Electronic Supplementary Information

Efficient Charge Generation and Collection in Organic Solar Cells Based on Low Band Gap Dyad Molecules

Seiichiro Izawa[a], Keisuke Tajima*[a,b], and Kazuhito Hashimoto*[a,b]

[a]Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan; [b]HASHIMOTO Light Energy Conversion Project, Exploratory Research for Advanced Technology (ERATO), Japan Science Technology Agency (JST)

E-mail: *k-tajima@light.t.u-tokyo.ac.jp*, *hashimoto@light.t.u-tokyo.ac.jp*

Materials and instruments

All chemicals were purchased from Sigma-Aldrich, Tokyo Kasei Kogyo, or Wako Chemicals and used without further purification. Cyclic voltammetry was measured on an HSV-100 automatic polarization system at Hokuto Denko Company. Anhydrous chloroform was used as the solvent under N_2, and 0.1 M tetrabutylammomium hexafluorophosphate was used as a supporting electrolyte. Glassy carbon was used as the working electrode, Pt wire was used as the counter electrode, and a Ag/AgCl wire was used as the reference electrode. UV-vis absorption spectra were measured on a V-670 system (Nippon Bunko Company). ^{1}H NMR spectra were measured in $CDCl_3$ containing 1% v/v TMS on an Oxford superconducting magnet system (500 MHz). Matrix-assisted laser desorption/ionization/time-of-flight (MALDI-TOF) MS spectra were measured with dithranol as matrix on an Applied Biosystems BioSpectrometry

Workstation spectrometer (Voyager-DE STR). High-performance liquid chromatography was carried out on a system with a CBM-20A controller (Shimadzu), an LC-6AD pump (Shimadzu), an SPD-20A UV-vis detector, and a Luna Silica column (particle size: 5 μm, column length: 250 mm, and inner diameter: 21.2 mm) (Phenomenex).

Synthetic procedures

The synthetic route to the low band gap dyad molecules is shown in Fig. S1. The details of the synthetic procedures, and the spectral data from ^{1}H-NMR spectroscopy and MALDI-TOF-MS, are described below. In MALDI-TOF-MS, Na^+ was sometimes attached to the detected compounds. The following compounds were synthesized according to procedures in the literature: 3,6-dithiophene-2-yl-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (S1),[1] 17-tosyloxy-3,6,9,12,15-pentaoxaheptadecane-1-ol (S4),[2] 5-tributylstannyl-2-hexylthiophene (S9),[3] and [6,6]-phenyl-C_{61}-butyric acid (S12).[4]

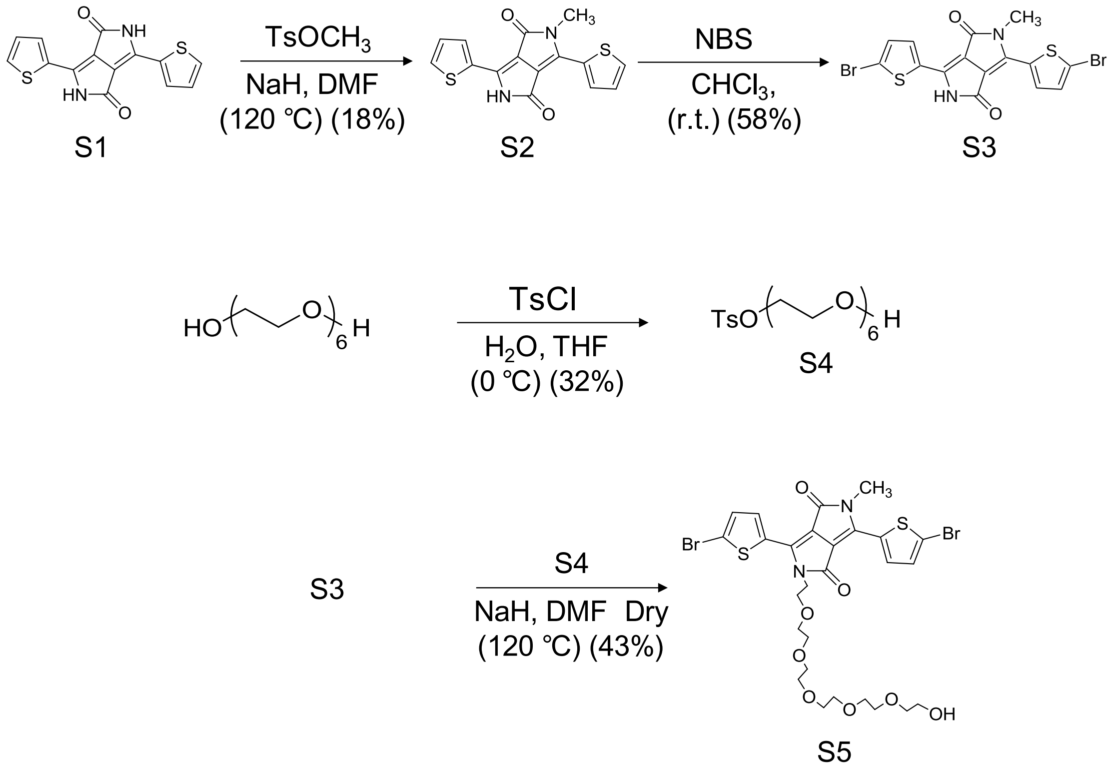

Figure S1: Synthesis route to low band gap dyad molecules

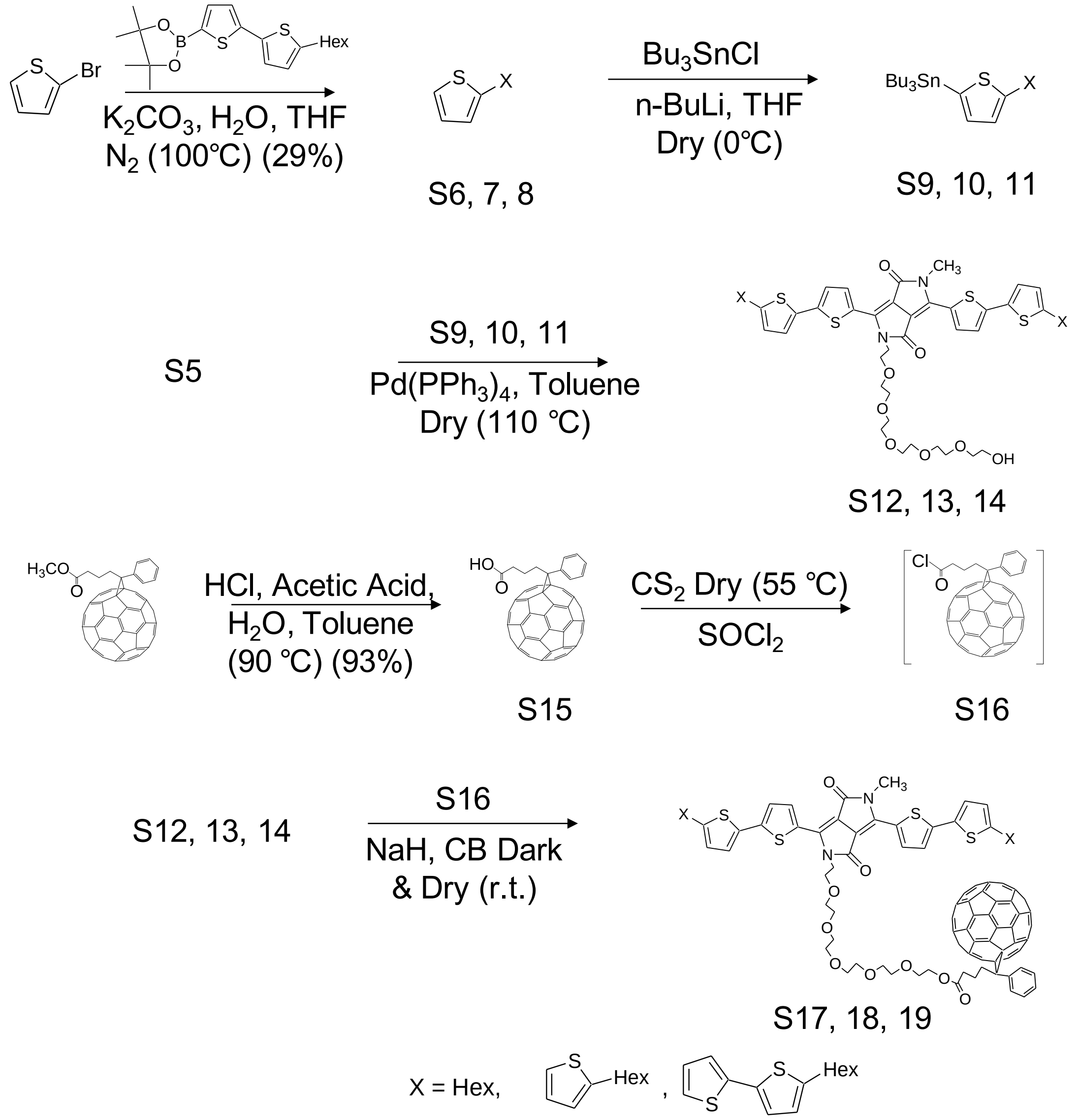

Figure S1: Synthesis route to low band gap dyad molecules

3,6-Dithiophene-2-yl-2-methyl-5-hydropyrrolo[3,4-*c*]pyrrole-1,4-dione (S2)

S1 (13.5 g, 45 mmol), NaH (oil dispersion 50~72%, 3.6 g), and DMF (800 mL) were added to a 1-L three-neck round-bottom flask under N_2. Methyl-*p*-toluenesulfonate (10.2 mL, 67.5 mmol) was mixed with DMF (100 mL), and added dropwise via a dropping funnel. The reaction mixture was stirred overnight at 120 °C and then cooled to room temperature. Acetic acid (25 mL) was added to the solution, and the mixture was stirred at room temperature for 1 h, and then poured into 4.5 L of water, and stirred at room temperature for 30 min. The solid was collected by vacuum filtration, washed with several portion of distilled water, washed with methanol, and then air dried. The crude product was extracted with $CHCl_3$ by Soxhlet extraction. The product was recrystallized from $CHCl_3$ and washed with $CHCl_3$, yielding a dark green solid (2.54 g, 18%)

^{1}H NMR (DMSO-d6, 500 MHz): δ (ppm): 11.35 (s, 1H), 8.74-8.75 (m, 1H), 8.31-8.32 (m, 1H), 8.06-8.07 (m, 1H), 7.99-8.00 (m, 1H), 7.40-7.42 (m, 1H), 7.31-7.33 (m, 1H), 3.52 (s, 3H)

3,6-Bis(5-bromothiophene-2-yl)-2-methyl-5-hydropyrrolo[3,4-*c*]pyrrole-1,4-dione (S3)

In a 500-mL round-bottom flask covered with aluminum foil, compound S2 (3.30 g, 10.5 mmol) was dissolved in 330 mL of $CHCl_3$ and stirred at room temperature for 15 min. *N*-Bromosuccinimide (4.10 g, 23 mmol) was then added, and the reaction mixture was kept at room temperature with stirring for 48 h. The reaction mixture was poured into 1 L of methanol, and the resulting suspension was filtered and washed with methanol, yielding a purple solid (2.83 g, 58%).

^{1}H NMR (DMSO-d6, 500 MHz): δ (ppm): 11.42 (s, 1H), 8.44-8.45 (d, 1H), 7.97-7.98 (d, 1H), 7.53-7.54 (d, 1H), 7.46-7.47 (d, 1H), 3.45 (s, 3H), MALDI-TOF-MS (*m/z*): 472.99 (M^+)

3,6-Bis(5-bromothiophene-2-yl)-2-methyl-5-(3,6,9,12,15-pentaoxaheptadecane-18-ol)-pyrrolo[3,4-*c*]pyrrole-1,4-dione (S5)

S3 (0.74 g, 1.6 mmol) and *t*-BuOK (0.26 g, 2.3 mmol) were added to a two-neck 100-mL round-bottom flask and vacuum dried overnight. The flask was then filled with N_2. Anhydrous DMF (25 mL) was added, and the reaction mixture was stirred for 1 h at 120 ºC. Dried S4 was added with anhydrous DMF (5 mL), and the reaction mixture was stirred overnight at 120 ºC. The solution was cooled to room temperature, and water (300 mL) and acetic acid (560 μL) were added. The reaction mixture was extracted with $CHCl_3$. The solution was purified by column chromatography using silica gel and $CHCl_3$/methanol (4:1) as eluent and then by HPLC using $CHCl_3$/methanol (100:1) as eluent. Solvent was removed in vacuo, yielding a purple solid (0.50 g, 42%)

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 8.61-8.62 (d, 1H), 8.50-8.51 (d, 1H), 7.24-7.25 (d, 1H), 7.20-7.21 (d, 1H), 4.16-4.20 (m, 2H), 3.57-3.77 (m, 22H) 3.55 (s, 3H), MALDI-TOF-MS (*m/z*): 759.11 ($[M + Na]^+$)

5-*n*-hexyl-[2,2';5',2"]-terthiophene (S8)

2-Bromothiophene (485 μL, 5.00 mmol), toluene (30 mL), 5'-***n***-hexyl-2,2'-bithiophene-5-boronic acid pinacol ester (1.88 g, 5.00 mmol) dissolved in THF (30 mL), and K_2CO_3 (2.07 g, 15.0 mmol) dissolved in water (10 mL) were added to a 100-mL two-neck round-bottom flask under N_2. The solution was degassed for 30 min, and tetrakis(triphenylphosphine)palladium(0) (57.8 mg, 0.0500 mmol) was added. The reaction mixture was then refluxed at 110 ºC for 24 h. After cooling to room temperature, the mixture was extracted with ether and purified by column chromatography using silica gel and hexane as eluent. Solvent was removed in vacuo, yielding a sticky yellow-white solid (475 mg, 29%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.20-7.21 (d, 1H), 7.15-7.16 (d, 1H), 7.05-7.06 (d, 1H), 6.97-7.02 (m, 3H), 6.68-6.69 (d, 1H), 2.78-2.81 (t, 2H), 1.64-1.72 (m, 2H), 1.35-1.41 (m, 2H), 1.30-1.33 (m, 4H), 0.88-0.91 (t, 3H)

General synthesis (S10, 11)

S7 (purchased) (1.29 mmol) or S8 (1.29 mmol) and anhydrous THF (6 mL) were added to a 100-mL two-neck round-bottom flask under N_2 and stirred for 10 min at 0 ºC. Then, *n*-butyllithium hexane solution (1.64 M, 865 μL, 1.42 mmol) was added and the reaction mixture was stirred for 30 min at 0 ºC. Tributyltin chloride (384 μL, 1.42 mmol) was added, and the reaction mixture was stirred for 2 h at room temperature. Water was added to quench the reaction. The mixture was extracted with ether and purified by column chromatography using alumina and hexane with triethylamine (5%) as eluent. The solvent was removed in vacuo, yielding a colorless transparent liquid.

***Compound S10*: 5-tributylstannyl-5'- *n*-hexyl-[2,2']-bithiophene** (yield: 60%)

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.20-7.21 (d, 1H), 7.03-7.04 (d, 1H), 6.96-6.97 (d, 1H), 6.65-6.66 (d, 1H), 2.76-2.78 (t, 2H), 1.63-1.71 (m, 2H), 1.53-1.61 (m, 6H), 1.28-1.38 (m, 12H), 1.09-1.12 (m, 6H), 0.87-0.92 (m, 12H)

***Compound S11*: 5-tributylstannyl-5"- *n*-hexyl-[2,2';5',2"]-terthiophene** (yield: 73%)

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 7.27-7.28 (d, 1H), 7.04-7.06 (m, 2H), 6.96-6.99 (m, 2H), 6.67-6.68 (d, 1H), 2.76-2.80 (t, 2H), 1.63-1.71 (m, 2H), 1.53-1.61 (m, 6H), 1.28-1.38 (m, 12H), 1.09-1.12 (m, 6H), 0.88-0.92 (m, 12H)

General synthesis (S12, 13, 14)

S5 (92 mg, 0.125 mmol), S9, 10, or 11 (0.375 mmol) and anhydrous toluene (10 mL) were added to a 50-mL two-neck round-bottom flask under N_2. The solution was degassed for 30 min, and tetrakis(triphenylphosphine)palladium(0) (10 mg, 0.013 mmol) was added. The reaction mixture was refluxed at 110 ºC for 24 h and then purified by column chromatography using silica gel and $CHCl_3$/methanol (4:1) as eluent and by HPLC using $CHCl_3$/methanol (100:1) as eluent. Solvent was removed in vacuo, yielding a blue-purple solid.

***Compound S12*: 3,6-bis-(5”-*n*-hexyl-[5,2’]bithiophene-2-yl)-2-methyl-5-(3,6,9,12,15-pentaoxaheptadecane-18-ol)-pyrrolo[3,4-*c*]pyrrole-1,4-dione** (yield: 62%)

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 8.87-8.88 (d, 1H), 8.78-8.79 (d, 1H), 7.26-7.27 (d, 1H), 7.22-7.23 (d, 1H), 6.73-6.75 (m, 2H), 4.31-4.32 (m, 2H), 3.80-3.81 (m, 2H), 3.57-3.66 (m, 23H), 2.79-2.82 (t, 4H), 1.66-1.72 (m, 4H), 1.36-1.42 (m, 4H), 1.30-1.34 (m, 8H), 0.89-0.91 (t, 6H, CH_2-$\mathit{CH_3}$), MALDI-TOF-MS (*m/z*): 934.52 ($[M + Na]^+$)

***Compound S13*: 3,6-bis-(5”-*n*-hexyl-[5,2’;5’,2”]terthiophene-2-yl)-2-methyl-5-(3,6,9,12,15-pentaoxaheptadecane-18-ol)-pyrrolo[3,4-*c*]pyrrole-1,4-dione** (yield: 62%)

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 8.88-8.89 (d, 1H), 8.80-8.81 (d, 1H), 7.30-7.31 (m, 1H), 7.27-7.28 (m, 1H), 7.23-7.24 (m, 2H), 7.02-7.05 (m, 4H), 6.70-6.71 (m, 2H), 4.31-4.32 (m, 2H), 3.80-3.81 (m, 2H), 3.57-3.66 (m, 23H), 2.79-2.82 (t, 4H), 1.66-1.72 (m, 4H), 1.36-1.42 (m, 4H), 1.30-1.34 (m, 8H), 0.89-0.91 (t, 6H), MALDI-TOF-MS (*m/z*): 1097.48 ($[M + Na]^+$)

***Compound S14*: 3,6-bis-(5”-*n*-hexyl-[5,2’;5’,2”;5”,2’”]quaterthiophene-2-yl)-2-methyl-5-(3,6,9,12,15-pentaoxaheptadecane-18-ol)-pyrrolo[3,4-*c*]pyrrole-1,4-dione** (yield: 62%)

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 8.80-8.81 (d, 1H), 8.74-8.75 (d, 1H), 7.07-7.08 (d, 1H), 7.02-7.05 (m, 3H), 6.85-7.6.91 (m, 8H), 6.62-6.63 (d, 1H), 6.59-6.60 (d, 1H), 4.31-4.32 (m, 2H), 3.78-3.79 (m, 2H), 3.53-3.70 (m, 23H), 2.73-2.76 (t, 4H), 1.64-1.67 (m, 4H), 1.30-1.42 (m, 12H), 0.89-0.91 (t, 6H), MALDI-TOF-MS (*m/z*): 1262.30 ($[M + Na]^+$)

General synthesis (S17, 18, 19)

S15 (0.0930 mmol) was added to a 50-mL two-neck round-bottom flask under N_2, and then distilled CS_2 (25 mL) and thionyl chloride (402 μL, 2.05 mmol) were added. The reaction mixture was refluxed overnight at 55 ºC. The solvent was removed, and the crude product was dried at 80 ºC for 3 h; then, anhydrous chlorobenzene (10 mL) and NaH (oil dispersion 50~72%, 10.1 mg), which had been washed with hexane, were added. The flask was covered with aluminum foil, and S12, 13, or 14 (0.0465 mmol) was added. The reaction mixture was stirred at room temperature for 48 h and then purified by column chromatography using silica gel and $CHCl_3$ as eluent and by HPLC using $CHCl_3$ as eluent. The obtained product was reprecipitated in hexane and filtered, yielding a blue solid.

Compound S17 **(4T dyad):**

3,6-bis-(5”-*n*-hexyl-[5,2’]bithiophene-2-yl)-2-methyl-5-(3,6,9,12,15,18-hexaoxa-19-carbonyl-23-phenyl[6.6]C_{61}-tricosane)-pyrrolo[3,4-*c*]pyrrole-1,4-dione (yield: 13%)

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 8.87-8.88 (d, 1H), 8.78-8.79 (d, 1H), 7.90-7.91 (d, 2H), 7.51-7.54 (m, 2H), 7.44-7.47 (m, 1H), 7.25-7.26 (d, 1H), 7.22-7.23 (d, 1H), 7.16-7.17 (m, 2H), 6.74-6.75 (m, 2H), 4.29-4.30 (m, 2H), 4.22-4.23 (m, 2H), 3.79-3.80 (m, 2H), 3.57-3.68 (m, 21H), 2.87-2.89 (m, 2H), 2.81-2.83 (t, 4H), 2.53-2.54 (m, 2H), 2.14-2.15 (m, 2H), 1.68-1.71 (m, 4H), 1.37-1.40 (m, 4H), 1.32-1.33 (m, 8H), 0.89-0.91 (t, 6H), MALDI-TOF-MS (*m/z*): 1789.72 (M^+)

Compound S18 **(6T dyad): 3,6-bis-(5”-*n*-hexyl-[5,2’;5’,2”]terthiophene-2-yl)-2-methyl-5-(3,6,9,12,15,18-hexaoxa-19-carbonyl-23-phenyl[6.6]C_{61}-tricosane)-pyrrolo[3,4-*c*]pyrrole-1,4-dione** (yield: 47%)

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 8.87-8.88 (d, 1H), 8.80-8.81 (d, 1H), 7.89-7.90 (d, 2H), 7.50-7.53 (m, 2H), 7.45-7.50 (m, 1H), 7.24-7.25 (d, 1H), 7.21-7.22 (d, 1H), 7.18-7.19 (d, 2H), 6.99-7.01 (m, 4H), 6.68-6.69 (m, 2H), 4.28-4.29 (m, 2H), 4.21-4.22 (m, 2H), 3.79-3.80 (m, 2H), 3.58-3.67 (m, 21H), 2.87-2.89 (m, 2H), 2.78-2.80 (t, 4H), 2.52-2.53 (m, 2H), 2.13-2.15 (m, 2H), 1.67-1.70 (m, 4H), 1.36-1.40 (m, 4H), 1.32-1.33 (m, 8H), 0.89-0.92 (t, 6H), MALDI-TOF-MS (*m/z*): 1954.08 (M^+)

Compound S19 **(8T dyad): 3,6-bis-(5”-*n*-hexyl-[5,2’;5’,2”;5”,2’”]quaterthiophene-2-yl)-2-methyl-5-(3,6,9,12,15,18-hexaoxa-19-carbonyl-23-phenyl[6.6]C_{61}-tricosane)-pyrrolo[3,4-*c*]pyrrole-1,4-dione** (yield: 13%)

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 8.80-8.81 (d, 1H), 8.74-8.75 (d, 1H), 7.02-7.08 (m, 4H), 6.85-6.91 (m, 8H), 6.59-6.60 (d, 1H), 6.62-6.63 (d, 1H), 4.30-4.31 (m, 2H), 4.20-4.22 (m, 2H), 3.82-3.83 (m, 2H), 3.57-3.67 (m, 21H), 2.85-2.86 (m, 2H), 2.78-2.81 (t, 4H), 2.50-2.52 (m, 2H), 2.11-2.13 (m, 2H), 1.67-1.70 (m, 4H), 1.36-1.40 (m, 4H), 1.32-1.33 (m, 8H), 0.87-0.91 (t, 6H), MALDI-TOF-MS (*m/z*): 2118.32 (M^+)

DFT calculations

Density functional theory (DFT) calculations were conducted using B3LYP/6-31G. The target compounds in the calculation were 3,6-bis-(5’’-methyl-[5,2’]bithiophene-2-yl)-2,5-methyl-pyrrolo[3,4-*c*]pyrrole-1,4-dione (D4), 3,6-bis-(5’’-methyl-[5,2’;5’,2’’]terthiophene-2-yl)-2,5-methyl-pyrrolo[3,4-*c*]pyrrole-1,4-dione (D6), and 3,6-bis-(5’’-methyl-[5,2’;5’,2’’;5’’,2’’’]quaterthiophene-2-yl)-2,5-methyl-pyrrolo[3,4-*c*]pyrrole-1,4-dione (D8). The calculated energies of the HOMO and LUMO in the ground-state optimized geometry, and the band gaps between them, are summarized in Table S1 for 4T, 6T, and 8T. From D4 to D8, a continuous decrease in band gap was observed due to the increase in conjugation length, and the decrease in the LUMO level was larger than the increase in the HOMO level. The optimized structures of the molecular orbital are shown in Fig. S2.

Material	HOMO/eV	LUMO/eV	Band Gap/eV
D4	-4.66	-2.59	2.07
D6	-4.62	-2.69	1.93
D8	-4.61	-2.74	1.87

Table S1: Summary of DFT calculations

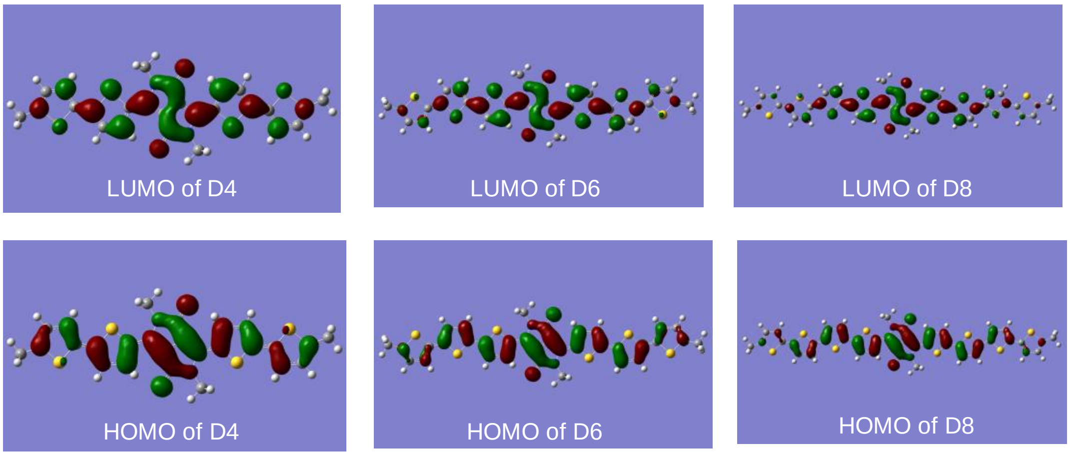

Figure S2: Optimized structures of molecular orbitals

Photovoltaic devices preparation and measurement

With the dyads, photovoltaic devices were prepared in a structure of ITO/PEDOT–PSS/Ca/Al. An indium tin oxide (ITO)-coated glass substrate (sheet resistance: 10 Ω sq^{-1}, Geomatech, Japan) was cleaned by ultrasonication in detergent, water, acetone, 2-propanol, and water. After the substrate was dried, PEDOT–PSS (H. C. Stark) was spin-coated (4000 rpm) onto ITO. The film was dried at 150 ºC under N_2 for 20 min. After cooling the substrate, $CHCl_3$ solution of dyad (4T: 20 mg/mL; 4T: 20 mg/mL; 8T: 15 mg/mL) was spin-coated (2500 rpm). Finally, Ca (20 nm) and Al (40 nm) electrodes were evaporated onto the organic layer under high vacuum (6×10^{-4} Pa). After Ca and Al evaporation, devices with 6T and 8T dyads were thermally annealed at 110 °C for 5 min under N_2 atmosphere.

I-*V* characteristics of the devices were measured under simulated solar light illumination (AM 1.5, 100 mW cm^{-2}) from a 150 W xenon lamp (PEC-L11, Peccell Technologies, Inc., Japan). The light intensity was calibrated with a standard silicon solar cell (BS520, Bunkoh-Keiki, Japan). The active area of the devices was defined to be 0.06 cm^2 by a photomask. The external quantum efficiency (EQE) of the devices was measured on a Hypermonolight SM-250F system (Bunkoh-Keiki, Japan).

AFM images and film thickness

Atomic force microscopy (AFM) images were obtained on a Digital Instrumental Nanoscope 31 operated in tapping mode. Surface images of the optimized devices with 4T, 6T, and 8T dyads are shown in Figure S3. There were no obvious differences in film morphology between the three dyad devices. The film surfaces were rather flat and smooth.

As measured by surface profilometry (Dektak 6M, ULVAC, Japan), 4T, 6T, and 8T films were 90, 100, and 70 nm in thickness, respectively.

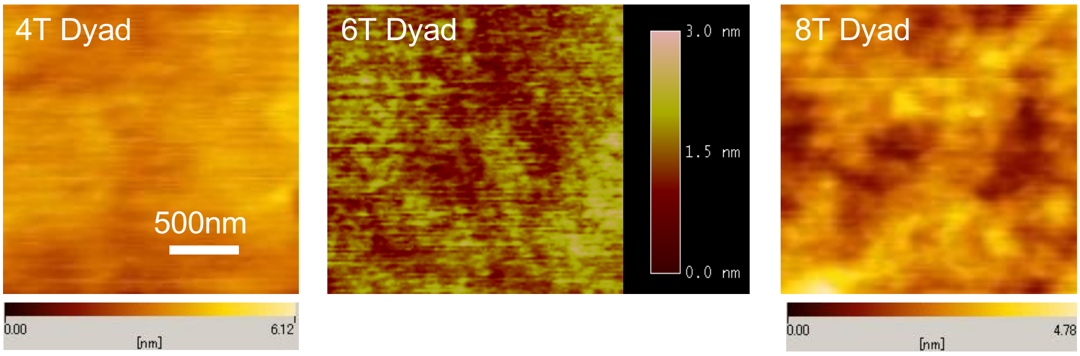

Figure S3: AFM images

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