LED) at 195–958 lx used in this study. *J*–*V* curves (solid lines: 958 lx; dashed lines: 478 lx; dotted lines: 195 lx) of optimized binary/ternary blend and PM6-based (b) OSC or (c) ST-OSCs at various indoor light intensities. (d) Photographs of optimized binary/ternary ST-OSCs. (e) Photographs of self-powered thermo-hygrometer powered by eco-friendly ternary conventional ST-OSC module under 3000 K LED at 195 lx.

number of photons could be harvested even at a low light intensity.

First, the indoor photovoltaic performances for opaque OSCs were evaluated at various low illuminances of 195-958 lx, as shown in Fig. 6b. (3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2):BTP-eC9 and PM6:BTPeC9 achieved 18.2% and 20.8% PCEs at 958 lx, respectively. The efficiency difference between these two devices was only 2.6%, which was lower than that at 1 sun illumination. Furthermore, the PCEs of the binary OSC were satisfactory with values of 17.0% and 14.7% at 478 lx and 195 lx, respectively. This result is owing to the high J_{sc} , which is maintained in low-light environments, indicating the potential of D- π =A building blocks for indoor OSC applications. Next, the ternary OSC unexpectedly achieved the highest PCE of 20.9%, which was slightly higher than that of PM6:BTP-eC9 at 958 lx. To the best of our knowledge, this is the highest indoor performance among the low-bandgap donor and acceptor combinations, with a band gap lower than 1.4 eV, that have been reported to date [71]. However, the PCEs of the ternary OSC decreased abruptly to 18.7% and 16.5% at 478 and 195 lx, respectively, when compared with those of the PM6:BTP-eC9 device. This result is due to the relatively low FF values. The indoor photovoltaic parameters for the OSCs are summarized in Table S38. All OSCs exhibited high reliability even under low illuminance conditions, as shown in Fig. S117–119. Additionally, Fig. S120 shows the comparison of the PCEs in terms of the light intensity.

To better understand the dependence of photovoltaic performance on light intensity, the dark current characteristics [51,72], exciton dissociation and charge collection efficiencies [6,7,9,18,19,23,33,50], charge recombination behaviors [8,9,15,19,51], nanoscale morphologies [17,28,29,31,43,64,65], domain sizes [4,16,28,50], and charge carrier lifetimes [4,10,23,28] of the optimized devices were systematically analyzed, as shown in Fig. S121-130 and Tables S39-41. Further details are presented in the SI. Briefly, the P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2)-based ternary blend had the highest PCE at 958 lx owing to the high J_{sc} derived from its excellent nanoscale morphology, which was the among the three photoactive combinations. However, the ternary blend device showed a very strong dependence on FF under lower illuminance conditions. In particular, as observed from the 2D-GIWAXS and time-resolved PL analyses, the domain sizes and charge carrier lifetimes of the ternary blend were very similar to those of the PM6 blend. Therefore, the high trap-assisted recombination under low illuminance conditions may have been derived from layers outside the photoactive laver.

ST-OSCs have significant potential for double-sided energy harvesting from both the solar and indoor illuminations because they can be integrated into various electronic devices, including wearable/flexible devices and indoor smart sensors for the Internet of Things (IoT). Considering the actual exposure environments—for example, when integrated into windows or portable devices—ST-OSCs can continuously generate high or low power during the day or night, respectively. Therefore, it is crucial to utilize both the sun and indoor light sources. However, only a few studies have simultaneously utilized these conditions [6,50,53]. Therefore, we evaluated the indoor photovoltaic performance for ST-OSCs and proposed several important techniques (ETL [51], DBR [8,10,28,37,73,74], and hollow electrode issues) to realize stable and high performance in low-light environments, as shown in Fig. 6b, S131–134 and Tables S42–45. Further details are presented in the SI.

The indoor photovoltaic performances of the binary and ternary ST-OSCs optimized using the abovementioned technologies are shown in Fig. 6c. The relevant parameters are summarized in Table S46. In particular, the binary and ternary ST-OSCs were introduced Ag electrodes of 10 nm which were thinner than those of PM6 (15 nm) to preserve the high transparent properties. Figs. S135–137 indicate that all ST-OSCs maintain high reliability. Despite possessing relatively thin electrodes, the binary and ternary ST-OSCs demonstrated reasonable photovoltaic parameters depending on the light intensity. First, the binary ST-OSC exhibited a high PCE of 12.4% owing to the enhancement

of FF at 958 lx compared to those obtained under 1 sun illumination. However, the PCEs of binary ST-OSC were 11.3% and 9.9% due to the gradual decrease in $V_{\rm oc}$ and FF at 478 lx and 195 lx, respectively (Fig. S138). This trend may be because the extremely low light intensity increases the carrier density loss in the trap state (Fig. S139). Next, the ternary ST-OSC increased the efficiency by approximately 35% at 958 lx when compared to that at 1 sun illumination, producing the best PCE of 15.7%. Remarkably, the substantial decrease in the FF, which was observed under low-light conditions in the opaque device, was not observed and was minimized in the translucent device (Fig. S140). As a result, the PCEs achieved 14.7% and 13.4% at 478 and 195 lx, respectively. A similar trend was observed in the PM6-based ST-OSC; however, it was not unexpected, considering the introduction of a relatively thick photoactive layer and Ag (Fig. S141).

The color quality of the binary and ternary ST-OSCs based on P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2) may be assessed using the Commission Internationale d'Eclairage (CIE) 1931 (x, y) chromaticity diagram, as illustrated in Fig. S142. As depicted in Fig. 6d, both devices afforded clear visualization. The binary ST-OSC, in particular, displayed color coordinates of (0.306, 0.337), a correlated color temperature of 6,815 K, and an infrared photon rejection rate (IRR) of 81.5% with an AVT of 44.5% and a CRI of 81.4. These values were very close to those of 6,500 K illuminant D65, which provides artificial daylight (0.313, 0.329). Furthermore, an IRR over 80% are suitable for realizing efficient window applications. The AVT of the binary ST-OSC further demonstrates the reliability, as accredited by the Korea Laboratory Accreditation Scheme, Republic of Korea (Fig. S143). Table S47 summarizes the parameters related to the transparent properties of the two ST-OSCs in detail.

The indoor performance of the P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2)-based binary and ternary ST-OSCs could be further improved by incorporating the AVT into a new concept, known as light utilization indoor efficiency (LUIE). LUIE, which is similar to LUE, has a trade-off relationship between the PCE and AVT and is a direct parameter to measure the efficiency of ST-OSC indoor performance, as expressed by the following equation:

$$LUIE = PCE_{indoor} \times AVT \tag{1}$$

where AVT is calculated using the equation proposed by Yang and Lunt [75]. The Vis region was limited to 380–780 nm. The PCE_{Indoor} is defined by the reliable PCE measured in a low-light environment in which the emission spectrum and input power density of the indoor light source have been determined using spectrometric measurements. [70]. The LUIE can be an essential criterion for consumers or users to make sensible decisions by considering the actual application environment of the ST-OSCs. The PCE and LUE (or LUIE) values of all ST-OSCs for various light conditions are presented in Fig. S144. Although the PM6-based ST-OSC showed the highest PCEs under all light conditions, the P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2)-based binary and ternary ST-OSCs can perform better than those of PM6 when its effectiveness was assessed using LUE or/and LUIE.

Briefly, the effectiveness of ST-OSCs was the highest with an LUE of 4.38% for binary blends under 1 sun illumination and with a LUIE of 5.52% (5.48%) for the binary blend (ternary blend) at 958 lx. The ternary OSC had a distinct advantage, achieving the highest LUIEs of 5.13% and 4.67% under light intensities of 478 lx and 195 lx, respectively. It is noteworthy that the LUIE values of binary and ternary ST-OSCs can be further increased when 2,700 K LED is introduced with a relatively enhanced emission in the long-wavelength region. Table 1 summarizes the photovoltaic and transparent parameters of eco-friendly binary/ternary OSC/ST-OSCs with respect to the light intensity. Because illuminance levels below 1000 lx are employed in indoor environments, such as offices and living rooms, the LUIE values of both binary and ternary ST-OSCs are significant [49–51]. Comprehensively, the performance indicators for LUE and LUIE will enable ST-OSCs to examine the

Table 1

Photovoltaic and transparent parameters of eco-friendly binary/ternary OSC/ST-OSCs based on P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2): PM6: BTP-eC9 with respect to light intensity.

Device (condition ^a)	Light intensity (source) [lux]	P _{in} [μW cm ⁻²]	$V_{\rm oc}[V]$	J _{sc} [μA cm ⁻²]	J _{cal} [μA cm ⁻²]	FF [%]	P _{out} [μW cm ⁻²]	PCE _{max} / PCE ^b _{ave} [%]	AVT [%]	LUE (LUIE) [%]
000 (1 0.0.1 0 VV) ^C	(AM 1 50)	100.000	0.005	25 420	04 001	66.0	14.000	140/120 + 0.22		
USC (1.0:0:1.2, XY)	(AM 1.5G)	100,000	0.825	25,420	24,291	67.7	14,009	$14.0/13.8 \pm 0.22$	-	-
	958 (2000 K LED)	337.07	0.052	138.87	134.07	07.7	61.30	$18.2/17.9 \pm 0.20$		
	(3000 K LED)	160 70	0.614	60 7E	67 15	67.0	28 60	$17.0/16.7 \pm 0.97$		
	4/8 (2000 K LED)	106.76	0.014	09.75	07.45	07.0	20.09	$17.0/10.7 \pm 0.27$		
	(3000 K LED)	60 62	0 570	27 50	27.40	61 E	10.11	$14.7/14.4 \pm 0.20$		
	(2000 K LED)	08.03	0.370	27.50	27.40	04.5	10.11	$14.7/14.4 \pm 0.29$		
ST OSC (1 0.0.1 2 VV) ^{d, e}	(3000 K LED)	100.000	0 000	10 040	17.045	69 E	0.924	$0.9/0.5 \pm 0.24$	44 E0	4 20
S1-OSC (1.0:0:1.2, XY)	(AM 1.5G)	227.07	0.642	10,042	17,045	66 E	9,034	$9.0/9.3 \pm 0.34$ 12.4/12.1 ± 0.20	44.50	4.30 (E EE)
	936 (2000 K LED)	337.07	0.043	97.80	93.20	00.5	41.04	$12.4/12.1 \pm 0.39$		(3.33)
	(3000 K LED)	160 70	0.600	40.16	16 74	62.0	10.12	$11.2/11.0 \pm 0.41$		(E 02)
	(3000 K LED)	100.70	0.009	49.10	40.74	03.9	19.15	$11.3/11.0 \pm 0.41$		(3.03)
	(5000 K EED)	60 62	0 550	10.00	19.06	60.9	6 76	$0.0/0.6 \pm 0.42$		(4.40)
	(3000 K LED)	08.05	0.339	19.90	10.90	00.8	0.70	9.9/9.0 ± 0.42		(4.40)
OSC (0.4.0.6.1.2. TL) ^c	(AM 1 5C)	100.000	0.827	26 251	25 226	75.9	16 455	$165/164 \pm 0.13$		
036 (0.4.0.0.1.2, 11)	058	337.07	0.657	149.19	141.60	73.0	70.20	$10.3/10.4 \pm 0.13$ $20.0/20.7 \pm 0.10$	-	-
	(3000 K LED)	337.07	0.037	140.10	141.09	12.2	70.29	$20.9/20.7 \pm 0.19$		
	(3000 K LED) 478	168 78	0.612	74 18	70.97	69 5	31 55	$18.7/18.5 \pm 0.22$		
	(3000 K LED)	100.70	0.012	74.10	/0.5/	09.5	51.55	$10.7/10.0 \pm 0.22$		
	105	68 63	0 570	30.21	28.83	65.6	11 30	$165/162 \pm 0.27$		
	(3000 K LED)	00.05	0.370	30.21	20.05	03.0	11.50	10.3/10.2 ± 0.2/		
OSC (0.4.0.6.1.2. TL) ^d	(AM 1 5G)	100.000	0.832	25 550	25 470	76.3	16 209	$16.2/16.0\pm0.21$		
056 (0.4.0.0.1.2, 11)	958	337.07	0.650	145 50	144 60	74.6	70 55	$\frac{10.2}{10.0} \pm 0.21$ 20.9/20.7 ± 0.23		
	(3000 K LED)	337.07	0.050	145.50	14.00	74.0	/0.55	20.9/20.7 ± 0.25		
	478	168 78	0.611	74 50	72 42	74 5	33 91	$20.1/19.9 \pm 0.22$		
	(3000 K LFD)	100.70	0.011	7 1.00	/ 2. 12	7 1.0	00.91	20.1/19.9 ± 0.22		
	195	68 63	0 586	30.95	29 42	734	13 38	$195/192 \pm 026$		
	(3000 K LFD)	00.00	0.000	00.90	23.12	/0.1	10.00	19.0/19.2 ± 0.20		
ST-OSC (0.4.0.6.1.2. TL) ^{d,}	(AM 1 5G)	100.000	0.819	19 093	19 048	74 2	11 601	$11.6/11.3 \pm 0.34$	34 86	4 04
e	958	337.07	0.654	110.28	105.04	73.4	52.94	$15.7/15.4 \pm 0.36$	01.00	(5.48)
	(3000 K LED)	00/10/	01001	110.20	100101	,	02131	1007 1017 ± 0100		(0110)
	478	168.78	0.623	55.08	52.62	72.4	24.84	$14.7/14.4 \pm 0.39$		(5.13)
	(3000 K LED)							,		(0120)
	195	68.63	0.583	22.42	21.36	70.3	9.19	$13.4/13.1 \pm 0.41$		(4.67)
	(3000 K LED)									()
OSC (0:1.0:1.2, CF) ^{c, f}	(AM 1.5G)	100,000	0.845	26.010	24,710	76.8	16.873	$16.9/16.6 \pm 0.29$	_	_
···· , ·· ,	958	337.07	0.665	141.01	140.88	74.8	70.14	$20.8/20.5 \pm 0.31$		
	(3000 K LED)							,		
	478	168.78	0.637	70.82	70.55	73.6	33.20	$19.7/19.3 \pm 0.36$		
	(3000 K LED)									
	195	68.63	0.602	28.73	28.66	70.2	12.14	$17.7/17.3 \pm 0.38$		
	(3000 K LED)									
ST-OSC (0:1.0:1.2, CF) ^{d-g}	(AM 1.5G)	100,000	0.817	20,868	20,135	77.7	13,248	$13.2/12.9 \pm 0.27$	17.35	2.30
	958	337.07	0.663	116.35	115.54	75.3	58.09	$17.2/16.7 \pm 0.44$		(2.99)
	(3000 K LED)									
	478	168.78	0.633	58.49	57.88	73.5	27.21	$16.1/15.6 \pm 0.49$		(2.80)
	(3000 K LED)									
	195	68.63	0.605	23.55	23.49	72.2	10.29	$15.0/14.4 \pm 0.51$		(2.60)
	(3000 K LED)									

^a Annealing at 100 °C for 10 min; ^b Average PCE values calculated from 10 independent cells; ^c OSC device configuration (ITO/PEDOT:PSS/Active layer/PNDIT-F3N/Ag); ^d OSC/ST-OSC device configuration (ITO/PEDOT:PSS/Active layer/PDINN/Ag); ^e ST-OSCs used the top electrode of Ag (10 nm)/WO₃ (30 nm); ^f The processing solvent is CF; ^g ST-OSC used the top electrode of Ag (15 nm)/WO₃ (30 nm).

primary exposure environment to the light source of the practical application to be integrated and will assist in making wise decisions for emplacement.

In addition to the small-area prototype, we demonstrated the feasibility of scaling up large-area modules using a ternary blend, which performed satisfactorily under both 1 sun and low-light illumination conditions. The series resistance of a large-area module is generally higher than that of the unit cell, and the voltage across the series resistance of the device is low due to the extremely low photocurrent at a low light intensity. In other words, because the series resistance does not affect the device performance, large-area OSC/ST-OSC modules with an indoor solar power may be highly desirable [31,50]. Therefore, we first fabricated eco-friendly ternary OSC/ST-OSC modules with a total active area of 4.7 cm². These modules consisted of three sub-cells (stripe) connected in series and were monolithically integrated via ITO-to-Ag interconnects in a way similar to that described by Facchetti et al. [52]. Further details are presented in the SI (Figs. S145–148 and Tables S48–53).

Briefly, the opaque OSC module achieved an excellent PCE of 13.6% ($V_{oc} = 2.486$ V, $J_{sc} = 7.93$ mA cm⁻², and FF = 69.0%) under 1 sun illumination. Furthermore, a PCE of 19.3% ($V_{oc} = 2.047$ V, $J_{sc} = 41.28 \ \mu\text{A cm}^{-2}$, and FF = 77.1%) and an output power (P_{out}) of 65.18 $\mu\text{W cm}^{-2}$ obtained in the same module measured under a 958 lx LED illumination, which is the highest indoor performance reported for OSC modules based on low-band-gap photoactive layer combinations to date. Despite a further decrease in the light intensities, the PCE and P_{out} values maintained a satisfactory performance with values of 18.4% and 31.08 $\mu\text{W cm}^{-2}$ at 478 lx and 16.8% and 11.50 $\mu\text{W cm}^{-2}$ at 195 lx, respectively. Next, the PCE and LUE of the ST-OSC module were 10.3% and 3.09% under 1 sun illumination, respectively. Although it is a relatively

poor performance compared to that of the opaque module under 1 sun illumination, the ST-OSC module showed LUIEs of 4.25%–2.97% with increased PCEs of 14.2%–9.9% at 958–195 lx. Notably, based on the previous studies, the V_{oc} values of 2.056–1.592 V and P_{out} values of 47.76–6.82 μ W cm⁻² of the ST-OSC module were sufficient to drive many mini-electronic applications, such as calculator, wristwatch, and radio-frequency identification tags [50,51]. Therefore, as observed in Fig. 6e and Video S1, we successfully demonstrate that the ST-OSC module can provide stable power in real time up to 195 lx by completely replacing the 1.5 V battery of the electronic thermohygrometer.

To verify the industrial scalability of the ST-OSC module, we also fabricated the air-processed eco-friendly inverted ternary OSC/ST-OSC modules based on P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2). Most OSC/ ST-OSC devices are generally manufactured and encased under relatively demanding inert atmosphere conditions owing to the stability issues. However, considering the large-scale manufacturing process of actual OSCs/ST-OSCs, it is crucial to process and optimize the photoactive layer in the ambient environment. The details are presented in the SI (Figs. S149–154 and Tables S54–61). The opaque inverted OSC module yielded a high performance with a PCE of 12.4% ($V_{oc} = 2.476$ V, $J_{\rm sc}$ of 7.68 mA cm⁻², and FF = 65.4%) under 1 sun illumination compared to that of the conventional OSC module. Furthermore, the inverted OSC module showed significantly uniform and stable PCEs of 16.8%-14.9% at low-light intensities at 958-195 lx. This result is achieved because in addition to the enhanced shunt resistance in the module, the dependency of FF on the light intensity is relatively low at a low light intensity. Finally, the inverted ST-OSC module was developed

by replacing WO₃ as conventional DBR layer with the same thickness of MoO₃. As a result, the module achieved an adequate PCE of 8.8% at 1 sun. A higher AVT of 32.11% was produced despite introducing a thicker 15 nm Ag layer compared to that of the conventional ST-OSC module. The difference in AVT values exists because in the inverted structure, the ETL and hole transport layer (HTL) are converted into more transparent layers, and formed oxide-metal-oxide multilayers, such as MoO₃/Ag/ MoO₃, with high refractive index [73]. Therefore, the inverted ST-OSC module showed high LUIEs of 3.90%-3.35% with increased PCEs of 12.1%-10.4% under low-light conditions at 958-195 lx. As a conventional ST-OSC module, the $V_{\rm oc}$ (1.957–1.753 V) and $P_{\rm out}$ values (40.94–7.17 μ W cm⁻²) of inverted ST-OSC module can be also drive the thermo-hygrometer under all low-light conditions (Fig. S155 and Video S2). Significantly, the color coordinates presented the neutral CIE approaching the white point compared to those of the conventional ternary ST-OSC, and the color discrimination and heat dissipation were relatively improved. Table 2 summarizes the photovoltaic and transparent parameters of eco-friendly ternary OSC/ST-OSC modules with respect to the light intensity. These results obtained for ternary OSC/ST-OSC modules with the inverted structure are very worth because they were obtained by processing the material with an eco-friendly solvent under ambient O₂ and humidity conditions to facilitate commercial mass production.

3.5. Part V: Potential of D-=A donor materials for commercialization of ST-OSCs

The typical low-band-gap D-A donor polymer-based OSCs show a Voc

Table 2

Photovoltaic and transparent parameters of eco-friendly ternary OSC/ST-OSC modules with conventional and inverted structures based on P(3IN = 0.3)(3IN2F = 0.5) (BDD = 0.2):PM6:BTP-eC9 with respect to light intensity.

Device (condition ^a)	Light intensity(source) [lux]	$P_{\rm in}$ [µW cm ⁻²]	$V_{\rm oc}[V]$	J _{sc} [μA cm ⁻²]	FF[%]	P _{out} [μW cm ⁻²]	PCE _{max} /PCE ^b _{ave} [%]	AVT [%]	LUE(LUIE) [%]
OSC module (0.4:0.6:1.2, TL) ^c	(AM 1.5G) 958 (3000 K LED) 478 (3000 K LED)	100,000 337.07 168.78	2.486 2.047 1.971	7,925 41.28 20.83	69.0 77.1 75.7	13,569 65.18 31.08	$13.6/13.4 \pm 0.19$ $19.3/19.0 \pm 0.29$ $18.4/18.1 \pm 0.34$	-	_
	195 (3000 K LED)	68.63	1.864	8.37	73.7	11.50	16.8/16.4 ± 0.39		
ST-OSC module (0.4:0.6:1.2, TL) ^{c, d}	(AM 1.5G) 958 (3000 K LED)	100,000 337.07	2.487 2.056	6,182 33.81	67.0 68.7	10,301 47.76	$\begin{array}{c} 10.3/10.0\pm0.34\\ 14.2/13.9\pm0.38\end{array}$	30.02	3.09 (4.25)
	478 (3000 K LED) 195	168.78 68.63	1.827 1.592	17.16 6.88	62.6 62.3	19.63 6.82	$\begin{array}{c} 11.6/11.2\pm0.41\\ 9.9/9.5\pm0.44\end{array}$		(3.49) (2.97)
	(3000 K LED)								
OSC module (0.4:0.6:1.2, TL) ^e	(AM 1.5G) 958 (3000 K LED)	100,000 337.07	2.476 1.954	7,678 39.90	65.4 72.8	12,433 56.76	$\begin{array}{c} 12.4/12.2\pm0.24\\ 16.8/16.6\pm0.20\end{array}$	-	_
	478 (3000 K LED) 195	168.78 68.63	1.888 1.794	20.13 8.06	71.7 70.6	27.25 10.21	$\begin{array}{l} 16.1/15.9\pm 0.24\\ \\ 14.9/14.6\pm 0.32\end{array}$		
	(3000 K LED)				<i>(</i>))				
ST-OSC module (0.4:0.6:1.2, TL) ^{e, 1}	(AM 1.5G) 958 (3000 K LED)	100,000 337.07	2.406 1.957	5,715 32.28	63.9 64.8	8,786 40.94	$\begin{array}{l} 8.8/8.5 \pm 0.26 \\ 12.1/11.8 \pm 0.32 \end{array}$	32.11	2.82 (3.90)
	478 (3000 K LED) 195	168.78 68.63	1.851 1.753	16.10 6.44	64.5 63.5	19.21 7.17	$\begin{array}{l} 11.4/11.1 \pm 0.33 \\ 10.4/10.1 \pm 0.34 \end{array}$		(3.66) (3.35)
	(3000 K LED)								

^a Annealing at 100 °C for 10 min; ^b Average PCE values calculated from 10 independent cells; ^c Conventional OSC module configuration (ITO/PEDOT:PSS/Active layer/PDINN/Ag); ^d Conventional ST-OSC module with the same configuration of the opaque module used the top electrode of Ag (13 nm)/WO₃ (30 nm); ^e Inverted OSC module configuration (ITO/ZnO/Active layer/MoO₃/Ag); ^f Inverted ST-OSC module with the same configuration of the opaque module used the top electrode of MoO₃ (10 nm)/Ag (15 nm)/MoO₃ (30 nm).

of 0.8 V or less owing to the high HOMO level of the polymer. In contrast, the unique D– π =A polymers exhibited relatively high V_{oc} values of 0.81–0.88 eV with donor band gap (E_g^{donor}) values of 1.57–1.73 eV, except for P(3BA). To investigate the changes in V_{oc} with the structure, energy loss (E_{loss}) calculations for nine D– π =A polymers, as well as P(3CHO) and PM6, were performed systematically, as shown in Fig. 7a–c. The details are presented in the SI (Fig. S156 and Table S62) [15,17–19,49,76].

Briefly, for polymers discussed in the Part I, E_{loss} values can be reduced as much the strength and size of EWG decreased, and the planarity of EWG relatively increased. Therefore, the IN and TC groups are promising candidates for high-performance $D-\pi=A$ donor materials. Next, for polymers discussed in the Part II, the introduction of halogenation and terpolymer strategies simultaneously lowered E_g^{donor} and $E_{\rm loss}$ values compared to those of polymers discussed in the Part I. Among them, P(3IN2F) with two fluorine effects showed the lowest E_{loss} of 0.511 eV and the highest V_{oc} of 0.878 V despite a low E_g^{donor} of 1.61 eV. This result provides valuable insights for the further development of polymers with high V_{oc} and low band gaps. Finally, among the D- π =A donor polymers, P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2) with the highest efficiency and lowest E_{g}^{donor} of 1.57 eV showed a suitable E_{loss} of 0.561 eV owing to the incorporation of the BDD unit, which is almost identical to that of PM6 with an E_{g}^{donor} of 1.82 eV. However, this polymer had a V_{oc} of approximately 0.83 V, indicating that the scope for further improvements. These results suggest that for fabricating an efficient D- π =A donor, it may be necessary to adjust the component ratio, such that a synergy between the halogenation effect and copolymer design approach is obtained. Additionally, exploring various combinations of promising derivatives may also be beneficial.

To improve the understanding of the new D– π =A polymer materials from the structural design perspective, compatibility between the donor and acceptor was examined, and the results are presented in Fig. S157 and Table S63 [17,28,44,46,56,64]. The D– π =A polymers with BA, IN, and TC incorporated as EWGs showed higher surface tensions than the typical D–A polymer, P(3CHO), and even is similar to that of BTP-eC9. Therefore, the D– π =A polymers can be mixed with BTP-eC9 more effectively than with P(3CHO). However, a high compatibility between the donor and acceptor may decrease the domain purity and consequently affect the photovoltaic performance. Despite the miscibility with BTP-eC9 being significantly high, P(3IN) and P(3TC) demonstrated high lamellar and π - π stacking properties in blend films. These crystalline properties were retained even after blending with BTP-eC9, resulting in a photovoltaic performance higher than that of P(3CHO). Additionally, compatibility can be controlled by systematically performing halogenation on the polymer backbone of the D- π =A structure. Significantly, the photovoltaic performance can be further improved by incorporating highly crystalline moieties, without losing the transparent properties of the D- π =A structure.

To further investigate the charge and energy transfer properties between the D– π =A polymer and BTP-eC9, the PLQ rates for the donor to blend (D \rightarrow B) and the acceptor to blend (A \rightarrow B) were assessed by measuring the PL spectra of pure donor/acceptor films and blended films (Fig. S158 and Table S64) [28,31,36,43,44,54-56,68]. The extinction efficiency of the Part I polymers steadily increased in the order of 3BA, 3IN, and 3TC, which were introduced as EWGs. With the halogenation and the terpolymer strategies, the Part II polymers efficiently minimized the HOMO and LUMO offsets when compared to those of the Part I polymers, and the $PLQ_{A \rightarrow B}$ efficiency of the fluorineintroduced terpolymer significantly improved. Finally, in case of the Part III polymers, the inclusion of BDD increased the PLQ efficiency more effectively in both the terpolymer and quaterpolymer. Particularly, the PLQ_{D→B} and PLQ_{A→B} values of P(3IN = 0.3)(3IN2F = 0.5) (BDD = 0.2), which showed the highest photovoltaic performance, reached 97.32% and 96.14%, respectively. These values are higher than those of PM6, indicating effective exciton dissociation. These findings are consistent with the trend in J_{sc} s observed for OSCs and complement previously discussed analysis results of 2D-GIWAXS, charge mobility, and morphological characteristics [60,64-66].

Notably, from a structural perspective, $D-\pi=A$ polymers exhibit significantly larger Stokes shifts than those of ordinary D–A polymers. The Stokes shift, which can be calculated by the difference between maximum absorption and emission positions, provides information



Fig. 7. (a) Normalized EQE and (b) EQE_{EL} curves of donor materials discussed in Parts I–III. (c) Comparison of open-circuit voltages and specific energy loss values in each optimized device. (d) PL spectra of donor materials and UV–Vis absorption spectra of NFAs (dotted and solid lines, respectively). (e) EQE curves and integrated current densities (solid and dotted lines, respectively) of P(3IN):NFA and modified quaterpolymer-based OSCs. (f) Comparison of LUE (or LUIE) and calculated SF values of eco-friendly solvent-processed ST-OSCs fabricated in this study and previous studies.

about the molecular reorganization energy between the ground and excited states [24,59]. As shown in Fig. 7d, the Stokes shift of P(3CHO) was 114 nm, whereas P(3TC) showed a significantly larger value of 380 nm. This result is because of large structural differences between the excited and ground states resulting from considerable molecular rearrangement during photoexcitation because P(3TC) has a larger dihedral angle than that of P(3CHO), as revealed by the abovementioned DFT calculation results [77]. Consequently, P(3TC) consumes more energy in the non-radiative transition than P(3CHO) when blended with BTP-eC9, resulting in a relatively large ΔE_3 value, as shown in the energy loss calculations. However, this characteristic can be sufficiently improved through halogenation and terpolymer/quaterpolymer strategies. It is noteworthy that P(3IN2F), in which two F atoms were introduced, exhibited the lowest non-radiative loss while demonstrating the largest Stokes shift. As shown in Fig. 7e and S159 and Table S65, the large Stokes shift of P(3TC) enabled an efficient energy transfer with NFAs, such as IEICO-4F and 6TIC-4F, which had band gaps lower than that of BTP-eC9. Moreover, the polymer blends with IECO-4F and 6TIC-4F provide significantly enhanced transparent properties with an AVT of 64.98%-67.04% and a CRI of 97.02-97.49 compared to those of BTPeC9 (Fig. S160 and Table S66).

The newly synthesized P(3TC = 0.3)(3IN2F = 0.5)(BDD = 0.2)-based device had stronger photo-response in the 450–800 nm region owing to structural modification by introducing 3TC instead of 3IN in P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2). Notably, the enhanced photovoltaic performances in indoor light may be expected because the spectral range corresponds to the major light-emitting region of the LED spectrum. Furthermore, the modified P(3TC = 0.3)(3IN2F = 0.5)(3CI = 0.2) by introducing 3-chlorothiophene instead of BDD in P(3TC = 0.3)(3IN2F = 0.5)(BDD = 0.2), simultaneously retained a high PCE and decreased a SC. Fig. S161–164 and Tables S67–69 show the theoretical, physical, optical, and electrochemical properties of the two newly synthesized quaterpolymers. Therefore, it will be provided the improved ST-OSCs in the near future if the D– π =A polymer is applied to the acceptor that can reduce energy loss while improving the photovoltaic and transparent parameters through rational structural design.

For the commercialization of OSCs, it is necessary to identify the application that can emphasize the unique features of the associated technology and build a specific high-performance photoactive layer combination suitable for the required application. Most high-performance photoactive materials, however, require hazardous toxic solvents, and the SC of the raw materials, namely, the donor and acceptor, is still high [28,43]. These are critical disadvantages in terms of scalability and commercial production. From the perspective of structural design, it is need to promote high performance while considering the use of eco-friendly solvents and low SC to fully realize the beneficial functionalities provided by OSCs. Therefore, the terpolymers/quaterpolymers with D– π =A structures, which are developed based on low-cost strategies, show great potential as donor materials for high-performance ST-OSCs because they can be treated with eco-friendly solvents.

To assess their cost effectiveness, we used a simpler and more reliable SF calculation compared to that of SC [78]. However, no clearly defined SF calculation method has been reported for a terpolymer/ quaterpolymer to date. Therefore, a new mathematical approach based on logical analysis and the premise in the existing literature that "the beginning ingredient is a chemical that can be obtained on the market in sufficient quantities to generate hundreds of kilograms of polymers" was developed. Detailed arithmetic processes and explanations can be found in the SI (also provided in Spreadsheet). Briefly, the SF was determined by assigning a weight based on the polymerization molar ratio to each of the number of synthetic steps (NSS) and the reciprocal yield (RY) of the final monomers utilized in polymer synthesis. Additionally, if the synthesis stages between the monomers overlap while calculating the SF of the terpolymer/quaterpolymer, NSS and RY are used only once and substituted in the arithmetic formula of the final monomer with a reasonably large molar ratio. This concept is also applicable to smallmolecule donor/acceptor calculations. This metric would be more reliable in terms of industrial mass production as the use of final monomers with low NSS and RY can reduce costs.

Based on our calculations, most of the D- π =A polymers have low NSSs of 8-11.5 and high overall yields, as illustrated in Figs. S165-177 and Table S70. Particularly, all quaterpolymers had high PCEs of 13.7–14.0% and low SF values of 17.75–18.23. Furthermore, the ternary OSC using PM6 with the highest PCE of 17.3% showed a slightly increased SF of 27.60 (Table S71). These results are further highlighted by comparing the LUE (or LUIE) and SF values to those of eco-friendly solvent-processed ST-OSCs (SF calculations of representative donor polymers are provided in Figs. S178-184 and Table S72), as shown in Fig. 7f and Table S73. For clarity, SF is stated as a value multiplied by 100 after calculating the reciprocal. Briefly, only a few donor materials for eco-friendly ST-OSCs have been researched so far. Most of these performed in PTB7-Th and PM6, which had relatively high SF values of 31.76 and 33.83 [4,8,9,30-32,50,79-81]. Therefore, among 48 ST-OSC results, the P(3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2)-based binary ST-OSCs with the lowest SF and highest LUE (or LUIE) can be ranked on top level. In the case of ternary ST-OSCs, the addition of PM6 raised the SF marginally; however, the cost still remained lower than those of other donor materials. Therefore, it can be still considered superior because of its higher LUE (or LUIE) and higher photovoltaic performance compared to those of binary devices. Finally, the ternary ST-OSC modules had the mid-upper ranking with a reasonable LUE (or LUIE). Overall, it has been proven that the potential for industrialization is quite high because the P (3IN = 0.3)(3IN2F = 0.5)(BDD = 0.2)-based ST-OSCs owing to many advantages such as high efficiency, high transparency, low cost, and ecofriendly processability.

4. Conclusion

In this study, we developed low-cost donor polymers with high visible transmission based on a unique $D-\pi=A$ building block for fabricating efficient ST-OSCs. To improve their photovoltaic performance, rational molecular structure design strategies were proposed, and structure-property relationship were systematically investigated. Basically, the D unit is responsible for the solubility of the polymer because of 2DBDT, and its conjugated structure extended to the 2D plane induces a dominant face-on structure in the polymer. Furthermore, in the case of the π =A unit, thiophene was chosen as a π -spacer to reduce the steric hindrance with the neighboring 2DBDT. Additionally, the physical, optical, and electrochemical properties of the polymer were optimized by introducing several EWGs linked to vinylene at its third position. In summary, the stacking properties of the polymer were enhanced by altering the electron withdrawing strength and planarity of the EWGs. Next, halogenation and terpolymer design were introduced simultaneously to decrease the HOMO offset between the polymer and acceptor and to achieve high solubility in eco-friendly solvents. Subsequently, the optimal quaterpolymer was fabricated by adding a BDD unit to compensate for the crystallinity of the polymer backbone. Finally, ternary devices reached the highest efficiency owing to the optimization of the proportion of the edge-on dominant PM6.

We considered a material perspective to fulfill the high industry demands for semitransparent solar cells. Consequently, P(3IN = 0.3) (3IN2F = 0.5)(BDD = 0.2) with improvements in cost, processability, stability, and performance were successfully developed for ST-OSCs. In particular, the photovoltaic performances of ST-OSCs were evaluated under both outdoor and indoor illumination conditions considering the application environment of the ST-OSCs. In addition, LUIE, which is an indicator that can assess the light utilization characteristics of ST-OSCs under indoor illumination conditions, is proposed for the first time. Furthermore, a novel SF calculation metric has been proposed based on the molar ratio of the final monomers introduced to assess the cost potential of terpolymers/quaterpolymers. This approach enables the

comparison of the cost-effectiveness for the material in terms of dependability. Finally, from a commercialization perspective, the airprocessed eco-friendly ternary ST-OSC module was replaced to the power source of the electronic thermo-hygrometer to demonstrate its stable operation up to 195 lx. The efficiency and transparency derived from D– π =A polymers and ST-OSC technologies could be improved further by modifying the molecular structure. Conclusively, these results may be universally applied to building/vehicle windows, electronic devices, and IoT sensors in the near future, significantly enhancing the commercialization potential of ST-OSCs.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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This paper was supported by Konkuk University in 2019. S. J. J. conceived all the ideas, designed and performed the experiments (synthesis of monomers, polymerizations, computing simulations, device fabrication, LUIE calculations, SF calculations, and most data collection/ analysis). S. J. J. wrote the original draft. Y. C. K. conducted the optical simulations and fabricated the conventional/inverted OSC/ST-OSC modules. J. Y. K. contributed to the indoor solar cell tests/calibrations and AFM measurements. J. H. K. contributed to the ternary OSC optimization. N. G. Y. contributed to 2D-GIWAXS measurements. Y. J. L. contributed to scale-up for monomers. H. S. L. contributed to the exciton dissociation and charge collection measurements. Y. H. K. contributed to the synthesis of P(NDIT-F3N). G. W. K. and E. M. J. contributed to the UV and CV measurements. B. L. and C. Y. contributed to energy loss calculations. All authors contributed to the results and discussion. D. K. M. reviewed and edited the draft paper and planned and directed the project.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2023.144850.

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