Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information (ESI)

Organic energy-harvesting devices achieving power conversion efficiencies over 20% under ambient indoor lighting

Ryota Arai,*[ac] Seiichi Furukawa,[ab] Narumi Sato[ab] and Takuma Yasuda*[ab]

[a]Department of Applied Chemistry, Graduate School of Engineering, Kyushu University,
744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan
[b]INAMORI Frontier Research Center (IFRC), Kyushu University,
744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan
[c]Ricoh Company, Ltd., 16-1 Honda-machi, Numazu, Shizuoka 410-8505, Japan

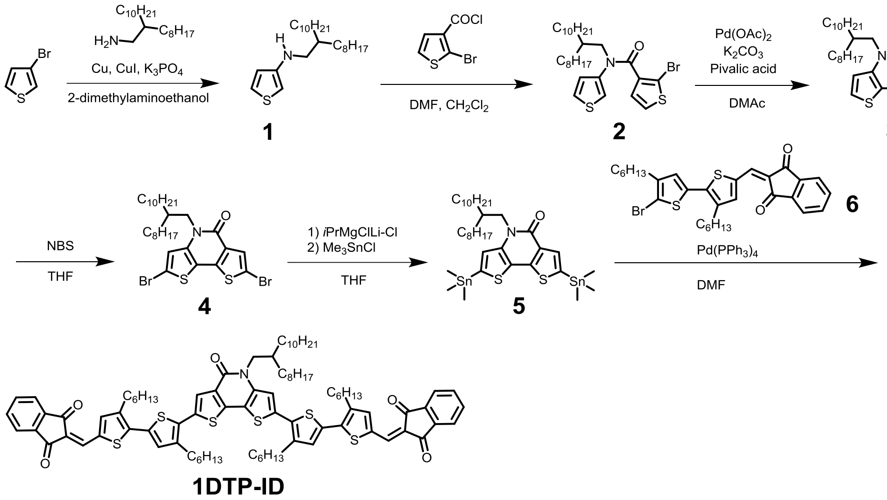
*E-mail: yasuda@ifrc.kyushu-u.ac.jp (T.Y.); ryota.arai@jp.ricoh.com (R.A.)

Contents:

Materials

All commercially available reagents and solvents were used without further purification unless otherwise noted. *N*-Phenyl-2-phenyl[60]fulleropyrrolidine (PNP)[S1] was received from Harves Co., Ltd. AZO nanoparticle ink (N-20X) was purchased from Avantama Corp. and used as received. 2-((5'-Bromo-3,4'-dihexyl-[2,2'-bithiophen]-5-yl)methylene)-1H-indene-1,3(2H)-dione (**6**) was prepared according to our previous work.[S2] All reactions were carried out under a nitrogen atmosphere in dry solvents using standard Schlenk techniques.

Synthesis



Scheme S1. Synthetic routes for **1DTP-ID**.

***N*-(2-octyldodecyl)thiophen-3-amine (1):** A mixture of 3-bromothiophene (24.4 g, 150 mmol), 2-octyldodecan-1-amine (53.5 g, 180 mmol), Cu powder (0.94 g, 15 mmol), CuI (I) (2.86 g, 15 mmol) and K_3PO_4 (63.38 g, 300 mmol) in 2-dimethylaminoethanol (150 mL) was stirred for 45 h at 80 °C. After cooling to room temperature, the reaction mixture was poured into water, and the product was extracted with hexane. The combined organic layer was dried over anhydrous Na_2SO_4. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: hexane) and dried under vacuum to afford **1** as a brown oil (yield = 52.2 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (dd, J = 5.2, 2.8 Hz, 1H), 6.61 (dd, J = 5.2, 1.6 Hz, 1H), 5.91 (dd, J = 2.8, 1.6 Hz, 1H), 3.57 (br, 1H), 2.96 (d, J = 6.0 Hz, 2H), 1.62-1.55 (m, 1H), 1.35-1.20 (m, 32H), 0.88 (t, J = 6.8 Hz, 6H).

2-Bromo-*N*-(2-octyldodecyl)-*N*-(thiophen-3-yl)thiophene-3-carboxamide (2): To a solution of 2-bromothiophene-3-carboxylic acid (20.7 g, 100 mmol) in dry CH_2Cl_2 (150 mL) and dimethylformamide (few drops) was added oxalyl chloride (19.0 g, 150 mmol) slowly. The mixture was stirred for 20 h at room temperature. Then, the solvent and excessive oxalyl chloride were removed under reduced pressure to obtain 2-bromothiophene-3-carbonyl chloride. To a solution of 2-bromothiophene-3-carbonyl chloride in dry THF was added slowly a solution of **1** (41.7 g, 110 mmol) in triethylamine (20 mL) and dry THF (150mL) at 0 °C. The mixture was stirred overnight at room temperature. The resulting mixture was poured into water and extracted with hexane. The combined organic layer was dried over anhydrous Na_2SO_4. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: hexane/chloroform = 3:1, v/v) and dried under vacuum to afford **2** as a brown oil (yield = 37.4 g, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (s, 1H), 7.00 (dd, *J* = 3.2, 2.0 Hz, 1H), 6.85 (s, 1H), 6.78 (s, 1H), 6.57 (d, *J* = 4.4 Hz, 1H), 3.80 (d, *J* = 6.4 Hz, 2H), 1.62-1.55 (m, 1H), 1.35-1.20 (m, 32H), 0.90-0.85 (m, 6H). MS (MALDI-TOF): *m/z* 567.22 $[M]^+$; found 568.02.

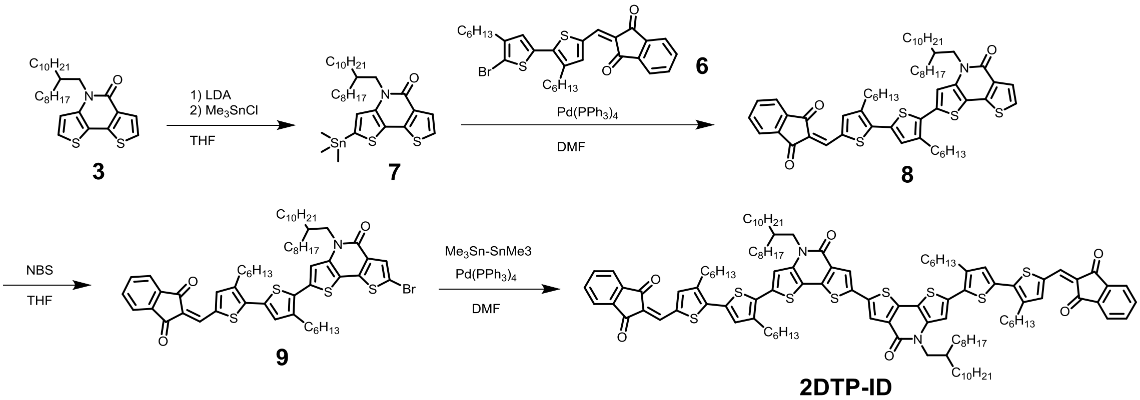
4-(2-Octyldodecyl)dithieno[3,2-b:2',3'-d]pyridin-5(4H)-one (3): A mixture of **2** (33.0 g, 60 mmol), $Pd(OAc)_2$ (II) (1.35 g, 6.0 mmol), K_2CO_3 (12.44 g, 90 mmol), and pivalic acid (2.04 g, 20 mmol) in dry DMF (300 mL) was stirred for 18 h at 110°C. After cooling to room temperature, the reaction mixture was poured into water, and the product was extracted with hexane. The combined organic layer was dried over anhydrous Na_2SO_4. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: hexane) and dried under vacuum to afford **3** as a brown oil (yield = 22.0 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 5.2 Hz, 1H), 7.43 (d, *J* = 5.2 Hz, 1H), 7.23 (d, *J* = 5.2 Hz, 1H), 7.08 (d, *J* = 5.2 Hz, 1H), 4.21 (d, *J* = 6.0 Hz, 2H), 2.03-1.95 (m, 1H), 1.40-1.15 (m, 32H), 0.90-0.84 (m, 6H). MS (MALDI-TOF): *m/z* 487.29 $[M]^+$; found 488.04.

2,7-Dibromo-4-(2-octyldodecyl)dithieno[3,2-b:2',3'-d]pyridin-5(4H)-one (4): To a solution of **3** (9.76 g, 20 mmol) in dry THF (100 mL) was added slowly NBS (7.12 g, 40 mmol). The mixture was stirred for 20 h at room temperature. The mixture was poured into water, and the product was extracted with hexane. The combined organic layer was dried over anhydrous Na_2SO_4. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: hexane/chloroform = 1:1, v/v) and dried under vacuum to afford **4** as a yellow oil (yield = 5.16 g, 40%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (s, 1H), 7.05 (s, 1H), 4.20-4.10 (br, 2H), 1.96-1.91 (m, 1H), 1.54-1.28 (m, 36H), 0.90-0.86 (m, 6H). MS (MALDI-TOF): *m/z* 643.12 $[M]^+$; found 643.92.

4-(2-Octyldodecyl)-2,7-bis(trimethylstannyl)dithieno[3,2-b:2',3'-d]pyridin-5(4H)-one (5): To a solution of **4** (1.50 g, 2.32 mmol) in dry THF (30 mL) was added slowly *i*PrMgCl-LiCl

(1.3 M in THF, 3.92 mL, 5.10 mmol) at −20°C. The mixture was stirred for 1 h at that temperature. Then, trimethyl tin chloride (1.39 g, 6.96 mmol) was added, and the mixture was stirred overnight at room temperature. The reaction mixture was added to water, and the product was extracted with hexane. The combined organic layer was dried over anhydrous Na_2SO_4. After filtration and evaporation, the product was dried under vacuum to afford **5** as a yellow brown oil (yield = 1.75 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (s, 1H), 7.07 (s, 1H), 4.27-4.20 (m, 2H), 2.02-1.94 (m, 1H), 1.65-1.51 (m, 4H), 1.40-1.20 (m, 32H), 0.89-0.86 (m, 6H), 0.45 (s, 9H), 0.42 (s, 9H). MS (MALDI-TOF): *m/z* 813.22 [M]$^+$; found 814.02.

1DTP-ID: A mixture of **5** (0.488 g, 0.60 mmol) and **6** (0.684 g, 1.20 mmol), $Pd(PPh_3)_4$ (0.016 g, 0.014 mmol) in dry DMF (50 mL) was stirred overnight at 80 °C. After cooling to room temperature, the reaction mixture was poured into methanol, and the formed precipitate was collected by filtration. The product was purified by silica gel column chromatography (eluent: chloroform/hexane = 3:1, v/v) and dried under vacuum to afford **1DTP-ID** as a deep blue solid (yield = 0.26 g, 30%). This material was further purified by recycling preparative GPC (eluent: chloroform) prior to use. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01-7.93 (m, 4H), 7.90 (s, 1H), 7.89 (s, 1H), 7.82-7.74 (m, 7H), 7.35 (s, 1H), 7.34 (s, 1H), 7.13 (s, 1H), 4.31-4.18 (m, 2H), 2.92-2.83 (m, 8H), 2.10-1.99 (m, 1H), 1.81-1.70 (m, 8H), 1.51-1.17 (m, 56H), 0.96-0.89 (m, 12H), 0.85 (m, 6H). MS (MALDI-TOF): *m/z* 1463.66 [M]$^+$; found 1464.53. Anal. Calcd (%) for $C_{89}H_{109}NO_5S_6$: C 72.96, H 7.50, N 0.96; found: C 72.87, H 7.54, N 1.12.



Scheme S2. Synthetic routes for **2DTP-ID**.

4-(2-Octyldodecyl)-2-(trimethylstannyl)dithieno[3,2-b:2',3'-d]pyridin-5(4H)-one (7): To a solution of **3** (976 mg, 2.00 mmol) in dry THF (10 mL) was added slowly LDA (0.394 M in THF, 6.6 mL, 2.6 mmol) at −78°C. The mixture was stirred for 1 h at −40°C. Then, trimethyl tin chloride (1.39 g, 6.96 mmol) was added, and the mixture was stirred overnight at room temperature. The reaction mixture was added into water, and the product was extracted with hexane. The combined organic layer was dried over anhydrous Na_2SO_4. After filtration and evaporation, the product was dried under vacuum to afford **7** as a yellow brown oil (yield = 1.22 g, 94%). ^{1}H NMR (400 MHZ, $CDCl_3$): δ 7.69 (d, J = 5.5 Hz, 1H), 7.20 (d, J = 5.3 Hz, 1H), 7.08 (s, 1H), 4.28-4.17 (m, 2H), 2.04-1.95 (m, 1H), 1.60-1.13 (32H), 0.90-0.86 (m, 6H), 0.46 (s, 9H). MS (MALDI-TOF): *m/z* 651.26 $[M]^+$; found 652.26.

2-((3,4'-Dihexyl-5'-(4-(2-octyldodecyl)-5-oxo-4,5-dihydrodithieno[3,2-b:2',3'-d]pyridin-2-yl)-[2,2'-bithiophen]-5-yl)methylene)-1H-indene-1,3(2H)-dione (8): A mixture of **7** (1.04 g, 1.6 mmol), **6** (0.91 g, 1.60 mmol), $Pd(PPh_3)_4$ (0.056 g, 0.050 mmol) in dry DMF (10 mL) was stirred overnight at 70 °C. After cooling to room temperature, the reaction mixture was poured into methanol, and the formed precipitate was collected by filtration. The product was purified by silica gel column chromatography (eluent: chloroform/hexane = 3:1, v/v) and dried under vacuum to afford **8** as a black solid (yield = 0.77 g, 49%). ^{1}H NMR (400 MHZ, $CDCl_3$): δ 8.00-7.94 (m, 2H), 7.90 (s, 1H), 7.82-7.77 (m, 3H), 7.72 (d, J = 5.3 Hz, 1H), 7.34 (s, 1H), 7.25 (d, 1H), 7.14 (s, 1H), 4.29-4.19 (m, 2H), 2.91-2.84 (m, 4H), 2.09-1.99 (m, 1H), 1.79-1.70 (m, 4H), 1.49-1.18 (m, 44H), 0.94-0.82 (m, 12H). MS (MALDI-TOF): *m/z* 975.48 $[M]^+$; found 976.89.

2-((5'-(7-Bromo-4-(2-octyldodecyl)-5-oxo-4,5-dihydrodithieno[3,2-b:2',3'-d]pyridin-2-yl)-3,4'-dihexyl-[2,2'-bithiophen]-5-yl)methylene)-1H-indene-1,3(2H)-dione (9): To a solution of **8** (0.68 g, 0.7 mmol) in dry THF (30 mL) was added slowly NBS (0.13 g, 0.74 mmol). The mixture was stirred for 14 h at room temperature. The reaction mixture was added into water, and the product was extracted with hexane. The combined organic layer was dried over anhydrous Na_2SO_4. After filtration and evaporation, the product was purified by reprecipitation (chloroform/methanol) and dried under vacuum to afford **9** as a black solid (yield = 0.6 g, 89%). ^{1}H NMR (400 MHZ, $CDCl_3$): δ 8.00-7.95 (m, 2H), 7.89 (s, 1H), 7.81-7.77 (m, 3H), 7.67 (s, 1H), 7.33 (s, 1H), 7.11 (s, 1H), 4.25-4.15 (m, 2H), 2.90-2.82 (m, 4H), 2.06-1.97 (m, 1H), 1.77-1.69 (m, 4H), 1.49-1.18 (m, 44H), 0.95-0.82 (m, 12H). MS (MALDI-TOF): *m/z* 1053.39 $[M]^+$; found 1053.72.

2DTP-ID: A mixture of **9** (0.63 g, 0.60 mmol), hexamethyl ditin (0.10 g, 0.30 mmol), $Pd(PPh_3)_4$ (0.02 g, 0.017 mmol) in dry DMF (20 mL) was stirred overnight at 80 °C. After cooling to room temperature, the reaction mixture was poured into methanol, and the formed precipitate was collected by filtration. The product was washed by methanol, and purified by silica gel column chromatography (eluent: chloroform/hexane = 3:1, v/v) and dried under vacuum to afford

2DTP-ID as a black solid (yield = 0.13 g, 24%). This material was further purified by recycling preparative GPC (eluent: chloroform) prior to use. ^{1}H NMR (400 MHZ, $CDCl_3$): δ 7.96-7.87 (m, 4H), 7.78-7.70 (m, 6H), 7.62 (s, 2H), 7.21 (s, 2H), 6.99 (s, 2H), 4.29-4.12 (m, 4H), 2.87-2.78 (m, 8H), 2.04-1.95 (m, 2H), 1.79-1.70 (m, 8H), 1.53-1.18 (m, 88H), 0.99-0.92 (m, 12H), 0.86-0.81 (12H). MS (MALDI-TOF): *m/z* 1948.94 $[M]^+$; found 1949.43. Anal. calcd (%) for $C_{118}H_{152}N_2O_6S_8$: C 72.64, H 7.85, N 1.44; found: C 72.58, H 7.88, N 1.54.

Fabrication of OPV Devices

Pre-patterned ITO-coated glass or polyethylene telephthalate (PET) substrates with a gas barrier layer were cleaned by sequentially sonicating in detergent solution, deionized water, acetone, and isopropanol for 15 min each, and then subjected to UV/ozone treatment for 30 min. A dispersion of AZO nanoparticles (N-20X) was spin-coated (3000 rpm) and annealed at 100 °C for 10 min in air to form an AZO thin layer. Thus fabricated AZO layer was pretreated with a solution of 4-dimethylaminobenzoic acid in ethanol (1 mg mL^{-1}) before depositing each active layer. Bulkhetero junction (BHJ) active layers based on 1DTP-ID:PNP or 2DTP-ID:PNP were then prepared by spin-coating from their chloroform solutions (total concentration: 30 mg mL^{-1}) after passing through a 0.45 μm PTFE membrane filter. Finally, 10 nm thick MoO_3 and 100 nm thick Ag layers were sequentially deposited on top of the active layer under high vacuum through a shadow mask to pattern the electrodes. The active area of the small-area cells was 6 mm^2. The active area of the large-area PET modules was defined by the overlapped regions of the ITO patterns and active layers (see Fig. 6b). As a result, the total functional active area of each module was calculated as 9.6 cm^2, which is the sum of the area (~1.6 cm^2) of six series-connected sub-cells.

Measurements

The current density–voltage (*J*–*V*) curves of the fabricated OPV devices were measured using a computer-controlled ADCMT 6241 source measure unit in air, under illumination from either an AM 1.5G solar simulator (100 mW cm^{-2}) or a white LED, without using masks. To simulate indoor lighting conditions, an LED lamp CDS-90α (Cosmo Techno Corp.) was employed. The illuminance of the incident light was modulated from 200 to 10000 lx, which corresponds to 57.9–2895 μW cm^{-2}, by changing the distance between the OPV device and LED light source. The illuminance was measured using a Digital Lux Meters 51012 (Yokogawa Test & Measurement Corp.), which was calibrated and certified by ensuring the linearity of illuminance in the range of 9–900000 lx from the maker. The power densities were determined from the respective illumination spectra of the white LED light, using a spectroradiometer C-7000 (Sekonic Corp.), which was calibrated and certified with a calibration error within 1% by comparing the standard instrument.

In general, indoor light intensity is described by illuminance, a measure relating the sensitivity of human eye. Conversion of illuminance (L, in lx = lm m^{-2}) to irradiance (P, in W m^{-2}) per unit wavelength λ is given by:

$$L(\lambda) = K_\mathrm{m} \cdot V(\lambda) \cdot P(\lambda) \qquad \text{(S1)}$$

where K_m is the maximum spectral luminous efficiency for human photonic vision (K_m = 683 lm W^{-1}) and V is the spectral luminous efficiency function. The human eye is only capable of detecting light within a visible region from 380 (violet) to 780 nm (red), and its sensitivity peaks around 555 nm and not constant within this range. An irradiance of P = 100 mW cm^{-2} for the AM 1.5G solar spectrum corresponds to an illuminance of L = 100000 lx, according to Equation S1.

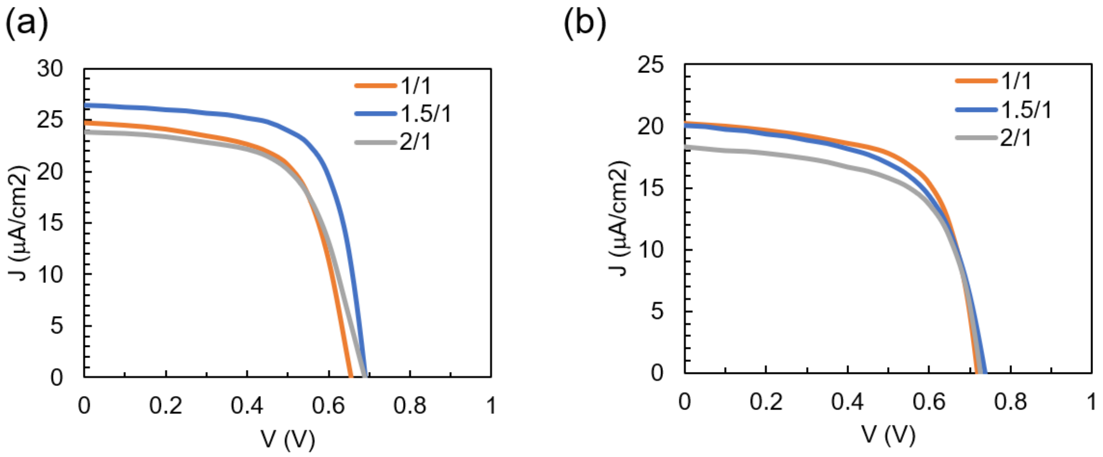


Fig. S1 *J*–*V* curves for the OPVs based on (a) **1DTP-ID:PNP** and (b) **2DTP-ID:PNP** with different D:A blend ratios under white LED illumination at 200 lx (7500 K).

Table S1 Photovoltaic parameters for the OPVs based on **1DTP-ID:PNP** and **2DTP-ID:PNP** with different D:A blend ratios under white LED illumination at 200 lx (7500 K).

active layer	D:A [w/w]	thickness [nm]	J_{sc} [μA cm^{-2}]	V_{oc} [V]	FF [%]	P_{out} [μW cm^{-2}]	PCE [%]
1DTP-ID:PNP	1:1	183	24.65	0.65	0.63	10.1	14.4
	1.5:1	**181**	**26.42**	**0.69**	**0.68**	**12.4**	**17.7**
	2:1	185	23.78	0.69	0.61	9.9	14.2
2DTP-ID:PNP	**1:1**	**148**	**19.96**	**0.72**	**0.65**	**9.3**	**13.3**
	1.5:1	145	20.27	0.74	0.59	8.8	12.6
	2:1	159	18.31	0.73	0.63	8.3	11.9

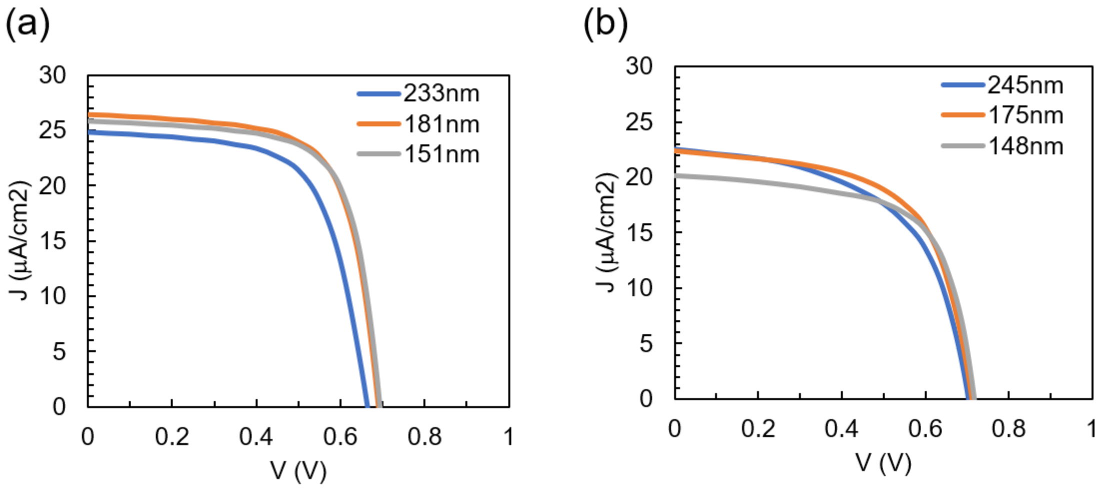


Fig. S2 *J*–*V* curves for the OPVs based on (a) **1DTP-ID:PNP** (1.5:1, w/w) and (b) **2DTP-ID:PNP** (1:1, w/w) with different active layer thickness under white LED illumination at 200 lx (7500 K).

Table S2 Photovoltaic parameters for the OPVs based on **1DTP-ID:PNP** and **2DTP-ID:PNP** with different active layer thickness under white LED illumination at 200 lx (7500 K).

active layer	thickness [nm]	D:A [w/w]	J_{sc} [μA cm^{-2}]	V_{oc} [V]	FF [%]	P_{out} [μW cm^{-2}]	PCE [%]
1DTP-ID:PNP	233	1.5:1	24.7	0.66	64	10.5	15.0
	181	1.5:1	**26.4**	**0.69**	**68**	**12.4**	**17.7**
	151	1.5:1	25.7	0.69	69	12.3	17.6
1DTP-ID:PNP	245	1:1	22.5	0.70	56	8.9	12.7
	175	1:1	**22.4**	**0.71**	**61**	**9.7**	**13.9**
	148	1:1	19.6	0.72	65	9.3	13.3

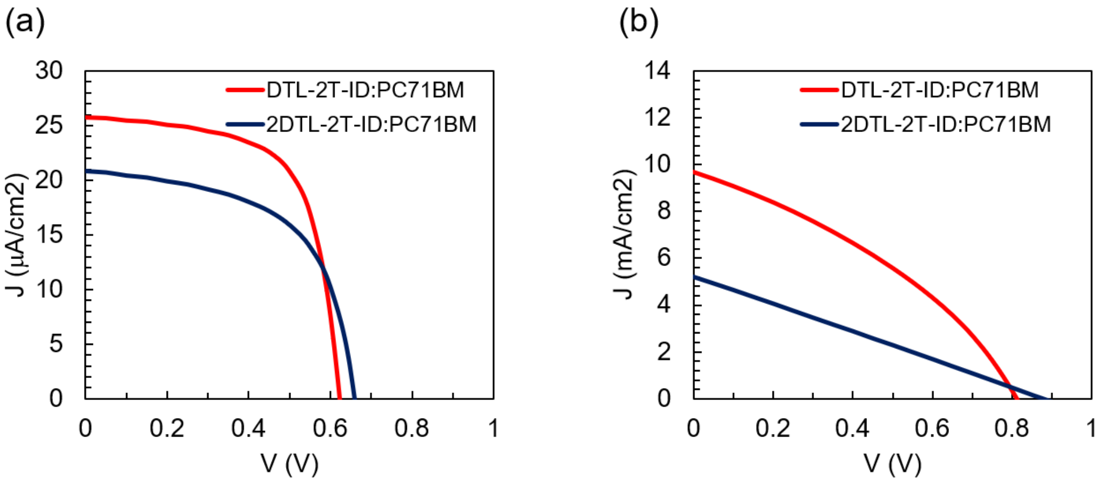


Fig. S3 *J*–*V* curves for the OPVs based on **1DTP-ID**:$PC_{71}BM$ (1.5:1, w/w) and **2DTP-ID**:$PC_{71}BM$ (1:1, w/w) under (a) white LED illumination at 200 lx (7500K) and (b) 1-sun illumination.

Table S3 Photovoltaic parameters for the OPVs based on **1DTP-ID**:$PC_{71}BM$ and **2DTP-ID**:$PC_{71}BM$ under white LED illumination at 200 lx (7500K) and 1-sun illumination.

active layer	condition	thickness [nm]	D:A [w/w]	J_{sc} [μA cm^{-2}]	V_{oc} [V]	FF [%]	P_{out} [μW cm^{-2}]	PCE [%]
1DTP-ID: $PC_{71}BM$	200 lx	184	1.5:1	25.3	0.62	65	10.2	14.6
	1-sun	184	1.5:1	9.7×10^3	0.81	0.36	2.8×10^3	2.8
1DTP-ID: $PC_{71}BM$	200 lx	160	1:1	20.54	0.66	0.583	7.9	11.2
	1-sun	160	1:1	5.2×10^3	0.88	0.25	1.2×10^3	1.2

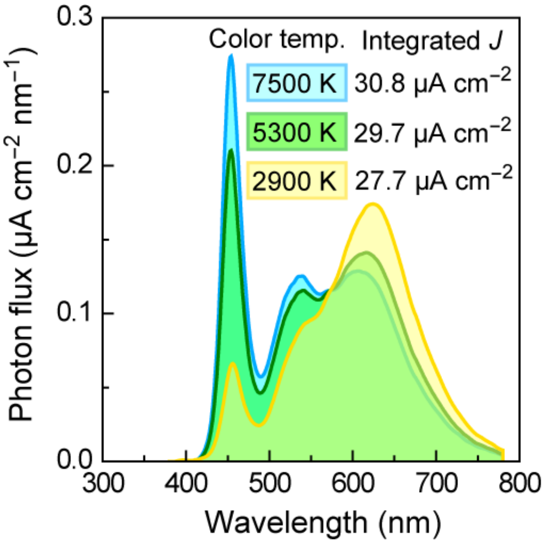


Fig. S4 Photon flux against wavelength for incident LED light sources with different color temperatures. The current density (*J*) values integrated in the range of 380–780 nm are given.

References

(S1) M. Karakawa, T. Nagai, K. Adachi, Y. Ie and Y. Aso, *J. Mater. Chem. A*, 2014, **2**, 20889.

(S2) H. Komiyama, T. To, S. Furukawa, Y. Hidaka, W. Shin, T. Ichikawa, R. Arai and T. Yasuda, *ACS Appl. Mater. Interfaces*, 2018, **10**, 11083.