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Supplementary Information

Quasi-solid-state dye-sensitized indoor photovoltaics with efficiencies exceeding 25%

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The supplementary information file includes 20 pages, experimental sections, 7 figures, 6 tables and 12 references.

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Experimental section

Materials

Poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP, average M_w ~400,000), poly(methylmethacrylate) (PMMA, M_w ~120,000), ammonium hexafluorophosphate (NH_4PF_6, 99.99%), 3,4-ethylenedioxythiophene (EDOT, 97%) and titanium diisopropoxide bis(acetylacetonate) (75 wt.% in isopropanol) were purchased from Aldrich Chemistry. 2,2′-Bipyridyl (99+%), cobalt(II) chloride hexahydrate ($CoCl_2\cdot 6H_2O$, 98%) and nitrosyl tetrafluoroborate ($NOBF_4$, 98%) were procured from Alfa Aesar. Lithium perchlorate ($LiClO_4$, 98%) and titanium(IV) chloride ($TiCl_4$, 98%) were obtained from Fluka. Ethanol (99.9%), methanol (99.8%) and sodium dodecyl sulfate (SDS, ultrapure bioreagent) were acquired from J. T. Baker. 4-*tert*-butylpyridine (*t*BP, $C_9H_{13}N$, 96%) and *tert*-butanol [$(CH_3)_3COH$, 99%] were received from Sigma-Aldrich. Acetonitrile (CH_3CN, 99.5%) were procured from Riedel-de Haën. Titanium dioxide pastes of 30 NR-D (for transparent layer) and PST-400C (for light-scattering layer) were purchased from Greatcell Solar and JGC C&C (JGC Catalysts and Chemicals Ltd.), respectively. Three dye sensitizers: 3-{6-{4-[*bis*(2′,4′-dihexyloxybiphenyl-4-yl)amino-]phenyl}-4,4-dihexyl-cyclopenta-[2,1-*b*:3,4-*b*′]dithiphene-2-yl}-2-cyanoacrylic acid (called Y123), (E)-3-(5-(4-(*bis*(2′,4′-dibutoxy-[1,1′- biphenyl]-4-yl)amino)phenyl)thiophen-2-yl)-2-cyanoacrylic acid (known as D35 or Dyenamo Orange), (E)-3-(4-(6-(7-(4-(*bis*(2′,4′-dibutoxy-[1,1′-biphenyl]-4-yl)amino)phenyl)benzo[c][1, 2,5]thiadiazol-4-yl)-4,4-*bis*(2-ethylhexyl)-4H-cyclopenta[2,1-*b*:3,4-*b*′]dithiophen-2-yl)phenyl)-2-cyanoacrylic acid (called XY1b) were obtained from Dyenamo AB. All chemicals were used as received without further purification.

Experimental section

Fabrication of counter electrodes

Two kinds of counter electrodes were employed in this work. The platinum (Pt) electrode was prepared by sputtering. The Pt catalysts were deposited onto fluorine-doped tin oxide-coated glass substrates (FTO, TEC 7, 2.2 mm thick) using a sputter coater (108auto, Cressington Scientific Instruments). The sputtering parameters, including controlled current of 40 mA, argon pressure of 0.06 mbar and coating time of 140 sec, were adopted for fabrication of each Pt electrodes. The other counter electrode was prepared by electrodeposition of polymer materials. A two-electrode electrochemical system and a potentiostat (CHI627D, CH Instruments) were used; both of electrodes were cleaned FTO substrates, and the electrolyte consists of 0.1 M SDS and 0.01 M EDOT in deionized water. The electrodeposition was performed by scanning the potential between –1 and 1.4 V for 5 cycles at a scan rate of 50 mV sec^{-1}. After the deposition, substrates were rinsed by deionized water and dried by air, and the PEDOT electrodes were obtained.

Experimental section

Characterization

Absorption and transmittance spectra were measured using a UV-vis spectrometer (Cintra 10e, GBC Scientific Equipment). The cross-sectional morphology of TiO_2 thin films was examined using a scanning electron microscope (SEM, SU8010, Hitachi). Electrochemical impedance spectroscopy (EIS), Tafel polarization and photocurrent transient analyses were performed on a potentiostat equipped with an FRA module (PGSTAT30, Metrohm Autolab). The EIS measurements were conducted in the dark at a controlled potential, and 10 mV AC sinusoidal signals were applied over a frequency range of 100 mHz to 100 kHz. The scan rate adopted in the Tafel polarization analysis is 10 mV sec^{-1}. Photocurrent transients were traced under different lighting conditions.

Photovoltaic characteristics (*J*−*V* curves) of the studied DS*i*PV devices were recorded with a digital source meter, scanning from 0 V to the relevant open-circuit voltages, under sunlight or fluorescent-light conditions. A solar simulator (XES-301S, AM 1.5G, AAA class, San-Ei Electric) calibrated by a certified reference silicon cell was employed to generate sunlight. A homemade system was built for measuring indoor photovoltaic performance; this system was wrapped by black curtains and consisted of an upper board, a bottom platform and a motor-controlled lifter. Fluorescent tubes (TL5 Essential 14W/865, Philips) covered by woven wire meshes (20 mesh, Stainless Steel 304L) were fixed to the upper board. The lifter could adjust the distance between the board and platform. To achieve illuminances of 200, 600 and 1000 lux, three layers of wire meshes were used, and the distances were controlled as ~91, ~46 and ~33 cm, respectively; for the illuminances of 1500 and 2000 lux, the distances were ~49 and ~39 cm, and no mesh was employed. A digital light meter (YF-170, TENMARS ELECTRONICS) was used to examine the illuminance, and the spectral irradiance (incident power) was determined by a spectroradiometer (S-2440 model Ⅱ, SOMA OPTICS). External quantum efficiency spectra were measured using an Enlitech system (QE-R3011, xenon light source, DC mode).

Table S1 Electrochemical characteristics of the electrolytes prepared using the starting composition [0.22 M Co(II), 0.05 M Co(III), 0.1 M $LiClO_4$, 0.2 M *t*BP]

Electrolyte A	R_s [a] (Ω cm²)	R_{ct} [a] (Ω cm²)	R_d [a] (Ω cm²)	J_{lim} [b] (mA cm⁻²)	D [b] (cm² s⁻¹)
Liquid	1.39	8.32	8.33	6.38	3.97×10^{-6}
PVDF-HFP/PMMA 10/0	1.34	5.58	10.5	6.24	3.88×10^{-6}
PVDF-HFP/PMMA 9/1	1.37	8.78	10.3	5.68	3.52×10^{-6}
PVDF-HFP/PMMA 8/2	1.37	9.72	10.3	5.67	3.54×10^{-6}

Parameters acquired by the [a] EIS analysis and [b] Tafel polarization.

R_s: Series resistance.

R_{ct}: Charge transfer resistance at the Pt-electrode/electrolyte interface.

R_d: Diffusion resistance.

J_{lim}: Limiting current density.

D: Apparent diffusion coefficients related to the $Co(bpy)_3^{3+}$ species.

Table S2 Photovoltaic parameters of the Y123 DS*i*PV cells using the starting electrolyte composition under 1-sun irradiation

Electrolyte A	J_{sc} (mA cm^{-2})	V_{oc}[a] (V)	FF	PCE[b] (%)
Liquid	13.03	0.835 (0.621)	0.682	7.42 ± 0.10 (0.11)
PVDF-HFP/PMMA 10/0	12.96	0.846 (0.635)	0.676	7.41 ± 0.09 (0.10)
PVDF-HFP/PMMA 9/1	10.61	0.848 (0.652)	0.697	6.27 ± 0.11 (0.12)
PVDF-HFP/PMMA 8/2	8.26	0.826 (0.644)	0.715	4.88 ± 0.10 (0.11)

[a] The voltages at the maximum power point are shown in parentheses. [b] The PCE values are expressed as mean value ± margin of error (95% confidence interval), and the numbers shown in parentheses are standard deviations based on five cells.

Table S3 Photovoltaic parameters of the Y123 DS*i*PV cells using half numbers of redox couples [0.11 M Co(II) and 0.025 M Co(III)] under 200-lux fluorescent lighting (incident power: 68.2 μW cm^{-2})

Gel Electrolyte	J_{sc} (μA cm^{-2})	V_{oc}[a] (V)	FF	PCE[b] (%)
Electrolyte B 0.2 M *t*BP	25.87	0.625 (0.514)	0.745	17.7 ± 0.15 (0.17)
Electrolyte C 1.2 M *t*BP	23.92	0.692 (0.576)	0.780	18.9 ± 0.21 (0.23)

[a] The voltages at the maximum power point are shown in parentheses. [b] The PCE values are expressed as mean value ± margin of error (95% confidence interval), and the numbers shown in parentheses are standard deviations based on five cells.

Table S4 Photovoltaic parameters of the DS*i*PV cells (gel **electrolyte C**) with different cosensitization conditions under 200-lux fluorescent lighting (incident power: 68.2 μW cm^{-2})

Cosensitization	J_{sc} (μA cm^{-2})	V_{oc}[a] (V)	FF	PCE[b] (%)
D35/XY1b (9/1)	23.70	0.709 (0.598)	0.783	19.3 ± 0.13 (0.15)
D35/XY1b (7/3)	25.71	0.707 (0.592)	0.770	20.5 ± 0.16 (0.19)
D35/XY1b (1/1)	24.44	0.711 (0.574)	0.761	19.4 ± 0.18 (0.20)

[a] The voltages at the maximum power point are shown in parentheses. [b] The PCE values are expressed as mean value ± margin of error (95% confidence interval), and the numbers shown in parentheses are standard deviations based on five cells.

Table S5 Photovoltaic parameters of the conventional DS*i*PV cells (gel **electrolyte C**, D35/XY1b = 7/3) using PEDOT catalysts under various LED lighting

LED Lighting	J_{sc} (μA cm^{-2})	V_{oc}[a] (V)	FF	PCE[b] (%)
200 lux (70.0 μW cm^{-2})[c]	28.20	0.718 (0.599)	0.780	22.6 ± 0.21 (0.25)
600 lux (203 μW cm^{-2})[c]	84.08	0.757 (0.647)	0.790	24.8 ± 0.06 (0.07)
1000 lux (333 μW cm^{-2})[c]	141.1	0.775 (0.655)	0.792	26.0 ± 0.09 (0.10)

[a] The voltages at the maximum power point are shown in parentheses. [b] The PCE values are expressed as mean value ± margin of error (95% confidence interval), and the numbers shown in parentheses are standard deviations based on five cells. [c] Incident power.

Table S6 Comparison of various organic indoor photovoltaics at illuminance of around 1000 lux

Device	Features	Lighting and Illuminance	J_{sc} (μA cm^{-2})	V_{oc} (V)	FF	PCE (%)	Ref.
DSC	Quasi-Solid-State Gel EL[a] Cobalt Redox Couple D35 & XY1b Dyes PEDOT Catalyst	FL[b] Tube 1000 lux	137.6	0.770	0.786	25.3	This work
DSC	Copper Redox Couple D35 & XY1 Dyes PEDOT Catalyst	FL[b] Tube 1000 lux	138.0	0.797	0.80	28.9	[S1]
DSC	TY6 Dye with Coabsorbent	FL[b] Lamp 1200 lux	164	0.671	0.778	24.4	[S2]
DSC	YL4 Dye with Coabsorbent	FL[b] Lamp 1025 lux	224	0.576	0.63	25.0	[S3]
DSC	New DSC Architecture Copper Redox Couple XY1b & Y123 Dyes PEDOT Catalyst	FL[b] Tube 1000 lux	149.3	0.878	0.773	31.8	[S4]
DSC	Copper Redox Couple XY1 & 5T Dyes PEDOT Catalyst	FL[b] Lamp 1000 lux	131.2	0.860	0.78	29.2	[S5]
DSC	Copper Redox Couple XY1 & L1 Dyes PEDOT Catalyst	FL[b] Tube 1000 lux	147	0.910	0.77	34.0	[S6]
OPV	BTR:PC$_{71}$BM[c]	FL[b] Lamp 1000 lux	133.1	0.791	0.752	28.1	[S7]
OPV	PDTBTBz-2F$_{anti}$:PC$_{71}$BM[c]	LED 1000 lux	112.4	0.817	0.704	23.1	[S8]
OPV	PBDB-TF:IO-4Cl[c]	LED (2700 K) 1000 lux	90.6	1.10	0.791	26.1	[S9]
PSK[d]	Two-Step PC$_{61}$BM ETL[e]	FL[b] Lamp 1000 lux	132.26	0.84	0.75	26.3	[S10]
PSK[d]	Ambient Process	FL[b] Lamp 1000 lux	129.5	0.858	0.753	27.0	[S11]
PSK[d]	Triple-Anion PSK[d] Film	FL[b] Lamp 1000 lux	126.2	1.028	0.768	36.3[f]	[S12]

[a] Electrolyte. [b] Fluorescent. [c] Organic donor:acceptor system. [d] Perovskite. [e] Electron-transporting layer. [f] Record efficiency of the indoor photovoltaic.

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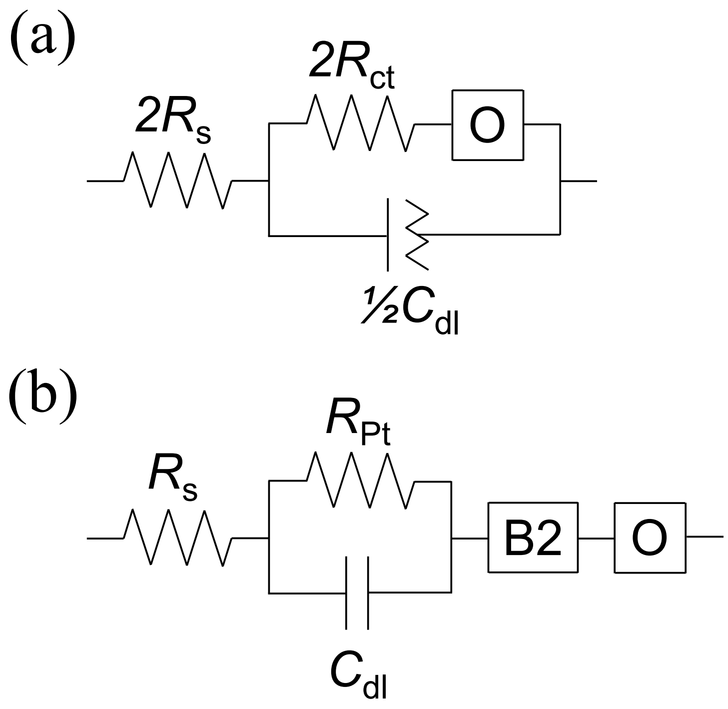

Fig. S1 Equivalent circuits adopted to fit the Nyquist spectra of (a) dummy and (b) DS*i*PV cells.

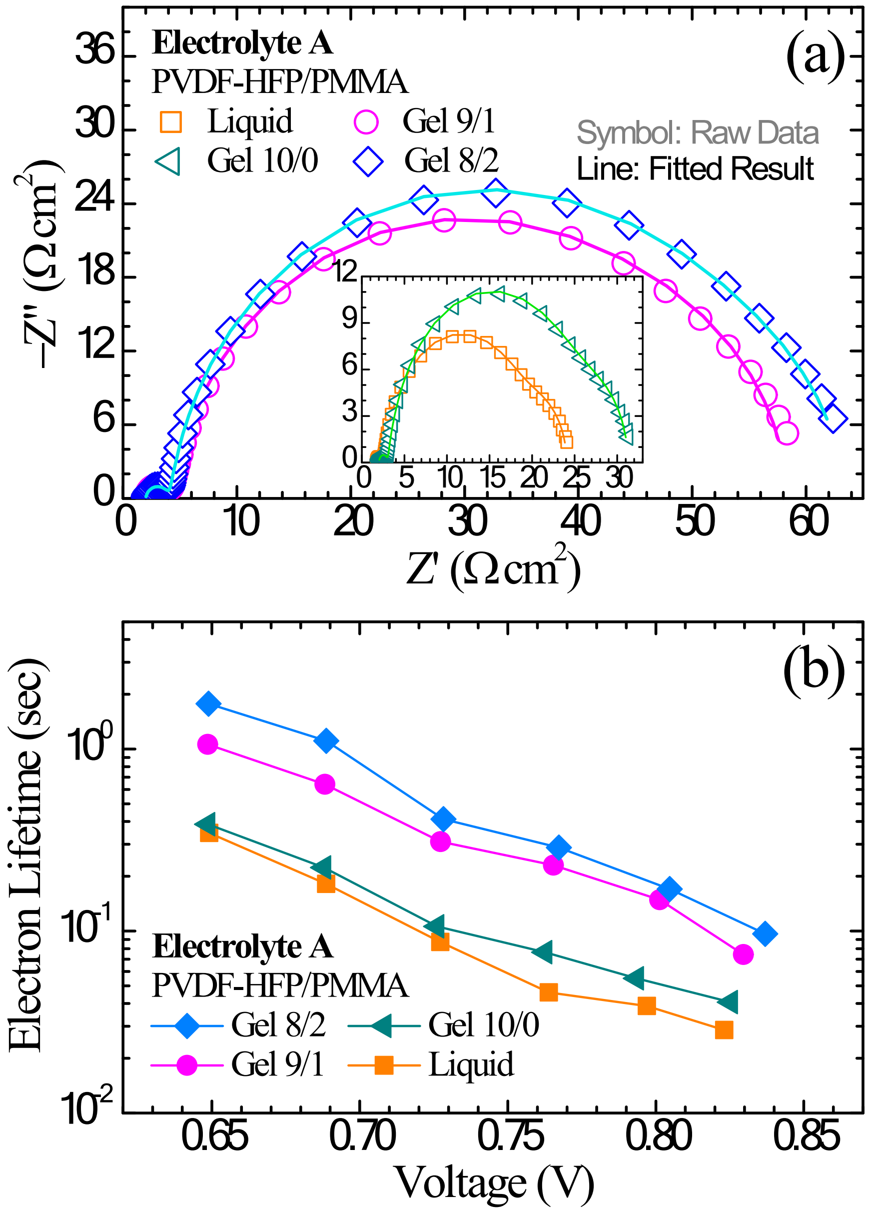

Fig. S2 Impedance characteristics of the Y123 DS*i*PV cells based on **electrolyte A**: (a) Nyquist spectra obtained at an applied voltage of 0.85 V; (b) electron lifetime as a function of corrected voltage.

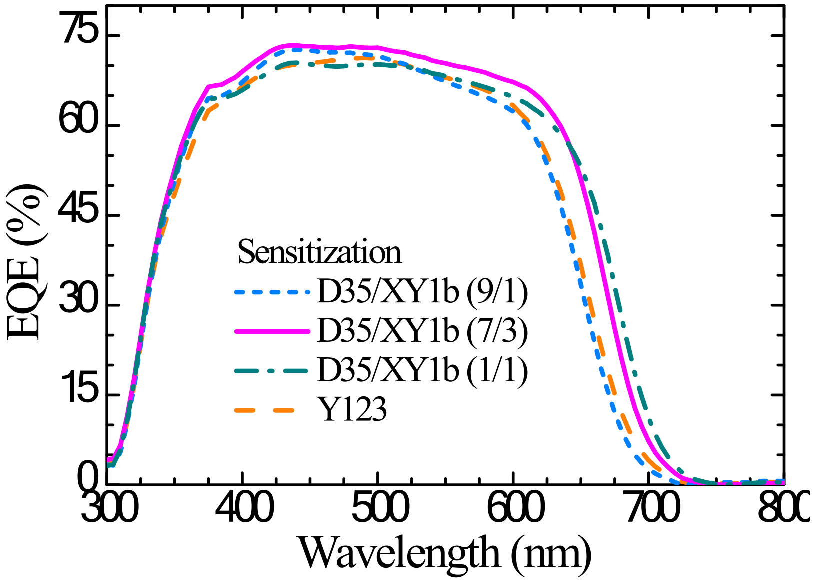

Fig. S3 EQE spectra of the DS*i*PV cells (gel **electrolyte C**) with different sensitization conditions.

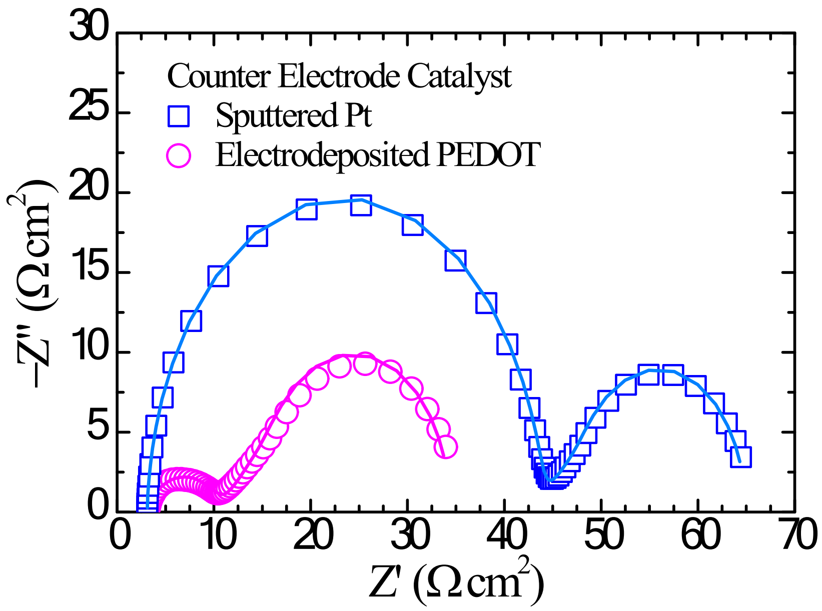

Fig. S4 Nyquist spectra related to the dummy cells (gel **electrolyte C**) assembled using Pt- and PEDOT-loaded electrodes (at 0 V).

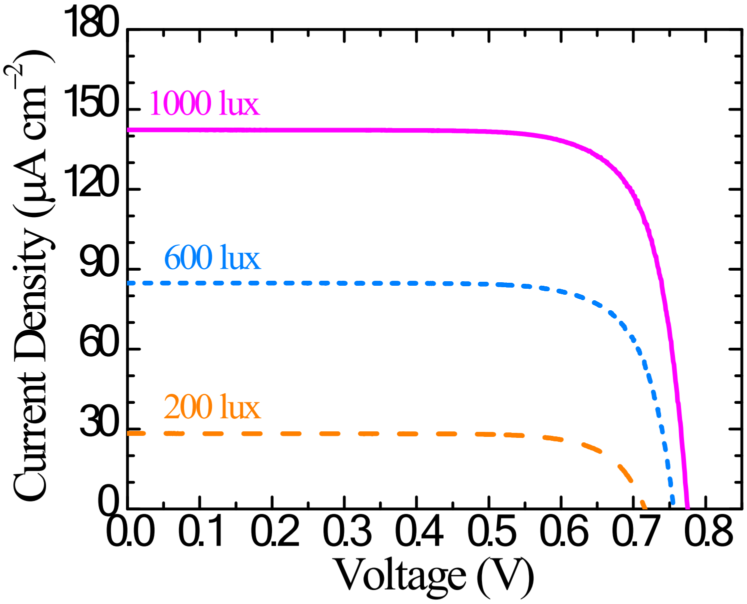

Fig. S5 J–V curves of the conventional DS*i*PV cells (gel **electrolyte C**, D35/XY1b = 7/3) using PEDOT catalysts under different LED lighting (6500 K).

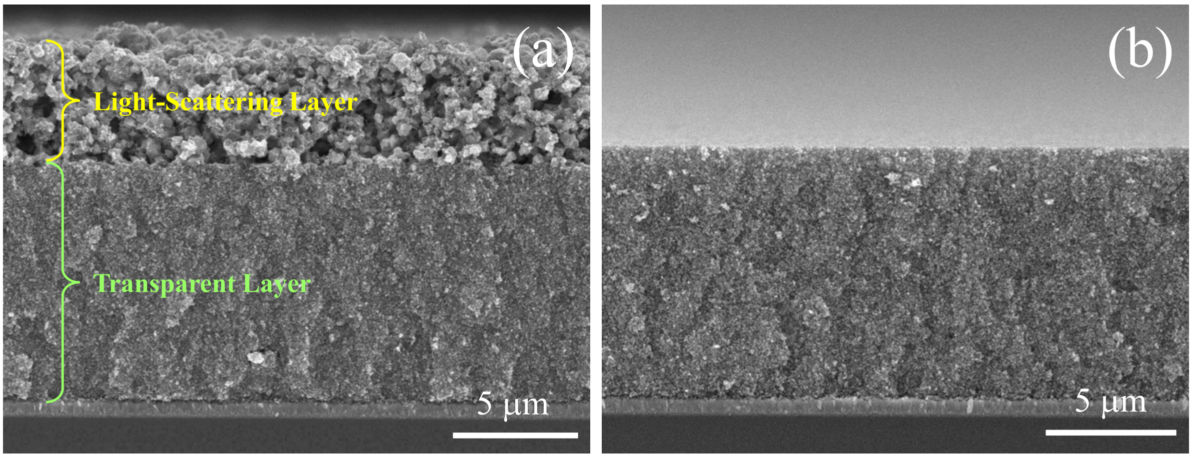

Fig. S6 Cross-sectional SEM images of the (a) double- and (b) single-layered TiO_2 thin films for assembling conventional and bifacial cells respectively.

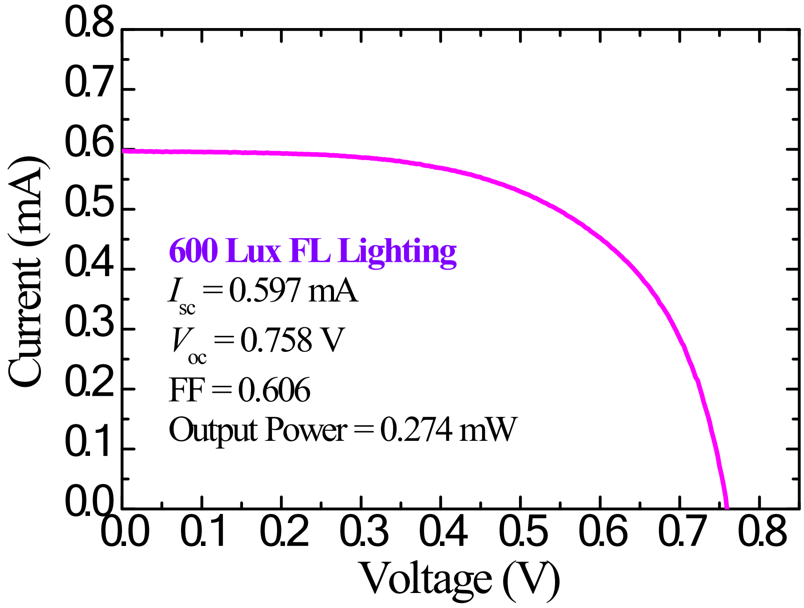

Fig. S7 Performance of an 11.2 cm^2 DS*i*PV module device measured under 600-lux fluorescent lighting.