Spectral splitting photovoltaics using perovskite and wideband dye-sensitized solar cells

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The extension of the light absorption of photovoltaics into the near-infrared region is important to increase the energy conversion efficiency. Although the progress of the lead halide perovskite solar cells is remarkable, and high conversion efficiency of > 20% has been reached, their absorption limit on the long-wavelength side is ~800 nm. To further enhance the conversion efficiency of perovskite-based photovoltaics, a hybridized system with near-infrared photovoltaics is a useful approach. Here we report a panchromatic sensitizer, coded DX3, that exhibits a broad response into the near-infrared, up to ~1100 nm, and a photocurrent density exceeding 30 mA cm−2 in simulated air mass 1.5 standard solar radiation. Using the DX3-based dye-sensitized solar cell in conjunction with a perovskite cell that harvests visible light, the hybridized mesoscopic photovoltaics achieved a conversion efficiency of 21.5% using a system of spectral splitting.
Dye-sensitized solar cells1–3 (DSSCs) and organic lead halide perovskite solar cells4–9 (PSCs) have attracted significant attention as next-generation low-cost photovoltaics because of the potential widespread applications10. Since the mesoscopic photovoltaics can be produced by simple solution processing, the technology shows potential for the large-scale mass production of solar cells. Furthermore, the power conversion efficiencies (PCEs) of lead halide PSCs have increased steeply over the past few years. However, the absorption range of lead halide PSCs is still limited to the visible region. In general, the PCE of a photovoltaic is limited by a voltage loss in the shorter wavelength region and an optical absorption loss in the longer wavelength region11,12. To reduce the energy losses, a multijunction architecture is effective. Although many inorganic semiconductor multijunction devices employing tandem or spectral splitting systems have been developed, their application is still limited because of problems in the production processes and total manufacturing costs. In contrast, several multijunction photovoltaics employing DSSCs17,18 or organic thin films19,20 are expected to be easier to produce, but their PCE currently remains at a relatively low level of ~10–12%. To improve the PCE of multijunction organic cells, two independent types of solar cells should be assembled, one showing a high photovoltage and the other a large response in the near-infrared (NIR) region. Although several trials for the realization of the NIR photovoltaic cells such as DSSC using osmium sensitizers21–24 or ruthenium sensitizers with large π-conjugated ligands25,26, organic thin-film solar cells27 and tin halide PSCs28,29 have been reported, the device performance remains low. Recently, DSSCs using a phosphine-coordinated ruthenium sensitizer (DX1), which exhibit a direct singlet-to-triplet transition in the NIR region, have been developed to yield a panchromatic photoresponse30. A mechanically stacked tandem DSSC comprises DX1 as the NIR sensitizer for the bottom cell and N719 as a visible sensitizer for the top cell was reported to have a PCE of 12% under reduced sunlight30. Using a PSC as the visible-light-absorbing cell should substantially increase the PCE. However, the NIR response of DX1 is insufficient for such a combination. Here, we present a molecular design for the panchromatic sensitizer and the development of a PSC/DSSC hybridized device by a spectral splitting system. The panchromatic ruthenium complexes DX2 (trans-dichloro-(methylphenylphosphine)–(2,2′,6′,2″-terpyridyl-4,4″-tricarboxylic acid-4-methyl ester)ruthenium(II)) and DX3 (trans-dichloro-(dimethylphenylphosphine)-(2,2′,6′,2″-terpyridyl-4,4″-tricarboxylic acid-4-methyl ester)ruthenium(II)) are engineered on the molecular level to increase the spin–orbit interactions, enhancing the direct singlet-to-triplet transition and extending its light-harvesting capacity further into the NIR region than that of DX1 with the tuning of triplet excited state levels by the replacement of the phosphate ligands. By associating a DX3-based DSSC with a PSC with an 18.4% PCE and negligible hysteresis, we achieved a PCE of 21.5%.

Results

Properties of the panchromatic sensitizer. The chemical structures of DX1, DX2 and DX3 are shown in Fig. 1a–c, respectively. DX2 and DX3 feature a methylidiphenylphosphine and

Figure 1 | Chemical structure and absorption spectra of DX1, DX2 and DX3. (a–c) Chemical structure of DX1, DX2 and DX3, respectively. A carboxy group of DX1 is replaced with a methyl ester group (blue part in DX2 and DX3) for the improvement of solubility in organic solvents. Bulky substituents (purple part) in the phosphate ligand are introduced to control the energy level of the excited triplet states. (d) Absorption and emission spectra of DX1, DX2 and DX3 in DMF solution. The emission spectra were measured at 77 K. (e) Absorption spectra of esterified DX3 in methylene dihalide (CH2X2:X = Cl, Br, I) solutions at 298 K. The lowest absorption peak was enhanced in the heavier halogenated solvent.
dimethylphenylphosphine ligand, respectively, with a weaker ligand field than that of the dimethoxymethylphosphine employed in the previously reported DX1 sensitizer. Since one of the three carboxyl groups on the tricarboxy-terpyridyl (tcterpy) ligand was esterified, the solubility of DX2 and DX3 was improved, as compared with DX1. The absorption spectra of DX1, DX2 and DX3 in $N,N$-dimethylformamide (DMF) solution are shown in Fig. 1d. DX2 and DX3 showed an intense ultraviolet absorption band at 318 nm that was assigned to the ligand-centred $\pi-\pi^*$ transition of the tricarboxy-terpyridyl ligand and broad absorption bands in the visible region that were assigned to metal-to-ligand charge-transfer transitions. DX2 and DX3 have absorption spectra similar to that of DX1 in the visible region. A notable difference is that the tail of the NIR band in DX3 is extended by 50 nm to a longer wavelength, as compared with DX1, especially DX3 showed the longest wavelength absorption up to 1,000 nm in these sensitizers. The calculated low-temperature absorption spectra of DX1 and DX3 in EtOH/2-methyl-THF are shown in Fig. 2a. The absorption spectrum of DX3 at 77 K becomes sharper, and a broad absorption band featuring a peak with a shoulder is observed at $\sim$790 nm. A similar absorption band structure was observed in the di-tert-butyl ester derivative of DX3 at 77 K in toluene (Supplementary Fig. 1). The absorption intensity in the NIR region of the esterified complex in a methylene dihalide solvent therefore diminishes in proportion to the atomic weight of the halogen atom (Supplementary Fig. 1). The absorption band at 790 nm was assigned to metal-to-ligand charge-transfer transitions. DX2 and DX3 showed an intense ultraviolet absorption band at 318 nm that was assigned to the ligand-centred $\pi-\pi^*$ transition of the tricarboxy-terpyridyl ligand and broad absorption bands in the visible region that were assigned to metal-to-ligand charge-transfer transitions. DX2 and DX3 have absorption spectra similar to that of DX1 in the visible region. A notable difference is that the tail of the NIR band in DX3 is extended by 50 nm to a longer wavelength, as compared with DX1, especially DX3 showed the longest wavelength absorption up to 1,000 nm in these sensitizers. The calculated low-temperature absorption spectra of DX1 and DX3 in EtOH/2-methyl-THF are shown in Fig. 2a. The absorption spectrum of DX3 at 77 K becomes sharper, and a broad absorption band featuring a peak with a shoulder is observed at $\sim$790 nm. A similar absorption band structure was observed in the di-tert-butyl ester derivative of DX3 at 77 K in toluene (Supplementary Fig. 1). The absorption intensity in the NIR region of the esterified complex in a methylene dihalide solvent therefore diminishes in proportion to the atomic weight of the halogen atom (Supplementary Fig. 1). The absorption band at 790 nm was assigned to metal-to-ligand charge-transfer transitions. DX2 and DX3 showed an intense ultraviolet absorption band at 318 nm that was assigned to the ligand-centred $\pi-\pi^*$ transition of the tricarboxy-terpyridyl ligand and broad absorption bands in the visible region that were assigned to metal-to-ligand charge-transfer transitions. DX2 and DX3 have absorption spectra similar to that of DX1 in the visible region. A notable difference is that the tail of the NIR band in DX3 is extended by 50 nm to a longer wavelength, as compared with DX1, especially DX3 showed the longest wavelength absorption up to 1,000 nm in these sensitizers. The calculated low-temperature absorption spectra of DX1 and DX3 in EtOH/2-methyl-THF are shown in Fig. 2a. The absorption spectrum of DX3 at 77 K becomes sharper, and a broad absorption band featuring a peak with a shoulder is observed at $\sim$790 nm. A similar absorption band structure was observed in the di-tert-butyl ester derivative of DX3 at 77 K in toluene (Supplementary Fig. 1). The absorption intensity in the NIR region of the esterified complex in a methylene dihalide solvent therefore diminishes in proportion to the atomic weight of the halogen atom (Supplementary Fig. 1). The absorption band at 790 nm was assigned to metal-to-ligand charge-transfer transitions.

According to the results of TD-DFT calculations based on perturbed SOC theory, the calculated spectrum was consistent with the SOC-TD-DFT calculation results (Supplementary Fig. 4). From the result of PSOC-TD-DFT, the triplet states (T1 and T2) and the singlet state (S1) of DX3 are mainly attributable to HOMO-1 the LUMO and HOMO-2, respectively (Supplementary Table 2). Supplementary Table 3 shows the contribution of the mixing of excited states by the PSOC effect; the relatively intense lower-energy band of DX3 (at 1.5381 eV) was ascribed to the mixed

Figure 2 | Calculated absorption spectra and excited states energy diagram of panchromatic sensitizers. (a) Low-temperature absorption spectra and calculated absorption spectra of DX1 and DX3 including spin-orbital coupling effects by SOC-TD-DFT. (b–e) Molecular orbitals of DX3. Highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals of DX3 as calculated using scalar relativistic DFT at the M06/TZP with ADF program. (f) Excited states energy diagram that showing SOC of DX1, DX2 and DX3.
states that contain the excited S1 state and excited triplet states (T1 and T2). Recently, De Angelis and co-workers attributed the lower-energy absorption band of DX1 to the mixing of the S1 and T2 states by SOC. In DX3, since the lower-energy level in the T2 triplet excited state is shifted close to the T1 state by destabilization of the HOMO-1 level (Supplementary Fig. 5), the excited T1 and T2 states have a similar electron distribution by configuration interaction. Accordingly, when the excited S1 state is mixed with the excited T1 and T2 states by SOC, DX3 indicated a red-shifted absorption band as compared with DX1 (Fig. 2f). On the basis of the perturbation theory, the oscillator strength of the singlet–triplet transition is inversely proportional to the energy difference between the singlet and triplet states. In the case of DX3, since the energy differences between S1 and the triplet states (T1 and T2) increased by destabilization at the HOMO-1 level, the oscillator strength of the lower-absorption band decreased. This trend is consistent with the experimental results.

To analyse the S–T transition states of DX3, we performed ultrafast transient absorption (TA) spectroscopy. Supplementary Figure 6 shows the TA spectra of methyl-esterified black dye and methyl-esterified DX3 excited at 750 and 800 nm, respectively. The photoinduced absorption (PA) band in NIR area (~1,000 nm) of black dye is attributed to a broad triplet absorption (T1n) band. Since esterified DX3 exhibited a similar PA band with esterified BD in NIR region, these PA bands in NIR part ~1,000 nm can be also assigned to a triplet absorption. In the sub-ps time-resolved pump-probe measurement, the triplet population at 990 nm of esterified black dye is grown in about 0.5 ps. It has been reported that the rising of the triplet population of black dye becomes relatively slow since it reflects the intersystem-crossing process from singlet to triplet excited states. In contrast, we found out that the growth of the triplet PA band at 990 nm in esterified DX3 is completed within 0.3 ps. The results suggested that by exciting the esterified DX3 in NIR absorption band, the slow intersystem-crossing process was not observed, while the triplet PA band can be already probed. Considering the time resolution of the TA measurement of <250 fs, we concluded that the triplet excited states of esterified DX3 are generated directly by S–T transition.

The air-sensitive phosphorescence observed in both DX1, DX2 and DX3 at 77 K in DMF exhibited similar wavelength peaks at 920, 923 and 924 nm, respectively (Fig. 1d). The emission maxima were red shift at room temperature. The emission peaks observed with DX1, DX2 and DX3 at 298 K in DMF at 952, 969, 976 nm, respectively. The results suggested that the glass-to-fluid transition affects the Ru-P or Ru-N bond length by rigidochromism. The phosphorescence spectrum overlapped with the absorption spectrum in the low-energy band. Despite the fact that the phosphorescence of DX3 is a metal-to-ligand charge-transfer transition, DX3 showed a relatively small Stokes shift of 1,700 cm⁻¹. The emission lifetime of the DX3 was 10 ns at 298 K, which is longer than 8 ns of DX1, and it had a sufficient lifetime relative to the electron injection rate. From differential pulse voltammetry of DX3 (Supplementary Fig. 7), the excited state of DX3 is expected to have a driving force comparable to that of DX1 for electron injection into the conduction band of TiO2.

Simple solar cell performance of DSSC and PSC. Figure 3a compares the incident photon-to-current efficiency (IPCE) spectra for the PSC to DSSCs using DX1, DX2 or DX3 as a sensitizer. While the PSC shows no photoresponse at wavelengths above 800 nm, the DX3-sensitized cell maintains a high IPCE values far beyond this limit. The IPCE exhibits a very high value—between 80 and 90% across a wide wavelength range between 400 and 850 nm—and reaches 70% at 900 nm with the tail extending to ~1,100 nm. This is a remarkable advance over the DX1 sensitizer, which absorbs light only up to 1,000 nm. To date, DX3 achieves the best solar light-harvesting capacity of

![Figure 3](https://example.com/figure3.png)

**Figure 3 | IPCE spectra and J–V characteristics of DSSCs and PSCs.** (a) IPCE and integrated current spectra of DSSCs made of DX3, DX1 and PSC. (b) Current-voltage curves of the same devices shown in Fig. 2a under solar illumination (AM1.5G, 100 mWcm⁻²). (c) Photocurrent density (blue) and power conversion efficiency (green) as a function of time for the PSC held to the voltage (red) of the maximum output power point.
all known sensitizers approaching that of silicon solar cells. Remarkably, the DX3 achieves this performance with a thousand times smaller sensitizer quantity than silicon. Figure 3b shows three photocurrent density versus voltage (J–V) curves for DSSC employing DX1, DX2 or DX3 measured under standard sunlight (air mass (AM) 1.5 G at 100 mW cm\(^{-2}\)). The device that used DX3 showed a high short-circuit current density (J\(_{SC}\)) of 30.3 mA cm\(^{-2}\) and an open-circuit voltage (V\(_{OC}\)) of 0.556 V, achieving an overall PCE of 10.2%. The photocurrent value of the DX3-sensitized cell is in agreement, within a 2% mismatch, with the calculated J\(_{SC}\) value from the overlap integration between the IPCE curve of DX3 and the AM1.5G spectral solar photon flux. This is the first time that a J\(_{SC}\) value over 30 mA cm\(^{-2}\) has been reached by a DSSC. The V\(_{OC}\) of 0.556 V is very respectable in view of its small optical bandgap of DX3 that amounts to 1.18 eV. The difference is 0.6 V, of which about 0.3 V represents the minimum voltage loss for a photovoltaic in AM1.5 sunlight\(^4\), while the remaining 0.3 eV is consumed to drive the electron injection from the excited DX3 into the TiO\(_2\) and its regeneration while the remaining 0.3 eV is consumed to drive the electron injection from the excited DX3 into the TiO\(_2\) and its regeneration.

The DX3-sensitized cell thus shows a large conversion efficiency into the infrared. The spectral mismatch is <2% (class AAA) from ultraviolet to infrared, according to AM1.5G. The PSC showed a V\(_{OC}\) of 1.12 V, a J\(_{SC}\) of 20.7 mA cm\(^{-2}\), a fill factor of 0.794 and an overall efficiency of 18.4%. The J–V curve showed negligible hysteresis between the forward and the reverse sweep (Supplementary Table 4). The transient photocurrent response at the applied voltage of 0.93 V (voltage of the maximum power point) becomes constant within 100 ms, and the stabilized conversion efficiency of 18.4% was sustained at least for 60 s (Fig. 3c).

Hybridized solar cell performance by a spectral splitting system. The hybridized solar cell employing a spectral splitting system (Fig. 4a) was constructed using dichroic mirrors at an angle of 45° with splitting edge wavelengths of 602, 654, 697, 733, 771 and 775 nm (Fig. 4b). In the experiments, a DX3-sensitized cell with 9.4% efficiency was used as the NIR cell (Supplementary Fig. 9). The reproducibility of these results was verified independently at the KAST, Kanagawa, Japan. The DSSC showed a V\(_{OC}\) of 0.544 V, a J\(_{SC}\) of 29.6 mA cm\(^{-2}\), a fill factor of 0.591 and an overall efficiency of 9.53% (Supplementary Fig. 10). The results were achieved with a dual-source solar simulator (YSS-T150A Yamashita Denso, Japan), which has different lamp types combined (xenon and hydrogen lamps) to extend the spectrum far into the infrared. The spectral mismatch is <2% (class AAA) from ultraviolet to infrared, according to AM1.5G. The measurement was performed at 25 ± 0.1 °C in a thermostat chamber, and the designated area of the cell was 0.1414 cm\(^2\). The results showed good agreement with the PCE measurements carried out in our own laboratory. The individual IPCE spectra (Fig. 4c) and the current–voltage characteristics of the visible and NIR light-harvesting cells measured under standard conditions are summarized in Fig. 4d–g and Supplementary Fig. 11. The IPCE spectra and the photocurrent value of the PSC were almost identical to the single cell at a splitting wavelength of longer than 771 nm. Figure 4g summarizes the total efficiency.

Figure 4 | Device structure, IPCE spectra and J–V characteristics of the hybridized cell. (a) Device structure of the hybridized cell using a dichroic spectrum splitter. (b) Transmittance spectra of dichroic mirrors under measurement conditions such as incident of a 45° angle. (c) IPCE spectra of the individual components of the hybridized cell with various dichroic mirrors: visible absorbing cell, PSC (solid line); near-IR absorbing cell, DX3-based DSSC (dashed line). (d–g) Photovoltaic parameter and total power conversion efficiency dependence on the splitting wavelength of the dichroic mirrors: PSC (red), DX3-based DSSC (blue) and total power conversion efficiency of the hybridized cell (green).
for the combination of the PSC and DSSC at each splitting wavelength. The PCE of the PSC increased as the splitting wavelength of the dichroic mirror gets longer, while the opposite trend was observed for the DSSC. The conversion efficiencies of the PSC reached a plateau at a splitting wavelength above 771 nm. At this wavelength, a maximum total PCE of 21.5% was achieved. This reduces resistive losses in each component due to the photocurrent are reduced as compared with those of a single cell. The ohmic loss is proportional to \( R_0^2 \), where \( R \) is the series resistance in the inner cell and \( I \) is the photocurrent. Spectral splitting reduced the photocurrent of the DSSC component to about one-third the value measured at full sunlight. This reduces resistive losses and augments the fill factor. As a consequence, the PCE of an individual DX3-sensitized cell increased to 11.7% at 20 mW cm\(^{-2}\) simulated sunlight (Supplementary Table S). This effect contributed to the high overall PCE of the hybridized cell.

Discussion

The cell structure can be simplified by fabricating a series-connected mechanically stacked tandem solar cell. To realize the series connection, it is necessary to adjust the light absorption band of each cell to match the splitting wavelength of ~680 nm. If the splitting wavelength is shifted to 680 nm, as seen in Fig. 4g, the photocurrent value of each cell is matched at a splitting wavelength of ~680 nm. Using a high-voltage PSC with a lead bromide perovskite, which shows the high-energy bandgap (~2.3 eV), the series-connected tandem cell would achieve up to 22% PCE. In addition, the tandem cell can also be used for applications such as the photolysis of water since the lead halide PSC shows the VOC of ~1.1 V, whereas it absorbs the part of sunlight until 680 nm (1.82 eV). Using a high-voltage PSC with a lead halide perovskite, the series-connected tandem solar cell would be important to develop an efficient transparent PSC and/or develop the sensitizers that absorb the longer wavelength sunlight.

In summary, we have successfully constructed hybrid mesoscopic photovoltaics using a perovskite cell with a high VOC and panchromatic DSSC by employing a broadband sensitizer, DX3, which was composed by molecular engineering based on triplet excited states. A single DX3-sensitized solar cell exhibited wide-ranging light absorption up to 1,100 nm and a very high photocurrent exceeding 30 mA cm\(^{-2}\). The PCE of the mesoscopic hybrid solar cell exceeds by a factor of two that of previously reported multijunction cells that employ organic photovoltaics. The performance of such solution-processed mesoscopic solar cells suggests that they have the potential to become an alternative to traditional inorganic semiconductor photovoltaics.

Methods

Synthesis of DX3. DX3 was synthesized as follows (the chemical reaction equations are shown in the Supplementary Methods): RuCl\(_3\) (TCl) was dissolved in dehydrated ethanol, and 4,4’-di-tert-butylcycaronyl-4’-methoxycarbonyl-2,2’-6’,2’-terpyridine (methods for synthesis of the ligand are described in the Supplementary Methods) was then added. The reaction mixture was refluxed under argon for 6 h. The reaction mixture was cooled to room temperature, the solvent was then removed and the residue was dissolved into dry CHCl\(_3\) at 0°C. NEt\(_3\) and dimethylphenylphosphine were then added to the reaction solution, and the reaction mixture was heated at 70°C for 10 min. After cooling the reaction mixture, most of the solvent was removed under vacuum. The reaction residue was purified on a silica gel column chromatography using a mixed solvent (CHCl\(_3\): MeOH = 8:5:1.5 v/v) as an eluent. After removal of the solvent, a black powder was obtained. The black powder was then added to CeF\(_2\)COOH, and the reaction mixture was stirred for 30 min at room temperature. After removal of the solvent, the brown product was precipitated with diethyl ether, and the brown powder was isolated by suction filtration and washed with diethyl ether. The brown powder was purified on a Sephadex LH-20 (GE Healthcare) column, using methanol as the eluent. The product was purified further by high-performance liquid chromatography system (Shimadzu) with high-performance liquid chromatography column (LiChrospher 100 DIOL, 40\(\mu\)m, 5-C18, 100 A\(\mu\)m, 4.6 x 250 mm). The obtained product was used for the tandem solar cell.

DSSC fabrication. A thin layer of TiO\(_2\) (Solaronix SA Ti-Nanoxide), containing a 24-μm-thick film of 20-nm particles, with a 4-μm-thick layer of 400-nm scattering particles was screen printed on an F-doped SnO\(_2\) (FTO) conducting glass with anti-reflective coating (Nippon Sheet Glass Co., Ltd, Tokyo; 10±3 Ω−1) using an automatic screen printer (Newlong Semitou Kogyo Co., Ltd, Tokyo) to guarantee repeatability. The prepared TiO\(_2\) electrodes were heated at 500°C for 30 min under a flowing atmosphere. The electrodes were then placed in a Teflon aqua for 30 min, after which the TiO\(_2\) electrodes were heated at 500°C for 30 min in a dry condition (dew point ~50°C) for a total of five times. The temperatures at which the electrodes were immersed in a TiCl\(_4\) aqueous solution were 10°C, 25°C, 2°C and 2°C, respectively. In the last heat treatment, the electrode was cooled to under 200°C before dipping into the dye solution. The DX2 and DX3 dye solutions were prepared in DMF with a concentration of 7.5 × 10\(^{-5}\) M respectively, and the electrodes were left in the dye solutions for 12 h. A sandwich cell was prepared using the dye-anchored TiO\(_2\) film as a working electrode and a counter electrode, which was coated with platinum. The two electrodes were superimposed with a polytetrafluoroethylene paste (DuPont-Mitsui Chemicals Co., Ltd, Tokyo) and a gas-permeable polymer (DulcoFlect, Luminar) that was interposed between the electrodes. This was followed by the deposition of a 100-μm-thick layer of TiO\(_2\) paste, which was dried in a hot oven at 150°C for 5 h. Finally, a Au counter electrode was deposited by thermal evaporation. Then the dried film was heated at a temperature of 180°C.

PSC fabrication. FTO (Pilkington, TEC8) substrate was cleaned in ultrasonic bath containing detergents for 30 min, and then a dense blocking layer of TiO\(_2\) (60 nm, bl-TiO\(_2\)) was deposited onto the FTO by spray pyrolysis using a 20-mM Titanium diisopropoxide bis(acetylacetonate) solution (Aldrich) at 450°C. A 100-nm thin mesoporous (mp) TiO\(_2\) was then deposited onto the FTO substrate using a 20-mM Mn\(_2\)(bipy)(acac)\(_2\) solution (Mabuchi) at 450°C (which was calibrated by AK300 at Kanagawa Academy of Science and Technology, Japan). The J–V curves were measured using a solar simulator (Newage Solar Simulator, 100 mW cm\(^{-2}\)) for 30 s. Finally, an Au counter electrode was deposited by thermal evaporation.

Solar cell characterization. For photovoltaic measurement of the solar cells, the irradiation source was a 450-W xenon light source (YS-80A; Yamashita Denso Co., Ltd, Japan), whose power of an AM1.5G, 100 mW cm\(^{-2}\) solar simulator was calculated using a reference Si photodiode BS-520 (Bunkoukeiki Co., Ltd, Japan), which was calibrated by AK300 (Konica Minolta, Inc., Japan) at Kanagawa Academy of Science and Technology, Japan. The J–V curves were measured employing an HSV-110 (Hokuto Denko Co., Ltd, Japan) potentiostat. The scan rate was fixed at 10 mV s\(^{-1}\). Measurement of the IPCE was a function of the excitation wavelength using the incident light from a 150-W xenon lamp SM-250E (Bunkoukeiki Co., Ltd, Japan), which was focused through an SM-25 monochrometer (Bunkoukeiki Co., Ltd, Japan). A light-shading mask was used on the photoanode of the solar cells to reduce scattered light from the edge of the glass substrate.

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the spectral mismatch were measured using the grating spectroradiometer (LS-100, EKO Instruments Co., Ltd., Japan).

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Authors contributions

T.Ki. and H.S. developed the basic concept. T.Ki. carried out the design and synthesis of the sensitizer fabrication of the DSSCs, and measurement of the solar cells. T.Ku. performed the ultrafast TA measurements. K.N., S.U. and H.S. supported construction of the DSSCs and the hybrid cell and provided technical advice. S.I.S., N.J.J., F.G., A.A., A.H., M.K.N. and M.G. planned the PSCs for the hybrid system and/or provided technical advice. T.Ki., H.S., A.H. and M.G. analysed the data and wrote the paper. H.S., S.I.S., A.H. and M.G. planned and directed the project. All authors discussed the results and reviewed the paper.

Additional information

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