Electronic supplementary information

Design of high-efficiency organic dyes for titania solar cells based on the chromophoric core of cyclopentadithiophene-benzothiadiazole

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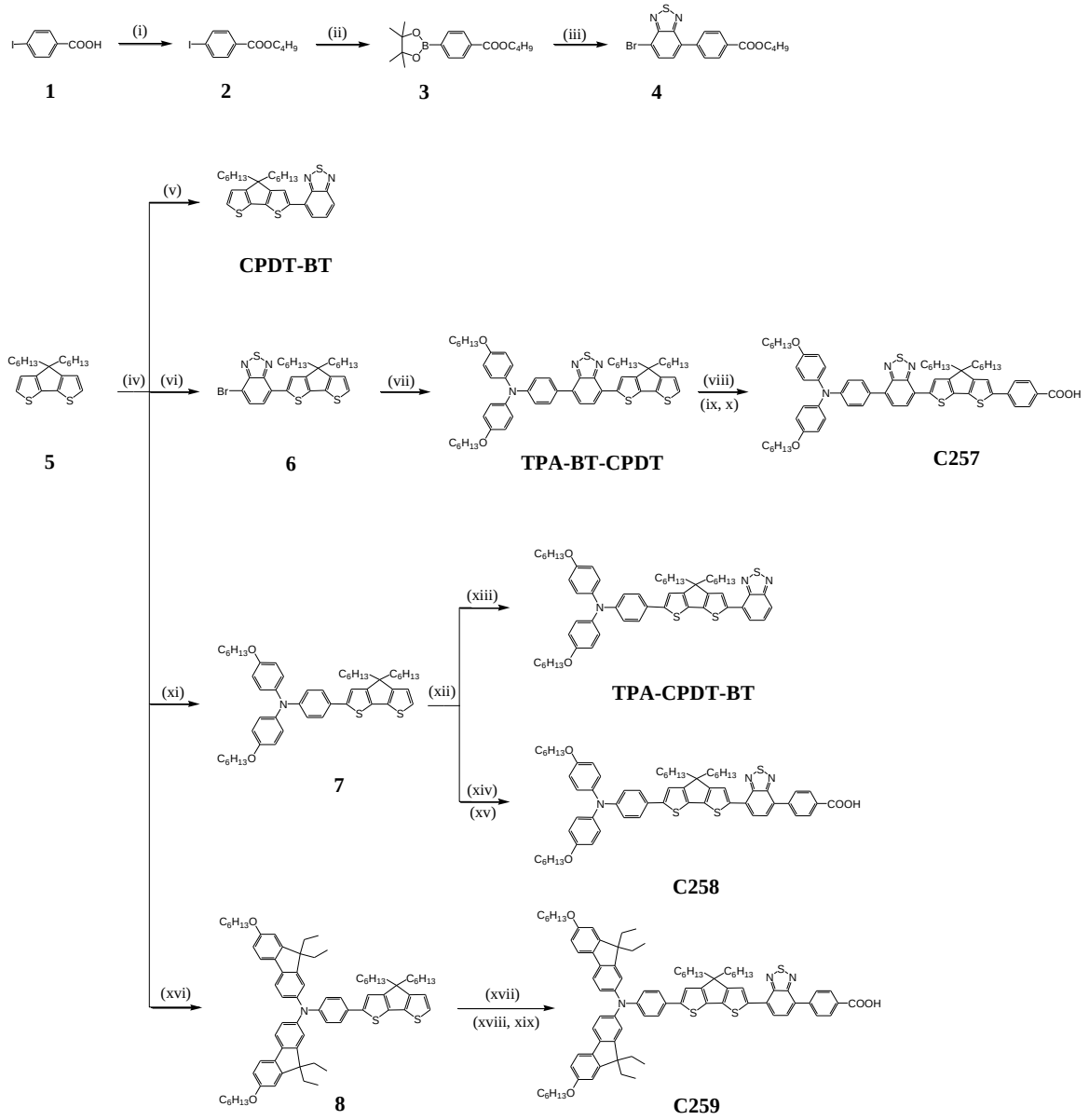
1 Experimental details

1.1 Materials

Acetonitrile, *tert*-butanol and tetrahydrofuran were distilled before use. 4,7-Dibromobenzo[*c*][1,2,5]thiadiazole,[S1] 4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*′]dithiophene (**5**),[S2] 4-bromobenzo[*c*][1,2,5]thiadiazole,[S3] 4,4,5,5-tetramethyl-2-{4-[*N*,*N*-bis(4-hexyloxyphenyl)amino]phenyl}-1,3,2-dioxaborolane[S2] and 4-(hexyloxy)-*N*-(4-(hexyloxy)phenyl)-*N*-(4-iodophenyl)aniline[S2] were synthesized according to the corresponding literature procedures. Other chemicals were purchased and used without further purification. The synthetic routes for **CPDT-BT**, **TPA-BT-CPDT**, **TPA-CPDT-BT**, **C257**, **C258** and **C259** are illustrated in Scheme S1.

Scheme S1 Synthetic routes of **CPDT-BT**, **TPA-BT-CPDT**, **TPA-CPDT-BT**, **C257**, **C258** and **C259** [a]

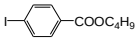


[a] Reagents and conditions: (i) 1-butanol, H_2SO_4, reflux, 20 h; (ii) bis(pinacolato)diboron, Pd(dppf)Cl_2, KOAc, DMSO, 45 °C, 12 h; (iii) 4,7-dibromobenzo[*c*][1,2,5]thiadiazole, Pd(PPh_3)$_4$, Na_2CO_3, ethanol/benzene/H_2O (v/v/v, 1/4/2), reflux, 2 h; (iv) *n*-BuLi, THF, –78 °C, 3 h; then Me_3SnCl, –78 °C to RT, 12 h; (v) 4-bromobenzo[*c*][1,2,5]thiadiazole, $Pd_2(dba)_3$, P(*t*-Bu)$_3$, CsF,

dioxane, 60 °C, 12 h; (vi) 4,7-dibromobenzo[*c*][1,2,5]thiadiazole, $Pd(PPh_3)_2Cl_2$, toluene, 60 °C, 1 h; (vii) 4,4,5,5-tetramethyl-2-{4-[*N*,*N*-bis(4-hexyloxyphenyl)amino]phenyl}-1,3,2-dioxaborolane, $Pd(PPh_3)_4$, Na_2CO_3, ethanol/benzene/H_2O (v/v/v, 1/4/2), reflux, 12 h; (viii) NBS, THF, RT, 12 h; (ix) **3**, $Pd(OAc)_2$, SPhos, K_3PO_4, dioxane/H_2O (v/v, 5/1), 60 °C, 12 h; (x) KOH, THF/H_2O (v/v, 3/1), reflux, 2 h; (xi) 4-(hexyloxy)-*N*-(4-(hexyloxy)phenyl)-*N*-(4-iodophenyl)aniline, $Pd_2(dba)_3$, P(*t*-Bu)$_3$, CsF, dioxane, 60 °C, 8 h; (xii) *t*-BuLi, THF, −78 °C, 3 h; then Me_3SnCl, −78 °C to RT, 12 h; (xiii) 4-bromobenzo[*c*][1,2,5]thiadiazole, $Pd_2(dba)_3$, P(*t*-Bu)$_3$, CsF, dioxane, 60 °C, 12 h; (xiv) **4**, $Pd_2(dba)_3$, P(*t*-Bu)$_3$, CsF, dioxane, 60 °C, 8 h; (xv) KOH, THF/H_2O (v/v, 3/1), reflux, 2 h; (xvi) *N*,*N*-bis[9,9-diethyl-7-(hexyloxy)-9*H*-fluoren-2-yl]-4-iodoaniline, $Pd_2(dba)_3$, P(*t*-Bu)$_3$, CsF, dioxane, 60 °C, 8 h; (xvii) *t*-BuLi, THF, −78 °C, 3 h; then Me_3SnCl, −78 °C to RT, 12 h; (xviii) **4**, $Pd_2(dba)_3$, P(*t*-Bu)$_3$, CsF, dioxane, 60 °C, 12 h; (xix) KOH, THF/H_2O (v/v, 3/1), reflux, 2 h. Herein, C_4H_9 and C_6H_{13} denote *n*-butyl and *n*-hexyl, respectively.

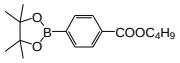
1.2 Synthetic procedures

1.2.1 Butyl 4-iodobenzoate (2)



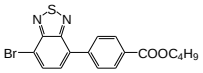
In a three-neck round-bottom flask was dissolved 4-iodobenzoic acid (**1**) (5.50 g, 22.18 mmol) in 1-butanol (50 mL). Concentrated sulfuric acid (1.5 mL) was added to the reaction mixture, whicn was refluxed for 20 h. Water was slowly added to quench the reaction and the solution was extracted three times with chloroform before the organic phase was washed with water and dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the crude product was purified by column chromatography (ethyl acetate/petroleum ether 60–90 °C, 1/20, v/v) on silica gel to yield a colorless oil as the desired product **2** (6.20 g, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H), 4.31 (t, J = 6.8 Hz, 2H), 1.74 (m, 2H), 1.46 (m, 2H), 0.97 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.96, 137.53, 130.88, 129.85, 100.47, 64.95, 30.59, 19.14, 13.67. MS (ESI) *m/z* calcd. for ($C_{11}H_{13}IO_2$): 304.0; Found: 305.0 ([M+H]$^+$). Anal. calcd. for $C_{11}H_{13}IO_2$: C, 43.44; H, 4.31. Found: C, 43.35; H, 4.33.

1.2.2 Butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (3)



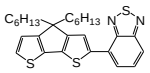
In a dried Schlenk tube were dissolved butyl 4-iodobenzoate (**2**) (6.10 g, 20.05 mmol), bis(pinacolato)diboron (25.45 g, 100.25 mmol) and KOAc (5.91 g, 49.72 mmol) in DMSO (100 mL). $Pd(dppf)Cl_2$ (0.74 g, 1.00 mmol) was added to the reaction mixture, which was stirred at 45 °C for 12 h. Water was added and the mixture was extracted three times with chloroform before the organic phase was washed with water and dried over anhydrous sodium sulfate. After solvent removel under reduced pressure, the crude product was purified by column chromatography (ethyl acetate/petroleum ether 60–90 °C, 1/200, v/v) on silica gel to yield a colorless oil as the desired product **3** (4.88 g, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, J = 8.4 Hz, 2H), 7.86 (d, J = 8.4 Hz, 2H), 4.31 (t, J = 6.8 Hz, 2H), 1.75 (m, 2H), 1.44 (m, 2H), 1.34 (s, 12H), 0.97 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.62, 134.56, 132.62, 128.47, 84.06, 64.84, 30.69, 24.80, 19.19, 13.70. MS (ESI) *m/z* calcd. for ($C_{17}H_{25}BO_4$): 304.2; Found: 305.2 ([M+H]$^+$). Anal. calcd. for $C_{17}H_{25}BO_4$: C, 67.12; H, 8.28. Found: C, 67.21; H, 8.24.

1.2.3 Butyl 4-(7-bromobenzo[*c*][1,2,5]thiadiazol-4-yl)benzoate (4)



In a dried Schlenk tube were dissolved **3** (4.00 g, 13.15 mmol), 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (4.64 g, 15.78 mmol) and Na_2CO_3 (16.37 g, 0.16 mol) in a solvent mixture of ethanol/benzene/H_2O (280 mL, 1/4/2, v/v/v). $Pd(PPh_3)_4$ (0.30 g, 0.26 mmol) was added to the reaction mixture, which was refluxed for 2 h. The mixture was extracted three times with chloroform before the organic phase was washed with water and dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the crude product was purified by column chromatography (ethyl acetate/petroleum ether 60–90 °C, 1/20, v/v) on silica gel to yield a colorless oil as the desired product **4** (3.34 g, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.16 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.4 Hz, 2H), 7.89 (d, J = 8.4 Hz, 1H), 7.57 (d, J = 8.4 Hz, 1H), 4.37 (t, J = 6.8 Hz, 2H), 1.79 (m, 2H), 1.50 (m, 2H), 1.00 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.11, 153.70, 152.68, 140.61, 132.62, 132.02, 130.34, 129.71, 128.96, 128.54, 114.04, 64.87, 30.67, 19.17, 13.67. MS (ESI) m/z calcd. for ($C_{17}H_{15}BrN_2O_2S$): 391.3. Found: 392.3 ($[M+H]^+$). Anal. calcd. for $C_{17}H_{15}BrN_2O_2S$: C, 52.18; H, 3.86; N, 7.16. Found: C, 52.33; H, 3.77; N, 7.09.

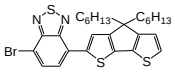
1.2.4 4-(4,4-Dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*′]dithiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (CPDT-BT)



In a three-neck flame-dried round-bottom flask was dissolved **5** (6.00 g, 17.3 mmol) in THF (50 mL) and cooled to −78 °C using a dry ice/acetone cold bath. Under argon, *n*-BuLi (10.8 mL, 1.6 M in hexanes, 17.3 mmol) was added dropwise to the reaction mixture, which was stirred for 3 h at −78 °C . After trimethylstannyl chloride (3.50 g, 17.3 mmol) was added in one portion *via* syringe, the mixture was slowly warmed up and stirred for 12 h at room temperature. Water was slowly added to terminate the reaction and the mixture was extracted three times with diethyl ether before the organic phase was washed with water and dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the crude product (4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*′]dithiophen-2-yl)trimethylstannane was used to synthesize **CPDT-BT**, **6**, **7** and **8** without further purification.

In a dried Schlenk tube were dissolved (4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*′]dithiophen-2-yl)trimethylstannane (0.10 g, 0.15 mmol) and 4-bromobenzo[*c*][1,2,5]thiadiazole (40 mg, 0.19 mmol) in dioxane (10 mL). P(*t*-Bu)$_3$ (21 μL, 10 wt% in hexanes, 0.0092 mmol), $Pd_2(dba)_3$ (2 mg, 0.0023 mmol) and CsF (51 mg, 0.34 mmol) were added to the reaction mixture, which was stirred at 60 °C for 12 h. Water was added to terminate the reaction and the mixture was extracted three times with chloroform before the organic phase was washed with water and dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the crude product was purified by column chromatography (toluene/petroleum ether 60–90 °C, 1/1, v/v) on silica gel to yield a red oil as the desired product **CPDT-BT** (54 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.06 (s, 1H), 7.81 (m, 2H), 7.55 (t, J = 8.0 Hz, 1H), 7.21 (d, J = 4.8 Hz, 1H), 6.96 (d, J = 4.8 Hz, 1H), 1.92 (m, 4H), 1.15 (m, 12H), 1.03 (m, 4H), 0.79 (t, J = 6.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.79, 155.54, 151.82, 138.97, 138.54, 136.42, 129.64, 128.39, 125.73, 123.59, 122.44, 121.63, 118.90, 53.71, 37.75, 31.55, 29.65, 24.50, 22.55, 13.99. MS (ESI) m/z calcd. for ($C_{27}H_{32}N_2S_3$): 480.2. Found: 481.2 ($[M+H]^+$). Anal. calcd. for $C_{27}H_{32}N_2S_3$: C, 67.45; H, 6.71; N, 5.83. Found: C, 67.22; H, 6.53; N, 5.92.

1.2.5 4-Bromo-7-(4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*′]dithiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (6)

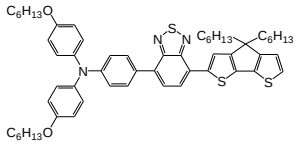


In a dried Schlenk tube were dissolved (4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*′]dithiophen-2-yl)trimethylstannane (1.14 g, 1.74 mmol) and 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (1.00 g, 3.48 mmol) in toluene (15 mL). $Pd(PPh_3)_2Cl_2$ (74 mg, 0.10 mmol) was added to the reaction mixture, which was stirred at 60 °C for 1 h. After solvent removal under reduced pressure, the

crude product was purified by column chromatography (toluene/petroleum ether 60–90 °C, 1/4, v/v) on silica gel to yield a red oil as the desired product **6** (0.40 g, 37% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (s, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.24 (d, J = 4.8 Hz, 1H), 6.97 (d, J = 4.8 Hz, 1H), 1.91 (t, J = 8.0 Hz, 4H), 1.15 (m, 12H), 1.03 (m, 4H), 0.79 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.08, 158.97, 153.80, 151.51, 139.19, 138.20, 136.34, 132.29, 128.00, 126.13, 123.92, 122.72, 121.71, 110.84, 53.81, 37.77, 31.57, 29.66, 24.53, 22.56, 13.99. MS (ESI) m/z calcd. for ($C_{27}H_{31}BrN_2S_3$): 558.1. Found: 559.1 ([M+H]$^+$). Anal. calcd. for $C_{27}H_{31}BrN_2S_3$: C, 57.95; H, 5.58; N, 5.01. Found: C, 58.13; H, 5.62; N, 4.99.

1.2.6

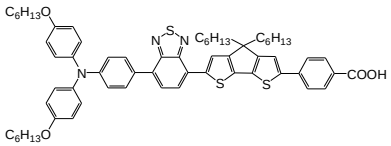
4-(7-(4,4-Dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*′]dithiophen-2-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)-*N*,*N*-bis(4-(hexyloxy)phenyl)aniline (TPA-BT-CPDT)



In a dried Schlenk tube were dissolved **6** (0.36 g, 0.64 mmol), 4,4,5,5-tetramethyl-2-{4-[*N*,*N*-bis(4-hexyloxyphenyl)amino]phenyl}-1,3,2-dioxaborolane (0.44 g, 0.78 mmol) and Na_2CO_3 (0.82 g, 7.68 mmol) in a solvent mixture of ethanol/benzene/H_2O (28 mL, 1/4/2, v/v/v). $Pd(PPh_3)_4$ (24 mg, 0.02 mmol) was added to the reaction mixture, which was refluxed for 12 h. The mixture was extracted three times with chloroform before the organic phase was washed with water and dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the crude product was purified by column chromatography (toluene/petroleum ether 60–90 °C, 1/3, v/v) on silica gel to yield a red powder as the desired product **TPA-BT-CPDT** (0.48 g, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.04 (s, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.82 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 7.6 Hz, 1H), 7.20 (d, J = 4.4 Hz, 1H), 7.12 (d, J = 8.8 Hz, 4H), 7.04 (d, J = 8.4 Hz, 2H), 6.96 (d, J = 4.4 Hz, 1H), 6.84 (d, J = 8.8 Hz, 4H), 3.94 (t, J = 6.4 Hz, 4H), 1.92 (m, 4H), 1.79 (m, 4H), 1.47 (m, 4H), 1.35 (m, 8H), 1.15 (m, 12H), 1.04 (m, 4H), 0.91 (m, 6H), 0.80 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.88, 158.65, 155.73, 154.04, 152.62, 148.89, 140.31, 139.50, 138.23, 136.63, 131.58, 129.59, 128.70, 126.96, 126.81, 126.24, 125.53, 124.40, 121.78, 121.66, 119.67, 115.30, 68.23, 53.75, 37.83, 31.58, 29.70, 29.30, 25.74, 24.55, 22.58, 14.01. MS (ESI) m/z calcd. for ($C_{57}H_{69}N_3O_2S_3$): 923.5. Found: 924.5 ([M+H]$^+$). Anal. calcd. for $C_{57}H_{69}N_3O_2S_3$: C, 74.06; H, 7.52; N, 4.55. Found: C, 74.12; H, 7.59; N, 4.53.

1.2.7

4-(6-(7-(4-(Bis(4-(hexyloxy)phenyl)amino)phenyl)benzo[*c*][1,2,5]thiadiazol-4-yl)-4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*′]dithiophen-2-yl)benzoic acid (C257)



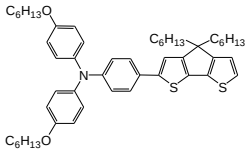
In a three-neck round-bottom flask was dissolved **TPA-BT-CPDT** (0.24 g, 0.26 mmol) in THF (10 mL) and cooled to 0 °C using an ice/water cold bath. NBS (49 mg, 0.27 mmol) was added to the reaction mixture, which was slowly warmed up and stirred for 12 h at room temperature. Chloroform was added before the organic phase was washed with water and dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the crude product was purified by column chromatography (toluene/petroleum ether 60–90 °C, 1/2, v/v) on silica gel to yield a red oil as the intermediate product 4-(7-(6-bromo-4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*′]dithiophen-2-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)-*N*,*N*-bis(4-(hexyloxy)p

henyl)aniline, which was used for the next reaction directly.

In a dried Schlenk tube were dissolved 4-(7-(6-bromo-4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*′]dithiophen-2-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)-*N*,*N*-bis(4-(hexyloxy)phenyl)aniline (0.26 g, 0.25 mmol) and **3** (77 mg, 0.25 mmol) in a solvent mixture of dioxane/H_2O (12 mL, 5/1, v/v). SPhos (4 mg, 0.005 mmol), $Pd(OAc)_2$ (2 mg, 0.005 mmol) and K_3PO_4 (0.27 g, 1.25 mmol) were added to the reaction mixture, which was stirred at 60 °C for 12 h. Chloroform was added before the organic phase was washed with water and dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the crude product was purified by column chromatography (toluene/petroleum ether 60–90 °C, 1/1, v/v) on silica gel to yield the desired butyl ester.

In a three-neck round-bottom flask were dissolved butyl ester (0.23 g, 0.21 mmol) and KOH (0.12 g, 2.10 mmol) in a solvent mixture of THF/H_2O (8 mL, 3/1, v/v). The reaction mixture was refluxed for 2 h and then cooled to room temperature. Chloroform was added before the organic phase was washed with 0.1 M hydrochloric acid and deionized water in turn and then dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the crude product was purified by column chromatography (chloroform/methanol, 10/1, v/v) on silica gel to yield a black solid as the desired product **C257** (0.22 g, 90% yield). ^{1}H NMR (400 MHz, THF-d_8) δ: 8.22 (s, 1H), 8.03 (m, 3H), 7.92 (d, J = 7.6 Hz, 2H), 7.75 (m, 3H), 7.58 (s, 1H), 7.09 (d, J = 8.4 Hz, 4H), 6.99 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 8.4 Hz, 4H), 3.95 (t, J = 6.0 Hz, 4H), 2.04 (m, 4H), 1.77 (m, 4H), 1.50 (m, 4H), 1.37 (m, 8H), 1.29 (m, 4H), 1.15 (m, 12H), 0.93 (m, 6H), 0.79 (m, 6H). ^{13}C NMR (100 MHz, THF-d_8) δ: 167.85, 161.06, 160.50, 157.46, 155.38, 154.03, 150.47, 145.40, 142.50, 141.81, 140.46, 139.43, 139.04, 133.09, 131.03, 130.92, 130.08, 128.21, 127.73, 127.28, 125.90, 125.71, 123.08, 120.84, 120.67, 116.53, 69.25, 55.65, 39.37, 33.42, 30.85, 30.79, 27.52, 25.99, 23.99, 14.86. HR-MS (MALDI-TOF) *m*/*z* calcd. for ($C_{64}H_{73}N_3O_4S_3$): 1043.47632. Found: 1043.47697. Anal. calcd. for $C_{64}H_{73}N_3O_4S_3$: C, 73.60; H, 7.04; N, 4.02. Found: C, 73.56; H, 7.10; N, 4.03.

1.2.8 4-(4,4-Dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*′]dithiophen-2-yl)-*N*,*N*-bis(4-(hexyloxy)phenyl)aniline (7)

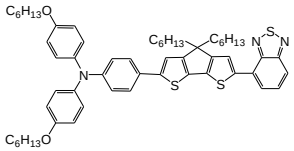


In a dried Schlenk tube were dissolved (4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*′]dithiophen-2-yl)trimethylstannane (2.21 g, 4.33 mmol) and 4-(hexyloxy)-*N*-(4-(hexyloxy)phenyl)-*N*-(4-iodophenyl)aniline (2.47 g, 4.33 mmol) in dioxane (20 mL). Then P(*t*-Bu)$_3$ (0.61 mL, 10 wt% in hexanes, 0.26 mmol), $Pd_2(dba)_3$ (59 mg, 0.065 mmol) and CsF (1.44 g, 9.53 mmol) were added to the reaction mixture, which was stirred at 60 °C for 8 h. Water was added to terminate the reaction and the mixture was extracted three times with chloroform before the organic phase was washed with water and dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the crude product was purified by column chromatography (toluene/petroleum ether 60–90 °C, 1/5, v/v) on silica gel to yield a viscous yellow liquid as the desired product **7** (2.60 g, 76% yield). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 7.46 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 4.8 Hz, 1H), 7.34 (s, 1H), 7.08 (d, J = 4.8 Hz, 1H), 7.01 (d, J = 8.4 Hz, 4H), 6.90 (d, J = 8.4 Hz, 4H), 6.78 (d, J = 8.4 Hz, 2H), 3.93 (t, J = 6.0 Hz, 4H), 1.18 (m, 4H), 1.69 (m, 4H), 1.41 (m, 4H), 1.31 (m, 8H), 1.09 (m, 12H), 0.88 (m, 10H), 0.77 (t, J = 7.2 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 158.96, 157.36, 155.48, 147.88, 144.44, 140.60, 136.85, 134.61, 127.51, 126.44, 125.79, 124.23, 121.56, 120.92, 116.36, 115.28, 68.28, 60.37, 53.62, 37.87, 31.61, 29.73, 29.34, 25.76, 24.50, 22.61, 14.03. MS (ESI) *m*/*z* calcd. for ($C_{51}H_{67}NO_2S_2$): 789.5. Found: 790.5 ([M+H]$^+$). Anal. calcd. for $C_{51}H_{67}NO_2S_2$: C, 77.52; H, 8.55; N, 1.77. Found: C, 77.21; H, 8.78; N, 1.89.

1.2.9

4-(6-(Benzo[*c*][1,2,5]thiadiazol-4-yl)-4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*′]dithiophen-2-yl)-*N*,*N*-bis(4-(hexyloxy)pheny

l)aniline (TPA-CPDT-BT)

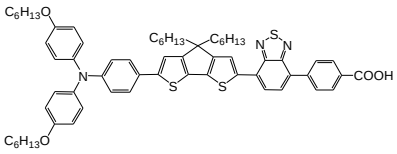


In a three-neck flame-dried round-bottom flask was dissolved **7** (2.40 g, 3.04 mmol) in THF (5 mL) and cooled to −78 °C using a dry ice/acetone cold bath. Under argon, *t*-BuLi (3.52 mL, 1.3 M in hexanes, 4.56 mmol) was added dropwise to the reaction mixture, which was stirred for 3 h at −78 °C. After trimethylstannyl chloride (0.90 g, 4.56 mmol) was added in one portion *via* syringe, the mixture was slowly warmed up and stirred for 12 h at room temperature. Water was added to terminate the reaction and the mixture was extracted three times with diethyl ether before the organic phase was washed with water and dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the crude product 4-(4,4-dihexyl-6-(trimethylstannyl)-4*H*-cyclopenta[1,2-*b*:5,4-*b*′]dithiophen-2-yl)-*N*,*N*-bis(4-(hexyloxy)phenyl)aniline was used to synthesize **TPA-CPDT-BT** and **C258** without further purification.

In a dried Schlenk tube were dissolved 4-(4,4-dihexyl-6-(trimethylstannyl)-4*H*-cyclopenta[1,2-*b*:5,4-*b*′]dithiophen-2-yl)-*N*,*N*-bis(4-(hexyloxy)phenyl)aniline (0.30 g, 0.24 mmol) and 4-bromobenzo[*c*][1,2,5]thiadiazole (63 mg, 0.29 mmol) in dioxane (10 mL). P(*t*-Bu)$_3$ (35 μL, 10 wt% in hexanes, 0.015 mmol), $Pd_2(dba)_3$ (4 mg, 0.0036 mmol) and CsF (80 mg, 0.53 mmol) were added to the reaction mixture, which was stirred at 60 °C for 12 h. Water was added to terminate the reaction and the mixture was extracted three times with chloroform before the organic phase was washed with water and dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the crude product was purified by column chromatography (toluene/petroleum ether 60–90 °C, 1/1, v/v) on silica gel to yield a red powder as the desired product **TPA-CPDT-BT** (0.17 g, 78% yield). ^{1}H NMR (400 MHz, THF-d_8) δ: 8.23 (s, 1H), 7.91 (d, J = 7.2 Hz, 1H), 7.83 (d, J = 8.8 Hz, 1H), 7.62 (t, J = 7.6 Hz, 1H), 7.45 (d, J = 8.8 Hz, 1H), 7.25 (s, 1H), 7.01 (d, J = 8.4 Hz, 4H), 6.89 (d, J = 8.4 Hz, 1H), 6.84 (d, J = 8.8 Hz, 2H), 3.93 (t, J = 6.4 Hz, 4H), 1.99 (m, 4H), 1.76 (m, 4H), 1.48 (m, 4H), 1.36 (m, 8H), 1.29 (m, 4H), 1.17 (m, 12H), 1.07 (m, 4H), 0.92 (t, J = 6.4 Hz, 6H), 0.79 (t, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, THF-d_8) δ: 160.95, 159.07, 156.99, 152.93, 149.43, 147.40, 141.60, 140.34, 140.14, 135.45, 130.84, 129.55, 128.81, 128.35, 127.51, 126.76, 124.48, 123.60, 121.64, 119.85, 117.40, 116.18, 68.93, 55.24, 39.13, 32.75, 30.89, 30.81, 30.48, 26.91, 25.62, 25.29, 25.09, 23.68, 14.55. MS (ESI) *m*/*z* calcd. for ($C_{57}H_{69}N_3O_2S_3$): 923.5. Found: 924.5 ([M+H]$^+$). Anal. calcd. for $C_{57}H_{69}N_3O_2S_3$: C, 74.06; H, 7.52; N, 4.55. Found: C, 74.29; H, 7.48; N, 4.46.

1.2.10

4-(7-(6-(4-(Bis(4-(hexyloxy)phenyl)amino)phenyl)-4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*′]dithiophen-2-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)benzoic acid (C258)



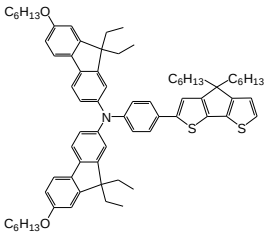
In a dried Schlenk tube were dissolved 4-(4,4-dihexyl-6-(trimethylstannyl)-4*H*-cyclopenta[1,2-*b*:5,4-*b*′]dithiophen-2-yl)-*N*,*N*-bis(4-(hexyloxy)phenyl)aniline (1.45 g, 1.52 mmol) and **4** (0.59 g, 1.52 mmol) in dioxane (40 mL). P(*t*-Bu)$_3$ (0.22 mL, 10 wt% in hexanes, 0.09 mmol), $Pd_2(dba)_3$ (22 mg, 0.02 mmol) and CsF (0.51 g, 3.34 mmol) were added to the reaction mixture, which was stirred at 60 °C for 8 h. Water was added to terminate the reaction and the mixture was extracted three times with chloroform before the organic phase was washed with water and dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the crude pruduct

was purified by column chromatography (toluene/petroleum ether 60–90 °C, 1/1, v/v) on silica gel to yield the desired butyl ester.

In a three-neck round-bottom flask were dissolved butyl ester (1.00 g, 0.91 mmol) and KOH (0.51 g, 9.09 mmol) in a solvent mixture of THF/H_2O (20 mL, 3/1, v/v). The reaction mixture was refluxed for 2 h and then cooled to room temperature. Chloroform was added before the organic phase was washed with 0.1 M hydrochloric acid and water in turn and then dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the crude product was purified by column chromatography (chloroform/methanol, 10/1, v/v) on silica gel to yield a black solid as the desired product **C258** (0.90 g, 74% yield). ^{1}H NMR (400 MHz, THF-d_8) δ: 11.44 (s, 1H), 8.29 (s, 1H), 8.18 (m, 4H), 8.06 (d, J = 7.6 Hz, 1H), 7.94 (d, J = 7.6 Hz, 1H), 7.48 (d, J = 8.4 Hz, 2H), 7.29 (s, 1H), 7.04 (d, J = 8.4 Hz, 4H), 6.92 (d, J = 8.4 Hz, 4H), 6.86 (d, J = 8.4 Hz, 2H), 3.96 (t, J = 6.4 Hz, 4H), 2.03 (m, 4H), 1.80 (m, 4H), 1.51 (m, 4H), 1.38 (m, 8H), 1.20 (m, 12H), 1.11 (m, 4H), 0.94 (t, J = 7.2 Hz, 6H), 0.81 (t, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, THF-d_8) δ: 164.37, 157.96, 156.01, 153.81, 151.75, 150.38, 146.27, 144.45, 139.24, 138.40, 137.60, 137.14, 132.31, 128.16, 127.95, 127.52, 126.69, 126.01, 125.12, 124.33, 123.59, 121.51, 120.38, 118.42, 114.22, 112.98, 65.74, 52.06, 35.94, 29.55, 27.69, 27.28, 23.71, 20.48, 11.34. HR-MS (MALDI-TOF) m/z calcd. for ($C_{64}H_{73}N_3O_4S_3$): 1043.47632. Found: 1043.47684. Anal. calcd. for $C_{64}H_{73}N_3O_4S_3$: C, 73.60; H, 7.04; N, 4.02. Found: C, 73.72; H, 6.98; N, 4.06.

1.2.11

***N*-(9,9-Diethyl-7-(hexyloxy)-9*H*-fluoren-2-yl)-*N*-(4-(4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*′]dithiophen-2-yl)phenyl)-9,9-diethyl-7-(hexyloxy)-9*H*-fluoren-2-amine (8)**

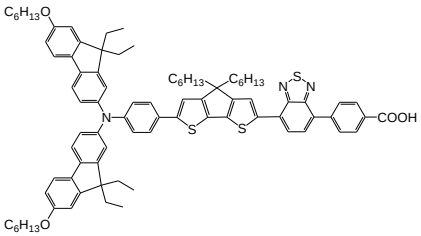


In a dried Schlenk tube were dissolved (4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*′]dithiophen-2-yl)trimethylstannane (1.62 g, 1.88 mmol) and *N*,*N*-bis[9,9-diethyl-7-(hexyloxy)-9*H*-fluoren-2-yl]-4-iodoaniline (1.15 g, 2.25 mmol) in dioxane (40 mL). Then P(*t*-Bu)$_3$ (0.26 mL, 10 wt% in hexanes, 0.11 mmol), $Pd_2(dba)_3$ (26 mg, 0.028 mmol) and CsF (0.63 g, 4.14 mmol) were added to the reaction mixture, which was stirred at 60 °C for 8 h. Water was added to terminate the reaction and the mixture was extracted three times with chloroform before the organic phase was washed with water and dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the crude product was purified by column chromatography (ethyl acetate/petroleum ether 60–90 °C, 1/100, v/v) on silica gel to yield a viscous yellow liquid as the desired product **8** (1.46 g, 72% yield). ^{1}H NMR (400 MHz, THF-d_8) δ: 7.54 (m, 3H), 7.51 (m, 3H), 7.28 (s, 1H), 7.21 (d, J = 4.8 Hz, 1H), 7.18 (s, 2H), 7.13 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 6.96 (d, J = 8.8 Hz, 1H), 6.89 (s, 2H), 6.85 (d, J = 8.8 Hz, 2H), 3.99 (t, J = 6.4 Hz, 4H), 1.92 (m, 12H), 1.80 (m, 4H), 1.52 (m, 4H), 1.38 (m, 8H), 1.16 (m, 12H), 1.00 (m, 4H), 0.93 (t, J = 6.4 Hz, 6H), 0.82 (t, J = 6.4 Hz, 6H), 0.38 (t, J = 6.8 Hz, 12H). ^{13}C NMR (100 MHz, THF-d_8) δ: 160.22, 159.97, 158.50, 152.41, 151.62, 148.56, 147.20, 145.50, 138.31, 137.78, 135.99, 135.28, 130.14, 126.73, 125.82, 124.46, 124.36, 122.43, 120.71, 120.44, 120.05, 117.79, 113.89, 110.28, 68.87, 57.07, 45.72, 39.09, 33.80, 32.81, 32.74, 30.86, 30.59, 26.96, 25.52, 23.68, 14.66, 9.23. MS (ESI) m/z calcd. for ($C_{73}H_{91}NO_2S_2$): 1077.65. Found: 1078.43 ([M+H]$^+$). Anal. calcd. for $C_{73}H_{91}NO_2S_2$: C, 81.29; H, 8.50; N, 1.30. Found: C, 81.08; H, 8.91; N, 1.19.

1.2.12

4-(7-(6-(4-(Bis(9,9-diethyl-7-(hexyloxy)-9*H*-fluoren-2-yl)amino)phenyl)-4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*′]dithiophe

n-2-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)benzoic acid (C259)



In a three-neck flame-dried round-bottom flask was dissolved **8** (0.48 g, 0.45 mmol) in THF (7 mL) and cooled to −78 °C using a dry ice/acetone cold bath. Under argon, *t*-BuLi (0.51 mL, 1.3 M in hexanes, 0.67 mmol) was added dropwise to the reaction mixture, which was stirred for 3 h at −78 °C. After trimethylstannyl chloride (0.13 g, 0.67 mmol) was added in one portion *via* syringe, the mixture was slowly warmed up and stirred for 12 h at room temperature. Water was added to terminate the reaction and the mixture was extracted three times with diethyl ether before the organic phase was washed with water and dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the crude product *N*-(9,9-diethyl-7-(hexyloxy)-9*H*-fluoren-2-yl)-*N*-(4-(4,4-dihexyl-6-(trimethylstannyl)-4*H*-cyclopenta[1,2-*b*:5,4-*b*′]dithiophen-2-yl)phenyl)-9,9-diethyl-7-(hexyloxy)-9*H*-fluoren-2-amine was used without further purification.

In a dried Schlenk tube were dissolved *N*-(9,9-diethyl-7-(hexyloxy)-9*H*-fluoren-2-yl)-*N*-(4-(4,4-dihexyl-6-(trimethylstannyl)-4*H*-cyclopenta[1,2-*b*:5,4-*b*′]dithiophen-2-yl)phenyl)-9,9-diethyl-7-(hexyloxy)-9*H*-fluoren-2-amine (0.55 g, 0.44 mmol) and **4** (0.12 g, 0.30 mmol) in dioxane (10 mL). P(*t*-Bu)$_3$ (0.042 mL, 10 wt% in hexanes, 0.02 mmol), $Pd_2(dba)_3$ (4 mg, 0.004 mmol) and CsF (98 mg, 0.65 mmol) were added to the reaction mixture, which was stirred at 60 °C for 8 h. Water was added to terminate the reaction and the mixture was extracted three times with chloroform before the organic phase was washed with water and dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the crude pruduct was purified by column chromatography (toluene/petroleum ether 60–90 °C, 1/1, v/v) on silica gel to yield the desired butyl ester.

In a three-neck round-bottom flask were dissolved butyl ester (0.36 g, 0.26 mmol) and KOH (0.15 g, 2.59 mmol) in a solvent mixture of THF/H_2O (8 mL, 3/1, v/v). The reaction mixture was refluxed for 2 h and then cooled to room temperature. Chloroform was added before the organic phase was washed with 0.1 M hydrochloric acid and water in turn and then dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the crude product was purified by column chromatography (chloroform/methanol, 10/1, v/v) on silica gel to yield a black solid as the desired product **C259** (0.30 g, 88% yield). ^{1}H NMR (400 MHz, THF-d_8) δ: 11.43 (s, 1H), 8.28 (s, 1H), 8.18 (d, J = 8.8 Hz, 2H), 8.15 (d, J = 8.8 Hz, 2H), 8.06 (d, J = 7.6 Hz, 1H), 7.92 (d, J = 7.6 Hz, 1H), 7.58 (s, 1H), 7.56 (m, 3H), 7.54 (d, J = 7.6 Hz, 2H), 7.36 (s, 1H), 7.17 (s, 2H), 7.13 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 6.88 (m, 3H), 6.85 (s, 1H), 4.00 (t, J = 6.4 Hz, 4H), 2.04 (m, 4H), 1.93 (m, 8H), 1.80 (m, 4H), 1.52 (m, 4H), 1.38 (m, 8H), 1.19 (m, 12H), 1.10 (m, 4H), 0.93 (t, J = 6.8 Hz, 6H), 0.81 (t, J = 6.8 Hz, 6H), 0.36 (t, J = 6.8 Hz, 12H). ^{13}C NMR (100 MHz, THF-d_8) δ: 167.59, 161.16, 160.30, 159.34, 154.96, 153.59, 152.45, 151.68, 148.89, 147.28, 147.14, 142.45, 140.74, 140.52, 138.49, 135.95, 135.29, 131.39, 131.24, 130.73, 129.91, 129.86, 129.19, 126.86, 124.78, 124.58, 124.21, 123.54, 120.73, 120.46, 120.19, 117.88, 113.95, 110.26, 68.89, 57.12, 55.31, 39.20, 33.78, 32.83, 32.76, 30.91, 30.60, 26.97, 25.69, 23.70, 14.56, 9.15. HR-MS (MALDI-TOF) m/z calcd. for ($C_{86}H_{97}N_3O_4S_3$): 1331.66412. Found: 1331.66438. Anal. calcd. for $C_{86}H_{97}N_3O_4S_3$: C, 77.49; H, 7.34; N, 3.15. Found: C, 77.33; H, 7.46; N, 3.07.

1.3 Computational details

All the calculations were carried out with Gaussian 09 program packages.[S4] The chromophore geometries were optimized by use of the hybrid B3LYP functional.[S5] The MPW1K functional with significant improvements on the description of charge-transfer excited states was used in the vertical excitation calculations.[S6] In all the calculations the 6-311G(d,p) basis set

was selected and the solvent (tetrahydrofuran) effect was simulated by the conductor-like polarizable continuum model (C-PCM).[S7]

1.4 Cell fabrication

A 4.6+4.7-μm-thick, bilayer-titania film made *via* screen-printing on a pre-cleaned fluorine-doped tin oxide (FTO) conducting glass (Nippon Sheet Glass, Solar, 4 mm thick) was used as the negative electrode of DSCs presented in this paper. A translucent layer of 25-nm-sized titania particles was first deposited on a FTO glass and further covered by a light-scattering layer of 350–450 nm sized titania particles (WER4-O, Dyesol). A circular titania electrode (~0.28 cm^2) was dye-loaded by immersing it into a 150 μM dye solution in a binary solvent of acetonitrile and *tert*-butanol (volume ratio, 1/1) for 12 h. For the high-efficiency cells, 300 or 150 μM **C239** was also added for **C258** or **C259**. The dye-grafted titania electrode was assembled with a gold coated FTO electrode (FTO/Cr/Au) by use of a 25-μm-thick Surlyn ring to produce a thin-layer electrochemical cell. A Co-bpy electrolyte consisting of 0.25 M tris(2,2′-bipyridine)cobalt(II) di[bis(trifluoromethanesulfonyl)imide], 0.05 M tris(2,2′-bipyridine)cobalt(III) tris[bis(trifluoromethanesulfonyl)imide], 0.5 M 4-*tert*-butylpyridine and 0.1 M LiTFSI in acetonitrile was applied for cell fabrication unless otherwise specified. The so-called Co-dmbpy electrolyte was formulated by just employing the corresponding cobalt complexes with the ligand of 4,4′-dimethyl-2,2′-bipyridine.

1.5 Instrumentation

Details on IPCE, *j–V*, TPD and charge extraction measurements have been described in our previous paper.[S8] UV-vis spectra were recorded on an Agilent G1103A spectrometer equipped with a silicon diode array detector. TCSPC measurements were carried out on a LifeSpec-II fluorescence spectrometer employing an EPL485 pulsed laser diode and a Hamamatsu H5773-04 photomultiplier. XPS spectra were recorded with an ESCALAB 250 spectrometer using the Al Kα radiation ($h\nu$=1486.6 eV) and an energy step of 0.1 eV. The electron take-off angle (α) was 90°. Photoelectron spectra were measured in the constant analyzer energy (CAE) mode. The spectra are energy calibrated by setting the $Ti2p_{3/2}$ signal to 458.6 eV.[S9] XRR measurements were carried out on a Bruker D8 discover reflectometer using the Cu Kα X-ray radiation (λ=1.542 Å). For accurate structure determination, atomic layer deposition (ALD) titania films on Si wafers were first heated at 150 °C for 1 h and cooled to 80 °C under a nitrogen atmosphere prior to immediate immersion into dye solutions to avoid water adsorption. The X-ray beam was collimated using a Göbel mirror with a 0.2 mm slit and a postsample parallel collimator. Reflectivity spectra were recorded over an angular range of $0.20^o \le 2\theta \le 8.00^o$, with a step size of 0.005^o and a counting time of 1 s per step. Collected reflectivity data were plotted as a function of perpendicular momentum transfer (Q_Z), $Q_z = 4\pi(\sin\theta)/\lambda$, and were refined by the MOTOFIT package[S10] to obtain structural parameters associated with the bare and dye-grafted titania films prepared by ALD. Initial structural models were prepared using estimated values of the X-ray scattering length density (SLD) of 31.2×10^{-6} $Å^{-2}$ for the ALD titania films and 10.0×10^{-6} $Å^{-2}$ for the dye layers. A native silicon oxide layer was not considered in the structural models, as little contrast was present between the SLD of the Si wafer (20.1×10^{-6} $Å^{-2}$) and that of the native oxide (18.9×10^{-6} $Å^{-2}$). The thickness, SLD and interfacial roughness of each layer were first estimated by the genetic optimization method and further refined by the Levenberg–Marquardt method until minimal χ^2 values were obtained.

1.6 References

[S1] B. A. D. Neto, A. S. A. Lopes, G. Ebeling, R. S. Gonçalves, V. E. U. Costa, F. H. Quina and J. Dupont, *Tetrahedron*, 2005, **61**, 10975.

[S2] R. Li, J. Liu, N. Cai, M. Zhang and P. Wang, *J. Phys. Chem. B*, 2010, **114**, 4461.

[S3] R. Wąsik, P. Wińska, J. Poznański and D. Shugar, *J. Phys. Chem. B*, 2012, **116**, 7259.

[S4] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision A.1, Gaussian, Inc., Wallingford CT, 2009.

[S5] C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

[S6] M. Pastore, E. Mosconi, F. De Angelis and M. Grätzel, *J. Phys. Chem. C*, 2010, **114**, 7205.

[S7] M. Cossi, N. Rega, G. Scalmani and V. Barone, *J. Comp. Chem.*, 2003, **24**, 669.

[S8] N. Cai, R. Li, Y. Wang, M. Zhang and P. Wang, *Energy Environ. Sci.*, 2013, **6**, 139.

[S9] E. M. J. Johansson, M. Hedlund, H. Siegbahn and H. Rensmo, *J. Phys. Chem. B*, 2005, **109**, 22256.

[S10] A. Nelson, *J. Appl. Cryst.*, 2006, **39**, 273.

2 Additional data and analysis

Table S1 The theoretical energy gap of frontier orbital, wavelength of maximum absorption, $S_0 \rightarrow S_1$ transition assignment for the herein studied chromophores in THF as well as the experimental wavelength and molar absorption coefficient of maximum absorption

Chromophore	$\Delta E_{H\rightarrow L}$ [eV][a]	$\Delta E_{H-1\rightarrow L}$ [eV][a]	λ_{max}^{calc} [nm][b]	Transition assignment[b]	λ_{max}^{meas} [nm]	ε_{max}^{meas} [10^3 M^{-1} cm^{-1}]
CPDT-BT	2.63	4.10	466	H→L (100%)	467	8.7
TPA-BT-CPDT	2.24	2.69	526	H→L (93%); H−1→L (7%)	525	29.1
C257	2.18	2.60	543	H→L (94%); H−1→L (6%)	538	37.8
TPA-CPDT-BT	2.12	2.75	516	H→L (82%); H−1→L (14%)	511	23.3
C258	1.96	2.60	563	H→L (86%); H−1→L (14%)	545	34.1

[a] The theoretical frontier energy gap were calculated at the B3LYP/6-311G(d,p) level. H and L represent HOMO and LUMO, respectively. [b] The theoretical wavelength of maximum absorption and transition assignments were calculated at the MPW1K/6-311G(d,p) level.

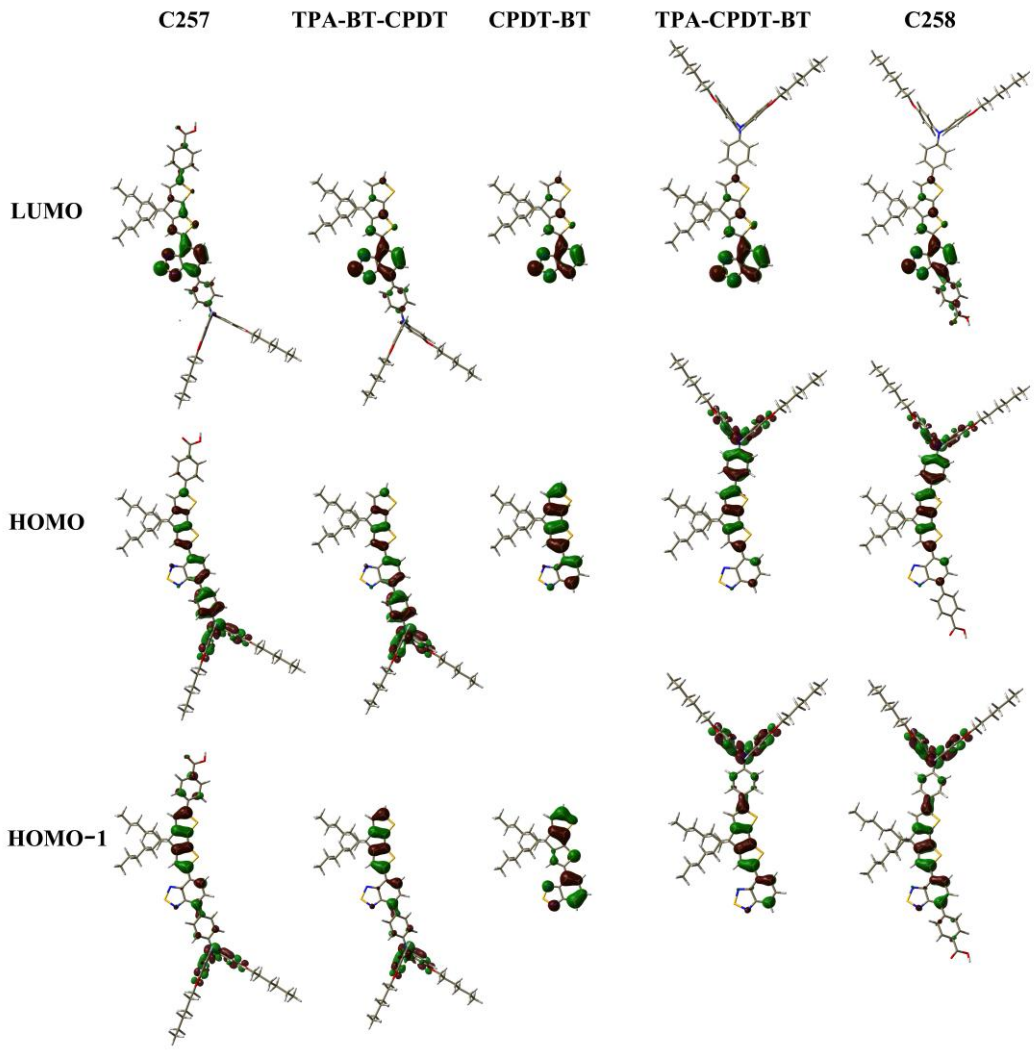


Fig. S1 Contour representations of frontier orbitals of the herein studied chromophores in THF. All the iodensity surface values are fixed at 0.03.

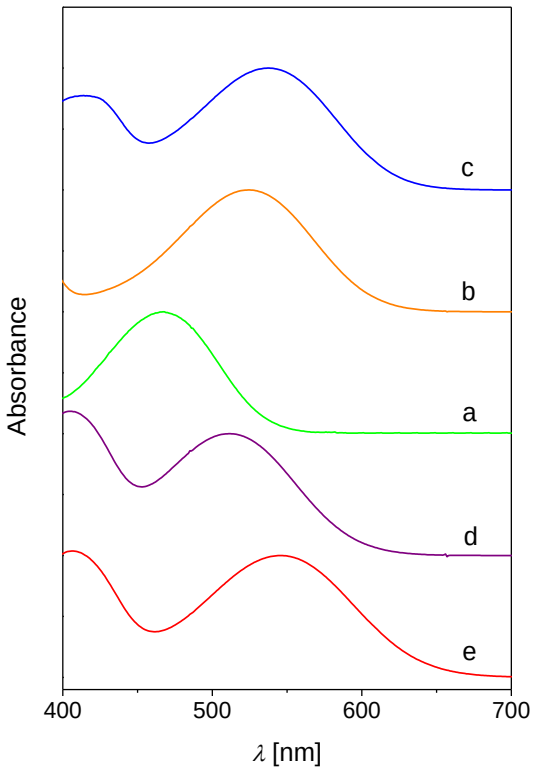


Fig. S2 Electronic absorption spectra of the THF solutions of 150 μM (a) **CPDT-BT**, (b), **TPA-BT-CPDT**, (c) **C257**, (d) **TPA-CPDT-BT** and (e) **C258**.

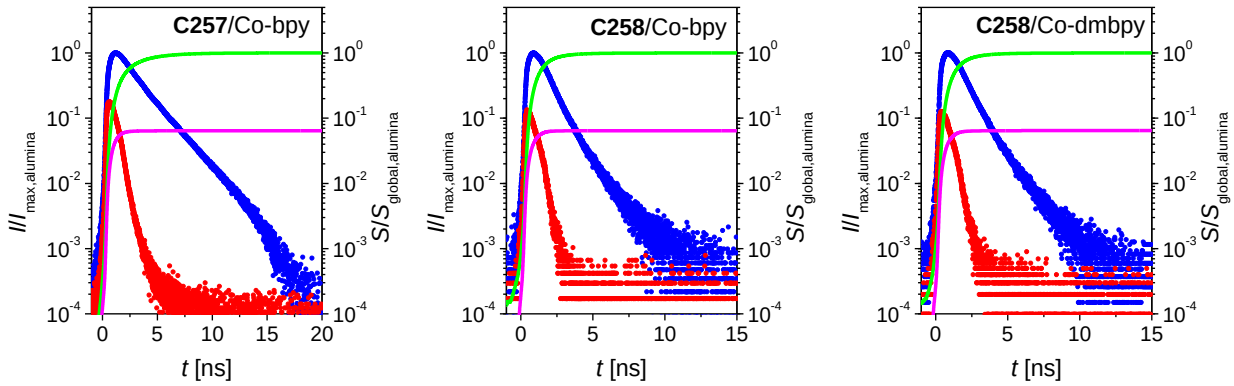


Fig.S3 Time-resolved PL decay traces for the dye-grafted alumina (blue line) and titania (red line) films immersed in the cobalt electrolytes for cell fabrication. The PL intensity (I) was corrected in term of the film absorbance at 482 nm and further normalized with respect to the PL maximum ($I_{max,alumina}$) for the corresponding alumina film. The PL integral area (S) for the alumina (green line) and titania (magenta line) films were normalized with respect to the PL global integral area ($S_{global,alumina}$) for the corresponding alumina film. Excitation wavelength: 482 nm; probe wavelength: 720 nm for **C257** and 740 nm for **C258**.

The possible influence of a fluctuation of the LUMO energy level of a dye molecule upon the yield of electron injection from its electrically excited-state to titania was examined by virtue of the time-correlated single photon counting technique, which has a very high sensitivity to the photons emitted from our samples. Utilizing a C**257** or **C258**-grafted nanoporous alumina film infiltrated with a cobalt electrolyte, we assembled a dummy cell exhibiting strong red light emission, upon exposing to high-repetition-rate trains of picosecond laser pulses at 482 nm. Owing to the absence of energy offsets for electron injection at the interface between alumina and dye molecules, the PL decays (blue lines in Fig. S3) could be ascribed to the radiative and nonradiative deactivation of excited-state dye molecules (D*). However, the replacement of alumina with titania exerts on significant PL quenching (red lines in Fig. S3), implying the occurrence of electron injection at the energy-offset interface between titania and dye molecules. By comparing the PL integral areas of the corresponding dye-grafted titania (magenta lines in Fig. S3) and alumina (green lines in Fig. S3) films, we estimated the electron injection yields of **C257** and **C258** in the titania cell with a Co-bpy electrolyte, being the same value of 94%. It is also valuable to note that the redox couple switch from Co-bpy to Co-dmbpy do not have an identical influence on the electron injection yield. On the basis of this analysis, a very efficient electron injection could be expected for the DSCs presented in this work, in spite of the presence of a minor quantity of non-electron-injecting dye molecules.

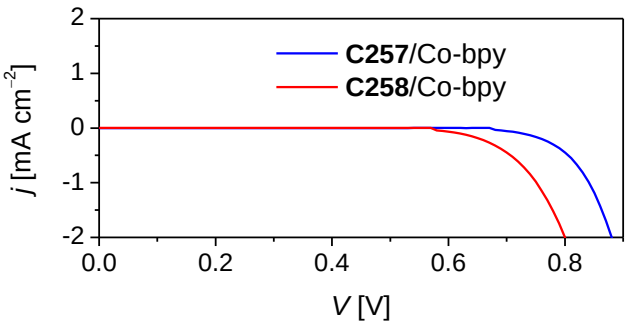


Fig. S4 *j*–*V* characteristics of the **C257** and **C25**8 cells with a Co-bpy electrolyte measured in the dark.

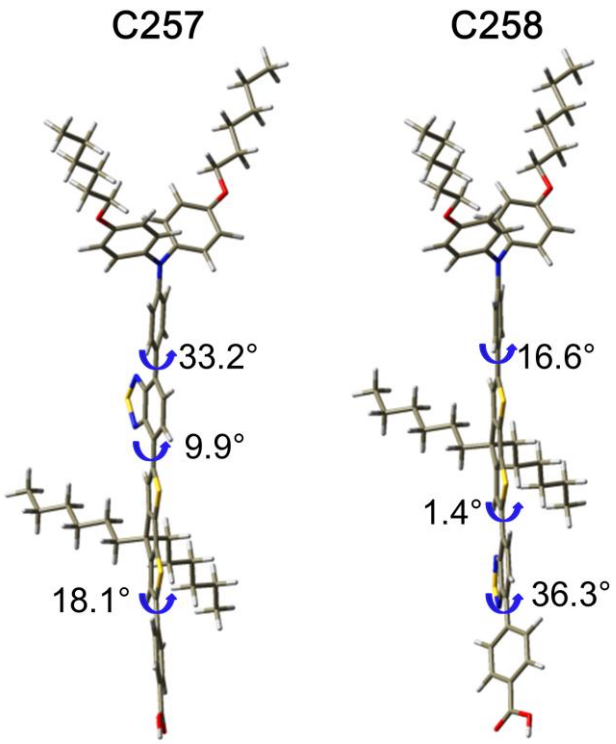


Fig. S5 Geometries and some dihedral angles of **C257** and **C258** optimized at the B3LYP/6-311G(d,p) level.