

Alkyl-Functionalized Organic Dyes for Efficient Molecular Photovoltaics

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Supporting Information

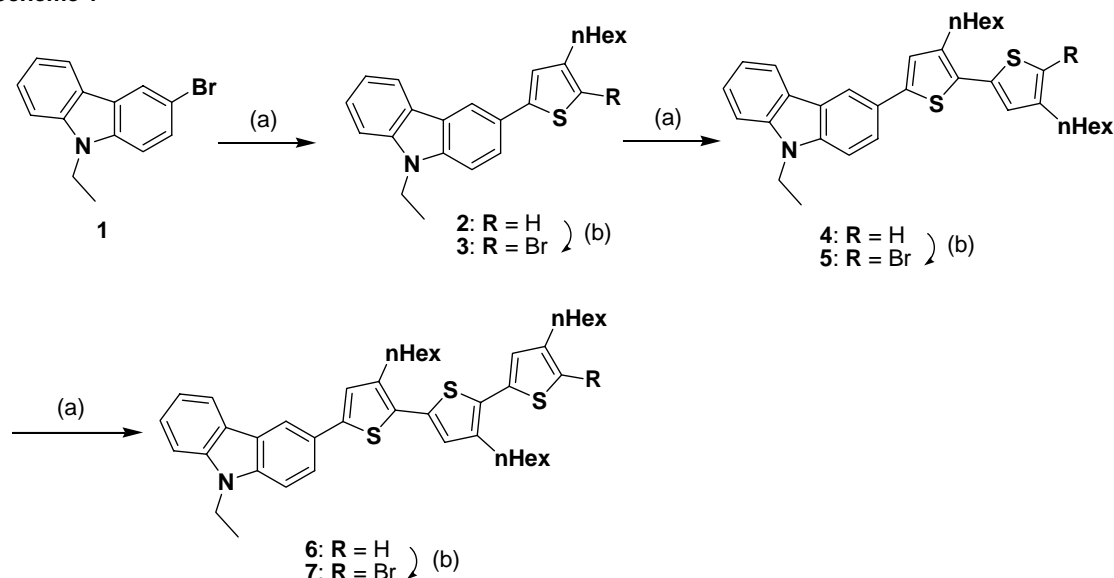
Experimental Section

General Procedure. ¹H NMR spectra were recorded on a Bruker Avance400 (400 MHz). ¹³C NMR spectra were recorded on a Bruker Avance400 (100 MHz). Chemical shifts are denoted in δ-unit (ppm) relative to CDCl₃, THF-*d*₈ or DMSO-*d*₆. The splitting patterns are designated as follows: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet) and br (broad). Elemental analyses were measured by a CE Instruments EA1110 automatic elemental analyzer. Column chromatography was performed on silica gel (Kanto, Silica Gel 60N, spherical, 40-50μm). Most of organic compound was finally purified by the preparative HPLC (YRU-880 detector from SHIMAMURA Tec.) on silica gel (pre-packed column, CPS-HS-221-05 or CPS-223L-1 from KUSANO KAGAKU) The solvents were distilled and dried, if necessary, by standard methods. Reagents and starting materials were used as obtained from Aldrich, Wako, Kanto Chemical, TCI, Merck. Absorption spectra were measured with a SHIMADZU UV-3101PC. The oxidation potential of the dye adsorbed on a TiO₂ film was measured by differential pulse voltammetry using a dye-coated TiO₂ electrode as the working electrode, a Pt counter electrode, and a Ag/Ag⁺

reference electrode (0.01 M AgNO₃ and 0.1 M tetrabutylammonium perchlorate in acetonitrile (AN)) in 0.1 M LiClO₄ / AN. The measurements were performed with an electrochemical analyzer (ALS, model 610B). The potential was calibrated against the ferrocene redox couple.

Synthesis of Dyes, MK-1 and MK-2

Scheme 1



(a) 5,5'-dimethyl-2-(4-*n*-hexylthiophen-2-yl)-1,3,2-dioxaborinane, Pd(PPh₃)₄, Na₂CO₃aq /DME (b) NBS /THF.

9-Ethyl-3-(4-*n*-hexylthiophen-2-yl)-9*H*-carbazole **2**. The mixture of 9-Ethyl-3-bromo-9*H*-carbazole **1** (550 mg, 2.01 mmol), 4-*n*-hexylthiophene-2-boronic acid ester (1120 mg, 4.01 mmol), tetrakis(triphenylphosphine)palladium (116 mg, 0.101 mmol) and 0.5 mL of 10% aqueous solution of Na₂CO₃ in dimethoxyethane (20 mL) was refluxed for 24 h. After cooling H₂O was added, and the reaction mixture was extracted with EtOAc three times. The combined organic layer was washed with H₂O and brine, dried over MgSO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography (hexane/EtOAc = 50/1) and successive HPLC on silica gel (hexane/EtOAc = 50/1) to obtain bithiophene **2** (337 mg, 0.93 mmol, 46%) as a slightly yellow oil, ¹H NMR (400 MHz, CDCl₃) δ 8.30 (1H, d, *J* = 1.8 Hz), 8.14 (1H, br d, *J* = 7.8 Hz), 7.72 (1H, dd, *J* = 8.5, 1.8 Hz), 7.49 (1H, ddd, *J* = 8.2, 7.0, 1.2 Hz), 7.41 (1H, br d, *J* = 8.2 Hz), 7.40 (1H, d, *J* = 8.5 Hz), 7.25 (1H, ddd, *J* = 7.8, 7.0, 1.0 Hz), 7.19 (1H, d, *J* = 1.2 Hz), 6.85 (1H, d, *J* = 1.2 Hz), 4.37 (2H, q, *J* = 7.2 Hz), 2.65 (2H, br t, *J* = 7.8 Hz), 1.73-1.65 (2H, m), 1.45 (3H, t, *J* = 7.2 Hz), 1.42-1.32 (6H, m), 0.91 (3H, t, *J* = 7.0 Hz), ¹³C NMR (100 MHz, CDCl₃) δ 145.3, 144.2, 140.3, 139.3, 125.9, 125.8, 124.1,

123.4, 123.2, 122.9, 120.5, 118.9, 118.2, 117.6, 108.58, 108.56, 37.5, 31.7, 30.7, 30.4, 29.1, 22.6, 14.1, 13.8. Anal. Calcd for C₂₄H₂₇NS: C, 79.73; H, 7.53; N, 3.87, S, 8.87. Found. C, 79.55; H, 7.44; N, 3.80, S, 9.03.

9-Ehtyl-3-(5-bromo-4-*n*-hexylthiophen-2-yl)-9*H*-carbazole 3. To the solution of 9-ethyl-3-(4-*n*-hexylthiophen-2-yl)-9*H*-carbazole **2** (199 mg, 0.55 mmol) in THF (10 mL) was added *N*-bromosuccinimide (103 mg, 0.57 mmol). The reaction mixture was stirred at room temperature for 30 min, and quenched with 10% aqueous solution of Na₂CO₃ and extracted with EtOAc three times. The combined organic layer was washed with H₂O and brine, dried over MgSO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography (hexane/EtOAc = 50/1) and successive HPLC on silica gel (hexane/EtOAc = 50/1) to obtain bromide **3** (169 mg, 0.38 mmol, 70%) as a colorless oil, ¹H NMR (400 MHz, CDCl₃) δ 8.23 (1H, d, *J* = 1.8 Hz), 8.13 (1H, br d, *J* = 7.8 Hz), 7.62 (1H, dd, *J* = 8.5, 1.8 Hz), 7.45 (1H, ddd, *J* = 8.3, 7.1, 1.2 Hz), 7.42 (1H, br d, *J* = 8.3 Hz), 7.38 (1H, d, *J* = 8.5 Hz), 7.26 (1H, ddd, *J* = 7.8, 7.1, 1.0 Hz), 7.05 (1H, s), 4.37 (2H, q, *J* = 7.2 Hz), 2.61 (2H, br t, *J* = 7.7 Hz), 1.71-1.63 (2H, m), 1.45 (3H, t, *J* = 7.2 Hz), 1.42-1.33 (6H, m), 0.93 (3H, t, *J* = 7.0 Hz), ¹³C NMR (100 MHz, CDCl₃) δ 145.0, 142.9, 140.2, 139.4, 125.9, 125.0, 123.5, 123.2, 122.7, 122.7, 122.5, 119.0, 117.2, 108.63, 108.56, 106.4, 37.4, 31.6, 29.7, 29.7, 29.0, 22.6, 14.1, 13.7. Anal. Calcd for C₂₄H₂₆BrNS: C, 65.45; H, 5.95; N, 3.18, S, 7.28. Found. C, 65.13; H, 5.94; N, 3.11, S, 7.20.

9-Ethyl-3-(3,4'-di-*n*-hexyl-[2,2']bithiophen-5-yl)-9*H*-carbazole 4. The Suzuki-coupling reaction of bromide **3** (169 mg, 0.38 mmol) with 4-*n*-hexylthiophene-2-boronic acid ester (215 mg, 0.77 mmol) existing Pd(PPh₃)₄ as a catalyst in DME (5 mL) was carried out in a similar manner to that of **2**. After cooling H₂O was added, and the reaction mixture was extracted with EtOAc three times. The combined organic layer was washed with H₂O and brine, dried over MgSO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography (hexane/EtOAc = 50/1) and successive HPLC on silica gel (hexane/EtOAc = 50/1) to obtain bithiophene **4** (173 mg, 0.33 mmol, 85%) as a slightly yellow oil, ¹H NMR (400 MHz, CDCl₃) δ 8.31 (1H, d, *J* = 1.8 Hz), 8.15 (1H, br d, *J* = 7.7 Hz), 7.72 (1H, dd, *J* = 8.5, 1.8 Hz), 7.50 (1H, ddd, *J* = 8.2, 7.0, 1.2 Hz), 7.42 (1H, br d, *J* = 8.2 Hz), 7.40 (1H, d, *J* = 8.5 Hz), 7.26 (1H, ddd, *J* = 7.7, 7.0, 1.0 Hz), 7.20 (1H, s), 7.01 (1H, d, *J* = 1.5 Hz), 6.90 (1H, d, *J* = 1.5 Hz), 4.37 (2H, q, *J* = 7.2 Hz), 2.81 (2H, br t, *J* = 7.8 Hz), 2.64 (2H, br t, *J* = 7.8 Hz), 1.77-1.63 (4H, m), 1.45 (3H, t, *J* = 7.2 Hz), 1.42-1.31 (12H, m), 0.92 (6H, t, *J* = 7.0 Hz), ¹³C NMR (100 MHz, CDCl₃) δ 143.5, 143.0, 140.3, 140.2, 139.4, 136.2, 129.2, 126.7, 125.9, 125.3, 124.8, 123.8, 123.3, 122.8, 120.5, 119.4, 119.0, 117.4, 108.6, 108.6, 37.5, 31.7, 31.7, 30.6, 30.5, 30.4, 29.5, 29.3, 29.0, 22.64, 22.62, 14.1, 14.1, 13.7. Anal. Calcd for C₃₄H₄₁NS₂: C, 77.37; H, 7.83; N, 2.65,

S, 12.15. Found. C, 77.96; H, 8.22; N, 2.61, S, 11.81.

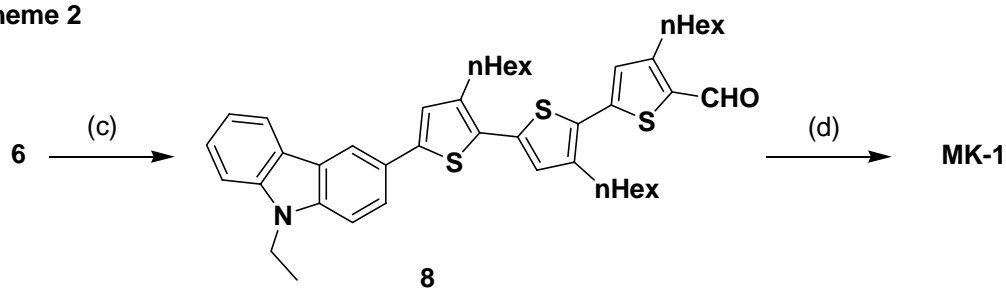
9-Ethyl-3-(5'-bromo-3,4'-di-*n*-hexyl-[2,2']bithiophen-5-yl)-9*H*-carbazole 5. The bromination of 9-ethyl-3-(3,4'-di-*n*-hexyl-[2,2']bithiophen-5-yl)-9*H*-carbazole **4** (173 mg, 0.33 mmol) with *N*-bromosuccinimide (61 mg, 0.34 mmol) in THF (5 mL) was carried out in a similar manner to that of **3**. The crude product was purified by column chromatography (hexane/EtOAc = 50/1) and successive HPLC on silica gel (hexane/EtOAc = 50/1) to obtain bromide **5** (193 mg, 0.32 mmol, 97%) as a slightly yellow oil, ¹H NMR (400 MHz, CDCl₃) δ 8.29 (1H, d, *J* = 1.8 Hz), 8.13 (1H, br d, *J* = 7.6 Hz), 7.70 (1H, dd, *J* = 8.5, 1.8 Hz), 7.49 (1H, ddd, *J* = 8.2, 7.0, 1.2 Hz), 7.42 (1H, br d, *J* = 8.2 Hz), 7.40 (1H, d, *J* = 8.5 Hz), 7.26 (1H, ddd, *J* = 7.6, 7.0, 1.0 Hz), 7.17 (1H, s), 6.85 (1H, s), 4.38 (2H, q, *J* = 7.2 Hz), 2.75 (2H, br t, *J* = 7.8 Hz), 2.58 (2H, br t, *J* = 7.8 Hz), 1.74-1.60 (4H, m), 1.45 (3H, t, *J* = 7.2 Hz), 1.42-1.31 (12H, m), 0.91 (6H, t, *J* = 7.0 Hz), ¹³C NMR (100 MHz, CDCl₃) δ 143.5, 142.3, 140.7, 140.2, 139.4, 136.1, 128.1, 126.0, 125.9, 125.0, 124.7, 123.7, 123.2, 122.7, 120.4, 119.0, 117.3, 108.6, 108.5, 107.9, 37.4, 31.7, 31.6, 30.6, 29.6, 29.5, 29.5, 29.3, 28.9, 22.63, 22.60, 14.1, 14.1, 13.7. Anal. Calcd for C₃₄H₄₀BrNS₂: C, 67.31; H, 6.65; N, 2.31, S, 10.57. Found. C, 67.57; H, 6.83; N, 2.33, S, 10.56.

9-Ethyl-3-(3,4',4''-tri-*n*-hexyl-[2,2',5',2'']terthiophen-5-yl)-9*H*-carbazole 6. The Suzuki-coupling reaction of bromide **5** (193 mg, 0.32 mmol) with 4-*n*-hexylthiophene-2-boronic acid ester (178 mg, 0.64 mmol) existing Pd(PPh₃)₄ as a catalyst in DME (5 mL) was carried out in a similar manner to that of **2**. The crude product was purified by column chromatography (hexane/EtOAc = 50/1) and successive HPLC on silica gel (hexane/EtOAc = 50/1) to obtain terthiophene **6** (214 mg, 0.31 mmol, 97%) as a yellow oil, ¹H NMR (400 MHz, CDCl₃) δ 8.31 (1H, d, *J* = 1.8 Hz), 8.14 (1H, br d, *J* = 7.5 Hz), 7.72 (1H, dd, *J* = 8.5, 1.8 Hz), 7.49 (1H, ddd, *J* = 8.2, 7.0, 1.2 Hz), 7.43-7.39 (2H, m), 7.26 (1H, ddd, *J* = 7.5, 7.0, 1.0 Hz), 7.19 (1H, s), 7.00 (1H, s), 6.98 (1H, d, *J* = 1.5 Hz), 6.90 (1H, d, *J* = 1.5 Hz), 4.38 (2H, q, *J* = 7.2 Hz), 2.83 (2H, br t, *J* = 7.8 Hz), 2.77 (2H, br t, *J* = 7.8 Hz), 2.62 (2H, br t, *J* = 7.8 Hz), 1.78-1.62 (6H, m), 1.46 (3H, t, *J* = 7.2 Hz), 1.43-1.31 (18H, m), 0.93-0.88 (9H, m), ¹³C NMR (100 MHz, CDCl₃) δ 143.5, 143.0, 140.33, 140.26, 139.41, 139.36, 135.6, 134.2, 130.4, 128.8, 127.9, 126.9, 125.9, 125.2, 124.9, 123.7, 123.3, 122.8, 120.4, 119.7, 119.0, 117.3, 108.6, 108.5, 37.4, 31.70, 31.67, 31.67, 30.9, 30.6, 30.5, 30.4, 30.3, 29.7, 29.34, 29.31, 29.25, 29.0, 22.64, 22.64, 22.62, 14.1, 14.1, 14.1, 13.7. Anal. Calcd for C₄₄H₅₅NS₃: C, 76.14; H, 7.99; N, 2.02, S, 13.86. Found. C, 76.70; H, 8.59; N, 1.95, S, 13.42.

9-Ethyl-3-(5''-bromo-3,4',4''-tri-*n*-hexyl-[2,2',5',2'']terthiophen-5-yl)-9*H*-carbazole 7. The bromination of terthiophene **6** (214 mg, 0.31 mmol) with *N*-bromosuccinimide (57 mg, 0.32

mmol) in THF (5 mL) was carried out in a similar manner to that of **3**. The crude product was purified by column chromatography (hexane/EtOAc = 50/1) and successive HPLC on silica gel (hexane/EtOAc = 50/1) to obtain bromide **7** (208 mg, 0.27 mmol, 87%) as a yellow oil, ^1H NMR (400 MHz, CDCl_3) δ 8.31 (1H, br s), 8.14 (1H, br d, $J = 7.7$ Hz), 7.72 (1H, br d, $J = 8.5$ Hz), 7.49 (1H, ddd, $J = 8.2, 7.1, 1.1$ Hz), 7.43-7.39 (2H, m), 7.26 (1H, ddd, $J = 7.7, 7.1, 1.0$ Hz), 7.18 (1H, s), 7.00 (1H, s), 6.86 (1H, s), 4.38 (2H, q, $J = 7.2$ Hz), 2.82 (2H, br t, $J = 7.8$ Hz), 2.73 (2H, br t, $J = 7.8$ Hz), 2.58 (2H, br t, $J = 7.8$ Hz), 1.78-1.60 (6H, m), 1.46 (3H, t, $J = 7.2$ Hz), 1.43-1.31 (18H, m), 0.93-0.89 (9H, m), ^{13}C NMR (100 MHz, CDCl_3) δ 143.3, 142.4, 140.6, 140.3, 140.0, 139.4, 135.5, 134.7, 130.8, 128.5, 127.9, 126.4, 125.9, 125.2, 124.9, 123.7, 123.3, 122.8, 120.5, 119.0, 117.4, 108.64, 108.59, 108.3, 37.5, 31.71, 31.66, 31.61, 30.6, 30.5, 29.7, 29.6, 29.5, 29.33, 29.29, 29.2, 28.9, 22.7, 22.63, 22.60, 14.13, 14.09, 14.09, 13.8. Anal. Calcd for $\text{C}_{44}\text{H}_{54}\text{BrNS}_3$: C, 68.37; H, 7.04; N, 1.81, S, 12.44. Found. C, 68.79; H, 7.29; N, 1.96, S, 12.22.

Scheme 2



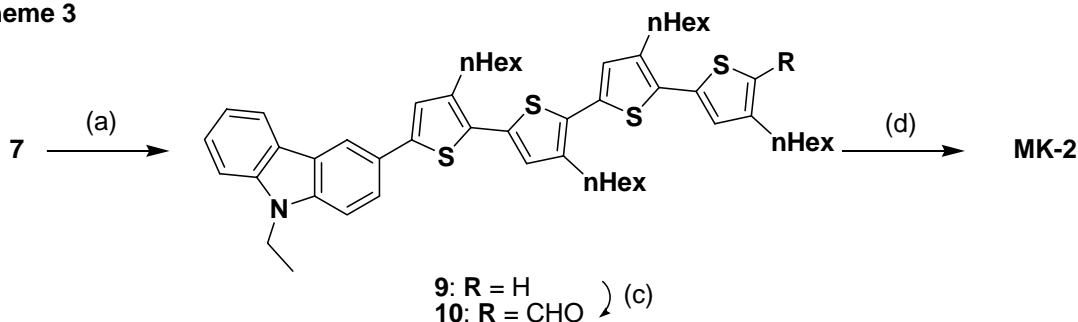
(c) POCl_3 -DMF /DMF (d) cyanoacetic acid, piperidine /toluene-AcCN

5''-(9-Ethyl-9H-carbazol-3-yl)-3',3'',4-tri-*n*-hexyl-[2,2',5',2'']terthiophene-5-carbaldehyde **8.** To a cold solution of terthiophene **6** (50 mg, 0.072 mmol) in dry DMF (1 mL) at 0 °C was added a Vilsmeier reagent, which was prepared with 0.05 mL of POCl_3 in DMF (0.2 mL). The mixture was stirred at 70 °C for 7 h, and quenched with 10% aqueous solution of NaOAc (30 mL) after cooling, and extracted with EtOAc three times. The combined organic layer was washed with H_2O and brine, dried over MgSO_4 , and evaporated under reduced pressure. The crude product was purified by column chromatography (hexane/EtOAc = 10/1) and successive HPLC on silica gel (hexane/EtOAc = 10/1) to obtain aldehyde **8** (33 mg, 0.046 mmol, 63%) as an orange oil, ^1H NMR (400 MHz, CDCl_3) δ 10.02 (1H, s), 8.31 (1H, d, $J = 1.8$ Hz), 8.14 (1H, br d, $J = 7.9$ Hz), 7.72 (1H, dd, $J = 8.5, 1.8$ Hz), 7.50 (1H, ddd, $J = 8.2, 7.1, 1.1$ Hz), 7.41 (1H, d, $J = 8.2$ Hz), 7.39 (1H, d, $J = 8.5$ Hz), 7.27 (1H, ddd, $J = 7.9, 7.1, 0.9$ Hz), 7.21 (1H, s), 7.06 (1H, s), 7.04 (1H, s), 4.36 (2H, q, $J = 7.2$ Hz), 2.95 (2H, br t, $J = 7.8$ Hz), 2.84 (4H, br t, $J = 7.8$ Hz), 1.80-1.68 (6H, m), 1.45 (3H, t, $J = 7.2$ Hz), 1.42-1.32 (18H, m), 0.95-0.90 (9H, m), ^{13}C NMR (100 MHz, CDCl_3) δ 181.6, 153.4, 145.3, 143.9, 142.5, 141.3, 140.4, 139.6, 136.6, 136.0, 128.9,

128.5, 128.1, 127.9, 126.0, 125.1, 125.0, 123.8, 123.4, 122.8, 120.5, 119.1, 117.5, 108.73, 108.67, 37.6, 31.69, 31.66, 31.5, 31.4, 30.5, 30.2, 29.83, 29.78, 29.32, 29.26, 29.0, 28.4, 22.63, 22.60, 22.5, 14.11, 14.08, 14.0, 13.8. Anal. Calcd for C₄₅H₅₅NOS₃: C, 74.85; H, 7.68; N, 1.94, S, 13.32. Found. C, 74.57; H, 7.90; N, 1.94, S, 12.87.

2-Cyano-3-[5''-(9-Ethyl-9H-carbazol-3-yl)-3',3'',4-tri-*n*-hexyl-[2,2',5',2'']terthiophen-5-yl] acrylic acid, MK-1. A mixture of aldehyde **8** (33 mg, 0.046 mmol) with cyanoacetic acid (8 mg, 0.092 mmol) in dry acetonitrile (0.5 mL) and dry toluene (1 mL) was refluxed in the presence of piperidine (0.5 mL) for 20 h. After cooling the mixture was diluted with dichloromethane, and the organic layer was washed with aqueous HCl (1N), H₂O and brine, dried over Na₂SO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography (CHCl₃ → CHCl₃/EtOH = 10/1) to obtain a dye **MK-1** (22 mg, 0.028 mmol, 61%) as dark-red solids, ¹H NMR (400 MHz, THF-*d*₈) δ 8.40 (1H, s), 8.39 (1H, br s), 8.14 (1H, br d, *J* = 7.7 Hz), 7.72 (1H, d, *J* = 8.0 Hz), 7.51-7.44 (2H, m), 7.42 (1H, br dd, *J* = 8.0, 7.1 Hz), 7.32 (1H, s), 7.21 (1H, s), 7.19 (1H, br dd, *J* = 7.7, 7.1 Hz), 7.12 (1H, s), 4.42 (2H, q, *J* = 7.2 Hz), 2.92-2.81 (6H, m), 1.80-1.65 (6H, m), 1.51-1.28 (18H, m), 1.39 (3H, t, *J* = 7.2 Hz), 0.94-0.90 (9H, m), ¹³C NMR (100 MHz, THF-*d*₈) δ 164.7, 155.4, 145.2, 144.8, 143.8, 143.4, 142.2, 141.5, 140.7, 137.9, 130.6, 129.8, 129.5, 128.8, 128.1, 126.8, 126.0, 125.9, 124.4, 124.4, 123.9, 121.2, 119.9, 118.0, 117.0, 109.8, 109.6, 98.0, 38.2, 32.7, 32.7, 32.6, 32.2, 31.37, 31.36, 30.9, 30.7, 30.3, 30.2, 29.9, 29.5, 23.6, 23.54, 23.47, 14.5, 14.5, 14.4, 14.1. Anal. Calcd for C₄₈H₅₆N₂O₂S₃: C, 73.05; H, 7.15; N, 3.55, S, 12.19. Found. C, 72.89; H, 7.46; N, 3.49, S, 11.65.

Scheme 3



9-Ethyl-3-(3,4',4'',4'''-tetra-*n*-hexyl-[2,2',5',2'',5'',2''']quaterthiophen-5-yl)-9H-carbazole **9.** The Suzuki-coupling reaction of bromide **7** (208 mg, 0.27 mmol) with 4-*n*-hexylthiophene-2-boronic acid ester (151 mg, 0.54 mmol) was carried out in a similar manner to that of **2**. The crude product was purified by column chromatography (hexane/EtOAc = 50/1) and successive HPLC on silica gel (hexane/EtOAc = 50/1) to obtain quaterthiophene **9** (231 mg,

0.27 mmol, 99%) as an orange oil, ^1H NMR (400 MHz, CDCl_3) δ 8.32 (1H, d, J = 1.8 Hz), 8.15 (1H, br d, J = 7.5 Hz), 7.73 (1H, dd, J = 8.5, 1.8 Hz), 7.50 (1H, ddd, J = 8.2, 7.0, 1.2 Hz), 7.43-7.39 (2H, m), 7.27 (1H, ddd, J = 7.5, 7.0, 1.0 Hz), 7.21 (1H, s), 7.02 (1H, s), 7.00 (1H, d, J = 1.3 Hz), 6.99 (1H, s), 6.91 (1H, d, J = 1.3 Hz), 4.38 (2H, q, J = 7.2 Hz), 2.87-2.75 (6H, m), 2.63 (2H, br t, J = 7.8 Hz), 1.80-1.62 (8H, m), 1.46 (3H, t, J = 7.2 Hz), 1.44-1.30 (24H, m), 0.95-0.89 (12H, m), ^{13}C NMR (100 MHz, CDCl_3) δ 143.6, 143.1, 140.4, 140.3, 139.6, 139.5, 139.4, 135.5, 134.3, 133.6, 130.8, 129.9, 128.8, 128.2, 128.1, 127.0, 125.9, 125.2, 125.0, 123.7, 123.3, 122.8, 120.5, 119.9, 119.0, 117.4, 108.65, 108.59, 37.5, 31.72, 31.69, 31.68, 31.68, 31.66, 30.6, 30.54, 30.49, 30.47, 30.4, 29.7, 29.5, 29.35, 29.27, 29.24, 29.0, 22.7, 22.64, 22.63, 22.61, 14.14, 14.11, 14.09, 14.09, 14.09, 13.8. Anal. Calcd for $\text{C}_{54}\text{H}_{69}\text{NS}_4$: C, 75.38; H, 8.08; N, 1.63, S, 14.91. Found. C, 75.90; H, 8.19; N, 1.69, S, 14.45.

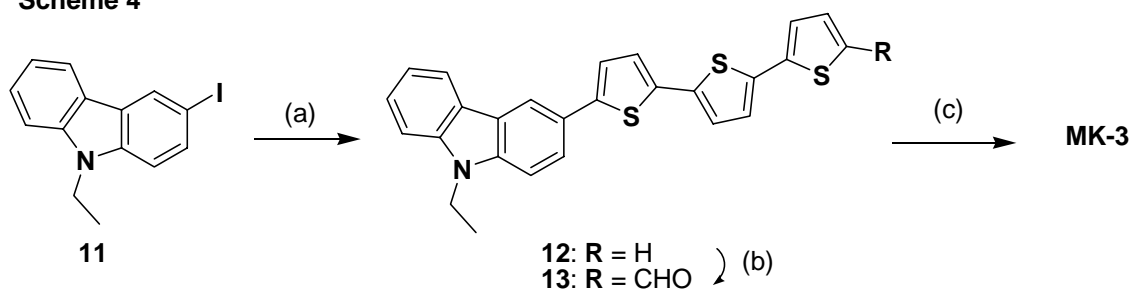
5'''-(9-Ethyl-9H-carbazol-3-yl)-3',3'',3''',4-tetra-*n*-hexyl-[2,2',5',2'',5'',2''']quaterthiophene-5-carbaldehyde **10.** To a cold solution of quaterthiophene **9** (231 mg, 0.27 mmol) in dry DMF (1 mL) at 0 °C was added a Vilsmeier reagent, which was prepared with 0.1 mL of POCl_3 in DMF (0.5 mL). The mixture was stirred at 70 °C for 7 h, and quenched with 10% aqueous solution of NaOAc (30 mL) after cooling, and extracted with EtOAc three times. The combined organic layer was washed with H_2O and brine, dried over MgSO_4 , and evaporated under reduced pressure. The crude product was purified by column chromatography (hexane/EtOAc = 15/1) and successive HPLC on silica gel (hexane/EtOAc = 10/1) to obtain aldehyde **10** (197 mg, 0.22 mmol, 83%) as a dark-orange oil, ^1H NMR (400 MHz, CDCl_3) δ 10.02 (1H, s), 8.31 (1H, d, J = 1.8 Hz), 8.14 (1H, br d, J = 7.9 Hz), 7.72 (1H, dd, J = 8.5, 1.8 Hz), 7.50 (1H, ddd, J = 8.2, 7.1, 1.1 Hz), 7.43-7.39 (2H, m), 7.27 (1H, ddd, J = 7.9, 7.1, 0.9 Hz), 7.21 (1H, s), 7.06 (1H, s), 7.02 (1H, s), 7.01 (1H, s), 4.38 (2H, q, J = 7.2 Hz), 2.95 (2H, br t, J = 7.8 Hz), 2.86-2.79 (6H, m), 1.80-1.68 (8H, m), 1.46 (3H, t, J = 7.2 Hz), 1.42-1.29 (24H, m), 0.95-0.88 (12H, m), ^{13}C NMR (100 MHz, CDCl_3) δ 181.4, 153.2, 145.1, 143.3, 142.4, 140.6, 140.4, 140.3, 139.4, 136.0, 135.9, 135.1, 129.15, 129.08, 128.44, 128.42, 128.0, 127.7, 125.9, 125.0, 124.9, 123.6, 123.2, 122.7, 120.4, 119.0, 117.3, 108.6, 108.5, 37.5, 31.66, 31.63, 31.60, 31.5, 31.3, 30.4, 30.3, 30.1, 29.8, 29.7, 29.5, 29.3, 29.23, 29.21, 28.9, 28.3, 22.62, 22.59, 22.56, 22.5, 14.09, 14.06, 14.02, 14.00, 13.7. Anal. Calcd for $\text{C}_{55}\text{H}_{69}\text{NOS}_4$: C, 74.36; H, 7.83; N, 1.58, S, 14.44. Found. C, 74.53; H, 8.20; N, 1.59, S, 14.16.

2-Cyano-3-[5'''-(9-Ethyl-9H-carbazol-3-yl)-3',3'',3''',4-tetra-*n*-hexyl-[2,2',5',2'',5'',2''']quaterthiophenyl-5-yl]acrylic acid **MK-2.** A mixture of aldehyde **10** (197 mg, 0.22 mmol) with cyanoacetic acid (38 mg, 0.44 mmol) in a mixed solvent of dry acetonitrile (1 mL) and dry toluene (2 mL) was refluxed in the presence of piperidine (1 mL) for 20 h. After cooling the

mixture was diluted with chloroform, and the organic layer was washed with aqueous HCl (1N), H₂O and brine, dried over Na₂SO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography (CHCl₃ → CHCl₃/ethanol = 10/1) to obtain a dye **MK-2** (182 mg, 0.19 mmol, 86%) as dark-red solids, ¹H NMR (400 MHz, THF-*d*₈) δ 8.41 (1H, s), 8.40 (1H, br s), 8.15 (1H, d, *J* = 7.7 Hz), 7.73 (1H, br d, *J* = 8.5 Hz), 7.52-7.48 (2H, m), 7.43 (1H, ddd, *J* = 8.0, 7.2, 0.8 Hz), 7.32 (1H, s), 7.24 (1H, s), 7.17 (1H, br t, *J* = 7.2 Hz), 7.13 (1H, s), 7.09 (1H, s), 4.43 (2H, q, *J* = 7.2 Hz), 2.93-2.82 (8H, m), 1.81-1.63 (8H, m), 1.51-1.28 (24H, m), 1.41 (3H, t, *J* = 7.2 Hz), 0.94-0.90 (12H, m), ¹³C NMR (100 MHz, THF-*d*₈) δ 164.6, 155.3, 144.7, 144.6, 143.8, 143.4, 141.6, 141.53, 141.50, 140.6, 137.1, 136.3, 130.7, 130.3, 130.1, 130.0, 129.1, 129.0, 128.2, 126.8, 126.0, 125.9, 124.40, 124.38, 123.9, 121.2, 119.8, 117.9, 117.0, 109.8, 109.6, 98.1, 38.2, 32.73, 32.68, 32.5, 32.2, 31.5, 31.4, 31.3, 30.8, 30.6, 30.4, 30.3, 30.22, 30.20, 30.1, 29.9, 29.5, 29.1, 23.58, 23.55, 23.54, 23.47, 14.53, 14.51, 14.50, 14.4, 14.1. Anal. Calcd for C₅₈H₇₀N₂O₂S₄: C, 72.91; H, 7.38; N, 2.93, S, 13.42. Found. C, 73.19; H, 7.42; N, 2.98, S, 13.42.

Synthesis of the dye, MK-3

Scheme 4



(a) 2-([2,2',5',2'']terthiophen-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, Pd(PPh₃)₄, Na₂CO₃ aq /DME
 (b) POCl₃-DMF /DMF (f) cyanoacetic acid, piperidine /CHCl₃-AcCN

9-Ethyl-3-([2,2',5',2'']terthiophen-5-yl)-9H-carbazole 12. The Suzuki-coupling reaction of iodide **11** (86 mg, 0.27 mmol) with terthiophene-2-boronic acid ester (150 mg, 0.40 mmol) and Pd(PPh₃)₄ (15 mg, 0.013 mmol) in DME (3 mL) was carried out in the presence of 0.2 mL of aqueous Na₂CO₃ at 60 °C for 10 h. After cooling the reaction mixture was diluted with chloroform and the organic layer was washed with H₂O and brine, and dried over MgSO₄. The solvent was evaporated under the reduced pressure. The crude product was purified by column chromatography (hexane/dichloromethane = 2/1) and successive HPLC on silica gel (hexane/EtOAc = 10/1) to obtain terthiophene **12** (66 mg, 0.15 mmol, 56%) as yellow solids, ¹H NMR (300 MHz, CDCl₃) δ 8.32 (1H, d, *J* = 1.7 Hz), 8.15 (1H, d, *J* = 7.7 Hz), 7.73 (1H, dd, *J* =

8.5, 1.7 Hz), 7.50 (1H, ddd, $J = 8.2, 7.1, 1.1$ Hz), 7.43 (1H, d, $J = 8.2$ Hz), 7.40 (1H, d, $J = 8.5$ Hz), 7.30-7.17 (5H, m), 7.11 (2H, dd, $J = 4.1$ Hz), 7.04 (1H, dd, $J = 5.2, 3.6$ Hz), 4.38 (2H, q, $J = 7.1$ Hz), 1.46 (3H, t, $J = 7.1$ Hz), ^{13}C NMR (75 MHz, CDCl_3) δ 144.9, 140.4, 139.6, 137.3, 136.6, 135.7, 135.0, 127.9, 126.1, 125.2, 125.1, 124.6, 124.38, 124.36, 123.9, 123.7, 123.6, 123.4, 122.8, 122.6, 120.6, 119.1, 117.6, 108.8, 108.7, 37.7, 13.8. Anal. Calcd for $\text{C}_{26}\text{H}_{19}\text{NS}_3$: C, 70.71; H, 4.34; N, 3.17, S, 21.78. Found. C, 70.54; H, 4.31; N, 3.15, S, 21.66.

5''-(9-Ethyl-9H-carbazol-3-yl)-[2,2',5',2'']terthiophenyl-5-carbaldehyde 13. To a cold solution of terthiophene **12** (66 mg, 0.15 mmol) in dry DMF (1 mL) at 0 °C was added a Vilsmeier reagent, which was prepared with 0.1 mL of POCl_3 in DMF (0.5 mL). The mixture was stirred at 70 °C for 4 h, and quenched with 10% aqueous solution of NaOAc (30 mL) after cooling, and extracted with dichloromethane three times. The combined organic layer was washed with H_2O and brine, dried over MgSO_4 , and evaporated under reduced pressure. The crude product was purified by column chromatography (hexane/EtOAc = 3/1) and recrystallization from hexane-chloroform to obtain aldehyde **13** (50 mg, 0.11 mmol, 71%) as orange needles, ^1H NMR (300 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$) δ 9.82 (1H, s), 8.30 (1H, br s), 8.14 (1H, br d, $J = 7.7$ Hz), 7.73 (1H, br d, $J = 8.3$ Hz), 7.69 (1H, d, $J = 3.8$ Hz), 7.54-7.42 (3H, m), 7.32-7.17 (6H, m), 4.36 (2H, br s), 1.45 (3H, t, $J = 7.1$ Hz), ^{13}C NMR (75 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$) δ 182.5, 146.8, 145.6, 141.0, 140.2, 139.4, 137.8, 134.0, 133.7, 127.0, 126.1, 125.5, 124.6, 124.1, 124.0, 123.8, 123.0, 122.7, 122.3, 120.4, 119.1, 117.4, 108.9, 108.7, 37.6, 13.8. Anal. Calcd for $\text{C}_{27}\text{H}_{19}\text{NOS}_3$: C, 69.05; H, 4.08, N, 2.98, S, 20.48. Found. C, 68.89; H, 4.09; N, 2.99, S, 20.32.

2-Cyano-3-[5''-(9-Ethyl-9H-carbazol-3-yl)-[2,2',5',2'']terthiophenyl-5-yl]acrylic acid MK-3. A mixture of aldehyde **13** (40 mg, 0.085 mmol) with cyanoacetic acid (14 mg, 0.17 mmol) in dry acetonitrile (2 mL) and chloroform (2 mL) was refluxed in the presence of piperidine (0.5 mL) for 4 h. After cooling the precipitates was filtrated, and the crude product was purified by recrystallization from chloroform-ethanol to obtain a dye **MK-3** (40 mg, 0.075 mmol, 87%) as dark-red solids, ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 8.50 (1H, s), 8.25 (1H, d, $J = 7.7$ Hz), 8.12 (1H, s), 7.78 (1H, dd, $J = 8.5, 1.7$ Hz), 7.72 (1H, d, $J = 3.8$ Hz), 7.66 (1H, d, $J = 8.8$ Hz), 7.62 (1H, d, $J = 8.5$ Hz), 7.53 (1H, d, $J = 3.8$ Hz), 7.50-7.45 (3H, m), 7.44 (1H, d, $J = 3.8$ Hz), 7.37 (1H, d, $J = 3.8$ Hz), 7.23 (1H, t, $J = 7.4$ Hz), 4.45 (2H, q, $J = 7.1$ Hz), 1.32 (3H, t, $J = 7.1$ Hz), ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) δ 163.2, 144.9, 141.4, 140.9, 140.3, 139.5, 137.6, 137.3, 135.9, 133.9, 133.6, 127.1, 126.4, 126.2, 125.0, 124.7, 124.4, 123.8, 123.7, 122.9, 122.3, 121.0, 119.3, 119.1, 117.5, 110.0, 109.6, 37.3, 13.9. Anal. Calcd for $\text{C}_{30}\text{H}_{20}\text{N}_2\text{O}_2\text{S}_3$: C, 67.14; H, 3.76; N, 5.22, S, 17.92. Found. C, 66.76; H, 3.51; N, 5.06, S, 17.92.

Preparation of Dye-sensitized TiO₂ Electrodes

Nanocrystalline TiO₂ photoelectrodes were prepared by a screen printing technique. TiO₂ nanoparticles and an organic TiO₂ paste for screen printing were prepared by methods reported in a previous paper (Wang, Z.-S.; Kawauchi, H.; Kashima, T.; Arakawa, H. *Coord. Chem. Rev.* **2004**, 248, 1381–1389). The TiO₂ paste consisted of TiO₂ nanoparticles (ca. 20 nm), ethyl cellulose as a binder, and α -terpineol as a solvent. The TiO₂ paste, which is commercially available (SOLARONIX, T), was also used. The TiO₂ paste was printed on a glass substrate coated with transparent conducting oxide (TCO, F-doped SnO₂) and subsequently sintered at 500 °C in air for 1 h. The thickness of the TiO₂ thin films, measured with an Alpha-Step 300 profiler (TENCOR INSTRUMENTS), was ca. 6.5 μ m. We also used thicker TiO₂ film electrodes (ca. 30 μ m) including a scattering layer, which consisted of large TiO₂ particles (av. 100 nm). The MK dyes were dissolved at a concentration of 0.3 mM in toluene (KANTO CHEMICAL). The TiO₂ films were immersed in the dye solutions and then kept at 25 °C for more than 12 h to allow the dye to adsorb to the TiO₂ surface.

Photovoltaic Measurements of the Solar Cells.

Each photovoltaic cell consisted of a dye-sensitized TiO₂ electrode, a Pt counter electrode sputtered (ca. 200 nm) onto TCO-coated glass plate, a film spacer (30 μ m thickness) and an organic electrolyte, was prepared. The apparent surface area of the TiO₂ film electrode was ca. 0.25 cm². The electrolyte was 0.6 M 1,2-dimethyl-3-n-propylimidazolium iodide (DMPIImI) + 0.1 M LiI + 0.05 M I₂ + 0.5 M 4-*tert*-butylpyridine (TBP) in AN. Reagent-grade LiI (WAKO CHEMICAL) and I₂ (WAKO) were used for the electrolyte. DMPIImI was purchased from TOMIYAMA PURE CHEMICAL INDUSTRIES Ltd.

The photovoltaic performance of the solar cells was measured with a source meter (ADVANTEST, R6246). We employed an AM 1.5G solar simulator (WACOM, WXS-80C-3 and YAMASHITA DENSO Co., YSS-150A) as the light source. The incident light intensity was calibrated by using a standard solar cell composed of a crystalline silicon solar cell and an IR-cut

off filter (SCHOTT, KG-5), giving the photoresponse range of amorphous silicon solar cell (produced and calibrated by Japan Quality Assurance Organization). We used an aperture mask (0.2354 cm^2) attached onto the top of the cells in the photovoltaic measurements. Action spectra of the monochromatic incident photon-to-current conversion efficiency (IPCE) of the solar cell were measured with a CEP-99W system (BUNKOH-KEIKI Co., Ltd.).

All data (J_{sc} , V_{oc} , FF , and η) are described in Table S1, and IV and Dark current spectra of DSSCs based on dyes, **MK-1**, **MK-2** and **MK-3** are shown in Figure S1. The each absorbed photon to current conversion efficiency (APCE) value of DSSCs with dyes, **MK-1**, **MK-2** and **MK-3** was calculated from the value of IPCE and absorbance at 500 nm based on the following equation, respectively, depicted in Table S2. Figure S2 shows action spectra of DSSCs based on dyes, **MK-1**, **MK-2** and **MK-3**. Each condition of the measurements are displayed in each caption, respectively.

$$LHE = 1 - 10^{-A}$$

$$APCE = \frac{IPCE}{LHE}$$

LHE: Light Harvesting Efficiency

A: absorbance

Dye	$J_{sc} / \text{mA cm}^{-2}$	V_{oc} / V	FF	$\eta (\%)$
N719^a	10.1	0.79	0.77	6.1
	10.5	0.79	0.76	6.3
MK-1^a	10.9	0.72	0.71	5.6
	11.1	0.71	0.71	5.6
MK-2^a	12.4	0.72	0.71	6.3
	12.3	0.72	0.71	6.3
MK-3^a	10.2	0.64	0.72	4.7
	10.8	0.63	0.71	4.8
MK-2^b	14.0	0.74	0.74	7.7
N719^c	16.1	0.76	0.74	9.1

Table S1. Photovoltaic performance of the DSSCs based on MK dyes. Incident light: AM 1.5G

(100 mW cm⁻²) with a mask (0.2354 cm²) and without an anti-reflection film. Electrolyte: 0.6 M DMPIImI + 0.1 M LiI + 0.05 M I₂ + 0.5 M TBP in acetonitrile. TiO₂ electrode: ca 0.25 cm² and film thickness ^a 6.5 μm, ^b 30 μm and ^c 16 μm.

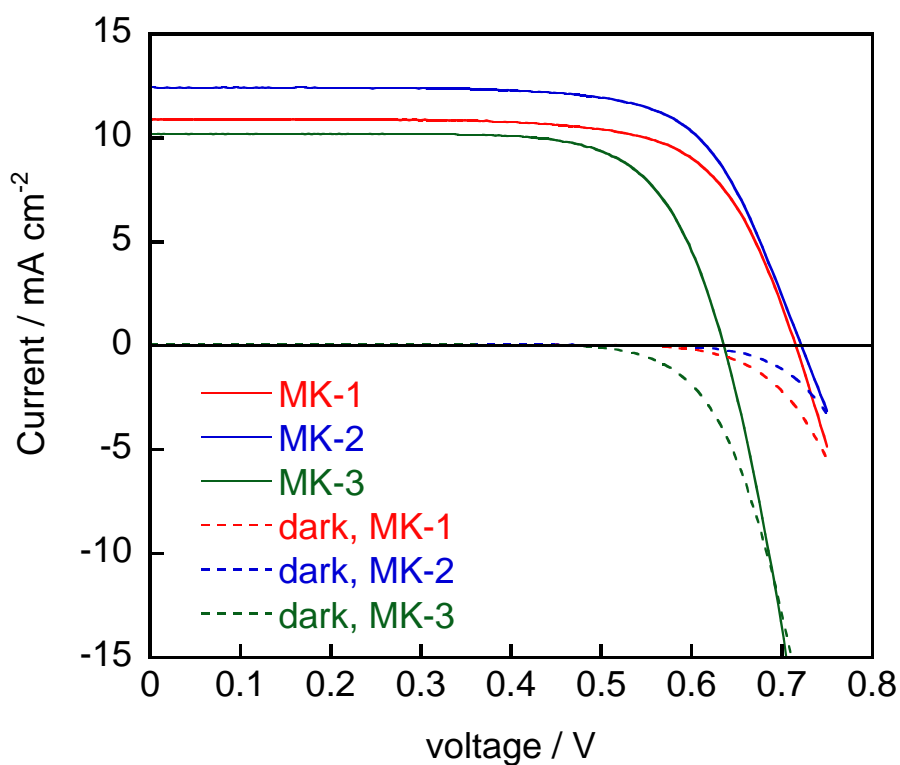


Figure S1. IV and Dark curves of DSSCs based on **MK-1**, **MK-2** and **MK-3**. Incident light: AM 1.5G (100 mW cm⁻²) with a mask (0.2354 cm²) and without an anti-reflection film. Electrolyte: 0.6 M DMPIImI + 0.1 M LiI + 0.05 M I₂ + 0.5 M TBP in acetonitrile. TiO₂ electrode: ca 0.25 cm² and film thickness 6.5 μm.

	IPCE	LHE	APCE
MK-1	0.67	0.94	0.71
MK-2	0.68	0.95	0.72
MK-3	0.59	0.96	0.61

Table S2. The value of APCEs of DSSCs bease on dyes, **MK-1**, **MK-2** and **MK-3**, respectively.

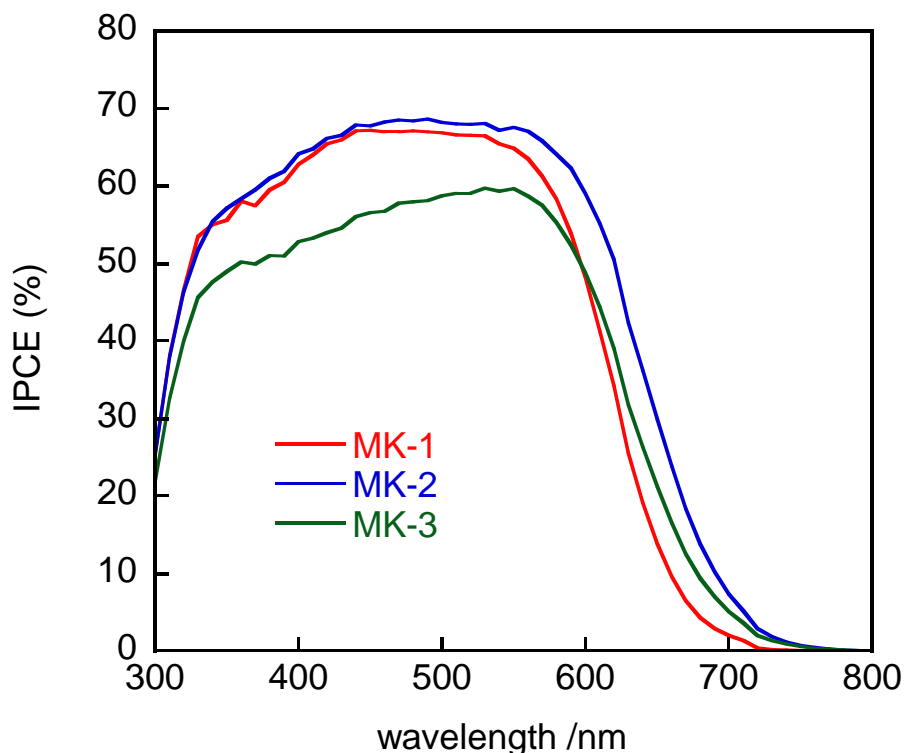


Figure S2. Action spectra of monochromatic incident photon-to-current conversion efficiency (IPCE) for DSSCs based on dyes, **MK-1**, **MK-2** and **MK-3**. These spectra were measured with a mask (0.2354 cm^2) and without an anti-reflection film. Electrolyte: 0.6 M DMPIImI + 0.1 M LiI + 0.05 M I_2 + 0.5 M TBP in acetonitrile. TiO_2 electrode: ca 0.25 cm^2 and film thickness $6.5 \text{ }\mu\text{m}$.

Transient Photovoltage Measurements

Electron lifetimes in the DSSCs were obtained by stepped light-induced transient measurements of photovoltage. For the measurements, TiO_2 electrodes were prepared from Solaronix-T by sintering at $550 \text{ }^\circ\text{C}$ for 30 min in air. Experimental procedure of the measurements is described in detail elsewhere (Nakade et al. *Langmuir* **2005**, 21, 10803-10807). In short, DSSCs were irradiated by a diode laser (Coherent, Lablaser, $\lambda = 635 \text{ nm}$) and the decay of open circuit voltage, caused by step-wise decrease of a small fraction of the laser intensity, was measured. The measurement was repeated with various initial laser intensities, giving different electron density in the DSSCs. Electron lifetime (τ) was obtained by fitting an exponential function, $\exp(-t/\tau)$, to

the voltage decay. The electron density used to plot Fig. 3 was estimated by the charge extraction method introduced by Peter and co-workers (Duffy et al. *Electrochemistry Communications* **2000**, 2, 658-662). Our experimental setup is described in a paper (Nakade et al. *Journal of Physical Chemistry B*, **2005**, 109, 3480-3487). In short, irradiated laser light was turned off simultaneously with the switch from open circuit to short circuit conditions. Then, the induced transient current was recorded, and then the amount of the charges in the DSSC at open circuit conditions was obtained by numerical integration of the current transient. The control of the laser intensity and circuit conditions was performed by LabVIEW with a DAQ card (National Instruments).