Electronic Supplementary Information for

Organic dye-sensitized solar cells with a cobalt redox couple: influences of π-linker rigidification and dye-bath solvent selection

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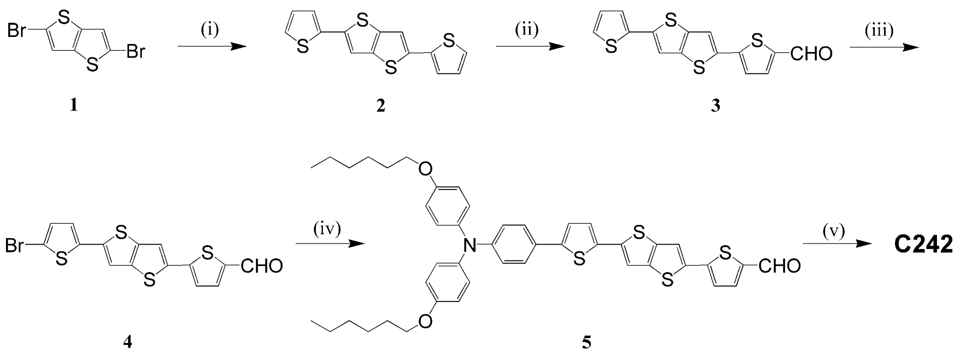
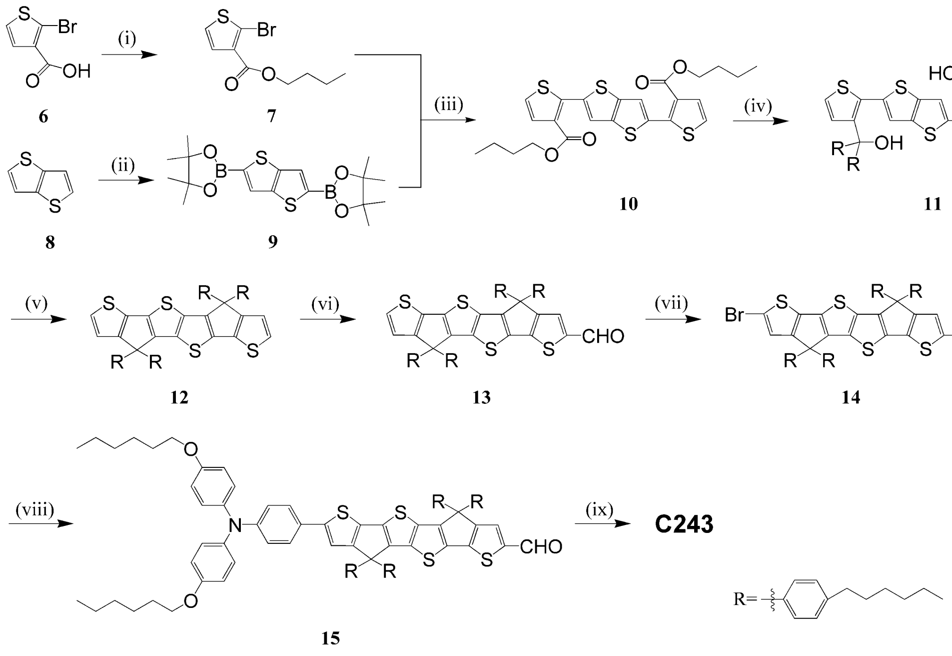
Dye synthesis

Scheme S1 Synthetic route of the C242 dye[a]



[a] Reagents: (i) 2-thiophene-boronic acid, palladium acetate, SPhos, K_3PO_4, dioxane/H_2O (*v*/*v*, 5/1); (ii) DMF, phosphoryl trichloride, 1,2-dichloroethane; (iii) NBS, THF; (iv) 4,4,5,5-tetramethyl-2-{4-[*N*,*N*-bis(4-hexyloxyphenyl)amino]phenyl}-1,3,2-dioxaborolane, palladium acetate, SPhos, K_3PO_4, dioxane/H_2O (*v*/*v*, 5/1); (v) cyanoacetic acid, piperidine, chloroform.

Scheme S2 Synthetic route of the C243 dye[a]



[a] Reagents: (i) butyl alcohol, H_2SO_4; (ii) *n*-butyllithium, THF, isopropyl pinacol borate; (iii) palladium acetate, SPhos, K_3PO_4, toluene; (iv) 4-hexyl-phenylbromide, Mg, THF; (v) Amberlyst 15, toluene; (vi) DMF, phosphoryl trichloride, 1,2-dichloroethane; (vii) NBS, THF; (viii) 4,4,5,5-tetramethyl-2-{4-[*N*,*N*-bis(4-hexyloxyphenyl)amino]phenyl}-1,3,2-dioxaborolane, palladium acetate, SPhos, K_3PO_4, dioxane/H_2O (*v*/*v*, 5/1); (ix) cyanoacetic acid, piperidine, chloroform.

*2,5-Di(thiophen-2-yl)thieno[3,2-b]thiophene (**2**).* To a stirred solution of **1** (1.240 g, 4.161 mmol), 2-thiophene-boronic acid (1.278 g, 9.986 mmol) and K_3PO_4 (8.832 g, 41.610 mmol) in dioxane/H_2O (*v*/*v*, 5/1, 86 mL) was added SPhos (68 mg, 0.166 mmol) and palladium acetate (37 mg, 0.166 mmol). The resulting mixture was stirred at 45 ^{o}C overnight and then cooled to room temperature. The solution was extracted with chloroform before the organic phase was washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography over silica gel with petroleum ether as the eluent to afford a yellow solid as the desired product **2** (1.139 g, 90% yield). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 7.66 (s, 2H), 7.56 (d, J = 5.4 Hz, 2H), 7.37 (d, J = 3.6 Hz, 2H), 7.12 (dd, J = 4.2, 4.8 Hz, 2H). Analytical data were consistent with previously reported results (X. Zhang and A. J. Matzger, *J. Org. Chem*., 2003, **68**, 9813).

*5-(5-(Thiophen-2-yl)thieno[3,2-b]thiophen-2-yl)thiophene-2-carbaldehyde (**3**).* To a stirred solution of **2** (0.500 g, 1.642 mmol) and anhydrous DMF (0.761 mL, 9.845 mmol) in 1,2-dichloroethane (25 mL) was added phosphoryl trichloride (0.219 mL, 2.463 mmol). The resulting mixture was stirred at 70 ^{o}C for 12 h and then cooled to room temperture. Saturated sodium acetate aqueous solution (25 mL) was added and the reaction was further stirred overnight. The solution was extracted with dichloromethane before the organic phase was washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography over silica gel with dichloromethane/petroleum ether (*v*/*v*, 1/1) as the eluent to afford an orange solid as the desired product **3** (0.408 g, 75% yield). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.90 (s, 1H), 8.02 (d, J = 4.2 Hz, 1H), 7.98 (s, 1H), 7.73 (s, 1H), 7.60 (d, J = 4.8 Hz, 1H), 7.58 (d, J = 3.6 Hz, 1H), 7.42 (d, J = 3.6 Hz, 1H), 7.14 (dd, J = 3.6, 4.8 Hz, 1H). ^{13}C NMR (150 MHz, THF-d_8) δ: 183.16, 147.58, 143.97, 142.15, 141.85, 140.18, 138.64, 138.58, 138.55, 129.34, 126.85, 125.72, 119.87, 117.24. MS (ESI) *m*/*z* calcd. for ($C_{15}H_8OS_4$): 331.9. Found: 355.0 ([M+Na]$^{+}$). Anal. Calcd. for $C_{15}H_8OS_4$: C, 54.19; H, 2.43. Found: C, 54.10; H, 2.52.

*5-(5-(5-Bromothiophen-2-yl)thieno[3,2-b]thiophen-2-yl)thiophene-2-carbaldehyde (**4**).* To a stirred solution of **3** (0.290 g, 0.872 mmol) in THF (50 mL) was added NBS (0.171 g, 0.959 mmol). The resulting mixture was stirred at room temperature overnight and evaporated to one quarter under reduced pressure. The residue was filtered and washed with water and dichloromethane to afford an orange powder as the desired product **4** (0.293 g, 82% yield). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.90 (s, 1H), 8.02 (d, J = 4.2 Hz, 1H), 7.98 (s, 1H), 7.73 (s, 1H), 7.59 (d, J = 4.2 Hz, 1H), 7.27 (m, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 182.58, 141.38, 139.51, 138.22, 137.44, 136.57, 131.07, 124,78, 124.77, 118.57, 116.57. MS (ESI) *m*/*z* calcd. for ($C_{15}H_7BrOS_4$): 409.9. Found: 410.8 ([M+H]$^{+}$). Anal. Calcd. for $C_{15}H_7BrOS_4$: C, 43.79; H, 1.72.

Found: C, 43.70; H, 1.77.

*5-(5-(5-(4-(Bis(4-(hexyloxy)phenyl)amino)phenyl)thiophen-2-yl)thieno[3,2-b]thiophen-2-yl)thiophene-2-carbaldehyde (**5**).* To a stirred solution of **4** (0.274 g, 0.666 mmol), 4,4,5,5-tetramethyl-2-{4-[*N*,*N*-bis(4-hexyloxyphenyl)amino]phenyl}-1,3,2-dioxaborolane (0.457 g, 0.799 mmol) and K_3PO_4 (0.707 g, 3.330 mmol) in dioxane/H_2O (*v*/*v*, 5/1, 36 mL) was added SPhos (5 mg, 0.013 mmol) and palladium acetate (3 mg, 0.013 mmol). The resulting mixture was stirred at 45 ^oC for 5 h and then cooled to room temperature. The solution was extracted with ethyl acetate before the organic phase was washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography over silica gel with dichloromethane/petroleum ether (*v*/*v*, 2/3) as the eluent to afford a reddish orange powder as the desired product **5** (0.475 g, 92% yield). ^1H NMR (600 MHz, DMSO-d_6) δ: 9.90 (s, 1H), 8.02 (d, J = 3.6 Hz, 1H), 7.97 (s, 1H), 7.71 (s, 1H), 7.57 (d, J = 3.6 Hz, 1H), 7.49 (d, J = 9.0 Hz, 2H), 7.38 (d, J = 3.6 Hz, 1H), 7.35 (d, J = 3.6 Hz, 1H), 7.05 (d, J = 9.0 Hz, 4H), 6.92 (d, J = 9.0 Hz, 4H), 6.77 (d, J = 9.0 Hz, 2H), 3.94 (t, J = 6.3 Hz, 4H), 1.71 (m, 4H), 1.41 (m, 4H), 1.31 (m, 8H), 0.89 (m, 6H). ^{13}C NMR (150 MHz, THF-d_8) δ: 183.09, 157.50, 150.29, 147.67, 146.03, 143.80, 142.45, 142.02, 141.69, 139.88, 138.54, 138.45, 136.15, 128.14, 127.44, 126.94, 126.69, 125.58, 123.80, 121.33, 119.85, 116.59, 116.54, 69.26, 33.07, 30.79, 27.22, 24.01, 14.87. MS (ESI) *m*/*z* calcd. for ($C_{45}H_{45}NO_3S_4$): 775.2. Found: 776.4 ($[M+H]^+$). Anal. Calcd. for $C_{45}H_{45}NO_3S_4$: C, 69.64; H, 5.84; N, 1.80. Found: C, 69.57; H, 5.91; N, 1.78.

*3-(5-(5-(5-(4-(Bis(4-(hexyloxy)phenyl)amino)phenyl)thiophen-2-yl)thieno[3,2-b]thiophen-2-yl)thiophen-2-yl)-2-cyano acrylic acid (**C242**).* To a stirred solution of **5** (0.330 g, 0.425 mmol) and cyanoacetic acid (0.109 g, 1.275 mmol) in chloroform (17 mL) was added piperidine (0.294 mL, 2.975 mmol). The resulting mixture was refluxed for 12 h and then cooled to room temperature before acidified with 2 M hydrochloric acid aqueous solution. The solution was extracted with chloroform before the organic phase was washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography over silica gel with methanol/toluene (*v*/*v*, 1/20) as the eluent to afford a purple powder as the desired product **C242** (0.285 g, 80% yield). ^1H NMR (600 MHz, THF-d_8) δ: 8.51 (s, 1H), 7.98 (d, J = 3.6 Hz, 1H), 7.95 (s, 1H), 7.67 (s, 1H), 7.59 (m, 3H), 7.43 (d, J = 4.2 Hz, 1H), 7.38 (d, J = 3.6 Hz, 1H), 7.20 (d, J = 9.0 Hz, 4H), 7.05 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 9.0 Hz, 4H), 4.11 (t, J = 6.3 Hz, 4H), 1.93 (m, 4H), 1.66 (m, 4H), 1.53 (m, 8H), 1.09 (t, J = 6.6 Hz ,6H). ^{13}C NMR (150 MHz, THF-d_8) δ: 164.55, 157.51, 150.30, 147.95, 146.64, 146.07, 142.68, 142.29, 141.70, 140.59, 140.10, 138.23, 136.26, 136.16, 128.15, 127.45, 126.96, 126.78, 125.64, 123.86, 121.32, 120.18, 117.19, 116.64, 116.56, 100.47, 69.28, 33.07,

30.79, 27.22, 24.01, 14.87. HR-MS (MALDI): *m*/*z* calcd for ($C_{48}H_{46}N_2O_4S_4$): 842.23404. Found: 842.23014. Anal. Calcd. for $C_{48}H_{46}N_2O_4S_4$: C, 68.38; H, 5.50; N, 3.32; Found: C, 68.30; H, 5.52; N, 3.29. IR (KBr): 1680 cm^{-1} (COOH), 2218 cm^{-1} (CN).

Butyl 2-bromothiophene-3-carboxylate (7). Catalytic amount of sulfuric acid (0.800 mL) was added to a stirred solution of **6** (8.000 g, 38.638 mmol) in anhydrous butyl alcohol (88 mL). The resulting mixture was stirred at 110 °C for 8 h and then cooled to room temperature. After the butyl alcohol was removed under reduced pressure, the crude product was dissolved into ethyl acetate, washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography over silica gel with ethyl acetate/petroleum ether (*v*/*v*, 1/50) as the eluent to afford a colorless oil as the desired product **7** (9.553 g, 94% yield). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 7.66 (d, J = 6.0 Hz, 1H), 7.34 (d, J = 5.4 Hz, 1H), 4.23 (t, J = 6.6 Hz, 2H), 1.67 (m, 2H), 1.42 (m, 2H), 0.92 (t, J = 7.5 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 161.22, 130.84, 128.93, 128.11, 118.98, 64.30, 30.08, 18.68, 13.51. MS (ESI) *m*/*z* calcd. for ($C_9H_{11}BrO_2S$): 262.0. Found: 285.2 ($[M+Na]^+$). Anal. Calcd. for $C_9H_{11}BrO_2S$: C, 41.08; H, 4.21. Found: C, 41.01; H, 4.25.

*4,4,5,5-Tetramethyl-2-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thieno[3,2-b]thiophen-2-yl)-1,3,2-dioxaborolane (**9**).* *n*-Butyllithium (46.798 mL, 74.877 mmol) was added dropwise to a stirred solution of **8** (5.000 g, 35.656 mmol) in anhydrous THF (80 mL) at –78 °C. The resulting mixture was stirred at the same temperature for 30 min and then warmed up to room temperature. After stirring for 1.5 h, the solution was cooled to –78 °C and isopropyl pinacol borate (16.003 mL, 78.443 mmol) was added. The reaction was stirred overnight at room temperature and then quenched by adding saturated ammonium chloride aqueous solution (20 mL). The mixture was filtered and washed with water and ethyl acetate to obtain a solid. The crude product was recrystallized with ethyl acetate to afford an off-white powder as the desired product **9** (11.745 g, 84% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.76 (s, 2H), 1.36 (s, 24H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 146.65, 128.88, 84.33, 24.77. MS (ESI) *m*/*z* calcd. for ($C_{18}H_{26}B_2O_4S_2$): 392.1. Found: 393.4 ($[M+H]^+$). Anal. Calcd. for $C_{21}H_{30}S_2$: C, 55.13; H, 6.68. Found: C, 55.06; H, 6.75.

*Dibutyl 2,2′-(thieno[3,2-b]thiophene-2,5-diyl)bis(thiophene-3-carboxylate) (**10**).* To a stirred solution of **7** (1.930 g, 7.331 mmol), **9** (1.150 g, 2.933 mmol) and K_3PO_4 (2.490 g, 11.732 mmol) in toluene (20 mL) was added SPhos (12 mg, 0.029 mmol) and palladium acetate (7 mg, 0.029 mmol). The resulting mixture was refluxed overnight and then cooled to room temperature. Water (50 mL) was added and the solution was extracted with ethyl acetate before the organic phase was washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography over silica gel with toluene as the eluent to afford a yellow-green solid as the desired product **10** (1.228 g, 83% yield). ^{1}H NMR (600 MHz, THF-d_8) δ: 7.98 (s, 2H), 7.66 (d, J = 5.4 Hz, 2H), 7.60 (d, J = 5.4 Hz, 2H), 4.40 (t, J = 6.6 Hz, 4H), 1.82 (m, 4H), 1.53 (m, 4H), 1.07 (t, J = 7.5 Hz, 6H). ^{13}C NMR (150 MHz, THF-d_8) δ: 163.73, 143.78, 141.93, 137.74, 131.91, 130.22, 126.15, 122.75, 65.59, 32.17, 20.60, 14.52. MS (ESI) *m*/*z* calcd. for ($C_{24}H_{24}O_4S_4$): 504.1. Found: 526.8 ($[M+Na]^+$). Anal. Calcd. for $C_{24}H_{24}OS_4$: C, 57.11; H, 4.79. Found: C, 57.05; H, 4.85.

*(2-(5-(3-(Bis(4-hexylphenyl)(hydroxy)methyl)thiophen-2-yl)thieno[3,2-b]thiophen-2-yl)thiophen-3-yl)bis(4-hexylphenyl)methanol (**11**).* To a suspended solution of magnesium chips (1.000 g, 41.152 mmol) and 4-hexyl-phenylbromide (6.921 g, 28.700 mmol) in anhydrous THF (38 mL) was added a few crystals of iodine to initiate reaction. The resulting mixture was refluxed for 2 h and then cooled to room temperature. **10** (1.036 g, 2.463 mmol) was added before the reaction was refluxed for another 1 h. The solution was cooled to room temperature again and poured into cold 1 M hydrochloric acid aqueous solution. The solution was extracted with ethyl acetate before the organic phase was washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography over silica gel with dichloromethane/petroleum ether (*v*/*v*, 1/1) as the eluent to afford a viscous yellow oil as the desired product **11** (1.558 g, 63%). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 7.40 (d, J = 5.4 Hz, 2H), 7.08 (d, J = 7.8 Hz, 8H), 7.00 (d, J = 8.4 Hz, 8H), 6.77 (s, 2H), 6.51 (d, J = 5.4 Hz, 2H), 6.36 (s, 2H), 2.48 (m, 8H), 1.48 (m, 8H), 1.24 (m, 24H), 0.83 (t, J = 6.6 Hz, 12H). ^{13}C NMR (150 MHz, THF-d_8) δ: 147.33, 146.76, 142.44, 140.57, 138.23, 134.75, 133.12, 128.85, 128.66, 124.24, 122.03, 80.73, 36.79, 33.15, 32.89, 30.43, 23.99, 14.93. MS (ESI) *m*/*z* calcd. for ($C_{64}H_{76}O_2S_4$): 1004.5. Found: 1027.7 ($[M+Na]^+$). Anal. Calcd. for $C_{64}H_{76}O_2S_4$: C, 76.44; H, 7.62. Found: C, 76.37; H, 7.71.

*5,5,10,10-Tetrakis(4-hexylphenyl)-3,5,8,10-tetrahydro-cyclopenta[1,2-b:5,4-b']dithiophene[2',1':4,5]thieno[2,3-d]thiophene (**12**).* To a stirred solution of **11** (1.130 g, 1.124 mmol) in toluene (122 mL) was added Amberlyst 15 (0.629 g). The resulting mixture was refluxed for 3 h and then cooled to room temperature. The solution was filtered and washed with toluene and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel with petroleum ether as the eluent to afford a yellow solid as the desired product **12** (0.567 g, 52% yield). ^{1}H NMR (600 MHz, THF-d_8) δ: 7.47 (d, J = 4.8 Hz, 2H), 7.29 (m, 10H), 7.22 (d, J = 7.8 Hz, 8H), 2.70 (t, J = 7.5 Hz, 8H), 1.73 (m, 8H), 1.47 (m, 24H), 1.04 (t, J = 6.3 Hz, 12H). ^{13}C NMR (150 MHz, THF-d_8) δ: 158.86, 149.93, 142.91, 141.47, 138.26, 138.13, 136.32, 129.73, 129.16, 127.06, 124.71, 63.51, 36.86, 33.14, 32.87, 30.54, 23.93, 14.88. MS (ESI) *m/z* calcd. for ($C_{64}H_{72}S_4$): 968.5. Found: 969.3 ($[M+H]^+$). Anal. Calcd. for $C_{64}H_{72}S_4$: C, 79.29; H, 7.49. Found: C, 79.22; H, 7.51.

*5,5,10,10-Tetrakis(4-hexylphenyl)-3,5,8,10-tetrahydro-cyclopenta[1,2-b:5,4-b']dithiophene[2',1':4,5]thieno[2,3-d]thiophene-2-carbaldehyde (**13**).* To a stirred solution of **12** (0.297 g, 0.307 mmol) and anhydrous DMF (0.066 mL, 0.865 mmol) in 1,2-dichloroethane (10 mL) was added phosphoryl trichloride (0.059 mL, 0.461 mmol). The resulting mixture was stirred for 4 h at room temperature and then saturated sodium acetate aqueous solution (10 mL) was added. After stirring at room temperature overnight, the solution was extracted with dichloromethane before the organic phase was washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography over silica gel with dichloromethane/petroleum ether (*v*/*v*, 1/1) as the eluent to afford an orange solid as the desired product **13** (0.262 g, 85% yield). ^{1}H NMR (600 MHz, THF-d_8) δ: 9.94 (s, 1H), 8.04 (s, 1H), 7.55 (d, J = 4.2 Hz, 1H), 7.32 (m, 5H), 7.29 (d, J = 7.8 Hz, 4H), 7.24 (m, 8H), 2.72 (m, 8H), 1.73 (m, 8H), 1.49 (m, 24H), 1.04 (m, 12H). ^{13}C NMR (150 MHz, THF-d_8) δ: 182.91, 159.88, 158.74, 153.70, 149.88, 147.63, 145.77, 143.41, 143.11, 141.15, 141.02, 140.48, 139.42, 137.82, 137.00, 136.06, 133.11, 129.95, 129.83, 129.10, 128.27, 124.80, 63.73, 63.56, 36.85, 33.13, 32.86, 30.53, 23.93, 14.88. MS (ESI) *m/z* calcd. for ($C_{65}H_{72}OS_4$): 996.4. Found: 997.3 ($[M+H]^+$). Anal. Calcd. for $C_{65}H_{72}OS_4$: C, 78.26; H, 7.28. Found: C, 78.19; H, 7.33.

*7-Bromo-5,5,10,10-tetrakis(4-hexylphenyl)-3,5,8,10-tetrahydro-cyclopenta[1,2-b:5,4-b']dithiophene[2',1':4,5]thieno[2,3-d]thiophene-2-carbaldehyde (**14**).* To a stirred solution of **13** (0.260 g, 0.261 mmol) in THF (10 mL) was added NBS (51 mg, 0.287 mmol). The resulting mixture was stirred overnight and then the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography over silica gel with dichloromethane/petroleum ether (*v*/*v*, 1/1) as the eluent to afford a orange solid as the desired product **14** (0.272 g, 97% yield). ^{1}H NMR (600 MHz, THF-d_8) δ: 9.94 (s, 1H), 8.04 (s, 1H), 7.45 (s, 1H), 7.31 (d, J = 7.8 Hz, 4H), 7.28 (d, J = 8.4 Hz, 4H), 7.25 (m, 8H), 2.72 (t, J = 7.8 Hz, 8H), 1.74 (m, 8H), 1.47 (m, 24H), 1.04 (t, J = 6.6 Hz, 12H). ^{13}C NMR (150 MHz, THF-d_8) δ: 182.95, 158.91, 158.51, 153.64, 149.39, 147.47, 145.98, 143.45, 143.37, 140.51, 140.42, 140.23, 139.15, 138.50, 137.50, 136.59, 133.08, 129.96, 129.08, 129.05, 128.10, 113.87, 64.19, 63.73, 36.84, 33.14, 32.86, 30.53, 23.94, 14.88. MS (ESI) *m/z* calcd. for ($C_{65}H_{71}BrOS_4$): 1074.4. Found: 1075.5 ($[M+H]^+$). Anal. Calcd. for $C_{65}H_{71}BrOS_4$: C, 72.53; H, 6.65. Found: C, 72.49; H, 6.73.

*7-(4-(N,N-Bis(4-hexyloxyphenyl)amino)phenyl)-5,5,10,10-tetrakis(4-hexylphenyl)-3,5,8,10-tetrahydro-cyclopenta[1,2-b:5,4-b']dithiophene[2',1':4,5]thieno[2,3-d]thiophene-2-carbaldehyde (**15**).* To a stirred solution of **14** (0.260 g, 0.242

mmol), 4,4,5,5-tetramethyl-2-{4-[*N*,*N*-bis(4-hexyloxyphenyl)amino]phenyl}-1,3,2-dioxaborolane (0.166 g, 0.290 mmol) and K_3PO_4 (0.257 g, 1.210 mmol) in dioxane/H_2O (*v*/*v*, 5/1, 15 mL) was added SPhos (2 mg, 0.005 mmol) and palladium acetate (1 mg, 0.005 mmol). The resulting mixture was stirred at 45 ^{o}C for 5 h and then cooled to room temperature. The solution was extracted with ethyl acetate before the organic phase was washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography over silica gel with dichloromethane/petroleum ether (*v*/*v*, 1/2) as the eluent to afford a red powder as the desired product **15** (0.321 g, 92% yield). ^{1}H NMR (600 MHz, THF-d_8) δ: 9.94 (s, 1H), 8.03 (s, 1H), 7.58 (d, J = 8.4 Hz, 2H), 7.54 (s, 1H), 7.33 (m, 8H), 7.25 (m, 8H), 7.17 (d, J = 9.0 Hz, 4H), 7.03 (d, J = 9.0 Hz, 2H), 7.00 (d, J = 9.0 Hz, 4H), 4.10 (t, J = 6.6 Hz, 4H), 2.71 (m, 8H), 1.92 (m, 4H), 1.74 (m, 8H), 1.66 (m, 4H), 1.51 (m, 32H), 1.09 (t, J = 6.6 Hz, 6H), 1.04 (t, J = 6.0 Hz, 12H). ^{13}C NMR (150 MHz, THF-d_8) δ: 182.82, 161.00, 158.68, 157.38, 153.82, 149.95, 149.10, 148.38, 147.67, 145.65, 143.39, 143.06, 141.79, 141.49, 141.01, 140.49, 139.46, 136.72, 135.97, 135.46, 133.09, 129.96, 129.84, 129.17, 129.12, 128.07, 127.88, 127.15, 121.69, 119.49, 116.49, 69.25, 63.87, 63.71, 36.86, 33.14, 33.06, 32.89, 32.87, 30.79, 30.55, 30.53, 27.22, 24.00, 23.94, 14.88. MS (ESI) *m*/*z* calcd. for ($C_{95}H_{109}NO_3S_4$): 1439.7. Found: 1440.5 ([M+H]$^+$). Anal. Calcd. for $C_{95}H_{109}NO_3S_4$: C, 79.17; H, 7.62; N, 0.97. Found: C, 79.11; H, 7.71; N, 0.93.

3-(7-(4-(N,N-Bis(4-hexyloxyphenyl)amino)phenyl)-5,5,10,10-tetrakis(4-hexylphenyl)-3,5,8,10-tetrahydro-cyclopenta[1,2-b:5,4-b′]dithiophene[2′,1′:4,5]thieno[2,3-d]thiophene-2-yl)-2-cyanoacrylic acid (***C243***). To a stirred solution of **15** (0.300 g, 0.208 mmol) and cyanoacetic acid (53 mg, 0.625 mmol) in chloroform (15 mL) was added piperidine (0.143 mL, 1.456 mmol). The resulting mixture was refluxed for 20 h and then cooled to room temperature before acidified with 2 M hydrochloric acid aqueous solution. The solution was extracted with chloroform before the organic phase was washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography over silica gel with methanol/toluene (*v*/*v*, 1/20) as the eluent to afford a purple-black powder as the desired product **C243** (0.297 g, 95% yield). ^{1}H NMR (600 MHz, THF-d_8) δ: 8.48 (s, 1H), 8.02 (s, 1H), 7.59 (d, J = 9.0 Hz, 2H), 7.55 (s, 1H), 7.34 (d, J = 8.4 Hz, 4H), 7.32 (d, J = 7.8 Hz, 4H), 7.25 (m, 8H), 7.17 (d, J = 9.0 Hz, 4H), 7.03 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 9.0 Hz, 4H), 4.10 (t, J = 6.3 Hz, 4H), 2.70 (m, 8H), 1.93 (m, 4H), 1.74 (m, 8H), 1.66 (m, 4H), 1.51 (m, 32H), 1.09 (t, J = 7.2 Hz, 6H), 1.04 (t, J = 6.6 Hz, 12H). ^{13}C NMR (150 MHz, THF-d_8) δ: 164.94, 161.20, 158.86, 157.40, 154.22, 150.01, 149.52, 149.16, 148.62, 147.64, 143.47, 143.13, 141.99, 141.81, 141.01, 140.39, 138.31, 136.85, 135.98, 135.46, 134.61, 130.00, 129.87, 129.16, 129.11, 127.90, 127.19, 121.68, 119.51, 117.75, 116.50, 96.93, 69.26, 63.90, 63.56, 36.86, 33.14, 33.06, 32.87, 30.78, 30.55, 27.22, 24.01, 23.94, 14.88. HR-MS (MALDI): *m*/*z* calcd for ($C_{98}H_{110}N_2O_4S_4$): 1507.73484. Found: 1507.73716. Anal. Calcd. for $C_{98}H_{110}N_2O_4S_4$: C, 78.04; H, 7.35; N, 1.86; Found: C, 77.97; H, 7.42; N, 1.84. IR (KBr): 1680 cm^{-1} (COOH), 2215 cm^{-1} (CN).

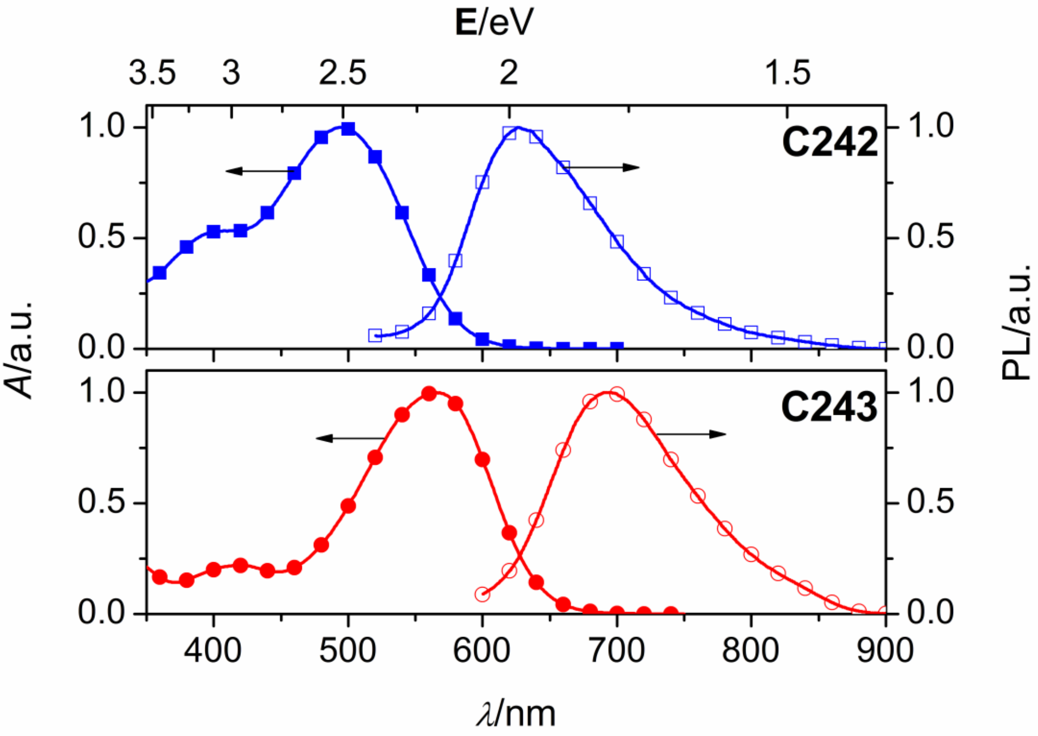


Fig. S1 Static electronic absorption and PL spectra of 200 μM **C242** and **C243** in THF.

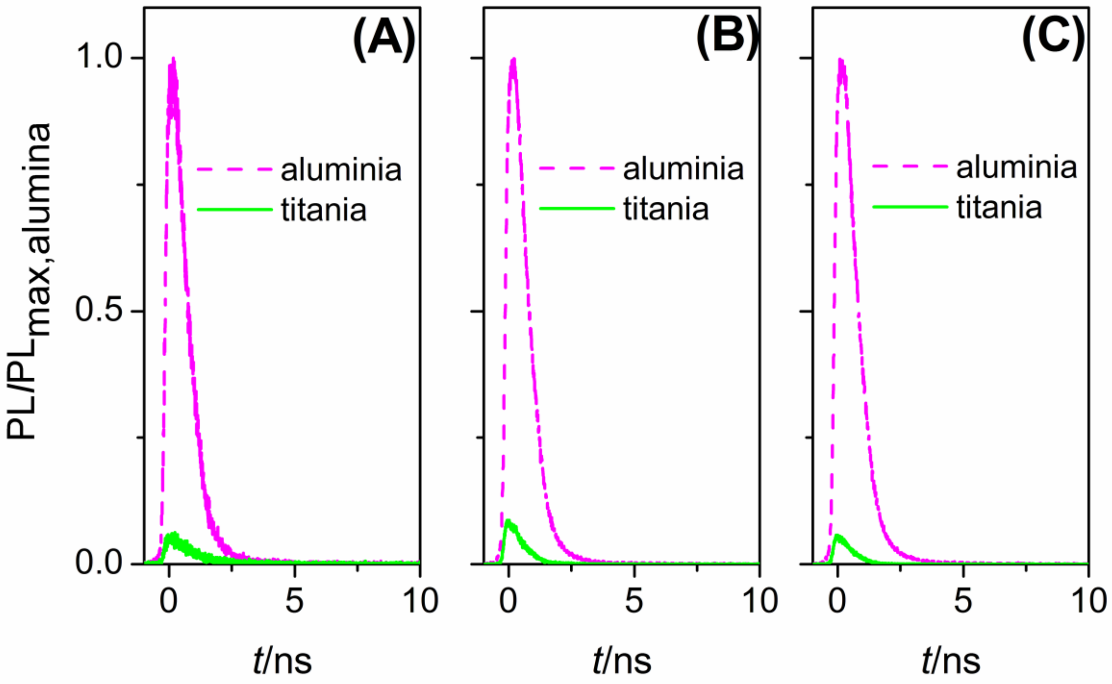


Fig. S2 PL decay traces of alumina and titania films coated with (**A**) **C242** from THF, (**B**) **C243** from THF and (**C**) **C243** from the binary solvent of THF and AN. Excitation wavelength: 488 nm. PL was corrected in regard to the absorbance at 488 nm and normalized with respect to the maximum PL intensity of a dye-coated alumina film (PL$_{max,alumina}$).

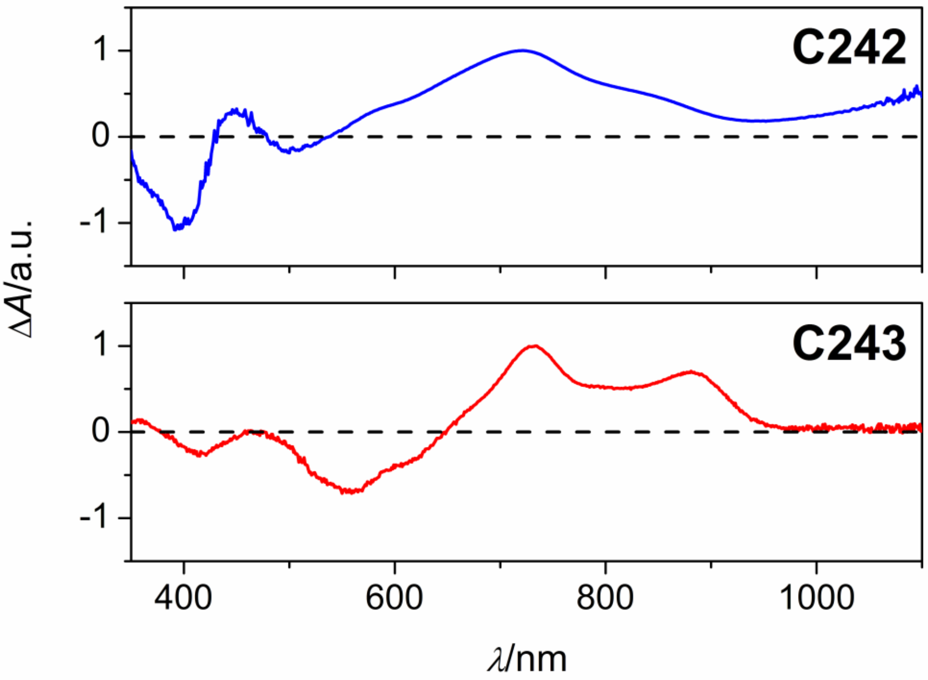
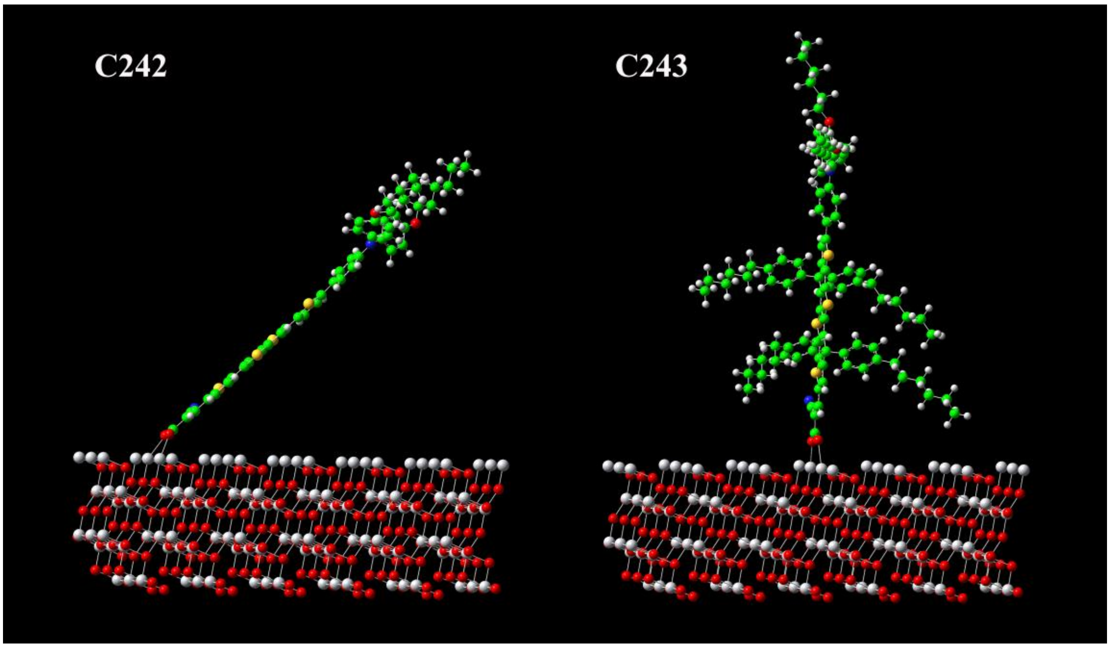


Fig. S3 Wavelength-dependent absorption change after applying a positive potential bias to a dye-coated titania film immersed in EMITFSI.

Scheme S3 Pictorial adsorption geometries of C242 and C243 on the surface of titania



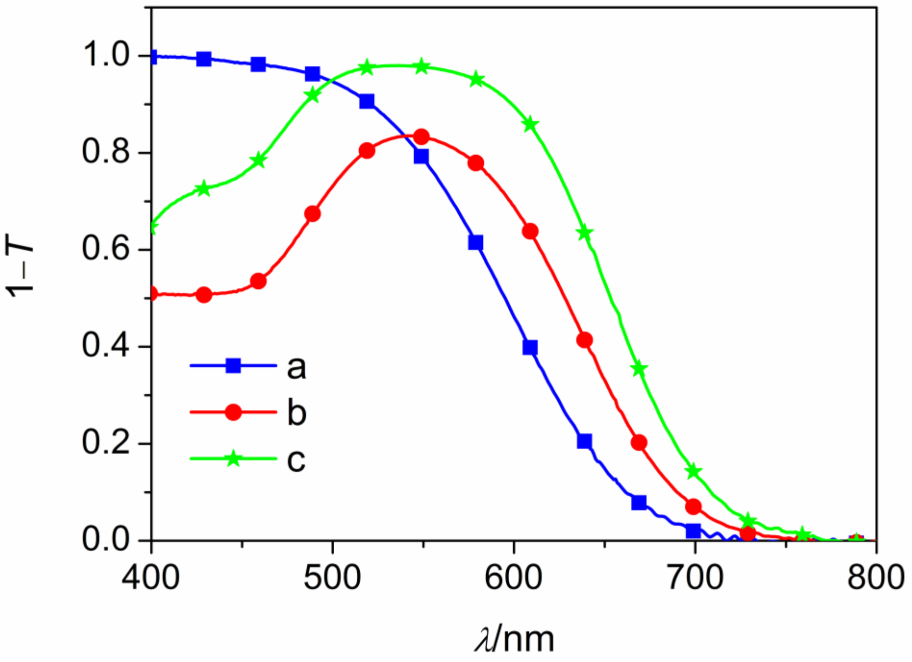


Fig. S4 Absorption spectra of 2.4-µm titania films coated with (a) **C242** from THF, (b) **C243** from THF and (c) **C243** from the binary solvent of THF and AN, immersed in the cobalt electrolyte for DSC fabrication.

Table S1 Photovoltaic parameters measured at an irradiation of the 100 mW cm^{-2}, simulated AM1.5 sunlight[a]

dye	bath solvent	cell code	j_{sc}/mA cm^{-2}	V_{oc}/V	FF	η/%
C242	THF	a-1	12.92	0.72	0.756	7.0
		a-2	12.94	0.71	0.755	6.9
		a-3	12.97	0.72	0.759	7.1
C243	THF	b-1	13.55	0.72	0.764	7.5
		b-2	13.50	0.72	0.763	7.4
		b-3	13.45	0.72	0.763	7.4
C243	THF+AN	c-1	15.67	0.75	0.756	8.9
		c-2	15.30	0.75	0.770	8.8
		c-3	15.66	0.75	0.752	8.8

[a] The validity of our photovoltaic data is confirmed by comparing the calculated j_{sc} via wavelength integration of the product of the standard AM1.5 emission spectrum (ASTM G173-03) and measured IPCE spectra with the experimental j_{sc}, showing a less than 5% error. Also note that all our cells show a linear dependence of photocurrent on light intensity.

Table S2 Experimental intensity (*I*) of Ti2$p_{3/2}$ signal and calculated mean thickness of a dye coating on titania

sample	bath solvent	$I_{\mathrm{Ti\ 2p3/2}}$/a.u.	*d*/Å
TiO_2	—	23962	—
C242/TiO_2	THF	15511	18.4
C243/TiO_2	THF	21657	4.3
	THF+AN	11240	32.2