Hexylthiophene-Functionalized Carbazole Dyes for Efficient Molecular Photovoltaics: Tuning of Solar-Cell Performance by Structural Modification

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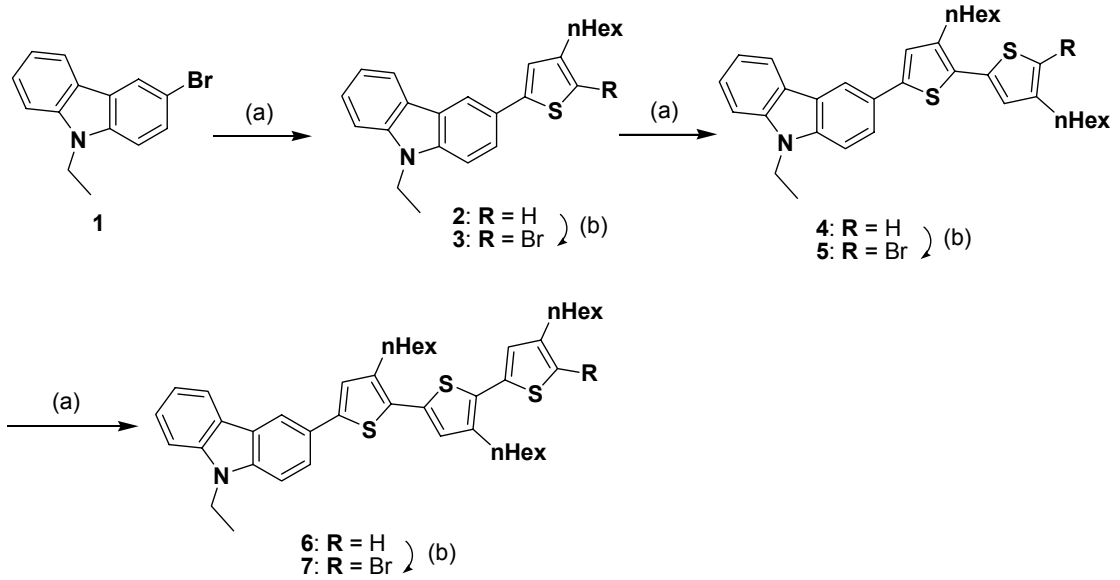
Supporting Information

Syntheses of the MK Dyes

General Procedure. ^{1}H NMR spectra were recorded on a Varian VXR-300 (300 MHz) and Burker Avance 400 (400 MHz). ^{13}C NMR spectra were recorded on a Varian VXR-300 (75 MHz) and Burker Avance 400 (100 MHz). Chemical shifts are denoted in δ-unit (ppm) relative to $CDCl_3$, 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 compounds were 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.

Synthesis of Dyes, MK-1 and MK-2

Scheme 1



(a) 5,5'-dimethyl-2-(4-*n*-hexylthiophen-2-yl)-1,3,2-dioxaborinane, $Pd(PPh_3)_4$, Na_2CO_3aq /DME (b) NBS /THF.

9-Ehtyl-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 mml), 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 Na_2CO_3 in dimethoxyethane (20 mL) was refluxed for 24 h. After cooling H_2O was added, and the reaction mixture was 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 = 50/1) and successive HPLC on silica gel (hexane/EtOAc = 50/1) to obtain bithiophene **2** (337 mg, 0.93 mml, 46%) as a slightly yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) 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), ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{24}H_{27}NS$: 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-ehtyl-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 Na_2CO_3 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 = 50/1) and successive HPLC on silica gel (hexane/EtOAc = 50/1) to obtain bromide **3** (169 mg, 0.38 mml, 70%) as a colorless oil, ^{1}H NMR (400

MHz, $CDCl_3$) 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), ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{24}H_{26}BrNS$: 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 $Pd(PPh_3)_4$ as a catalyst in DME (5 mL) was carried out in a smilar manner to that of **2**. After cooling H_2O was added, and the reaction mixture was 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 = 50/1) and successive HPLC on silica gel (hexane/EtOAc = 50/1) to obtain bithiophene **4** (173 mg, 0.33 mml, 85%) as a slightly yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) 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), ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{34}H_{41}NS_2$: 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.

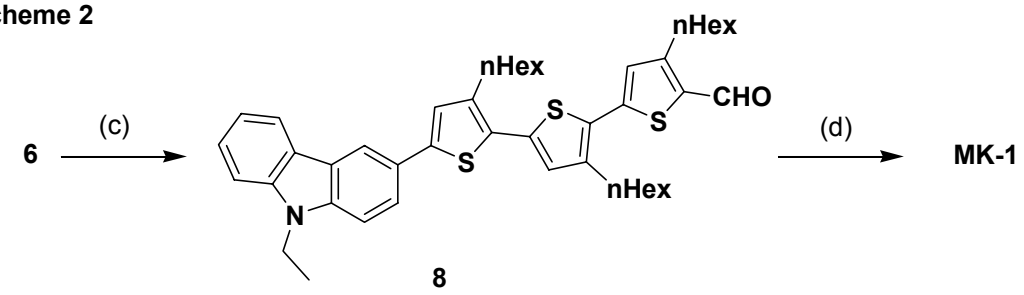
9-Ethyl-3-(5'-bromo-3,4'-di-*n*-hexyl-[2,2']bithiophen-5-yl)-9*H*-carbazole 5. The bromination of 9-ethyl-3-(3,4'-di-*n*-hexyl-[2,2']bithiophen-5-yl)-9*H*-carbazole **4** (173 mg, 0.33 mmol) with *N*-bromosuccinimide (61 mg, 0.34 mmol) in THF (5 mL) was carried out in a similar manner to that of **3**. 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 mml, 97%) as a slightly yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) 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), ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{34}H_{40}BrNS_2$: 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 $Pd(PPh_3)_4$ as a catalyst in DME (5 mL) was carried out in a smilar 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, ^{1}H NMR (400 MHz, $CDCl_3$) 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), ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{44}H_{55}NS_3$: 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 mml, 87%) as a yellow oil, ^{1}H 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 $C_{44}H_{54}BrNS_3$: 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



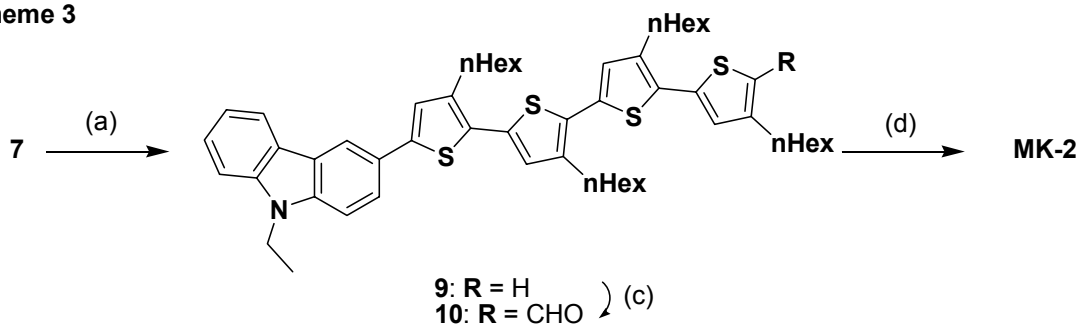
(c) $POCl_3$-DMF /DMF (d) cyanoacetic acid, piperidine /toluene-AcCN

5''-(9-Ethyl-9*H*-carbazol-3-yl)-3',3'',4-tri-*n*-hexyl-[2,2',5',2'']terthiophene-5-carbaldehy-de 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 mml, 63%) as an orange oil, ^{1}H 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 $C_{45}H_{55}NOS_3$: 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-9*H*-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), H_2O and brine, dried over Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by column chromatography ($CHCl_3$ → $CHCl_3$/EtOH = 10/1) to obtain a dye **MK-1** (22 mg, 0.028 mmol, 61%) as dark-red solids, ^{1}H 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), ^{13}C 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 $C_{48}H_{56}N_2O_2S_3$: 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)-9*H*-carbazo-le 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 smilar 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, ^{1}H 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 $C_{54}H_{69}NS_4$: 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.

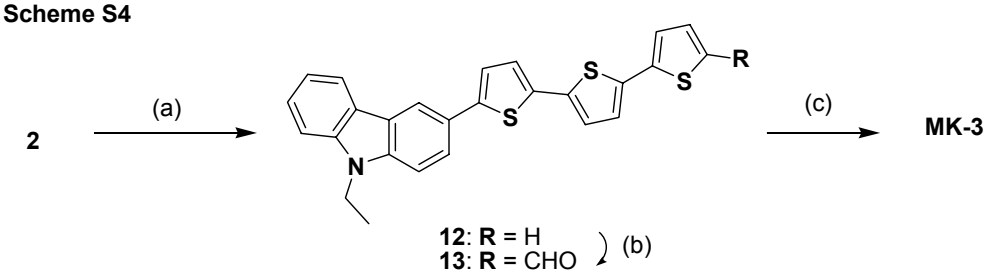
5'''-(9-Ethyl-9*H*-carbazol-3-yl)-3',3'',3''',4-tetra-*n*-hexyl-[2,2',5',2'',5'',2''']quaterthiop-hene-5-car baldehyde 10. To a cold solution of quaterthiophene **9** (231 mg, 0.27 mmol) in dry DMF (1 mL) at 0 °C was added a Vilsmeier reagent, which was prepared with 0.1 mL of $POCl_3$ in DMF (0.5 mL). 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 mml, 83%) as a dark-orange oil, ^{1}H 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 $C_{55}H_{69}NOS_4$: 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-9*H*-carbazol-3-yl)-3',3'',3''',4-tetra-*n*-hexyl-[2,2',5',2'',5'',2''']-quaterthio phenyl-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), H_2O and brine, dried over Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by column chromatography ($CHCl_3$ → $CHCl_3$/ethanol = 10/1) to obtain a dye **MK-2** (182 mg, 0.19 mmol, 86%) as dark-red solids, ^{1}H 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), ^{13}C 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 $C_{58}H_{70}N_2O_2S_4$: 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 S4



(a) [2,2',5',2'']terthiophene-5-boronic acid neopentyl ester, $Pd(PPh_3)_4$, Na_2CO_3aq /DME (b) $POCl_3$-DMF /DMF (f) cyanoacetic acid, piperidine /$CHCl_3$-AcCN

9-Ethyl-3-([2,2',5',2'']terthiophen-5-yl)-9*H*-carbazole 12. A Suzuki-coupling reaction of iodide **2** (86 mg, 0.27 mmol) with terthiophene-2-boronic acid neopentyl ester (150 mg, 0.40 mmol) and $Pd(PPh_3)_4$ (15 mg, 0.013 mmol) in DME (3 mL) was carried out in the presence of 0.2 mL of aqueous Na_2CO_3 at 60 °C for 10 h. After cooling the reaction mixture was diluted with chloroform and the organic layer was washed with H_2O and brine, and dried over $MgSO_4$. 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 a yellow solid, ^{1}H NMR (300 MHz, $CDCl_3$) 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 $C_{26}H_{19}NS_3$: 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.

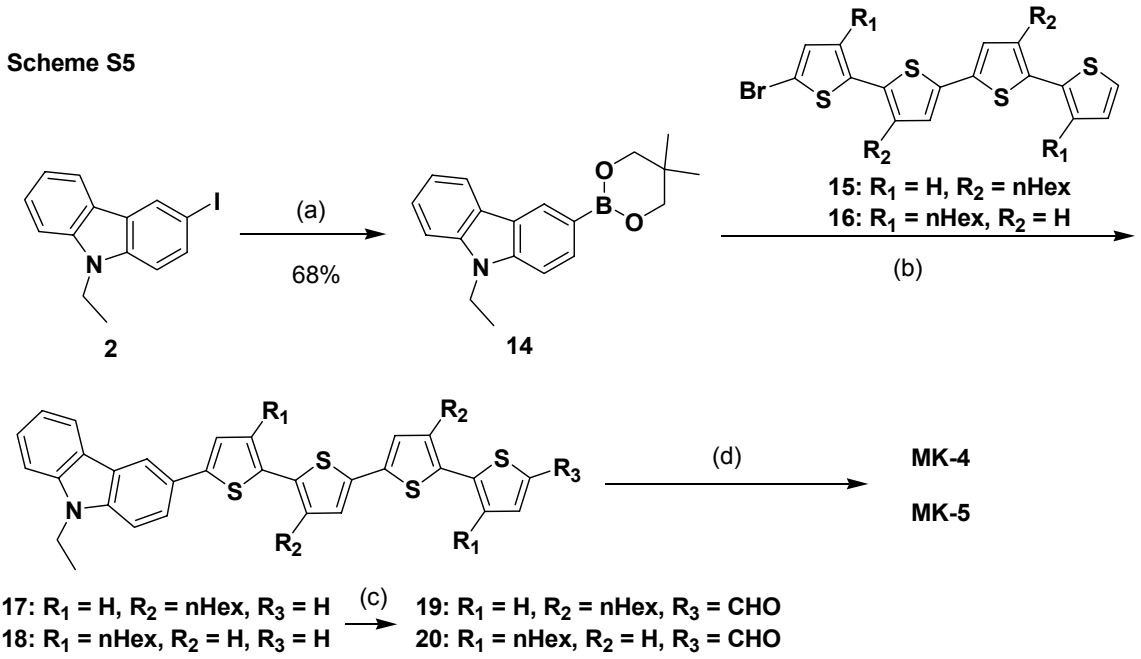
5''-(9-Ethyl-9*H*-carbazol-3-yl)-[2,2',5',2'']terthiophenyl-5-carbaldehyde 13. To a cold solution of terthiophene **12** (66 mg, 0.15 mmol) in dry DMF (1 mL) at 0 °C was added a Vilsmeier reagent, which was prepared with 0.1 mL of $POCl_3$ in DMF (0.5 mL). The mixture was stirred at 70 °C for 4 h, and 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, ^{1}H NMR (300 MHz, $C_2D_2Cl_4$) 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, $C_2D_2Cl_4$) 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 $C_{27}H_{19}NOS_3$: 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-9*H*-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 recrystalization from chloroform-ethanol to obtain a dye **MK-3** (40 mg, 0.075 mmol, 87%) as a dark-red solid, ^{1}H NMR (300 MHz, 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, 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 $C_{30}H_{20}N_2O_2S_3$: 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.

Syntheses of the dyes, MK-4 and MK-5

Scheme S5



(a) (i) *n*-BuLi /THF (ii) $B(OMe)_3$ (iii) 2,2-dimethyl-1,3-propandiol (b) $Pd(PPh_3)_4$, Na_2CO_3aq /DME (c) $POCl_3$-DMF /DMF (d) cyanoacetic acid, piperidine /AcCN-toluene

9-Ethylcarbazole-3-boronic acid neopentyl ester 14. To a cold solution of 3-iodo-9-ethylcarbazole (540 mg, 1.68 mmol) in THF (20 mL) at –78 °C was dropwised a 1.6 M solution (1.26 mL) of n-butyllithium in n-hexane. After stirred for 1h at –78 °C, trimethylborate (0.38 mL, 2.02 mmol) was added. The reaction mixture was allowed to warm up to room temperature. After warmed 2,2-dimethyl-1,3-propandiol (184 mg, 1.76 mmol) was added, and the mixture was stirred overnight at room temperature. The reaction mixture was

quenched by addition of water, 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 = 20/1), and the obtained product was used for the next coupling reaction without a further purification.

9-Ethyl-3-(3',4''-di-*n*-hexyl-[2,2',5',2'',5'',2''']quaterthiophen-5-yl)-9*H*-carbazole 17. A Suzuki-coupling reaction of bromide **15** (183 mg, 0.32 mmol) with boronic acid neopentyl ester **14** (130 mg, 0.42 mmol) was carried out in a similar manner to that of **5**. 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 **17** (197 mg, 0.29 mmol, 90%) as an orange solid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (1H, d, *J* = 1.7 Hz), 8.18 (1H, br d, *J* = 7.7 Hz), 7.75 (1H, dd, *J* = 8.5, 1.7 Hz), 7.52 (1H, ddd, *J* = 8.2, 7.1, 1.1 Hz), 7.43 (1H, d, *J* = 8.5 Hz), 7.39 (1H, d, *J* = 8.5 Hz), 7.33 (1H, dd, *J* = 5.2, 1.1 Hz), 7.31 (1H, d, *J* = 3.8 Hz), 7.29 (1H, m), 7.18 (1H, dd, *J* = 3.6, 1.1 Hz), 7.16 (1H, d, *J* = 3.8 Hz), 7.10 (1H, dd, *J* = 5.2, 3.6 Hz), 7.058 (1H, s), 7.055 (1H, s), 4.36 (2H, q, *J* = 7.1 Hz), 2.85 (2H, t, *J* = 7.7 Hz), 2.78 (2H, t, *J* = 7.7 Hz), 1.81-1.65 (4H, m), 1.46 (3H, t, *J* = 7.1 Hz), 1.42-1.31 (12H, m), 0.96 (3H, t, *J* = 6.7 Hz), 0.95 (3H, t, *J* = 6.7 Hz), ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.5, 140.4, 140.3, 140.0, 139.5, 136.0, 135.0, 134.4, 134.1, 130.1, 129.4, 127.4, 126.6, 126.5, 126.2, 126.0, 125.7, 125.24, 125.20, 123.9, 123.4, 122.8, 122.3, 120.6, 119.1, 117.6, 108.7, 108.6, 37.6, 31.7, 31.6, 30.48, 30.46, 29.5, 29.4, 29.3, 29.2, 22.62, 22.61, 14.12, 14.09, 13.8. Anal. Calcd for $C_{42}H_{45}NS_4$: C, 72.89; H, 6.55; N, 2.02; S, 18.53. Found: C, 72.72; H, 6.34; N, 2.02; S, 18.41.

9-Ethyl-3-(3,3'''-di-*n*-hexyl-[2,2',5',2'',5'',2''']quaterthiophen-5-yl)-9*H*-carbazole 18. A Suzuki-coupling reaction of bromide **16** (226 mg, 0.39 mmol) with boronic acid neopentyl ester **14** (180 mg, 0.59 mmol) was carried out in a similar manner to that of **5**. 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 **18** (166 mg, 0.24 mmol, 61%) as an orange oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (1H, br s), 8.15 (1H, br d, *J* = 7.7 Hz), 7.72 (1H, br d, *J* = 8.0 Hz), 7.50 (1H, br dd, *J* = 8.0, 7.1 Hz), 7.42 (1H, br d, *J* = 7.7 Hz), 7.40 (1H, d, *J* = 8.0 Hz), 7.26 (1H, br dd, *J* = 8.0, 7.1 Hz), 7.21-7.15 (4H, m), 7.09 (1H, br s), 7.04 (1H, d, *J* = 3.9 Hz), 6.95 (1H, d, *J* = 5.2 Hz)), 4.39 (2H, q, *J* = 7.1 Hz), 2.83-2.77 (4H, m), 1.81-1.61 (4H, m), 1.46 (3H, t, *J* = 7.1 Hz), 1.41-1.29 (12H, m), 0.93 (3H, t, *J* = 6.7 Hz), 0.91 (3H, t, *J* = 6.7 Hz), ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 140.7, 140.4, 139.7, 139.5, 136.8, 135.2, 130.3, 130.0, 128.5, 126.4, 126.0, 125.8, 125.2, 125.0, 123.8, 123.8, 123.8, 123.7, 123.7, 123.3, 122.8 120.5, 119.1, 117.4, 108.7, 108.6, 37.6, 31.70, 31.65, 30.6, 30.5, 29.7, 29.32, 29.27, 29.2, 22.64, 22.61, 14.12, 14.09, 13.8. Anal. Calcd for $C_{42}H_{45}NS_4$: C, 72.89; H, 6.55; N, 2.02; S, 18.53. Found: C, 72.48; H, 6.72; N, 1.97; S, 17.66.

5'''-(9-Ethyl-9*H*-carbazol-3-yl)-3',4''-di-*n*-hexyl-[2,2',5',2'',5'',2''']quaterthiophenyl-5-carbaldehyde 19. To a cold solution of quaterthiophene **17** (117 mg, 0.17 mmol) in dry DMF (2 mL) at 0 °C was added a Vilsmeier reagent, which was prepared with 0.1 mL of $POCl_3$ in DMF (2 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 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 = 7/1) and successive HPLC on silica gel (hexane/EtOAc = 5/1) to obtain aldehyde **19** (80 mg, 0.11 mmol, 66%) as a red solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (1H, s), 8.32 (1H, d, *J* = 1.7 Hz), 8.15 (1H, d, *J* = 7.7 Hz), 7.74 (1H, dd, *J* = 8.5, 1.7 Hz), 7.70 (1H, d, *J* =4.0 Hz), 7.50 (1H, ddd, *J* = 8.2, 7.1, 1.0 Hz), 7.42 (1H, d, *J* = 8.2 Hz), 7.41 (1H, d, *J* = 8.5 Hz), 7.30 (1H, d, *J* = 3.6 Hz), 7.27 (1H, br t, *J* = 7.4 Hz), 7.22 (1H, d, *J* = 4.0 Hz), 7.14 (1H, d, *J* = 3.6 Hz), 7.07 (1H, s), 7.04 (1H, s), 4.39 (2H, q, *J* = 7.2 Hz), 2.83 (2H, t, *J* = 7.8 Hz), 2.76 (2H, t, *J* = 7.8 Hz), 1.76-1.66 (4H, m), 1.46 (3H, t, *J* = 7.2 Hz), 1.43-1.30 (12H, m), 0.92 (3H, t, *J* = 6.7 Hz), 0.90 (3H, t, *J* = 6.7 Hz), ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.3, 146.1, 145.6, 143.0, 141.7, 140.3, 139.9, 139.4, 137.1, 136.7, 133.7, 133.4, 131.1, 128.1, 127.1, 126.6, 126.5, 125.9, 125.4, 125.0, 123.7, 123.3, 122.7, 122.1, 120.5, 119.0, 117.4, 108.7, 108.6, 37.5, 31.62, 31.58, 30.3, 30.0, 29.9, 29.5, 29.3, 29.2, 22.6, 22.5, 14.1, 14.0, 13.7. Anal. Calcd for $C_{43}H_{45}NOS_4$: C, 71.72; H, 6.30; N, 1.95; S, 17.81. Found: C, 72.02; H, 6.15; N, 1.95; S, 17.69.

5'''-(9-Ethyl-9*H*-carbazol-3-yl)-3,3'''-di-*n*-hexyl-[2,2',5',2'',5'',2''']quaterthiophenyl-5-carbaldehyde 20. To a cold solution of quaterthiophene **18** (384 mg, 0.56 mmol) in dry DMF (5 mL) at 0 °C was added a Vilsmeier reagent, which was prepared with 0.5 mL of $POCl_3$ in DMF (1.5 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 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 = 7/1) and successive HPLC on silica gel (hexane/EtOAc = 5/1) to obtain aldehyde **20** (179 mg, 0.25 mmol, 45%) as a red solid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.80 (1H, s), 8.31 (1H, br s), 8.14 (1H, d, *J* = 7.7 Hz), 7.71 (1H, d, *J* = 8.5 Hz), 7.56 (1H, s), 7.49 (1H, br dd, *J* = 8.0, 7.1 Hz), 7.41 (1H, d, *J* = 8.0 Hz), 7.38 (1H, d, *J* = 8.5 Hz), 7.27 (1H, br dd, *J* = 8.0, 7.1 Hz), 7.21-7.14 (4H, m), 7.08 (1H, d, *J* = 3.6 Hz), 4.35 (2H, q, *J* = 7.1 Hz), 2.83 (2H, t, *J* = 7.7 Hz), 2.81 (2H, t, *J* = 7.7 Hz), 1.81-1.63 (4H, m), 1.44 (3H, t, *J* = 7.1 Hz), 1.42-1.24 (12H, m), 0.95-0.87 (6H, m), ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.4, 143.8, 141.00, 140.96, 140.4, 140.3, 140.1, 139.5, 139.2, 139.0, 136.6, 135.3, 133.4, 128.3, 128.2, 126.0, 125.9, 125.1, 125.0, 124.6, 123.84, 123.80, 123.3, 122.8, 120.5, 119.1, 117.5, 108.7, 108.6, 37.6, 31.7, 31.6, 30.5, 30.1, 29.7, 29.4, 29.3, 29.1, 22.62, 22.57, 14.10, 14.05, 13.8. Anal. Calcd for $C_{43}H_{45}NOS_4$: C, 71.72; H, 6.30; N, 1.95; S, 17.81. Found: C, 71.74; H, 6.56; N, 1.97; S, 17.71.

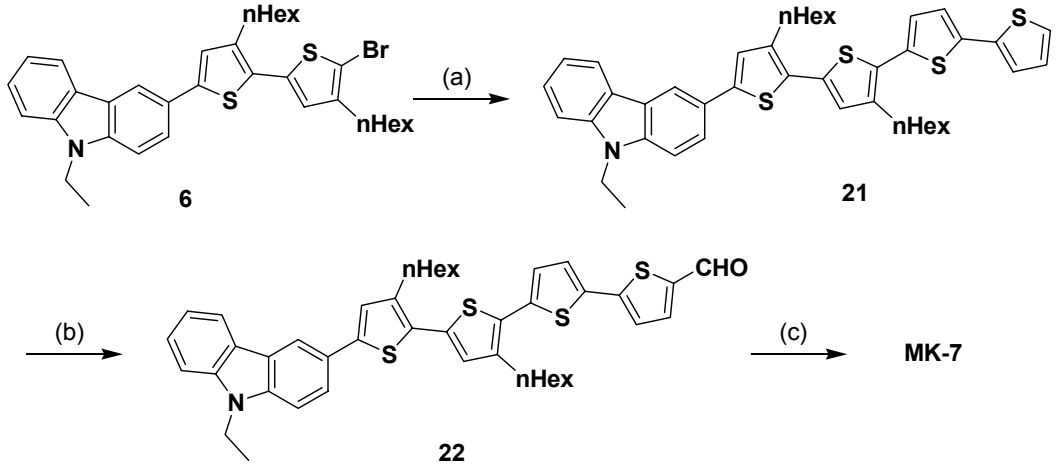
2-Cyano-3-[5'''-(9-Ethyl-9*H*-carbazol-3-yl)-3',4''-di-*n*-hexyl-[2,2',5',2'',5'',2''']-quaterthiophenyl-5-yl]acrylic acid MK-4. A mixture of aldehyde **19** (60 mg, 0.083 mmol) with cyanoacetic acid (14 mg, 0.17 mmol) in a mixed solvent of dry acetonitrile (2 mL) and dry toluene (2 mL) was refluxed in the presence of piperidine (0.3 mL) for 4 h. After cooling the mixture was diluted with dichloromethane, and the organic layer was washed with dil.HCl*aq*, H_2O and brine, dried over Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by column chromatography ($CHCl_3$ → $CHCl_3$/EtOAc = 1/1 → $CHCl_3$/ethanol = 5/1 →$CHCl_3$/ethanol = 3/1) to obtain a dye **MK-4** (40 mg, 0.051 mmol, 61%) as a dark-red solid, ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.40 (1H, d, *J* = 1.7 Hz), 8.19 (1H, br d , *J* = 7.6 Hz), 8.13 (1H, s), 7.73 (1H, dd, *J* = 8.5, 1.7 Hz), 7.69 (1H, d, *J* = 4.0 Hz), 7.59 (1H, br d, *J* = 7.7 Hz), 7.57 (1H, d, *J* = 8.5 Hz), 7.47 (1H, d, *J* = 3.8 Hz), 7.46 (1H, ddd, *J* = 8.2, 7.2, 1.2 Hz), 7.26 (1H, d, *J* = 4.0 Hz), 7.23 (1H, s), 7.23-7.19 (1H, m), 7.21 (1H, s), 7.14 (1H, d, *J* = 3.8 Hz), 4.43 (2H, q, *J* = 7.1 Hz), 2.81-2.75 (4H, m), 1.72-1.61 (4H, m), 1.44-1.26

(12H, m), 1.35 (3H, t, J = 7.1 Hz), 0.87 (3H, t, J = 7.0 Hz), 0.85 (3H, t, J = 7.0 Hz), ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.6, 145.1, 142.0, 140.8, 140.7, 140.1, 140.0, 139.3, 136.2, 135.59, 135.57, 135.4, 133.1, 132.7, 130.0, 128.2, 127.4, 127.1, 127.0, 126.0, 125.9, 124.4, 123.6, 122.8, 122.1, 120.5, 118.9, 118.4, 117.1, 109.5, 109.1, 107.7, 37.1, 30.91, 30.89, 29.63, 29.58, 29.1, 28.8, 28.43, 28.42, 21.9 21.9, 13.70, 13.68, 13.5. Anal. Calcd for $C_{46}H_{46}N_2O_2S_4$: C, 70.19; H, 5.89; N, 3.56, S, 16.29. Found: C, 69.54; H, 5.60; N, 3.87, S, 16.02.

2-Cyano-3-[5'''-(9-Ethyl-9*H*-carbazol-3-yl)-3,3'''-di-*n*-hexyl-[2,2',5',2'',5'',2''']-quaterthiophenyl -5-yl]acrylic acid MK-5. A mixture of aldehyde **20** (180 mg, 0.25 mmol) with cyanoacetic acid (43 mg, 0.50 mmol) in a mixed solvent of dry acetonitrile (2 mL) and dry toluene (1 mL) was refluxed in the presence of piperidine (0.5 mL) for 4 h. After cooling the mixture was diluted with dichloromethane, and the organic layer was washed with H_2O and brine, dried over Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by column chromatography ($CHCl_3$ → $CHCl_3$/ethanol = 9/1) to obtain a dye **MK-5** (185 mg, 0.24 mmol, 94%) as a dark-red solid, ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.46 (1H, s), 8.23 (1H, d, J = 7.7 Hz), 8.15 (1H, s), 7.70 (1H, dd, J = 8.5, 1.8 Hz), 7.63 (1H, s), 7.60 (1H, d, J = 8.5 Hz), 7.58 (1H, d, J = 8.5 Hz), 7.46 (1H, ddd, J = 8.1, 7.1, 1.0 Hz), 7.45 (1H, s), 7.37, (1H, d, J = 4.0 Hz), 7.36 (1H, d, J = 4.0 Hz), 7.27 (1H, d, J = 4.0 Hz), 7.22 (1H, br t, J = 7.6 Hz), 7.15 (1H, s), 4.41 (2H, q, J = 7.1 Hz), 2.76 (2H, t, J = 7.7 Hz), 2.73 (2H, t, J = 7.7 Hz), 1.72-1.55 (4H, m), 1.42-1.21 (12H, m), 1.30 (3H, t, J = 7.1 Hz), 0.87-0.82 (6H, m), ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.0, 143.2, 142.4, 141.1, 140.3, 140.0, 139.8, 139.4, 137.6, 136.6, 135.6, 134.8, 134.1, 133.3, 128.6, 127.5, 126.5, 126.4, 125.8, 125.6, 125.1, 124.4, 123.7, 122.9, 122.3, 120.9, 119.3, 118.4, 117.3, 109.8, 109.6, 105.9, 37.3, 31.3, 31.2, 30.0, 29.7, 29.4, 28.9, 28.8, 28.7, 22.30, 22.28, 14.17, 14.15, 13.9. Anal. Calcd for $C_{46}H_{46}N_2O_2S_4$: C, 70.19; H, 5.89; N, 3.56; S, 16.29. Found: C, 69.15; H, 5.79; N, 3.48; S, 16.65.

Synthesis of the dye, MK-7.

Scheme S6



(a) 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-bithiophene, $Pd(PPh_3)_4$, Na_2CO_3aq /DME (b) $POCl_3$-DMF /DMF (c) cyanoacetic acid, piperidine /AcCN-toluene.

9-Ethyl-3-(3',4-di-*n*-hexyl-[2,2',5',2'',5'',2''']quaterthiophen-5-yl)-9*H*-carbazole 21. A

Suzuki-coupling reaction of bromide **6** (336 mg, 0.55 mmol) with 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-bithiophene (243 mg, 0.83 mmol) was carried out in a similar manner to that of **5**. The crude product was purified by column chromatography (hexane/EtOAc = 50/1) and successive HPLC on silica gel (hexane/EtOAc = 25/1) to obtain quaterthiophene **21** (365 mg, 0.53 mmol, 95%) as an orange oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (1H, br s), 8.13 (1H, d, *J* = 7.7 Hz), 7.56 (1H, dd, *J* = 8.5, 1.7 Hz), 7.54-7.43 (3H, m), 7.29-7.19 (4H, m), 7.14 (1H, d, *J* = 3.9 Hz), 7.10 (1H, s), 7.05 (1H, d, *J* = 3.9 Hz), 7.03 (1H, s), 4.41 (2H, q, *J* = 7.1 Hz), 2.78 (2H, t, *J* = 7.7 Hz), 2.70 (2H, t, *J* = 7.7 Hz), 1.76-1.63 (4H, m), 1.48 (3H, t, *J* = 7.1 Hz), 1.44-1.24 (12H, m), 0.91 (3H, t, *J* = 6.7 Hz), 0.86 (3H, t, *J* = 6.7 Hz), ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4, 140.3, 139.2, 138.9, 138.3, 137.1, 136.8, 135.6, 135.1, 134.3, 128.7, 127.8, 127.1, 126.1, 126.01, 125.95, 125.9, 124.8, 124.3, 123.9, 123.5, 123.0, 122.8, 121.1, 120.4, 119.0, 108.6, 108.3, 37.5, 31.7, 31.6, 30.9, 30.4, 29.5, 29.23, 29.19, 28.8, 22.61, 22.59, 14.10, 14.06, 13.8. Anal. Calcd for $C_{42}H_{45}NS_4$: C, 72.89; H, 6.55; N, 2.02; S, 18.53. Found: C, 73.12; H, 6.91; N, 1.95; S, 17.79.

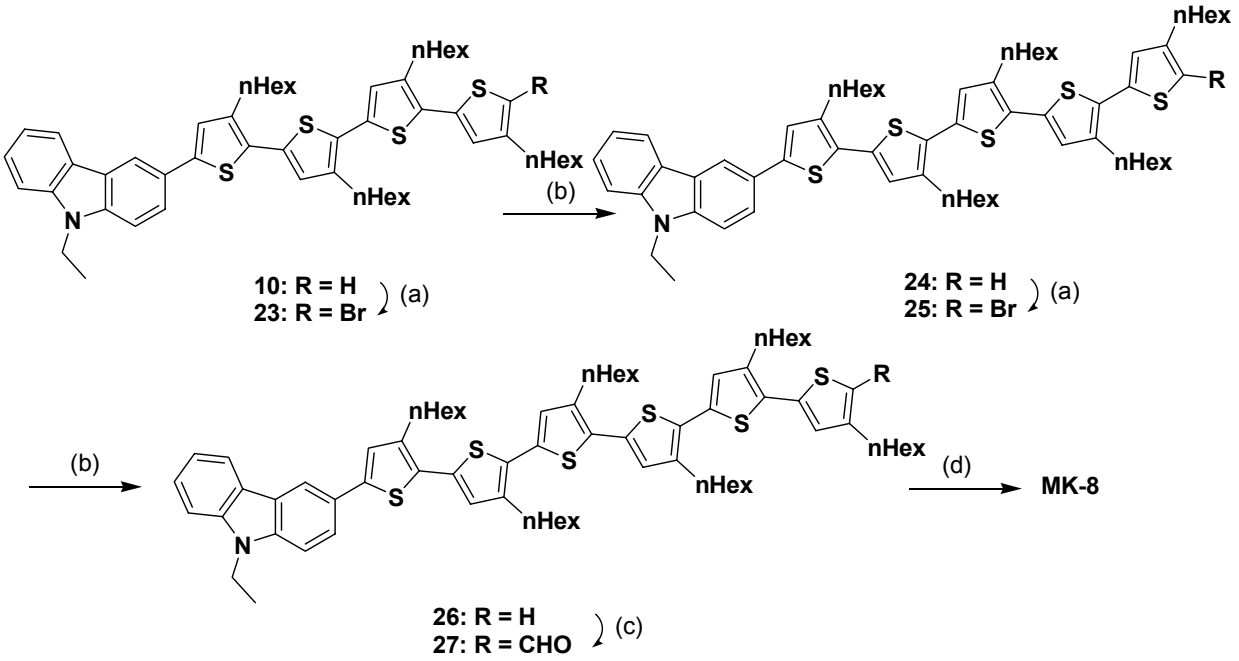
5'''-(9-Ethyl-9*H*-carbazol-3-yl)-3',4-di-*n*-hexyl-[2,2',5',2'',5'',2''']quaterthiophenyl-5-carbaldehyde 22. To a cold solution of quaterthiophene **21** (416 mg, 0.60 mmol) in dry DMF (5 mL) at 0 °C was added a Vilsmeier reagent, which was prepared with 0.5 mL of $POCl_3$ in DMF (2.4 mL). The mixture was stirred at 70 °C for 4 h, and quenched with 10% aqueous solution of NaOAc (30 mL) after cooling, and extracted with 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 = 6/1) to obtain aldehyde **22** (280 mg, 0.39 mmol, 65%) as a red solid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.86 (1H, s), 8.17 (1H, br s), 8.12 (1H, d, *J* = 7.7 Hz), 7.66 (1H, d, *J* = 3.8 Hz), 7.56 (1H, dd, *J* = 8.5, 1.7 Hz), 7.54-7.43 (3H, m), 7.32 (1H, d, *J* = 3.8 Hz), 7.29-7.23 (2H, m), 7.12 (1H, s), 7.09 (1H, d, *J* = 3.8 Hz), 7.04 (1H, s), 4.40 (2H, q, *J* = 7.1 Hz), 2.78 (2H, t, *J* = 7.7 Hz), 2.71 (2H, t, *J* = 7.7 Hz), 1.76-1.63 (4H, m), 1.48 (3H, t, *J* = 7.1 Hz), 1.44-1.24 (12H, m), 0.92 (3H, t, *J* = 6.6 Hz), 0.86 (3H, t, *J* = 6.6 Hz), ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.3, 146.9, 141.4, 141.2, 140.3, 139.3, 138.9, 138.7, 138.2, 137.4, 136.4, 134.9, 134.0, 128.1, 127.0, 126.5, 126.3, 126.2, 126.1, 126.0, 124.7, 123.8, 123.0, 122.7, 121.1, 120.4, 119.1, 108.6, 108.4, 37.6, 31.63, 31.61, 30.9, 30.3, 29.6, 29.3, 29.23, 29.7, 28.8, 22.6, 14.1, 14.0, 13.8. Anal. Calcd for $C_{43}H_{45}NOS_4$: C, 71.72; H, 6.30; N, 1.95, S, 17.81. Found: C, 71.43; H, 6.44; N, 1.80, S, 16.31.

2-Cyano-3-[5'''-(9-Ethyl-9*H*-carbazol-3-yl)-3',4-di-*n*-hexyl-[2,2',5',2'',5'',2''']-quaterthiophenyl -5-yl]acrylic acid MK-7. A mixture of aldehyde **22** (250 mg, 0.35 mmol) with cyanoacetic acid (59 mg, 0.69 mmol) in a mixed solvent of dry acetonitrile (2 mL) and dry toluene (1 mL) was refluxed in the presence of piperidine (0.5 mL) for 4 h. After cooling the mixture was diluted with dichloromethane, and the organic layer was washed with H_2O and brine, dried over Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by column chromatography ($CHCl_3$ → EtOAc → $CHCl_3$/ethanol = 5/1 → $CHCl_3$/ethanol = 1/1) to obtain a dye **MK-7** (132 mg, 0.17 mmol, 48%) as a dark-red solid, ^{1}H NMR (400 MHz, THF-d_8) δ 8.35 (1H, s), 8.13 (1H, s), 8.11 (1H, d, *J* = 7.6 Hz), 7.77 (1H, br s), 7.54-7.49 (3H, m), 7.46 (1H, br s), 7.43 (1H, ddd, *J* = 8.0, 7.0, 1.0 Hz), 7.37 (1H, br s), 7.21-7.16 (3H, m), 7.13 (1H, s), 4.45 (2H, q, *J* = 7.1 Hz), 2.72 (2H, t, *J* = 7.7 Hz), 2.72 (2H, t, *J* = 7.7 Hz), 1.76-1.65 (4H, m), 1.42 (3H, t, *J* = 7.1 Hz),

1.39-1.25 (12H, m), 0.91 (3H, t, J = 6.9 Hz), 0.84 (3H, t, J = 6.9 Hz), ^{13}C NMR (100 MHz, THF-d_8) δ 170.5, 169.3, 145.1, 141.6, 141.4, 140.3, 139.61 139.56, 138.6, 138.2, 137.0, 136.5, 136.3, 135.1, 129.5, 127.8, 127.0, 127.0, 126.94, 126.86, 126.7, 125.7 124.8, 124.1, 123.8, 121.6, 121.1, 119.8, 118.6, 109.5, 109.4, 105.2, 38.1, 32.7, 32.6, 31.8, 31.1, 30.6, 30.3, 30.2, 29.7, 23.6, 23.5, 14.6, 14.4, 14.1. Anal. Calcd for $C_{46}H_{46}N_2O_2S_4$: C, 70.19; H, 5.89; N, 3.56; S, 16.29. Found: C, 69.60; H, 5.64; N, 3.49; S, 16.13.

Synthesis of the dye, MK-8.

Scheme S7



(a) NBS /THF (b) 3-*n*-hexylthiophene-2-boronic acid neopentyl ester, $Pd(PPh_3)_4$, Na_2CO_3aq /DME (c) $POCl_3$-DMF /DMF (d) cyanoacetic acid, piperidine /AcCN-toluene.

9-Ethyl-3-(5'''-bromo-3',3'',3''',4-tetra-*n*-hexyl-[2,2',5',2'',5'',2''']quaterthiophen-5-yl)-9*H*-carbazole 23. A bromination of quaterthiophene **10** (1.11 g, 1.29 mmol) with *N*-bromosuccinimide (230 mg, 1.29 mmol) in THF (50 mL) was carried out in a similar manner to that of **4**. 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 **23** (945 mg, 1.01 mmol, 78%) as a yellow oil, ^{1}H NMR (400 MHz, THF-d_8) δ 8.18 (1H, br s), 8.12 (1H, d, J = 7.7 Hz), 7.57-7.50 (3H, m), 7.44 (1H, ddd, J = 8.2, 7.2, 1.0 Hz), 7.19 (1H, br t, J = 7.1 Hz), 7.17 (1H, s), 7.11 (1H, s), 7.03 (1H, s), 6.95 (1H, s), 4.47 (2H, q, J = 7.1 Hz), 2.84-2.75 (4H, m), 2.73 (2H, t, J = 7.8 Hz), 2.60 (2H, t, J = 7.8 Hz), 1.72-1.60 (8H, m), 1.43 (3H, t, J = 7.1 Hz), 1.42-1.25 (24H, m), 0.93-0.88 (9H, m), 0.84 (3H, t, J = 7.0 Hz), ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.4, 140.27, 140.26, 140.0, 139.2, 138.8, 138.3, 135.5, 135.4, 134.30, 134.29, 129.6, 128.8, 128.1, 127.1, 126.4, 126.00, 125.91, 124.8, 123.1, 122.8, 121.1, 120.4, 119.0, 108.54, 108.51, 108.3, 37.5, 31.7, 31.65, 31.65, 31.61, 31.0, 30.5, 30.4, 29.63, 29.55, 29.5, 29.3, 29.3, 29.20, 29.20, 28.9, 28.8, 22.62, 22.60, 22.60, 22.60, 14.1, 14.09, 14.09, 14.06, 13.8. Anal. Calcd for $C_{54}H_{68}BrNS_4$: C, 69.05; H, 7.30; N, 1.49; S, 13.66. Found: C, 69.59; H, 7.39; N, 1.51; S, 13.24.

9-Ethyl-3-(3',3'',3''',3'''',4-hepta-*n*-hexyl-[2,2',5',2'',5'',2''',5''',2'''']quinquithiophen-5-yl)-9*H*-car

bazole 24. A Suzuki-coupling reaction of bromide **23** (309 mg, 0.33 mmol) with 3-*n*-hexylthiophene-2-boronic acid neopentyl ester (138 mg, 0.49 mmol) was carried out in a similar manner to that of **5**. The crude product was purified by column chromatography (hexane/EtOAc = 50/1) and successive HPLC on silica gel (hexane/EtOAc = 25/1) to obtain quinquithiophene **24** (324 mg, 0.32 mmol, 96%) as an orange oil, ^{1}H NMR (400 MHz, THF-d_8) δ 8.18 (1H, br s), 8.12 (1H, d, *J* = 7.9 Hz), 7.60-7.51 (3H, m), 7.44 (1H, br t, *J* = 8.0 Hz), 7.19 (1H, br t, *J* = 7.8 Hz), 7.17 (1H, s), 7.11 (1H, s), 7.06 (1H, s), 7.04-7.03 (3H, m), 4.47 (2H, q, *J* = 7.2 Hz), 2.85-2.76 (6H, m), 2.73 (2H, t, *J* = 7.7 Hz), 2.63 (2H, t, *J* = 7.7 Hz), 1.73-1.60 (10H, m), 1.43 (3H, t, *J* = 7.0 Hz), 1.42-1.25 (30H, m), 0.94-0.82 (15H, m), ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 140.3, 140.2, 139.7 139.6, 139.3, 138.9, 138.3, 135.5, 135.4, 134.4, 133.8, 133.5, 130.9, 130.3, 129.0, 128.4, 128.4, 127.12, 127.08, 126.1, 125.99, 125.94, 124.9, 123.1, 122.8, 121.1, 120.5, 119.9, 119.0, 108.6, 108.4, 37.6, 31.68, 31.68, 31.68, 31.66, 31.65, 31.0, 30.55, 30.48, 30.48, 30.44, 30.38, 29.6, 29.4, 29.28, 29.26, 29.25, 29.24, 29.19, 29.0, 28.8, 22.64, 22.64, 22.64, 22.61, 22.60, 14.12, 14.10, 14.09, 14.08, 14.06, 13.8. Anal. Calcd for $C_{64}H_{83}NS_5$: C, 74.87; H, 8.15; N, 1.36; S, 15.62. Found: C, 74.42; H, 8.15; N, 1.36; S, 15.97.

9-Ethyl-3-(5’’’’-bromo-3’,3’’,3’’’,3’’’’,4-hepta-*n*-hexyl-[2,2’,5’,2’’,5’’,2’’’,5’’’,2’’’’]quinquithiophen-5-yl)-9*H*-carbazole 25. A bromination of quinquithiophene **24** (324 mg, 0.32 mmol) with *N*-bromosuccinimide (56 mg, 0.32 mmol) in THF (6 mL) was carried out in a similar manner to that of **4**. The crude product was purified by column chromatography (hexane/EtOAc = 25/1) and successive HPLC on silica gel (hexane/EtOAc = 25/1) to obtain bromide **25** (302 mg, 0.27 mmol, 87%) as a yellow oil, ^{1}H NMR (400 MHz, THF-d_8) δ 8.19 (1H, br s), 8.12 (1H, d, *J* = 7.7 Hz), 7.60-7.50 (3H, m), 7.44 (1H, ddd, *J* = 8.2, 7.1, 1.0 Hz), 7.19 (1H, ddd, *J* = 8.0, 7.1, 1.0 Hz), 7.18 (1H, s), 7.11 (1H, s), 7.06 (1H, s), 7.05 (1H, s), 6.95 (1H, s), 4.46 (2H, q, *J* = 7.1 Hz), 2.84-2.79 (4H, m), 2.76 (2H, t, J = 7.7 Hz), 2.73 (2H, t, *J* = 7.7 Hz), 2.60 (2H, t, *J* = 7.7 Hz), 1.75-1.60 (10H, m), 1.44 (3H, t, *J* = 7.1 Hz), 1.42-1.26 (30H, m), 0.94-0.88 (12H, m), 0.85 (3H, t, *J* = 6.9 Hz), ^{13}C NMR (100 MHz, THF-d_8) δ 142.5, 140.33, 140.30, 140.1, 139.9, 139.3, 138.9, 138.3, 135.5, 135.3, 134.4, 134.1, 129.9, 129.0, 128.4, 128.3, 127.1, 126.6, 126.1, 126.04, 125.96, 124.9, 123.1, 122.8, 121.2, 120.5, 119.1, 108.61, 108.57, 108.4, 37.7, 31.68, 31.68, 31.65, 31.65, 31.6, 31.0, 30.6, 30.5, 30.4, 29.6, 29.5, 29.5, 29.4, 29.3, 29.3, 29.3, 29.3, 29.2, 29.2, 28.9, 28.8, 22.63, 22.63, 22.63, 22.62, 22.60, 14.12, 14.11, 14.09, 14.09, 14.07, 13.9. Anal. Calcd for $C_{64}H_{82}BrNS_5$: C, 69.53; H, 7.48; N, 1.27; S, 14.50. Found: C, 69.34; H, 7.47; N, 1.26; S, 14.07.

9-Ethyl-3-(3’,3’’,3’’’,3’’’’,3’’’’’,4-hexa-*n*-hexyl-[2,2’,5’,2’’,5’’,2’’’,5’’’,2’’’’,5’’’’,2’’’’’]sexithiophen-5-yl)-9*H*-carbazole 26. A Suzuki-coupling reaction of bromide **25** (276 mg, 0.25 mmol) with 3-*n*-hexylthiophene-2-boronic acid neopentyl ester (105 mg, 0.37 mmol) was carried out in a similar manner to that of **5**. The crude product was purified by column chromatography (hexane/EtOAc = 25/1) and successive HPLC on silica gel (hexane/EtOAc = 25/1) to obtain sexithiophene **26** (288 mg, 0.24 mmol, 97%) as an orange oil, ^{1}H NMR (400 MHz, THF-d_8) δ 8.19 (1H, br s), 8.12 (1H, d, *J* = 7.8 Hz), 7.60-7.51 (3H, m), 7.44 (1H, ddd, *J* = 8.0, 7.0, 1.0 Hz), 7.19 (1H, br t, *J* = 7.4 Hz), 7.18 (1H, s), 7.12 (1H, s), 7.064 (1H, s), 7.061 (1H, s), 7.05 (1H, s), 7.03 (2H, m), 4.47 (2H, q, *J* = 7.1 Hz), 2.87-2.76 (8H, m), 2.73 (2H, t, *J* = 7.7 Hz), 2.63 (2H, t, *J* = 7.7 Hz), 1.77-1.64 (12H, m), 1.43 (3H, t, *J* = 7.1 Hz), 1.40-1.26 (36H, m), 0.95-0.89 (15H, m), 0.85

(3H, t, *J* = 6.9 Hz), ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 140.3, 140.2, 139.80, 139.76, 139.6 139.3, 138.9, 138.3, 135.5, 135.4, 134.4, 133.9, 133.6, 133.5, 131.0, 130.5, 130.3, 129.0, 128.5, 128.4, 128.4, 127.2, 127.1, 126.1, 126.03, 125.96, 124.9, 123.1, 122.8, 121.2, 120.5, 120.0, 119.1, 108.6, 108.4, 37.7, 31.69, 31.69, 31.69, 31.69, 31.66, 31.66, 31.0, 30.56, 30.50, 30.50, 30.50, 30.45, 30.4, 29.6, 29.45, 29.42, 29.29, 29.26, 29.26, 29.24, 29.24, 29.20, 29.0, 28.8, 22.64, 22.64, 22.64, 22.64, 22.62, 22.60, 14.12, 14.12, 14.10, 14.10, 14.09, 14.07, 13.9. Anal. Calcd for $C_{74}H_{97}NS_6$: C, 74.50; H, 8.20; N, 1.17; S, 16.13. Found: C, 74.16; H, 8.19; N, 1.20; S, 15.74.

5’’’’’-(9-Ethyl-9*H*-carbazol-3-yl)-3’,3’’,3’’’,3’’’’,3’’’’’,4-hexa-*n*-hexyl-[2,2’,5’,2’’,5’’,2’’’,5’’’,2’’’’,5’’’’,2’’’’’]sexithiophenyl-5-carbaldehyde 27. To a cold solution of sexithiophene **26** (253 mg, 0.21 mmol) in dry DMF (4 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 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 = 7/1) to obtain aldehyde **27** (97 mg, 0.081 mmol, 38%) as a dark-orange oil, ^{1}H NMR (400 MHz, THF-d_8) δ 10.03 (1H, s), 8.18 (1H, d, *J* = 1.0 Hz), 8.12 (1H, d, *J* = 7.7 Hz), 7.60-7.51 (3H, m), 7.44 (1H, ddd, *J* = 8.2, 7.0, 1.1 Hz), 7.19 (1H, ddd, J = 8.0, 7.0, 1.0 Hz), 7.19 (1H, s), 7.18 (1H, s), 7.12 (2H, s), 7.09 (1H, s), 7.07 (1H, s), 4.47 (2H, q, *J* = 7.1 Hz), 3.00 (2H, t, *J* = 7.8 Hz), 2.90-2.81 (8H, m), 2.73 (2H, t, *J* = 7.8 Hz), 1.77-1.66 (12H, m), 1.44 (3H, t, *J* = 7.1 Hz), 1.42-1.26 (36H, m), 0.94-0.88 (15H, m), 0.85 (3H, t, *J* = 7.0 Hz), ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.6, 153.3, 145.1, 142.5, 140.6, 140.33, 140.32, 140.1, 139.3, 138.9, 138.3, 136.2, 135.9, 135.5, 134.5, 134.3, 134.2, 129.9, 129.7, 129.4, 128.9, 128.8, 128.5, 128.4, 128.0, 127.1, 126.1, 126.05, 125.95, 124.9, 123.1, 122.8, 121.1, 120.5, 119.1, 108.6, 108.4, 37.6, 31.68, 31.68, 31.66, 31.64, 31.64, 31.5, 31.4, 31.0, 30.44, 30.41, 30.41, 30.2, 29.8, 29.6, 29.51, 29.47, 29.23, 29.23, 29.23, 29.23, 29.18, 29.0, 28.8, 28.5, 22.63, 22.63, 22.62, 22.59, 22.59, 22.5, 14.11, 14.11, 14.09, 14.05, 14.05, 14.04, 13.8. Anal. Calcd for $C_{75}H_{97}NOS_6$: C, 73.78; H, 8.01; N, 1.15; S, 15.76. Found: C, 73.37; H, 7.90; N, 1.10; S, 15.26.

2-Cyano-3-[5’’’’’-(9-Ethyl-9*H*-carbazol-3-yl)-3’,3’’,3’’’,3’’’’,3’’’’’,4-hexa-*n*-hexyl-[2,2’,5’,2’’,5’’,2’’’,5’’’,2’’’’,5’’’’,2’’’’’]sexithiophenyl-5-yl]acrylic acid MK-8. A mixture of aldehyde **27** (88 mg, 0.072 mmol) with cyanoacetic acid (12 mg, 0.14 mmol) in a mixed solvent of dry acetonitrile (2 mL) and dry toluene (1 mL) was refluxed in the presence of piperidine (0.5 mL) for 4 h. After cooling the mixture was diluted with dichloromethane, and the organic layer was washed with dil.HCl*aq*, H_2O and brine, dried over Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by column chromatography ($CHCl_3$ → EtOAc → $CHCl_3$/ethanol = 10/1 →$CHCl_3$/ethanol = 4/1) and subsequent recrystallization from $CHCl_3$-ethanol to obtain a dye **MK-8** (91 mg, 0.071 mmol, 99%) as dark-red solid, ^{1}H NMR (400 MHz, THF-d_8) δ 8.41 (1H, s), 8.19 (1H, br s), 8.11 (1H, d, *J* = 7.7 Hz), 7.60-7.50 (3H, m), 7.43 (1H, ddd, *J* = 8.2, 7.2, 1.0 Hz), 7.25 (1H, s), 7.19 (1H, br t, *J* = 7.2 Hz), 7.18 (1H,s), 7.13 (1H, s), 7.12 (1H, s), 7.09 (1H, s), 7.07 (1H, s), 4.46 (2H, q, *J* = 7.1 Hz), 2.91 (2H, t, *J* = 7.7 Hz), 2.89-2.80 (8H, m), 2.73 (2H, t, *J* = 7.7 Hz), 1.77-1.64 (12H, m), 1.43 (3H, t, *J* = 7.1 Hz), 1.46-1.26 (36H, m), 0.96-0.88 (15H, m), 0.85 (3H, t, J = 7.0 Hz), ^{13}C NMR (100 MHz, THF-d_8) δ 164.6, 155.4, 144.4, 143.9, 143.5, 141.7, 141.5, 141.3, 141.1, 140.4, 139.7, 139.6, 136.9, 136.7, 135.3, 135.2, 135.1, 130.90, 130.85, 130.79, 130.5, 130.2, 129.7, 129.6, 129.4, 128.4,

127.8, 126.93, 126.89, 126.7, 125.7, 124.2, 123.8, 121.8, 121.1, 119.8, 116.9, 109.6, 109.5, 98.3, 38.2, 32.68, 32.68, 32.68, 32.66, 32.63, 32.5, 32.2, 31.8, 31.43, 31.38, 31.35, 31.32, 30.8, 30.4, 30.3, 30.20, 30.20, 30.20, 30.20, 30.17, 30.1, 29.9, 29.6, 29.5, 23.55, 23.55, 23.55, 23.53, 23.51, 23.47, 14.51, 14.51, 14.51, 14.50, 14.48, 14.4, 14.1. Anal. Calcd for $C_{78}H_{98}N_2O_2S_6$: C, 72.73; H, 7.67; N, 2.17; S, 14.94. Found: C, 72.48; H, 7.74; N, 2.12; S, 14.67.

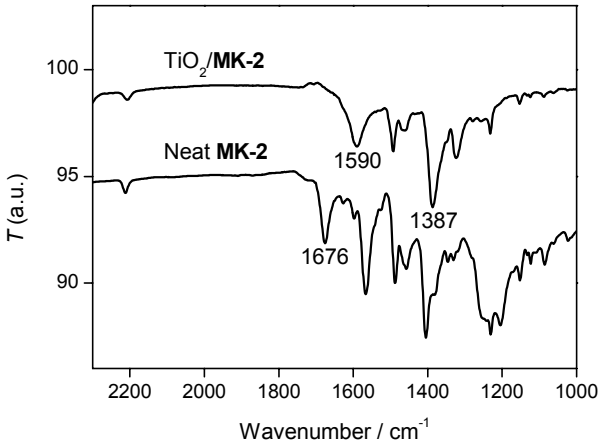


Figure S1. FT-IR spectra for neat **MK-2** and the dye-loaded TiO_2 film.

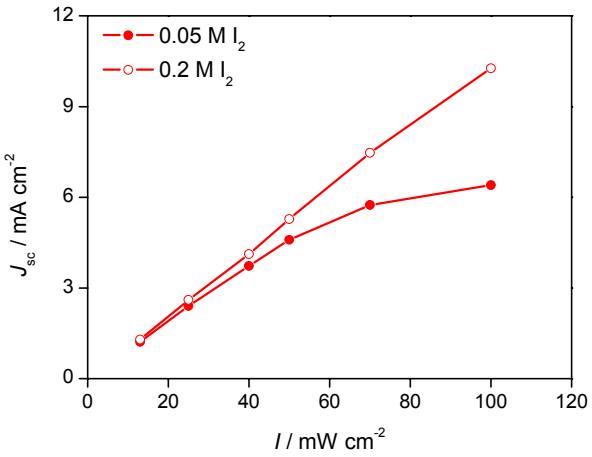


Figure S2. Relationship between J_{sc} and light intensity for a DSSC with **MK-5** using electrolyte containing 0.05 or 0.2 M I_2.