Reducing the transmission loss for below-gap photons is a straightforward way to break the limit of the energy-conversion efficiency of solar cells (SCs). The up-conversion of below-gap photons is very promising for generating additional photocurrent. Here we propose a two-step photon up-conversion SC with a hetero-interface comprising different bandgaps of Al$_{0.3}$Ga$_{0.7}$As and GaAs. The below-gap photons for Al$_{0.3}$Ga$_{0.7}$As excite GaAs and generate electrons at the hetero-interface. The accumulated electrons at the hetero-interface are pumped upwards into the Al$_{0.3}$Ga$_{0.7}$As barrier by below-gap photons for GaAs. Efficient two-step photon up-conversion is achieved by introducing InAs quantum dots at the hetero-interface. We observe not only a dramatic increase in the additional photocurrent, which exceeds the reported values by approximately two orders of magnitude, but also an increase in the photovoltage. These results suggest that the two-step photon up-conversion SC has a high potential for implementation in the next-generation high-efficiency SCs.
**Results**

**Concept of two-step photon up-conversion solar cell.** We propose a simple structure with a hetero-interface that demonstrates the concept of the TPU-SC. Here, the TPU is effectively realized at a hetero-interface comprising different bandgaps of III-V semiconductors instead of one IB in the bandgap. Figure 1a,b illustrate the schematic band diagram of the proposed TPU-SC with a diode structure of n-Al0.3Ga0.7As/Al0.3Ga0.7As/GaAs/p-GaAs on a p+-GaAs(001) substrate. A single InAs QD layer capped by 10 nm GaAs was inserted just below the Al0.3Ga0.7As layer to improve the TPU efficiency. Detailed device structure is described in the Methods section. Here, sunlight irradiates the n-Al0.3Ga0.7As layer to improve the TPU efficiency. 

**Figure 1** Schematic band diagram of TPU-SC. Diagrams (a) at the short-circuit condition and (b) at an operating condition. Sunlight irradiates the Al0.3Ga0.7As side. High-energy photons are absorbed in Al0.3Ga0.7As, and excited electrons and holes drift in opposite directions towards n-layer and p-layer, respectively. Below-gap photons for Al0.3Ga0.7As excite InAs QDs and GaAs. Long-lived electrons separated from holes are accumulated at the Al0.3Ga0.7As/GaAs hetero-interface, inducing a dramatic increase in the two-step photon up-conversion current. $E_f$ in (a) is the Fermi level. $E_{In}$ in (b) indicates the quasi-Fermi level of electrons and holes, respectively. $\Delta E_c$ and $\Delta E_v$ are the conduction band and VB discontinuities, respectively. Quantized states in InAs/GaAs QDs are drawn by horizontal dashed lines.
for GaAs and are efficiently pumped upwards into the Al0.3Ga0.7As barrier. As shown in Fig. 1b, the output voltage of TPU-SC corresponds to the gap of the quasi-Fermi levels for electrons in Al0.3Ga0.7As and holes in GaAs at an operating condition.

Measurement of external quantum efficiency. To demonstrate the TPU effect, we measured the EQE and its change (ΔEQE) that were produced by irradiating SC with IR light with photon energy lower than the fundamental edge of InAs QDs. All the measurements were performed at room temperature (290 K). Fig. 2a,b show the EQE and ΔEQE spectra for TPU-SC with InAs QDs, respectively. Without the IR illumination, two clear absorption edges appear at 685 and 875 nm in the EQE spectrum (black colour in Fig. 2a); these edges correspond to the bandgaps of Al0.3Ga0.7As and GaAs, respectively. The EQE signal for high-energy photons (above the bandgap of Al0.3Ga0.7As) decreases because of the shallow penetration of the incident light and significant carrier recombination at the surface, which are suppressed by introducing a wider-gap window layer. When excited above the bandgap of Al0.3Ga0.7As, the excited electrons and holes are collected at the corresponding electrodes. However, the behaviour of carriers generated by below-gap photons in Al0.3Ga0.7As is different. Below-gap photons are predominantly absorbed in i-GaAs and generate electrons and holes. The excited holes drift towards the p-layer of GaAs. On the other hand, the drift current of excited electrons is partially obstructed at the Al0.3Ga0.7As/GaAs interface, resulting in a significant drop of the EQE signal below the bandgap of Al0.3Ga0.7As. The excited photocurrent in the wavelength region between the bandgaps of Al0.3Ga0.7As and GaAs is caused by the thermal and tunnelling escape of the accumulated electrons at room temperature. In this wavelength region, the EQE signal also shows a gradual decrease with increasing wavelength because the optical absorption coefficient becomes small with increasing wavelength. In the near-IR wavelength region below the bandgap of GaAs, the EQE signal decreases drastically and shows a small structure at 912 nm that can be attributed to thermally excited carriers from the deep quantized states of the InAs wetting layer.

Figure 3a shows the temperature dependent EQE spectra. At low temperature, the absorption edges of Al0.3Ga0.7As and GaAs are relatively steep owing to the excitonic feature. With increasing the temperature, the absorption edges shift and the below-gap state attributed to the InAs-wetting layer appears gradually. The EQE signal from QDs was very weak and below the detection limit because of the deeper quantized state. Figure 3b shows the temperature dependence of the current density at 780 nm excited by a laser diode (LD). 780 nm photons directly excite i-GaAs. The excitation power density was 47 mW cm−2. The current density increases with increasing the temperature. The inset of Fig. 3b indicates the applied bias voltage dependence of the estimated thermal activation energy EA. EA monotonically decreases with increasing the electric field because of lowering the effective barrier height at the hetero-interface. EA shows the maximum of 221 ± 3 meV at 0.02 V. Conversely, applying higher positive bias voltage weakens the internal electric field significantly and makes flatter the band. As the forward current increases even at the same bias condition with increasing the temperature, the detected photocurrent decreases rapidly with flatten the band. Thereby, EA decreases and finally becomes negative with increasing the bias voltage. The maximum EA excellently coincides with the estimated CB discontinuity between Al0.3Ga0.7As and GaAs.

Figure 3c shows the temperature dependence of the current density at 912 nm corresponding to the wetting layer state. We recorded the current at the bias of 0.02 V. Here, the excitation light was produced by a supercontinuum laser, passed through a 270 nm single monochromator. The monochromatic excitation-laser line width was 9.6 nm. The EQE line width of the wetting layer state is ~15 nm and the temperature drift of the wetting layer state is ~2.9 nm, so that we fixed the excitation wavelength in this experiment. The evaluated thermal activation energy was 254 ± 5 meV. Photo-excited electrons are thermally excited from the GaAs edge to the Al0.3Ga0.7As one, from the InAs wetting layer state to the Al0.3Ga0.7As edge, and from the ground state of the QD transition to the GaAs edge. We did not confirm an obvious change caused by thermal excitation of holes, suggesting photo-excited holes reach the p-GaAs contact without captured at the hetero-interface. These optical responses are linear with the excitation density, and we did not observe any obvious nonlinear two-photon absorptions, as discussed later.
loss caused by the electron accumulation at the hetero-interface.

We defined \( \Delta \text{EQE} \) (blue colour in Fig. 2b) as the difference between the EQE obtained with and without the 1,300 nm LD illumination. The \( \Delta \text{EQE} \) enhancement was \( \approx 30\% \). We also observed an increase in the EQE signal attributed to the quantized states of the InAs wetting layer. However, \( \Delta \text{EQE} \) at the InAs QD ground state of 1,186 nm was very weak, suggesting that optical absorption in the single InAs QD layer with the in-plane QD density of \( \approx 1.0 \times 10^{10} \text{ cm}^{-3} \) is not enough to contribute to the change in the current generation at the QD ground state. Most of the excited electrons in GaAs were separated from the holes and accumulated at the \( \text{Al}_0.3\text{Ga}_{0.7}\text{As} / \text{GaAs} \) interface. Such densely accumulated long-lived electrons are easily pumped into the \( \text{Al}_0.3\text{Ga}_{0.7}\text{As} \) barrier by the 1,300 nm LD light, which accomplishes efficient TPU at the hetero-interface. Additionally, we fabricated a reference TPU-SC without InAs QDs. The EQE

**Figure 3** | EQE spectra measured at various temperatures and the temperature dependence of the current density. (a) EQE spectra for TPU-SC with InAs QDs at various temperatures. (b,c) show the temperature dependences of the current density at 780 and 912 nm, respectively. 780 and 912 nm photons directly excite i-GaAs and the InAs-wetting layer state, respectively. Magenta circles indicate the measured current density at the bias voltage of 0.02 V as a function of the temperature. The dashed line represents the result of the Arrhenius-type fitting. \( E_A \) is the estimated thermal activation energy.

**Figure 4** | Photoluminescence spectrum for TPU-SC with InAs QDs. (a) Photoluminescence spectra measured at various temperatures and (b) the temperature dependence of the integrated photoluminescence intensity.
and ΔEQE spectra for the reference TPU-SC are shown in Fig. 2c,d, respectively. The same absorption edges of Al0.3Ga0.7As and GaAs appear in the EQE spectrum. As shown in Fig. 2a,c, the EQE drop observed below the bandgap of Al0.3Ga0.7As was significant for TPU-SC with InAs QDs, which is caused by extra carrier recombination in QDs. As shown in Fig. 2d, ΔEQE is obviously generated even in TPU-SC with the hetero-interface of Al0.3Ga0.7As/GaAs without InAs QDs. Comparison between the ΔEQE spectra suggests that the hetero-interface containing InAs QDs improves the TPU efficiency for the accumulated electrons. The optical selection rule of the intersubband transition of electrons in an ideal two-dimensional structure is forbidden for light irradiating the two-dimensional plane perpendicularly. The finite thickness of the accumulation layer relaxes the selection rule, and, moreover, InAs QDs play a role enhancing the TPU efficiency. Generally, it is well known that the electronic wavefunctions in QDs are quantized on all three dimensions, and light of all polarization directions induces intersubband transitions. Thus, electrons at the hetero-interface obey the selection rule modified by QDs and are efficiently pumped into the CB of Al0.3Ga0.7As by the 1,300 nm LD illumination.

Short-circuit current generated by 780 nm photo-excitation. Figure 6 shows the short-circuit current density of TPU-SC with InAs QDs as a function of the excitation power density of a single-colour excitation light source. We used a 780 nm LD for excitation. The 780 nm photons traverse Al0.3Ga0.7As and directly excite the intrinsic layer of GaAs. The excited electrons drifted towards the n-layer and were obstructed at the hetero-interface; subsequently, they were partially extracted by thermal and tunnelling processes at the interface and finally reached the n-side electrode, generating a photocurrent. The accumulated electrons at the hetero-interface are partially extracted by thermal and tunnelling processes and thus generate electric power. By adding the 1,300 nm LD illumination, we observed an obvious enhancement in the photocurrent; for a density of 320 mW cm$^{-2}$, the photocurrent increased by 0.6 mA cm$^{-2}$. This value is rather high and approximately two orders of magnitude greater than previously reported values, as described in the Discussion section. Generally, the intraband excitation strength is proportional to the electron density in the initial state. Because of the carrier separation in the internal electric field, extremely long-lived electrons are densely accumulated at the hetero-interface and fill all the confinement states of the InAs QDs and the wetting layer. Here, it must be noted that we confirmed an increase in the photovoltage by adding the 1,300 nm LD illumination. This demonstrates that TPU enhances quasi-Fermi level splitting, which is a key feature that characterizes the operation of the TPU-SC. When irradiated by the 780 nm LD, the TPU-SC produces both photocurrent and photovoltage and the 780 nm photons traverse Al0.3Ga0.7As and excite GaAs. The excited electrons drift towards n-Al0.3Ga0.7As and are obstructed at the hetero-interface. The accumulated electrons at the hetero-interface are partially extracted by thermal and tunnelling processes and thus generate electric power. By adding the 1,300 nm LD illumination, we observed an obvious enhancement in the photocurrent; for a density of 320 mW cm$^{-2}$, the photocurrent increased by 0.6 mA cm$^{-2}$. This value is rather high and approximately two orders of magnitude greater than previously reported values, as described in the Discussion section. Generally, the intraband excitation strength is proportional to the electron density in the initial state. Because of the carrier separation in the internal electric field, extremely long-lived electrons are densely accumulated at the hetero-interface and fill all the confinement states of the InAs QDs and the wetting layer. Here, it must be noted that we confirmed an increase in the photovoltage by adding the 1,300 nm LD illumination. This demonstrates that TPU enhances quasi-Fermi level splitting, which is a key feature that characterizes the operation of the TPU-SC. When irradiated by the 780 nm LD, the TPU-SC produces both photocurrent and photovoltage and the 780 nm photons traverse Al0.3Ga0.7As and excite GaAs. The excited electrons drift towards n-Al0.3Ga0.7As and are obstructed at the hetero-interface.

Figure 7b,c summarize the 1,300 nm excitation power dependence of the change in the short-circuit current density, ΔJsc, and the open-circuit voltage, ΔVoc. ΔJsc and ΔVoc exhibit different behaviours according to a model proposed in the Methods section. ΔJsc is proportional to $P_{ex}^{0.73}$, where $P_{ex}$ is the 1,300 nm excitation power density. Generally, the short-circuit current has a linear relationship with the excitation density. The measured ΔJsc shows a sub-linear response. Figure 7d indicates the dependence of n value on the reverse-bias voltage in the relationship $J_{sc} \propto P_{ex}^{1.007}$ as the reverse-bias voltage increases; n increases and approaches unity. The dense space charge accumulated at the hetero-interface weakens the electric field, resulting in a sub-linear response to the excitation density because a stronger electric field improves the carrier collection efficiency.
of the TPU. Conversely, ΔV_{oc} increases non-linearly with the 1,300 nm excitation power density. A detailed model that reproduces ΔJ_{sc} and ΔV_{oc} is proposed and discussed in the Methods section. As given in equation (4), ΔV_{oc} is an increase against V_{oc,single} which is the open-circuit voltage measured at the single-colour excitation without the 1,300 nm LD illumination. The increase in ΔV_{oc} includes effect of the voltage boost effect at the hetero-interface, which follows an increase in the extra photon current ΔJ_{sc} created by the additional 1,300 nm LD illumination. Next, we demonstrated a difference between the TPU effect caused by the optical process and the thermal excitation effect. To confirm the contribution of 1,300 nm LD illumination to ΔV_{oc} we carefully measured ΔV_{oc} as a function of J_{sc} controlled by the 1,300 nm LD illumination or temperature. The results are summarized in Fig. 7e. The blue circles indicate ΔV_{oc} recorded by changing J_{sc} controlled by temperature. Here, the 1,300 nm LD does not shine the device. With increasing the temperature, J_{sc} increases because of increasing thermal carrier excitation, and, resultantly, ΔV_{oc} reduces. This is a well-known phenomenon. As the bandgap change in this temperature variation is ≈4.5 meV which is given by $5 \times 10^{-4} \text{eV K}^{-1}$ of the temperature dependence of the bandgap of GaAs, the observed change in ΔV_{oc} was almost caused by the thermal carrier excitation effect. Conversely, when the 1,300 nm LD with the excitation power density of 300 mW cm$^{-2}$ illuminates the device at 290 K, ΔV_{oc} slightly increases, despite increasing J_{sc} similarly. The clear difference between the thermal effect and the TPU by the second-photon flux proves the concept of the proposed TPU-SC.

**Theoretical prediction of the conversion efficiency.** Here, we estimate the expected conversion efficiency of the TPU-SC, using the detailed balance framework which considers a steady state
between carrier generation and recombination at the optimum operation point of SC\textsuperscript{1,25}. We ignore nonradiative processes in SC for predicting the ideal limit of the conversion efficiency. As shown in Fig. 2d, TPU itself occurs at the Al\textsubscript{0.3}Ga\textsubscript{0.7}As/GaAs hetero-interface, and InAs QDs play a role enhancing the TPU efficiency. Here, we neglected QD states enhancing the TPU efficiency in our calculation, and we simply assumed a perfect TPU at the hetero-interface. In this calculation, we consider that solar radiation is a black body with a temperature of 6,000 K and the temperature of the TPU-SC is 300 K. The calculation model assumes an absorptivity of 1 and good photon selectivity\textsuperscript{25}. We maintained the bandgap energy (1.80 eV) of Al\textsubscript{0.3}Ga\textsubscript{0.7}As fixed and varied the CB offset (\(E_d\)) and the VB offset (\(\Delta E\)). The TPU of electrons occurs at the potential discontinuity of \(E_2\). Figure 8 shows the calculated results as a function of \(E_2\) at a solar concentration of 1 and 1,000 suns. Increasing the \(E_2\) with a fixed \(\Delta E\) results in a decreasing \(E_1\) (see inset of Fig. 8). When \(E_2\) and \(\Delta E\) are zero, the conversion efficiency coincides with that of a single-junction Al\textsubscript{0.3}Ga\textsubscript{0.7}As/GaAs SC. Regardless of \(\Delta E\), the conversion efficiency increases as \(E_2\) increases because the contribution of the TPU increases, namely, the transmission loss decreases. Finally, the efficiency reaches a peak; under the one-sun irradiation, the maximum conversion efficiency is 44% at \(E_1 = 0.63\) eV when \(\Delta E = 0\). This value coincides with the efficiency calculated for the well-known ideal IBSC\textsuperscript{25}. Furthermore, under 1,000-sun irradiation, the conversion efficiency exceeds 50%, even at \(\Delta E = 0.2\) eV. The \(E_2\) at which the conversion efficiency exhibits a peak shifts with varying \(\Delta E\). Increasing the \(\Delta E\) leads to a monotonic decrease in the conversion efficiency, which is caused by a voltage loss at the hetero-interface. These results suggest that a zero VB discontinuity (\(\Delta E = 0\)) achieves maximum conversion efficiency. To reduce \(\Delta E\), the use of other material systems showing a type-II band alignment would accentuate the intrinsic nature of the TPU-SC.

**Figure 8 | Detailed balance calculation of TPU-SC.** The horizontal axis represents the conduction band offset (\(E_d\)), shown in the inset. The bandgap energy of the host material (Al\textsubscript{0.3}Ga\textsubscript{0.7}As) is fixed at 1.80 eV. The solid and dashed lines correspond to the results at a solar concentration of 1 and 1,000 suns, respectively. \(\Delta E\) is the VB offset (inset).

**Figure 9 | Schematic of the structure of the TPU-SC.** TPU-SC was fabricated using solid-source molecular beam epitaxy. The intrinsic layer comprises AlGaAs/GaAs. InAs QDs are inserted at the hetero-interface.

\[
\Delta J_{sc} = qN_{in} \{1 - \exp(-\alpha d)\},
\]  

where \(q\) is the elementary charge, \(N_{in}\) is the incident 1,300 nm photon flux, \(\alpha\) is the absorption coefficient and \(d\) is the thickness of absorber. When calculating \(N_{in}\), we considered a reflectivity of 29.8% at the SC surface. The maximum value of \(\alpha d\) estimated from equation (1) was \(9 \times 10^{-3}\), depending on the 1,300 nm excitation power density. \(d\) corresponds to the thickness of the electrons gas forming around the hetero-interface. Roughly assuming that the electron gas concentrates in the InAs QDs layer, \(d\) is considered to be the InAs-QD height of 3 nm; consequently, the maximum \(\alpha d\) becomes 30,000 cm\textsuperscript{-1}. This value is rather high compared to coefficients previously reported in the literature, which were in the range 400–2,000 cm\textsuperscript{-1} (refs 18,26,27). The developed TPU-SC presents extremely long-lived electrons accumulated at the hetero-interface that fill all the confinement states of the InAs QDs and wetting layer, leading to this strong intraband excitation. The additional 1,300 nm LD produces not only a dramatic increase in the photocurrent, which is two orders of magnitude greater than ever observed, but also an increase in the photovoltage. The typical illumination power density used in the experiment corresponded to approximately 17 suns. This concentration ratio is relatively low, demonstrating the efficient TPU effect, and is expected to be easily realized.

Next, we compare \(\Delta J_{sc}\) with results reported in several references. As shown in Fig. 7a, the maximum \(\Delta J_{sc}\) of our TPU-SC was 0.6 mA cm\textsuperscript{-2} at the additional 1,300 nm IR-LD power density of 320 mW cm\textsuperscript{-2}. In ref. 14, two-step photon absorption in GaSb/GaAs type-II QD-IBSC has been reported, where the maximum \(\Delta J_{sc}\) obtained by irradiating additional IR light with the intensity of 750 W cm\textsuperscript{-2} was estimated \(\sim 10\) nA cm\textsuperscript{-2} at 200 K and became smaller than 1 nA cm\textsuperscript{-2} at the temperature above 250 K. In ref. 38, we reported a saturable behaviour of \(\Delta J_{sc}\) in IBSC including InAs QDs embedded in Al\textsubscript{0.3}Ga\textsubscript{0.7}As/GaAs quantum well. In that study, the maximum \(\Delta J_{sc}\) was 0.15 \(\mu\)A cm\textsuperscript{-2} when excited by the additional IR light with the power density of 56 mW cm\textsuperscript{-2}. As the saturated \(\Delta J_{sc}\) is proportional to the IR power density, \(\Delta J_{sc}\) can be estimated to be 0.86 \(\mu\)A cm\textsuperscript{-2} at the IR power density of 320 mW cm\textsuperscript{-2} used in our experiment. Elborg...
et al. investigated the voltage dependence of extra photocurrent for the GaAs/Al0.28Ga0.72As QD-IBSC. In that literature, ΔIE was 0.44 μA cm⁻² when excited at the additional IR power density of 1.400 mW cm⁻². Sellers et al. investigated InAs/GaAs QD-IBSC inserting GaP strain-balancing layer between each QD layer. Here, the maximum ΔIE was 3 μA cm⁻² at the additional IR power density of 300 mW cm⁻². Thus, ΔIE of our TPU-SC exceeded all the reported values by greater than two orders of magnitude.

The SC device used in this study was designed and fabricated to demonstrate a strong TPU phenomenon. However, the SC structure presented in this paper is not the final version of this device. A detailed optimized design considering the theoretical predictions shown in Fig. 8 is necessary to achieve the best performance of the TPU-SC. For example, the position of the hetero-interface becomes important. Furthermore, as the cause for TPU reduces when the electric field is strongly reduced, we need to perform detailed simulations of the band profile at the operating point in order to maintain a moderate internal electric field. Here, the maximum D was 550 mW cm⁻². Sellers et al. investigated InAs/GaAs QD-IBSC. In that literature, the GaAs/Al0.28Ga0.72As QD-IBSC presented in this paper is not the final version of this structure. The data that support the findings of this study are available from the corresponding author upon request.

Methods

Solar cell fabrication. The TPU-SC was fabricated on a p⁺-GaAs (001) substrate using solid-source molecular beam epitaxy. The detailed structure is illustrated in Fig. 9. A 150-nm-thick p-GaAs (Be: 2 x 10¹⁹ cm⁻³) buffer layer was grown over a 400-nm-thick p⁺-GaAs (Be: 1 x 10¹⁹ cm⁻³) buffer layer at a substrate temperature of 550 °C. The substrate temperature was monitored during the growth using an infrared pyrometer. Subsequently, an i layer with the structure Al0.3Ga0.7As/GaAs (1,140 nm) was deposited. The nominal thickness of InAs was 0.64 nm (2.1 monolayers). The typical height and width of the QDs was 3 and 20 nm, respectively, and the QD density was approximately 10¹⁹ cm⁻³. Layers were grown on the SC structure at a substrate temperature of 500 °C. Au/Au-Ge and Au/Au-Zn contacts were created on the top and the bottom surfaces, respectively. The dimensions of the SC were 4 x 4 mm². Note that the SC structure shown in Fig. 8 was fabricated to demonstrate the fundamental TPU effects on the SC characteristics. Further development, such as the optimization of the thickness and doping concentration of each layer as well as introduction of a window layer and anti-reflection coating, is required to obtain the best performance.

EQE and AEQE measurement. The EQE and AEQE measurement was conducted at various temperatures. The excitation light was produced by a tungsten halogen lamp, passed through a 140 mm single monochromator, and chopped by an optical chopper with a frequency of 800 Hz. The excitation power density depended on the wavelength. The recorded power density was approximately 2 W cm⁻², much lower than the QD current density of 10³ A cm⁻². The beam diameter of the monochromatic light was 1.2 mm on the SC surface. The photocurrent was detected by a lock-in amplifier synchronized with the optical chopper. Likewise, an infrared pyrometer measured the change in the EQE obtained with and without the 1,300 nm LD illumination. The excitation light was produced by a tungsten halogen lamp, passed through a 140 mm single monochromator, and chopped by an optical chopper with a frequency of 800 Hz. The excitation power density depended on the wavelength. The recorded power density was approximately 2 W cm⁻², much lower than the QD current density of 10³ A cm⁻². The beam diameter of the monochromatic light was 1.2 mm on the SC surface. The photocurrent was measured after two-colour photo-excitation measurements. The measurements were performed at 297 K without a temperature controller.

Modelling of ΔVoc and ΔΔIE. Generally, the short-circuit current has a linear relationship with the excitation density. However, as described in the Results section, ΔIE exhibited a clear sub-linear response to the excitation density; this is because dense space charge accumulated at the hetero-interface weakens the electric field and the carrier collection efficiency of the TPU decreases. Therefore, we introduced equation (1) as follows to interpret the results phenomenologically:

\[ \Delta V_{oc} = qN_n \left( \ln \left( \frac{I_s}{I_s + 1} \right) \right) \]

where \( q \) is the Boltzmann constant, \( T \) is the temperature, and \( I_s \) is the saturation current. For two-colour photo-excitation measurements, \( V_{oc,single} \) and \( V_{oc,diff} \) are divided into \( V_{oc single} \) and \( \Delta V_{oc} \), where \( V_{oc single} = \) the short-circuit current at the single-colour excitation. By substituting \( V_{oc,single} \) and \( I_s \), where \( \Delta V_{oc,single} = \Delta V_{oc,single} + \Delta \Delta IE \) is written as

\[ \Delta V_{OC} = \frac{qN_n}{q} \ln \left( \frac{I_{s,single} + \Delta \Delta IE}{I_s + 1} \right) - V_{oc,single}. \]

(4) Equation (4) was used to fit the results of Figs. 7b,c.

Data availability. The data that support the findings of this study are available from the corresponding author upon request.

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Author contributions
S.A. originated the concept, designed and carried out experiments, performed modelling and the data analysis and wrote the manuscript. H.T. and T. Kita designed and fabricated the solar devices. K.K. performed the theoretical calculation. T. Kita co-wrote the manuscript and was in charge of overall direction and planning.

Additional information
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