Electronic Supplementary Information

Benzothiadiazole-based photosensitizers for efficient and stable dye-sensitized solar cells and 8.7% efficiency semi-transparent mini-modules.

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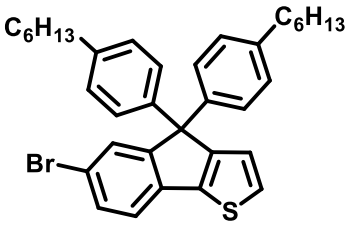
I. Synthesis and structural analysis

1. General methods

All reagents, chemicals and solvents were purchased from Sigma Aldrich, TCI Europe, AK Scientific or Acros Organics and were used as received. Anhydrous THF was obtained by distillation from sodium benzophenone under Argon atmosphere. Compound 1 was synthesised according to literature.[1]

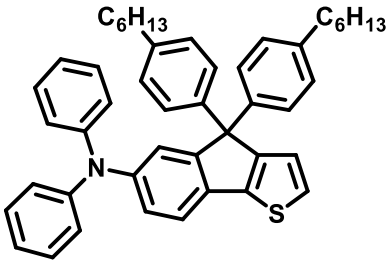
2. Synthetic procedures and analysis

Compound **2**



Under Argon, 1(4-bromophenyl)hexane (2.0 g, 8.29 mmol, 2.5 eq) is added to a suspension of Magnesium (202 mg, 8.29 mmol, 2.5 eq) in anhydrous THF (10 mL). The reaction mixture is stirred at 75°C for 1 hour. At RT, the Grignard intermediate is added to a solution of methyl 5-bromo-2-(thiophen-2-yl)benzoate (1.0 g, 3.37 mmol, 1.0 eq) in anhydrous THF (15 mL). The reaction mixture was stirred at reflux for 5 hours. After cooling to room temperature, the crude mixture was poured into 2M HCl (30 mL). The organic layer was extracted twice with ethyl acetate (2*20 mL). The combined organic layer is washed with water and brine, dried over sodium sulphate, filtered off and concentrated. The crude product is dissolved in glacial acetic acid (40 mL). After 30 min, 37% HCl (4 mL) is added and the mixture is heated at reflux for 5 hours. At room temperature, the acetic acid is removed under vacuum, and the crude product is taken up in pentane (50 mL). The organic layer is washed with water (20 mL) and dried over sodium sulphate, filtered and concentrated. The crude product is purified by column chromatography (SiO_2, neat *n*-hexane) to afford compound **2** as a colourless oil (1.40 g, 2.24 mmol, 73 %). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ (ppm): 7.47 (d, J = 1.7 Hz, 1 H), 7.40 (dd, J = 8.0, 1.8 Hz, 1 H), 7.31 (d, J = 4.9 Hz, 1 H), 7.30 (d, J = 8.0 Hz, 1 H), 7.08 (d, J = 8.4 Hz, 4 H), 7.04 (d, J = 8.4 Hz, 4 H), 6.99 (d, J = 4.9 Hz, 1 H), 2.58-2.51 (m, 4 H), 1.62-1.52 (m, 4 H), 1.38-1.23 (m, 12 H), 0.92-0.84 (m, 6 H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ (ppm): 156.2, 155.5, 141.4, 414.0, 139.7, 136.1, 130.5, 129.3, 128.4, 128.2, 127.4, 122.9, 120.3, 118.9, 35.3, 31.5, 31.1, 28.9, 22.4, 13.9. **HRMS (ESI):** calcd. for $C_{35}H_{40}BrS$: 571.2029, found $[M+H]^+$ = 571.2033 (1 ppm).

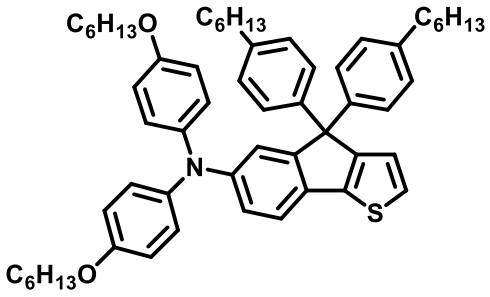
Compound **3**



Under argon, Pd_2dba_3 (4 mg, 4.4 µmol, 1% mol) and tri-*tert*-butylphosphine tetrafluoroborate (3 mg, 8.7 µmol, 2% mol) were dissolved with anhydrous toluene (5 mL). A solution of the compound **2** (250 mg, 0.437 mmol, 1.0 eq) and diphenylamine (81.4 mg, 481.0 µmol, 1.1 eq) in anhydrous toluene (10 mL) was added. Potassium tertbutoxide (161.9 mg, 1.44 mmol, 3.3 eq) is added and the mixture is stirred at reflux for 48 hours. The mixture is poured into 2M HCl (20 mL). The aqueous layer is extracted with DCM, washed with water, dried over Na_2SO_4 and concentrated. The crude product is purified by column chromatography (SiO_2, *n*-hexane:DCM 9:1) to afford compound **3** as a pale yellow oil (266 mg, 0.403 mmol, 92 %). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ (ppm): 7.29 (d, J = 8.2 Hz, 1 H), 7.24-7.16 (m, 6 H), 7.13-7.02 (m, 8 H), 7.02-6.92 (m, 8 H), 2.57-2.49 (m, 4 H) 1.61-152 (m, 4 H), 1.37-1.24 (m, 12 H), 0.92-0.82 (m, 6 H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ (ppm): 155.0, 147.5, 145.4, 141.7, 141.0, 131.9, 128.9, 127.9, 127.5, 126.7, 123.7, 123.01,

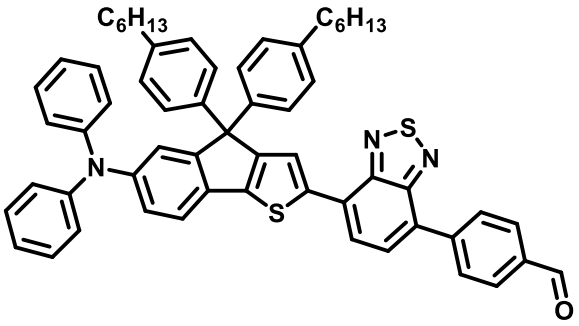
122.95, 122.5, 119.6, 62.6, 35.3, 31.5, 31.2, 29.5, 28.9, 22.4, 13.9. **HRMS (ESI):** calcd. for $C_{47}H_{49}NS$: 659.3580, found $[M]^+$= 659.3579 (0 ppm).

Compound **4**



Under argon, Pd_2dba_3 (6.4 mg, 7.0 µmol, 1% mol) and tri-*tert*-butylphosphine tetrafluoroborate (4.1 mg, 14.0 µmol, 2% mol) were dissolved with anhydrous toluene (5 mL). A solution of the compound **2** (400 mg, 0.700 mmol, 1.0 eq) and di(p-hexyloxyphenyl)amine (284 mg, 0.770 mmol, 1.1 eq) in anhydrous toluene (10 mL) was added. Potassium tert-butoxide (259 mg, 2.31 mmol, 3.3 eq) is added and the mixture is stirred at reflux for 48 hours. The mixture is poured into 2M HCl (20 mL). The aqueous layer is extracted with DCM, washed with water, dried over Na_2SO_4 and concentrated. The crude product is purified by column chromatography (SiO_2, *n*-hexane:DCM 9:1) to afford compound **4** as a pale yellow oil (353 mg, 0.410 mmol, 59 %). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ (ppm): 7.42 (d, *J* = 4.9 Hz, 1 H), 7.38 (d, *J* = 8.2 Hz, 1 H), 7.15-7.06 (m, 10 H), 7.04-6.99 (m, 4 H), 6.92-6.86 (m, 4 H), 6.82 (dd, 1 H, *J* = 8.2, 2.1 Hz), 4.00 (t, *J* = 6.5 Hz, 4 H), 2.63-2.56 (m, 4 H), 1.85-1.76 (m, 4 H), 1.67-1.58 (m, 4 H), 1.56-1.47 (m, 4 H), 1.45-1.30 (m, 20 H), 0.99-0.88 (m, 12 H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ (ppm): 157.0, 156.5, 156.1, 148.5, 143.7, 142.6, 142.3, 131.4, 129.6, 129.1, 128.2, 127.6, 124.8, 121.14, 121.10, 121.0, 116.7, 69.4, 64.2, 36.7, 33.0, 32.94, 32.85, 27.1, 23.88, 23.85, 14.90, 14.88.

Compound **5**

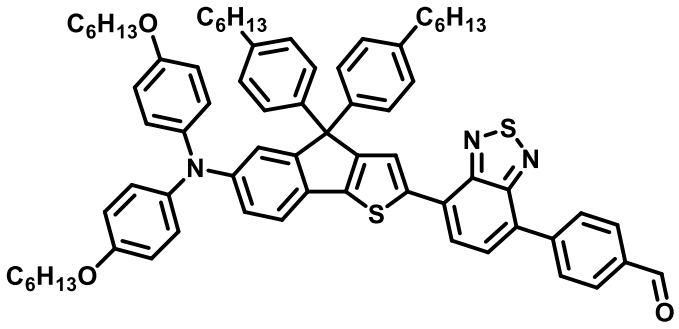


At -78°C, *n*-BuLi (279 µL, 418 µmol, 1.1 eq) is added to a solution of compound **3** (240 mg, 0.364 mmol, 1.0 eq) in anhydrous THF (15 mL). The solution is stirred for an hour at -78 °C before trimethyltin chloride (1 M solution in hexanes, 545 µL, 545 µmol, 1.5 eq). The solution is allowed to warm up at room temperature and further stirred for 2 hours. The reaction is quenched by addition of a saturated aqueous solution of ammonium chloride (10 mL). The organic phase is extracted with *n*-hexane (2*20 mL). The combined organic layer is washed with water and dried over Na_2SO_4, filtered off and concentrated under vacuum. The resulting light yellow oil was used in the next step without any further purification.

The crude tin derivative and 4-bromo-7-(4-formylbenzyl)-2,1,3-benzothiadiazole (93 mg, 291 µmmol, 0.8 eq) are dissolved in toluene (20 mL), and the solution is degassed by gentle bubbling with Argon. Pd_2dba_3 (6.7 mg, 7.27 µmol, 2% mol) and P(*o*-tolyl)$_3$ (4.4 mg, 14.55 µmol, 4% mol) are added and the reaction mixture is stirred at 110°C for 24 hours. The mixture is poured into 2M HCl (20 mL). The aqueous layer is extracted with DCM, washed with water, dried over Na_2SO_4 and concentrated. The crude product is purified by chromatography (SiO_2, *n*-hexane:DCM 6:4) to afford compound **5** as a dark red solid (195 mg, 75 %). **^{1}H NMR (CD_2Cl_2, 400 MHz):** δ (ppm): 10.09 (s, 1 H), 8.19 (d, *J* = 8.3 Hz, 2 H), 8.15 (s, 1 H), 8.02 (d, *J* = 8.5 Hz, 2 H), 7.97 (d, *J* = 7.6 Hz, 1 H), 7.81 (d, *J* = 7.6 Hz, 1 H), 7.42 (d, *J* = 8.2 Hz, 2 H), 7.30-6.94 (m, 21 H), 2.62-2.48 (m, 4 H), 1.68-1.45 (m, 4 H), 1.40-1.18 (m, 12 H), 0.94-0.79 (m, 6 H). **^{13}C NMR (CD_2Cl_2, 100 MHz):** δ (ppm): 192.0, 156.2, 155.6, 154.1, 152.7, 147.9, 146.9, 143.5, 143.4, 142.03, 141.95, 141.5, 136.1, 131.6, 130.7, 130.0, 129.5, 129.3, 128.6, 128.4, 128.0, 124.6, 124.3,

123.3, 123.1, 122.1, 120.6, 63.6, 35.8, 32.0, 31.8, 29.4, 22.9, 14.2. **Elem. Anal.:** Calcd for $C_{60}H_{55}N_3OS_2$: C, 80.23; H, 6.17; N, 4.68; S, 7.14. Found: C, 80.19; H, 6.06; N, 4.59; S, 6.71.

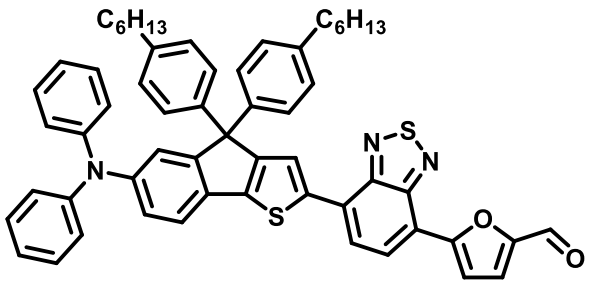
Compound **6**



At -78°C, *n*-BuLi (287 µL, 401 µmol, 1.1 eq) is added to a solution of compound **4** (300 mg, 349 µmol, 1.0 eq) in anhydrous THF (15 mL). The solution is stirred for an hour at -78 °C before trimethyltin chloride (1 M solution in hexanes, 523 µL, 523 µmol, 1.5 eq). The solution is allowed to warm up at room temperature and further stirred for 2 hours. The reaction is quenched by addition of a saturated aqueous solution of ammonium chloride (10 mL). The organic phase is extracted with n-hexane (2*20 mL). The combined organic layer is washed with water and dried over Na_2SO_4, filtered off and concentrated under vacuum. The resulting light yellow oil was used in the next step without any further purification.

The crude tin derivative and 4-bromo-7-(4-formylbenzyl)-2,1,3-benzothiadiazole (99 mg, 0.311 mmol, 0.9 eq)are dissolved in toluene (20 mL), and the solution is degassed by gentle bubbling with Argon. Pd_2dba_3 (6.4 mg, 7.0 µmol, 2% mol) and P(*o*-tolyl)$_3$ (4.2 mg, 14.0 µmol, 4% mol) are added and the reaction mixture is stirred at 110°C for 24 hours. The mixture is poured into 2M HCl (20 mL). The aqueous layer is extracted with DCM, washed with water, dried over Na_2SO_4 and concentrated. The crude product is purified by chromatography (SiO_2, *n*-hexane:DCM 1:1) to afford compound **6** as a purple solid (275 mg, 0.250 mmol, 81 %). **^{1}H NMR (CD_2Cl_2, 400 MHz):** δ (ppm): 10.17 (s, 1 H), 8.32 (s, 1 H), 8.30 (d, *J* = 8.3 Hz, 2 H), 8.13-8.08 (m, 3 H), 7.97 (d, *J* = 7.6 Hz, 1 H), 7.48 (d, 1 H, *J* = 8.3 Hz), 7.22-7.18 (m, 4 H), 7.17-7.13 (m, 4 H), 7.09 (d, 1 H, *J* = 3.1 Hz), 7.08-7.03 (m, 4 H), 6.93-6.88 (m, 4 H), 6.85 (dd, *J* = 8.3, 2.2 Hz, 1 H), 4.01 (t, *J* = 6.5Hz, 4 H), 2.64-2.57 (m, 4 H), 1.85-1.76 (m, 4 H), 1.66-1.57 (m, 4 H), 1.56-1.48 (m, 4 H), 1.43-1.28 (m, 20 H), 0.98-0.92 (m, 6 H), 0.91-0.86 (m, 6 H). **^{13}C NMR (CD_2Cl_2, 100 MHz):** δ (ppm): 192.6, 156.8, 156.1, 154.6, 153.2, 148.8, 144.7, 143.8, 143.0, 142.3, 141.5, 141.3, 137.1, 131.07, 131.05, 130.7, 130.5, 130.23, 130.17, 129.3, 128.8, 127.4, 125.3, 125.1, 121.2, 120.4, 119.8, 116.3, 68.9, 36.2, 32.5, 32.43, 32.35, 26.6, 23.4, 23.3, 14.41, 14.38.

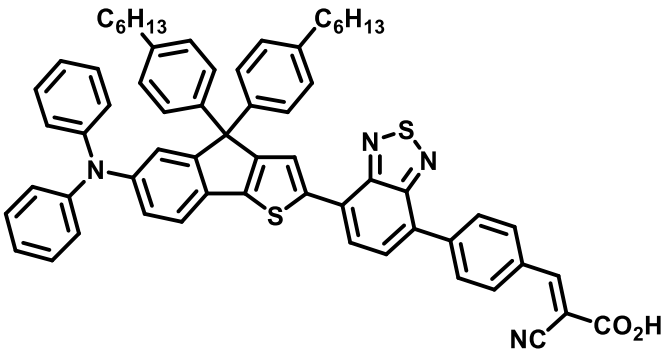
Compound **7**



At -78°C, *n*-BuLi (0.43 mL, 1.01 mmol, 1.05 eq) is added to a solution of compound **3** (650 mg, 0.98 mmol, 1.0 eq) in anhydrous THF (15 mL). The solution is stirred for an hour at -78 °C before trimethyltin chloride (1 M solution in hexanes, 1.0 mL, 1.0 mmol, 1.05 eq)). The solution is allowed to warm up at room temperature and further stirred for 2 hours. The reaction is quenched by addition of a saturated aqueous solution of ammonium chloride (10 mL). The organic phase is extracted with *n*-hexane (2*20 mL). The combined organic layer is washed with water and dried over Na_2SO_4, filtered off and concentrated under vacuum. The resulting light yellow oil was used in the next step without any further purification.

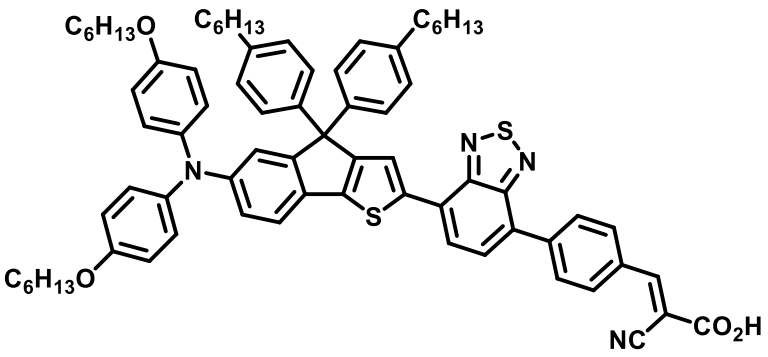
The crude tin derivative and 4-bromo-7-(4-formylbenzyl)-2,1,3-benzothiadiazole (243 mg, 0.78 mmol, 0.8 eq) are dissolved in toluene (20 mL), and the solution is degassed by gentle bubbling with Argon. Pd_2dba_3 (18 mg, 20 µmol, 2% mol)and P(*o*-tolyl)$_3$ (12mg, 40 µmol, 4% mol) are added and the reaction mixture is stirred at 110°C for 24 hours. The mixture is poured into 2M HCl (20 mL). The aqueous layer is extracted with DCM, washed with water, dried over Na_2SO_4 and concentrated. The crude product is purified by chromatography (SiO_2, cyclohexane:DCM 6:4) to afford compound **7** as a deep red solid (490 mg, 0.552 mmol, 70 %). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 9.72 (s, 1 H), 8.10 (s, 1 H), 8.42 (d, *J* = 7.8 Hz, 1 H), 8.09 (d, *J* = 3.7 Hz, 1 H), 7.74 (d, *J* = 7.8 Hz, 1 H), 7.37 (d, *J* = 8.2 Hz, 1 H), 7.25-7.18 (m, 5 H), 7.21 (d, *J* = 3.7 Hz, 1 H), 7.20 (d, *J* = 8.4 Hz, 4 H), 7.10-7.05 (m, 4 H), 7.02-6.96 (m, 3 H), 6.98 (d, *J* = 8.4 Hz, 4 H), 2.55 (t, *J* = 7.3 Hz, 4 H), 1.63-1.53 (m, 4 H), 1.38-1.25 (m, 12 H), 0.87 (t, *J* = 6.8 Hz, 6 H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 177.3, 156.0, 155.5, 152.2, 151.8, 147.5, 146.6, 144.3, 141.6, 141.4, 140.8, 131.3, 129.2, 128.3, 127.8, 126.5, 124.6, 124.5, 124.3, 124.1, 123.9, 123.6, 123.0, 122.9, 122.0, 120.4, 119.1, 118.8, 113.9, 63.3, 35.5, 31.7, 31.4, 29.1, 22.6, 14.1.

Compound **YKP-88**



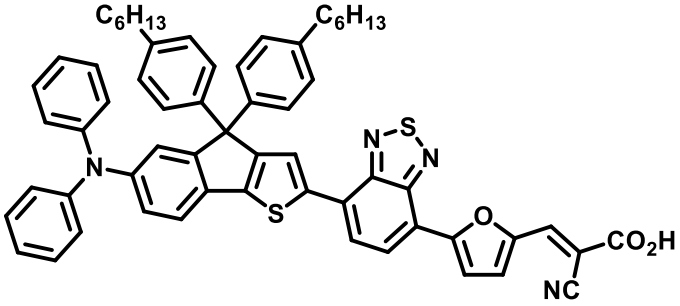
In an argon atmosphere, compound **5** (180 mg, 200 µmol, 1.00 eq) and cyanoacetic acid (85 mg, 1 mmol, 5.00 eq) are dissolved in a mixture of acetonitrile and chloroform (1:1 (v:v), 18 mL). A catalytic amount of piperidine is added and the solution is heated to reflux for 3 hours. Solvents are removed under reduced pressure. The residue is dissolved in chloroform, and the organic layer is washed with HCl aqueous solution (2 M), dried on Na_2SO_4 and concentrated. The crude solid is purified by column chromatography (DCM DCM/MeOH 95:5, DCM/MeOH/Acetic acid, 90:5:5) to afford the expected compound **YKP-88** as a dark red solid (179 mg, 93 %). **^{1}H NMR (THF-d_8, 400 MHz):** δ (ppm): 8.33 (s, 1 H), 8.31 (d, *J* = 8.3 Hz, 2 H), 8.27 (s, 1 H), 8.21 (d, *J* = 8.4 Hz, 2 H), 8.12-8.07 (m, 1 H), 8.00-7.95 (m, 1 H), 7.45 (d, *J* = 8.2 Hz, 1 H), 7.24-7.17 (m, 6 H), 7.15 (d, *J* = 8.2 Hz, 4 H), 7.08-7.01 (m, 8 H), 7.01-6.95 (m, 3 H), 2.59-2.52 (m, 4 H), 1.63-1.53 (m, 4 H), 1.38-1.27 (m, 12 H), 0.91-0.84 (m, 6 H). **^{13}C NMR (THF-d_8, 100 MHz): δ (ppm):** 164.2, 157.4, 156.8, 155.0, 154.4, 153.8, 149.1, 147.9, 144.8, 143.3, 142.9, 142.5, 133.0, 132.3, 131.3, 130.9, 130.4, 130.1, 129.4, 129.2, 125.7, 125.5, 124.3, 124.2, 123.5, 121.5, 116.7, 105.1, 64.7, 36.8, 33.1, 33.0, 31.1, 30.5, 23.9, 14.8. **HRMS (ESI):** calcd. for $C_{63}H_{56}N_4O_2S_2$964.3839, found $[M]^+$= 964.3835 (0 ppm).

Compound **YKP-137**



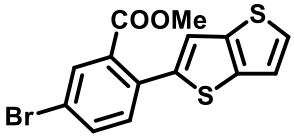
In an argon atmosphere, compound **6** (275 mg, 250 µmol, 1.00 eq) and cyanoacetic acid (213 mg, 2.5 mmol, 10.0 eq) are dissolved in a mixture of acetonitrile and chloroform (2:1 (v:v), 30 mL). A catalytic amount of piperidine is added and the solution is heated to reflux for 3 hours. Solvents are removed under reduced pressure. The residue is dissolved in chloroform, and the organic layer is washed with HCl aqueous solution (2 M), dried on Na_2SO_4 and concentrated. The crude solid is purified by column chromatography (DCM, DCM:MeOH 95:5, DCM:MeOH:Acetic acid, 90:5:5) to afford the expected compound **YKP-137** as a dark blue-purple solid (253 mg, 87 %). **^{1}H NMR (THF-d_8, 400MHz):** δ (ppm): 8.32 (m, 3 H), 8.24 (s, 1 H), 8.22 (m, 2 H), 8.07 (d, *J* = 7.6 Hz, 1 H), 7.96 (d, *J* = 7.7 Hz, 1 H), 7.36 (d, *J* = 8.3 Hz, 1 H), 7.18-7.12 (m, 4 H), 7.09 (d, *J* = 2.1 Hz, 1 H), 7.07-7.01 (m, 4 H), 7.00-6.95 (m, 4 H), 6.85-6.76 (m, 5 H), 3.92 (t, *J* = 6.4 Hz, 4 H), 2.61-2.51 (m, 4 H), 1.81-1.73 (m, 4 H), 1.64-1.54 (m, 4 H), 1.54-1.44 (m, 4 H), 1.43-1.27 (m, 20 H), 0.99-0.90 (m, 6 H), 0.90-0.84 (m, 6 H). **^{13}C NMR (THF-d_8, 100 MHz):** δ (ppm): 163.9, 156.6, 156.2, 154.5, 153.8, 153.3, 148.7, 144.8, 143.1, 142.4, 142.0, 141.6, 141.3, 132.4, 131.8, 130.1, 129.7, 129.0, 128.8, 127.1, 125.1, 124.9, 120.8, 120.6, 120.0, 115.9, 68.7, 64.2, 36.4, 32.7, 32.5, 30.3, 30.1, 26.8, 23.53, 23.47, 14.4. **ITMS (ESI):** calcd. for $C_{75}H_{80}N_4O_4S_2$ 1165.6, found $[M]^+$ = 1165.6.

Compound **DJ-214**



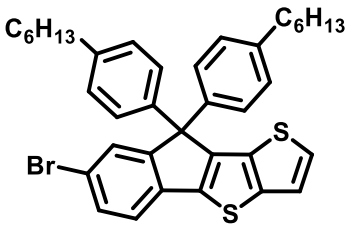
In an argon atmosphere, compound **7** (470 mg, 0.52 mmol, 1.0 eq) and cyanoacetic acid (225 mg, 2.65 mmol, 5.00 eq) are dissolved in a mixture of acetonitrile and chloroform (6:4, (v:v), 100 mL). A catalytic amount of piperidine is added and the solution is heated to reflux for 3 hours. Solvents are removed under reduced pressure. The residue is dissolved in chloroform, and the organic layer is washed with HCl aqueous solution (2 M), dried on Na_2SO_4 and concentrated. The crude solid is purified by column chromatography (DCM, DCM:MeOH 95:5, DCM:MeOH:Acetic acid, 90:5:5) to afford the expected compound **DJ-214** as a dark purple solid (472 mg, 93 %). **^{1}H NMR (THF-d_8, 400 MHz):** δ (ppm): 8.40-8.20 (m, 2 H), 7.09 (br. s, 2 H), 7.90 (br. s, 1 H), 7.42 (br. s, 2 H), 7.30-7.15 (m, 9 H), 7.15-6.95 (m, 11 H), 2.58 (t, J = 7.4 Hz, 4 H), 1.66-1.56 (m, 4 H), 1.43-1.27 (m, 12 H), 0.90 (t, J = 6.7 Hz, 6 H). **^{13}C NMR (THF-d_8, 100 MHz):** δ (ppm): 156.1, 155.5, 155.0, 151.9, 151.3, 148.6, 147.7, 146.6, 144.2, 141.9, 141.1, 136.8, 131.5, 129.0, 128.1, 127.8, 126.5, 124.4, 124.1, 122.82, 122.78, 122.0, 120.2, 118.9, 116.0, 114.7, 63.3, 35.4, 31.7, 31.6, 29.1, 22.5, 13.4. **HRMS (ESI):** calcd. for $C_{61}H_{54}N_4O_3S_2$ 954.36319, found $[M]^+$= 954.3630 (0 ppm).

Compound **8**



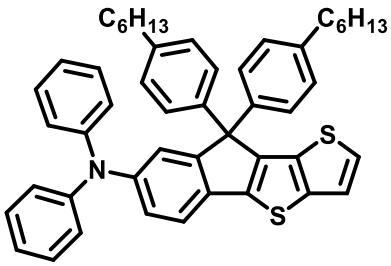
To a stirred solution of thienothiophene (2.0 g, 14.3 mmol, 1.0 eq) in anhydrous THF (40 mL) at -78 °C was added dropwise a solution of n-BuLi (2.5 M, 5.8 mL, 14.4 mmol, 1.01 eq) under argon. The resulting solution was stirred for 30 min. A solution of $ZnCl_2$ (2.1 g, 15.7 mmol, 1.1 eq) in anhydrous THF (15.7 mL) was then added dropwise to the reaction mixture, warmed up to room temperature and stirred for 30 min. To a solution of ethyl 5-bromo-2-iodobenzoate (4.62 g, 13.5 mmol, 0.95 eq) and $Pd(PPh_3)_4$ (1.48 g, 1.3 mmol, 9% mol) in anhydrous THF (60 mL), the above freshly prepared zinc reagent was added at room temperature under argon. The mixture was kept stirring at room temperature for 15 h. The reaction mixture was quenched with H_2O and extracted with ethyl acetate. The organic phase was washed with water followed by brine and dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude was further purified by column chromatography on silica gel (Petroleum Ether/CH_2Cl_2, 9:1) to obtain **8** as an off-white oil (4.3 g, 85 %). **^{1}H NMR (Acetone-d_6, 200 MHz):** δ (ppm): 7.88 (d, *J* = 2.0 Hz, 1 H), 7.80 (dd, *J* = 8.3, 2.1 Hz, 1 H), 7.62 (d, *J* = 5.2 Hz, 1 H), 7.57 (d, *J* = 8.3 Hz, 1 H), 7.48-7.38 (m, 2 H), 3.76 (s, 3 H). Spectroscopic analysis were coherent with the literature.[2]

Compound **9**



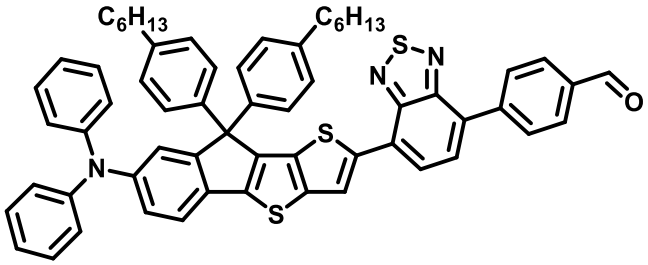
To a solution of 1-bromo-4-n-hexylbenzene (2.32 mL, 11.3 mmol, 4.5 eq) in dry THF (20 mL) was added slowly a 2.5 M n-butyllithium/hexane solution (3.96 mL, 9.9 mmol, 4.0 eq) at -78 °C. The resulting mixture was allowed to stir at -78 °C for 1 h, and then was added to a solution of the compound **8** (888 mg, 2.5 mmol, 1.0 eq) in dry THF (10 mL) at -78 °C dropwise. After the addition, the mixture was allowed to warm to room temperature and stirred for 3 h 30. Then the reaction mixture was quenched with water and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was dissolved in boiling acetic acid (20 mL), and concentrated HCl(aq) (2 mL) was added dropwise. After refluxed for 1 hour, the mixture was poured into ice water, extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using pentane as the eluent affording the desired colourless oil **9** (1.3 g, 83 %). **^{1}H NMR (Acetone-d_6, 400 MHz):** δ (ppm): 7.65-7.64 (m, 1H), 7.57-7.54 (m, 3 H), 7.49 (d, *J* = 5.3 Hz, 1 H), 7.17-7.10 (m, 8 H), 2.60-2.52 (m, 4 H), 1.62-1.52 (m, 4 H), 1.38-1.22 (m, 12 H), 0.90-0.82 (m, 6 H). **^{13}C NMR (Acetone-d_6, 100 MHz)** δ (ppm): 156.4, 147.5, 143.8, 142.9, 142.3, 140.5, 138.0, 134.3, 131.8, 129.9, 129.5, 128.8, 128.6, 121.65, 121.60, 119.9, 100.9, 64.3, 36.1, 32.4, 32.2, 29.8, 23.2, 14.3. **Elem. Anal.** Calcd for $C_{37}H_{39}{}^{79}BrS_2$: C, 70.79; H, 6.26; N, 0.00; S, 10.22. Found: C, 71.44; H, 6.31; N, 0.00; S, 10.09.

Compound **10**



The compound **9** (650 mg, 1.04 mmol, 1.0 eq), diphenylamine (166 mg, 0.98 mmol, 0.95 eq), potassium tert-butoxide (349 mg, 3.11 mmol, 3.0 eq), $Pd_2(dba)_3$ (47 mg, 0.05 mmol, 0.05 eq), and $(t\text{-}Bu)_3PHBF_4$ (30 mg, 0.10 mmol, 0.10 eq) were transferred to a Schlenk flask and connected to a Schlenk line. The flask was subjected to three vacuum/nitrogen refill cycles. Anhydrous toluene was added (10 mL), and the mixture was refluxed for 2 hours. The product was collected by extraction with addition of ethyl acetate and water, followed by a brine solution. The toluene/EtOAc layer was dried with Na_2SO_4, filtered, and concentrated. The collected residue was purified by silica gel column chromatography (Pentane/CH_2Cl_2, 9:1) afforded the desired yellow film **10** (585 mg, 83 %). **^{1}H NMR (Acetone-d_6, 400 MHz):** δ (ppm): 7.47-7.43 (m, 2 H), 7.42 (d, *J* = 5.3 Hz, 1 H), 7.28-7.21 (m, 5 H), 7.10-6.99 (m, 14 H), 6.97 (dd, *J* = 8.2, 2.1 Hz, 1 H), 2.58-2.50 (m, 4 H), 1.60-1.51 (m, 4 H), 1.36-1.24 (m, 12 H), 0.91-0.82 (m, 6 H). **^{13}C NMR (Acetone-d_6, 100 MHz)**: δ (ppm): 155.6, 148.5, 147.1, 146.2, 143.5, 142.52, 142.49, 141.1, 134.7, 133.3, 130.2, 129.3, 128.7, 127.6, 124.9, 123.89, 123.85, 122.7, 121.5, 120.6, 64.0, 36.1, 32.4, 32.2, 29.8, 23.3, 14.4. **Elem. Anal.** Calcd for $C_{49}H_{49}NS_2$: C, 82.19; H, 6.90; N, 1.96; S, 8.96. Found: C, 82.46; H, 6.89; N, 1.93; S, 8.87.

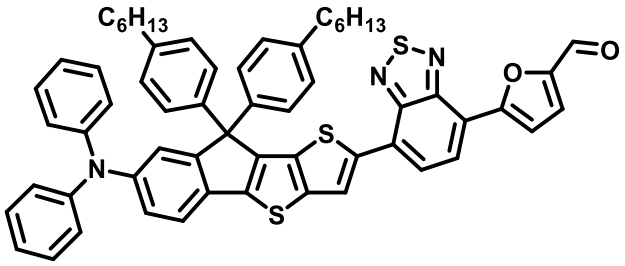
Compound **11**



To a stirred solution of **10** (250 mg, 0.35 mmol, 1.0 eq) in anhydrous THF (5 mL) at -78 °C was added dropwise a solution of nBuLi (2.5 M, 154 µL, 0.38 mmol, 1.1 eq) under argon. The resulting solution was stirred for 30 min at -78 °C. A solution of $ZnCl_2$ (57 mg, 0.42 mmol, 1.2 eq) in anhydrous THF (1 mL) was then added dropwise to the reaction mixture, warmed up to room temperature and stirred for 30 min. To a solution of 2 (106 mg, 0.33 mmol, 0.95 eq) and $Pd(PPh_3)_4$ (36 mg, 0.03 mmol, 9% mol) in anhydrous THF (5 mL), the above freshly prepared zinc reagent was added at room temperature under argon. The mixture was kept stirring at room temperature for 2 h. The reaction mixture was quenched with H_2O and extracted with ethyl acetate. The organic phase was washed with water followed by brine and dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude was further purified by column chromatography on silica gel (Pentane/CH_2Cl_2, 6:4 to 1:1) to obtain **11** as purple solid (215 mg, 68 %). **^{1}H NMR (CD_2Cl_2, 400 MHz):** δ (ppm): 10.09 (s, 1 H), 8.58 (s, 1 H), 8.17 (d, *J* = 8.3 Hz, 2 H), 8.01 (d, *J* = 8.3 Hz, 2 H), 7.89 (d, *J* = 7.6 Hz, 1 H), 7.78 (d, *J* = 7.6 Hz, 1 H), 7.37 (d, *J* = 8.22 Hz, 1 H), 7.27-7.20 (m, 5 H), 7.16-6.94 (m, 15 H), 2.59-2.53 (m, 4 H), 1.62-1.53 (m, 4 H), 1.38-1.23 (m, 12 H), 0.89-0.82 (m, 6 H). **^{13}C NMR (CD_2Cl_2, 100 MHz):** δ (ppm): 192.1, 155.4, 154.2, 152.9, 147.9, 147.0, 145.6, 145.1, 143.4, 143.0,

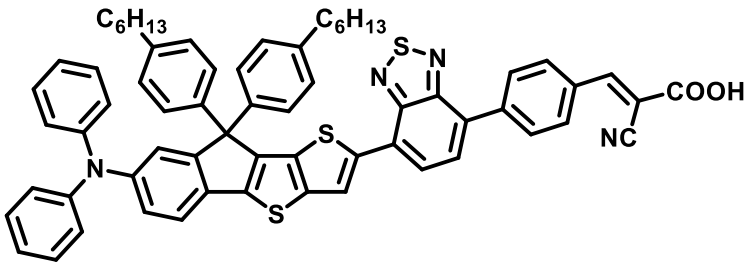
142.5, 140.5, 140.1, 136.2, 135.0, 132.3, 131.2, 130.13, 130.08, 129.6, 129.3, 128.9, 128.3, 128.1, 125.2, 124.7, 123.5, 123.2, 122.5, 121.9, 120.4, 63.5, 35.9, 32.1, 31.8, 29.5, 23.0, 14.3. **Elem. Anal.** Calcd for $C_{62}H_{55}N_3OS_3$: C, 78.03; H, 5.81; N, 4.40; S, 10.08. Found: C, 78.03; H, 5.79; N, 4.33; S, 10.15.

Compound **12**



To a stirred solution of **10** (200 mg, 0.28 mmol, 1.0 eq) in anhydrous THF (10 mL) at -78 °C was added dropwise a solution of nBuLi (2.5 M, 123 µL, 0.31 mmol, 1.1 eq) under argon. The resulting solution was stirred for 30 min at -78 °C. A solution of $ZnCl_2$ (46 mg, 0.34 mmol, 1.2 eq) in anhydrous THF (5 mL) was then added dropwise to the reaction mixture, warmed up to room temperature and stirred for 30 min. To a solution of **6** (78 mg, 0.25 mmol, 0.9 eq) and $Pd(PPh_3)_4$ (29 mg, 0.03 mmol, 9% mol) in anhydrous THF (5 mL), the above freshly prepared zinc reagent was added at room temperature under argon. The mixture was kept stirring at room temperature for 2 hours. The reaction mixture was quenched with H_2O and extracted with ethyl acetate. The organic phase was washed with water followed by brine and dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude was further purified by column chromatography on silica gel (Pentane/CH_2Cl_2, 1:1) to obtain **12** as a purple solid (72 mg, 30 %). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ (ppm): 9.71 (s, 1 H), 8.60 (s, 1 H), 8.21 (d, *J* = 7.8 Hz, 1 H), 7.86 (d, *J* = 3.7 Hz, 1 H), 7.80 (d, *J* = 7.7 Hz, 1 H), 7.41 (d, *J* = 3.8 Hz, 1 H), 7.32 (d, *J* = 8.2 Hz, 1 H), 7.28 (d, *J* = 2.0 Hz, 1 H), 7.25-7.19 (m, 4 H), 7.14 (d, *J* = 8.3 Hz, 4 H), 7.11-7.04 (m, 8 H), 7.04-6.96 (m, 3 H), 2.59-2.52 (m, 4 H), 1.63-1.54 (m, 4 H), 1.37-1.24 (m, 12 H), 0.89-0.83 (m, 6 H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ (ppm): 177.4, 155.32, 155.30, 152.4, 152.0, 151.9, 147.7, 146.7, 145.5, 145.3, 142.8, 141.9, 140.2, 139.6, 135.3, 132.1, 129.3, 128.8, 128.6, 128.1, 126.5, 124.6, 124.4, 123.1, 123.0, 121.9, 120.1, 119.6, 114.2, 63.3, 35.7, 31.9, 31.5, 29.3, 22.8, 14.2. **HRMS (ESI):** $[M]^{+\cdot}$= 943.3294 (0 ppm) (calcd. for $C_{60}H_{53}N_3O_2S_3$: 943.3294).

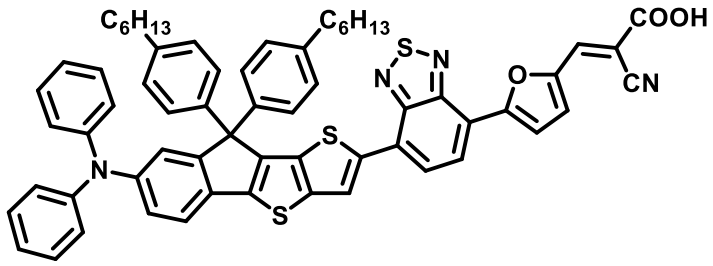
Compound **MG-207**



The compound **11** (201 mg, 0.21 mmol, 1.0 eq) and cyanoacetic acid (90 mg, 1.05 mmol, 5.0 eq) were dissolved in a mixture of acetonitrile (10 mL) and chloroform (5 mL). A few drops of piperidine were added and the reaction mixture was stirred at reflux for 3 hours. Solvents were removed under reduced pressure. The solid was taken in chloroform, washed with HCl 2 M, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography ($CHCl_3$/MeOH/AcOH, 1:0:0 to 95:5:0 to 90:5:5) to obtain the desired purple solid **MG-207** (213 mg, 99 %). **^{1}H NMR (THF-d_8, 400 MHz):** δ (ppm): 8.66 (s, 1 H), 8.31 (s, 1 H), 8.28 (d, *J* = 8.5 Hz, 2 H), 8.18 (d, *J* = 8.6 Hz, 2 H), 7.98 (d,

J = 7.6 Hz, 1 H), 7.93 (d, *J* = 7.6 Hz, 1 H), 7.41 (d, *J* = 8.22 Hz, 1 H), 7.28 (d, *J* = 2.0 Hz, 1 H), 7.24-7.17 (m, 4 H), 7.17-7.11 (m, 4 H), 7.10-7.03 (m, 8 H), 7.02-6.94 (m, 3 H), 2.60-2.50 (m, 4 H), 1.64-1.52 (m, 4 H), 1.39-1.23 (m, 12 H), 0.92-0.82 (m, 6 H). **^{13}C NMR (THF-d_8, 100 MHz)**: δ (ppm): 163.6, 155.9, 154.4, 153.7, 153.2, 148.4, 147.4, 146.3, 145.2, 143.3, 142.3, 142.1, 141.1, 140.6, 135.7, 132.9, 132.4, 131.6, 131.1, 130.3, 129.8, 129.4, 129.0, 128.7, 128.4, 125.5, 124.9, 123.7, 123.6, 122.8, 122.5, 120.6, 116.1, 104.4, 64.0, 36.2, 32.5, 32.3, 29.9, 23.3, 14.2. **HRMS (ESI):** $[M]^{+\cdot}$= 1020.3560 (0 ppm) (calcd. for $C_{65}H_{56}N_4O_2S_3$: 1020.3560).

Compound **MG-214**



The compound **12** (71 mg, 0.08 mmol, 1.0 eq) and cyanoacetic acid (32 mg, 0.38 mmol, 5.0 eq) were dissolved in a mixture of acetonitrile (10 mL) and chloroform (5 mL). A few drops of piperidine were added and the reaction mixture was stirred at reflux for 3 hours. Solvents were removed under reduced pressure. The solid was taken in chloroform, washed with HCl 2 M, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography ($CHCl_3$/MeOH/AcOH, 1:0:0 to 95:5:0 to 90:5:5) to obtain the desired purple solid **MG-214** (75 mg, 99 %). **^{1}H NMR (THF-d_8, 400 MHz):** δ (ppm): 8.65 (s, 1 H), 8.32 (d, *J* = 7.8 Hz, 1 H), 8.07-8.02 (m, 2 H), 7.91 (d, *J* = 3.8 Hz, 1 H), 7.45 (d, *J* = 3.8 Hz, 1 H), 7.40 (d, *J* = 8.2 Hz, 1 H), 7.29 (d, *J* = 2.0 Hz, 1 H), 7.24-7.17 (m, 4 H), 7.16-7.11 (m, 4 H), 7.10-7.03 (m, 8 H), 7.01-6.95 (m, 3 H), 2.59-2.52 (m, 4 H), 1.63-1.53 (m, 4 H), 1.40-1.24 (m, 12 H), 0.91-0.82 (m, 6 H). **^{13}C NMR (THF-d_8, 100 MHz)**: δ (ppm): 163.9, 156.0, 155.9, 152.8, 152.3, 149.3, 148.2, 147.4, 146.3, 145.6, 143.4, 142.3, 141.0, 140.6, 137.8, 136.2, 132.8, 129.8, 129.0, 128.6, 127.3, 125.5, 125.4, 124.9, 123.6, 123.1, 122.5, 120.6, 120.1, 116.5, 115.7, 99.9, 64.0, 36.2, 32.5, 32.3, 30.4, 29.9, 23.3, 14.2. **HRMS (ESI):** $[M]^{+\cdot}$= 1010.3352 (0 ppm) (calcd. for $C_{63}H_{54}N_4O_3S_3$: 1010.3353).

3. Cristal structure of RK1 and MG207

RK1 was recrystallized from methanol at room temperature yielding orange/red cristals. **MG207** was recrystallized from chloroform and methanol.

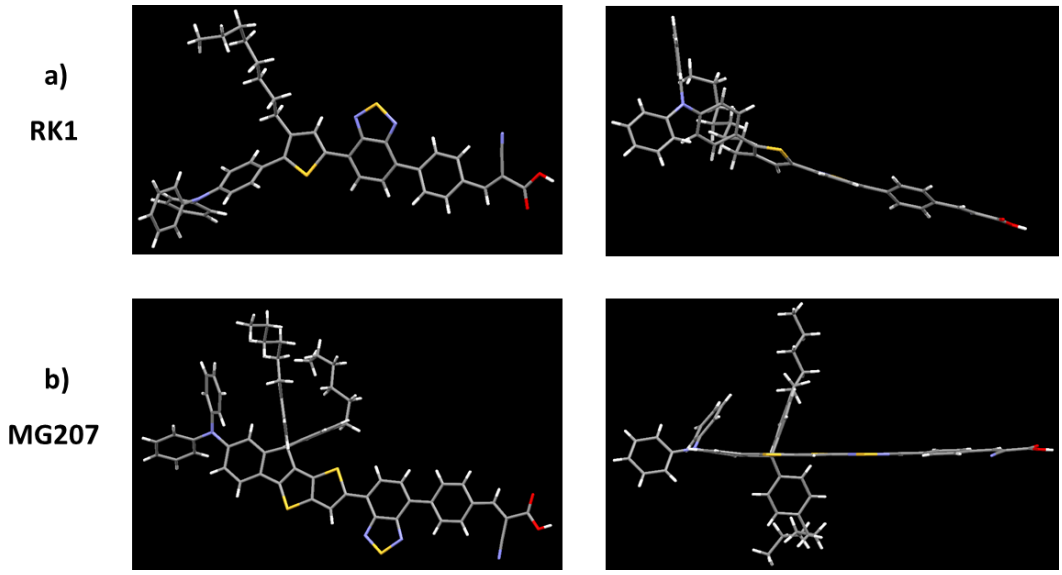


Figure S1: Crystal structure of **RK1** (a) and **MG207** (b) showing the planarization induced by the modification of the donating group.

Table S1: Technical details of data acquisition and selected refinement results for **RK1**.

Identification code	RK1
Empirical formula	$C_{47}H_{44}N_4O_3S_2$
Formula weight	776.98
Temperature/K	150(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.8890(4)
b/Å	11.1928(4)
c/Å	21.2986(9)
α/°	103.005(4)
β/°	98.248(4)
γ/°	101.816(4)
Volume/Å^3	1980.65(15)
Z	2
ρcalcg/cm^3	1.303
μ/mm^{-1}	0.183
F(000)	820
Crystal size/mm^3	0.994 x 0.123 x 0.047
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.123 to 30.508
Index ranges	-12<=h<=12, -15<=k<=15, -30<=l<=30
Reflections collected	47927
Independent reflections	12068 [R(int) = 0.0541]
Data/restraints/parameters	12068 / 138 / 676
Goodness-of-fit on F2	1.033
Final R indexes [I>=2σ (I)]	R1 = 0.0565, wR2 = 0.1128
Final R indexes [all data]	R1 = 0.0888, wR2 = 0.1254
Largest diff. peak/hole / e Å^{-3}	0.48/ -0.34

Table S2: Technical details of data acquisition and selected refinement results for **MG207**.

Identification code	MG207
Empirical formula	$C_{65}H_{56}N_4O_2S_3$
Formula weight	1021.31
Temperature/K	149(1)
Crystal system	triclinic
Space group	P-1
a/Å	11.0016(10)
b/Å	13.5748(10)
c/Å	18.1598(16)
α/°	81.736(7)
β/°	78.669(8)
γ/°	88.211(7)
Volume/Å^3	2631.6(4)
Z	2
ρ_{calc}g/cm^3	1.289
μ/mm^{-1}	0.192
F(000)	1076.0
Crystal size/mm^3	0.732 × 0.344 × 0.01
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.026 to 52.744
Index ranges	-13 ≤ h ≤ 13, -16 ≤ k ≤ 16, -22 ≤ l ≤ 22
Reflections collected	22914
Independent reflections	10717 [R_{int} = 0.1115, R_{sigma} = 0.1870]
Data/restraints/parameters	10717/168/744
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0924, wR_2 = 0.1874
Final R indexes [all data]	R_1 = 0.1950, wR_2 = 0.2459
Largest diff. peak/hole / e Å^{-3}	0.54/-0.40

II. Optoelectronic properties

1. UV-Visible absorption spectroscopy

a) UV-Vis spectra in solution

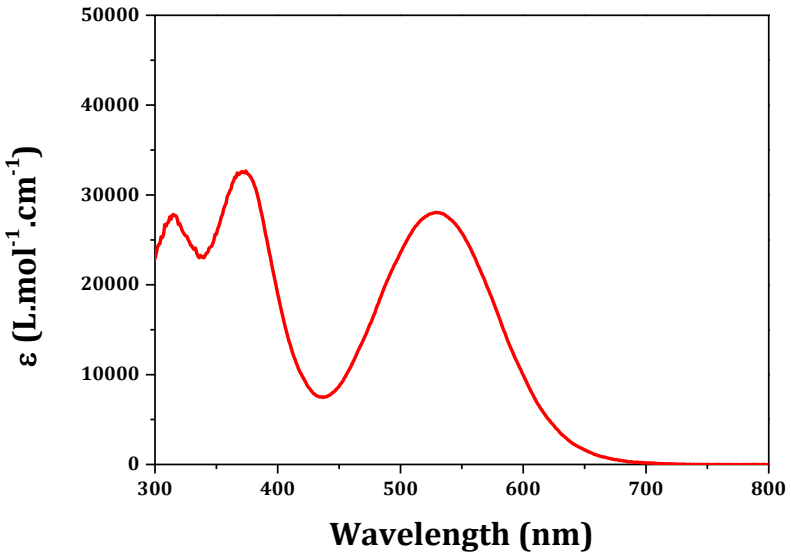


Figure S2: Absorption spectra of compound **YKP-88** (DCM, 10^{-5} M, 25°C).

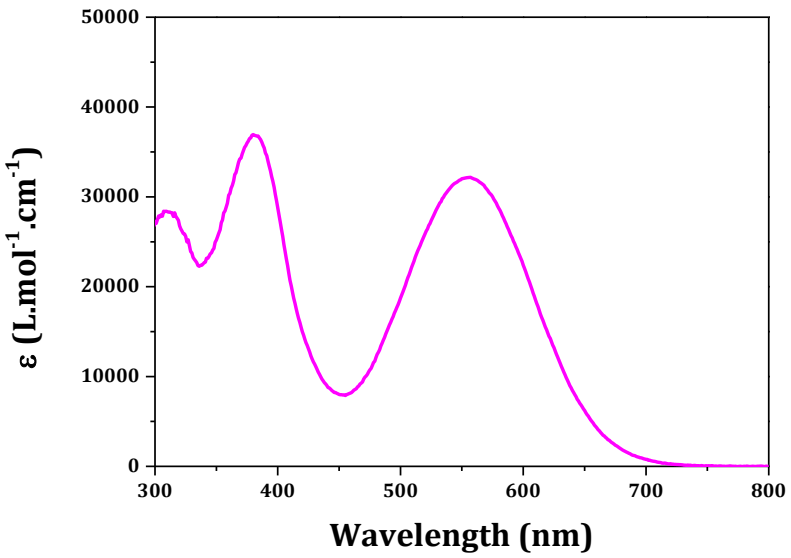


Figure S3: Absorption spectra of compound **YKP-137** (DCM, 10^{-5} M, 25°C).

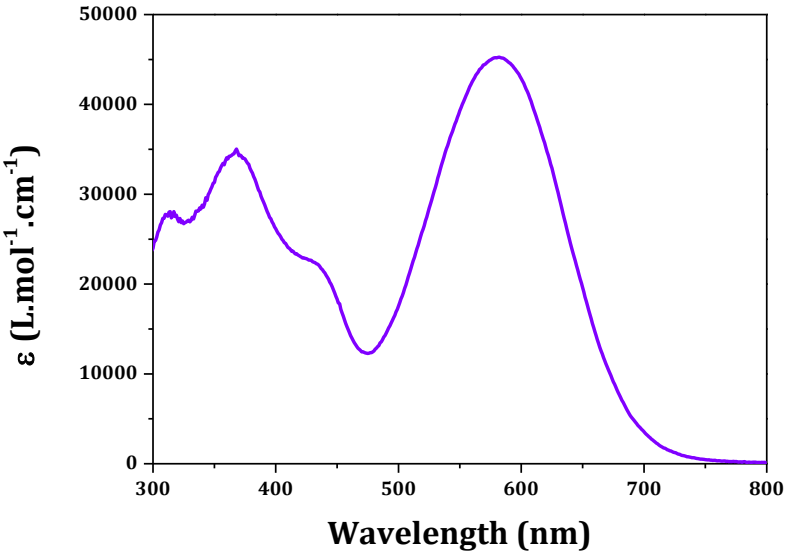


Figure S4: Absorption spectra of compound **DJ-214** (DCM, 10^{-5} M, 25°C).

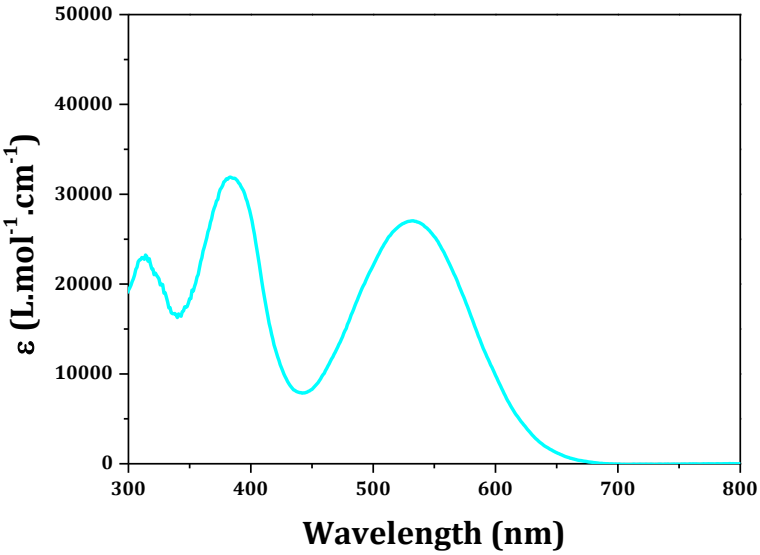


Figure S5: Absorption spectra of compound **MG-207** (DCM, 10^{-5} M, 25°C).

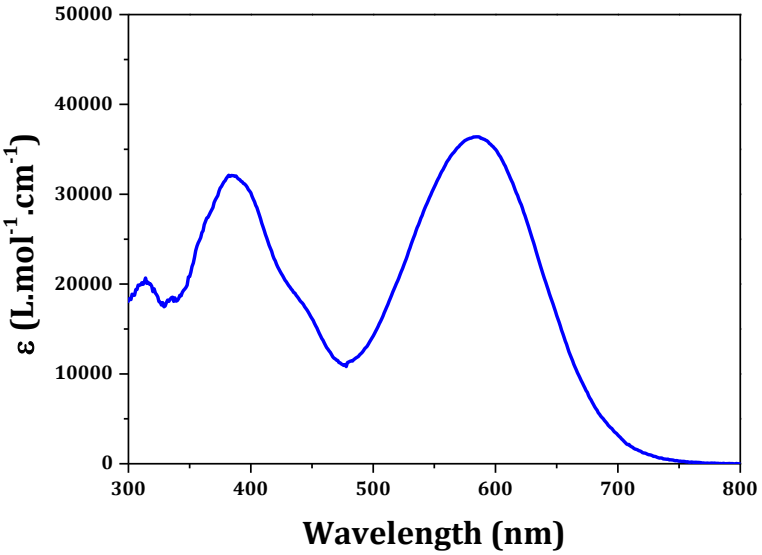


Figure S6: Absorption spectra of compound **MG-214** (DCM, 10^{-5} M, 25°C).

b) UV-Vis spectra of the dyes grafted on a 2µm thick TiO_2 surface

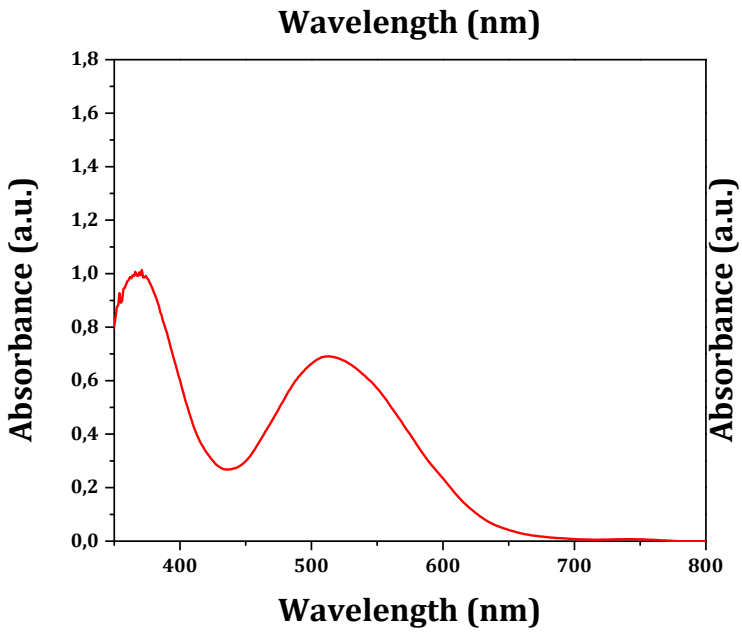


Figure S7: Absorption spectra of compound **YKP-88** (2 µm thick TiO_2).

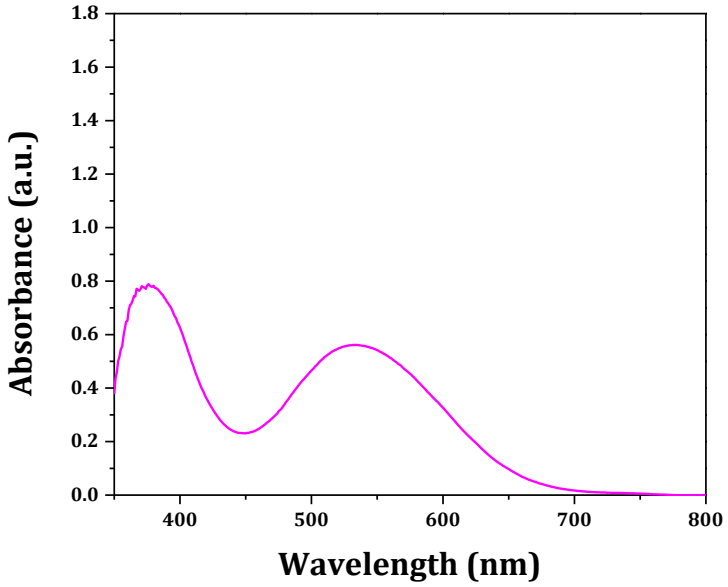


Figure S8: Absorption spectra of compound **YKP-137** (2 µm thick TiO_2).

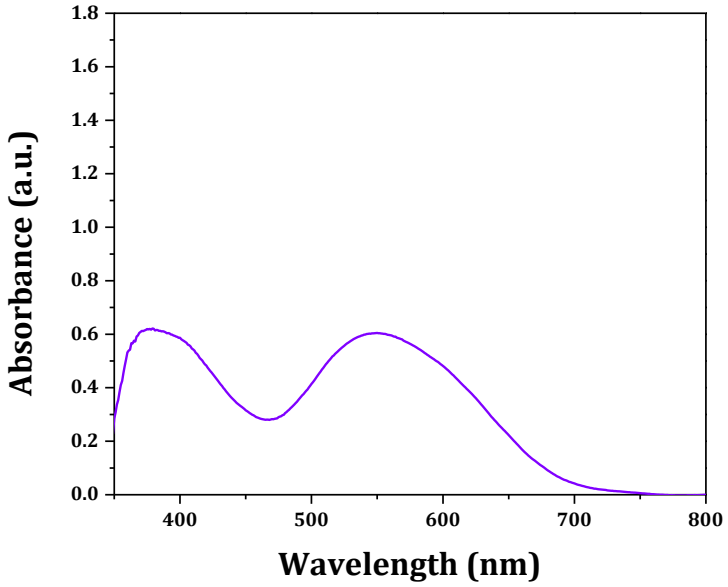


Figure S9: Absorption spectra of compound **DJ-214** (2 µm thick TiO_2).

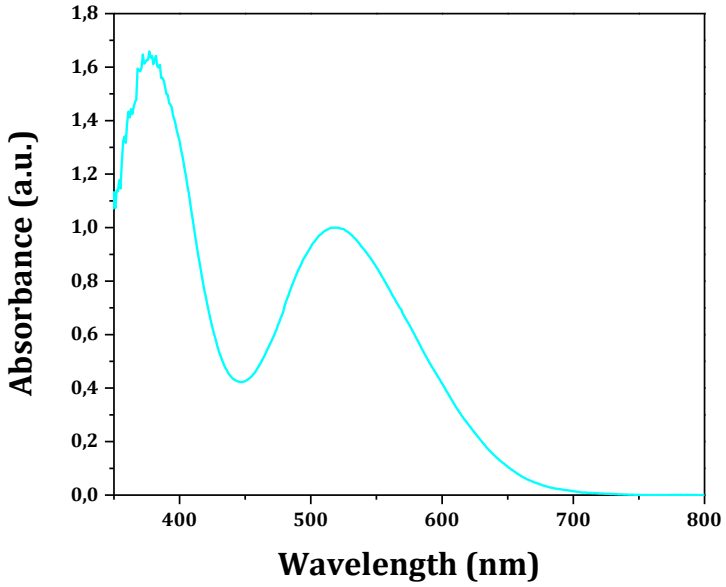


Figure S10: Absorption spectra of compound **MG-214** (2 µm thick TiO_2).

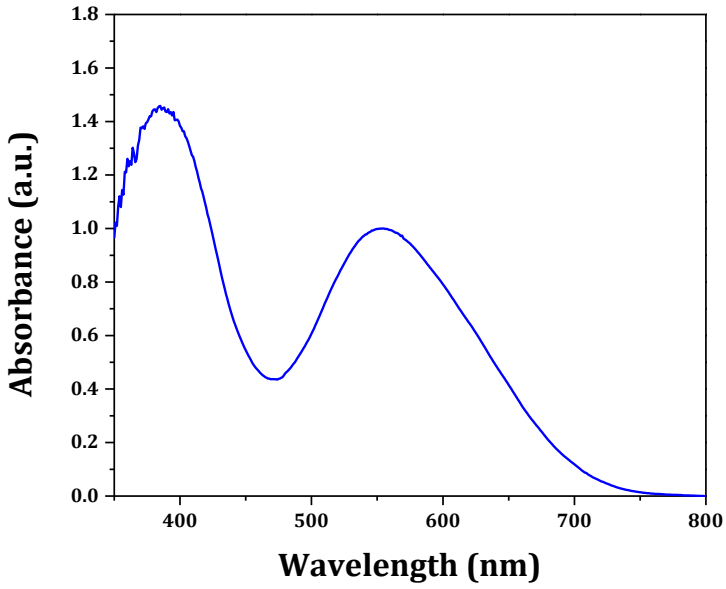


Figure S11: Absorption spectra of compound **MG-214** (2 µm thick TiO_2).

2. Cyclic voltammetry

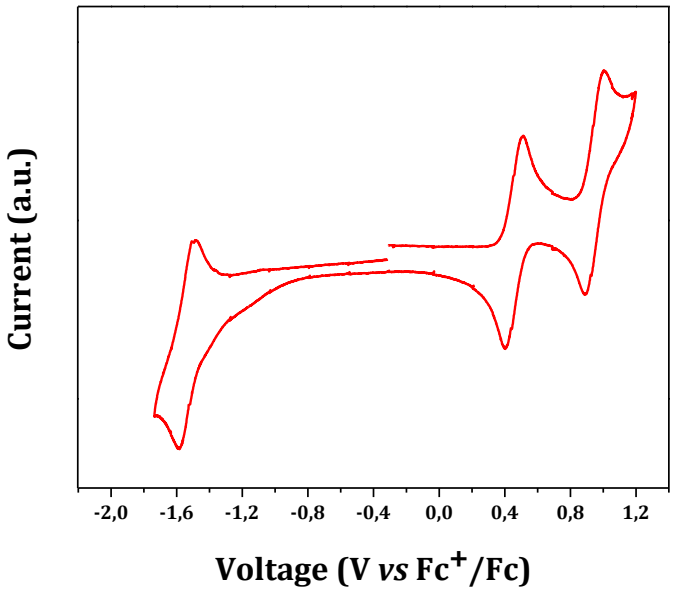


Figure S12: Cyclic voltammogram of compound **YKP-88** (2.10^{-3} M in deoxygenated and anhydrous DCM, $TBAPF_6$ 0.1M).

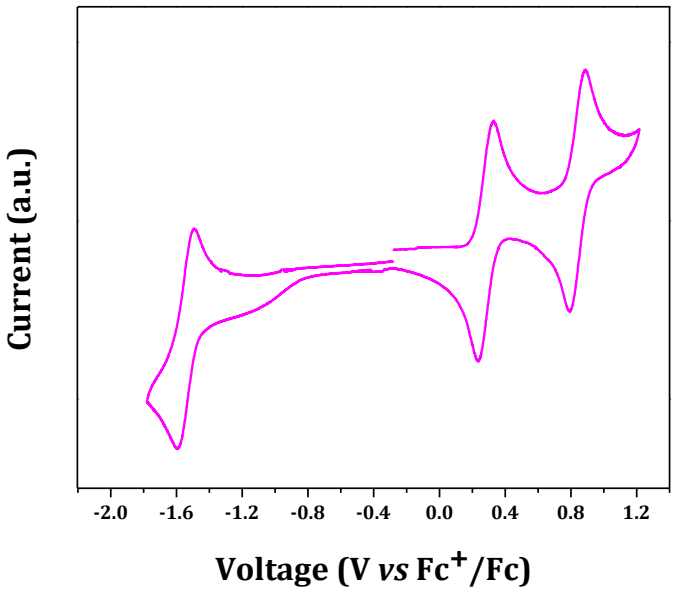


Figure S13: Cyclic voltammogram of compound **YKP-137** (2.10^{-3} M in deoxygenated and anhydrous DCM, $TBAPF_6$ 0.1M).

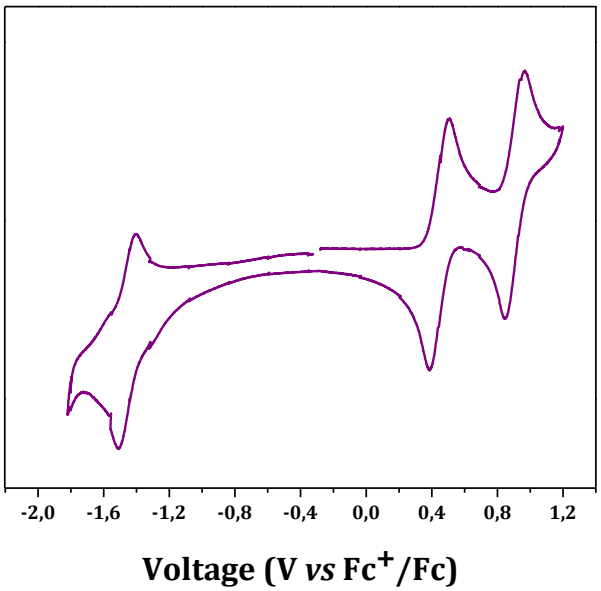


Figure S14: Cyclic voltammogram of compound **DJ-214** (2.10^{-3} M in deoxygenated and anhydrous DCM, $TBAPF_6$ 0.1M).

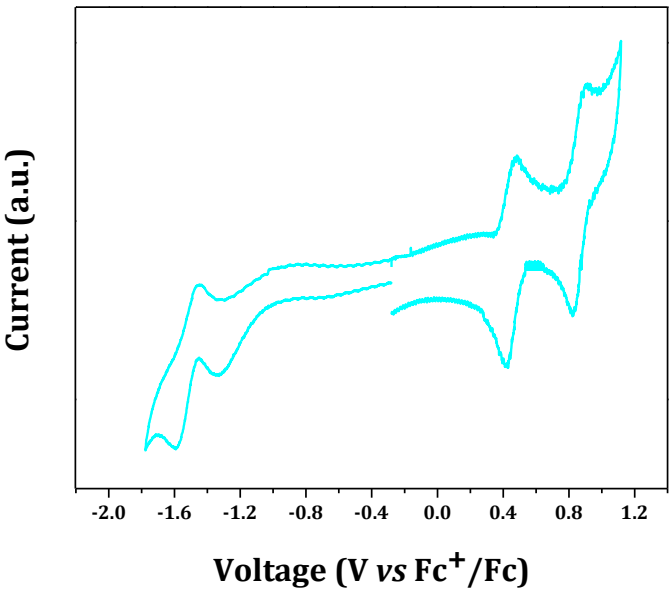


Figure S15: Cyclic voltammogram of compound **MG-207** (2.10^{-3} M in deoxygenated and anhydrous DCM, $TBAPF_6$ 0.1M).

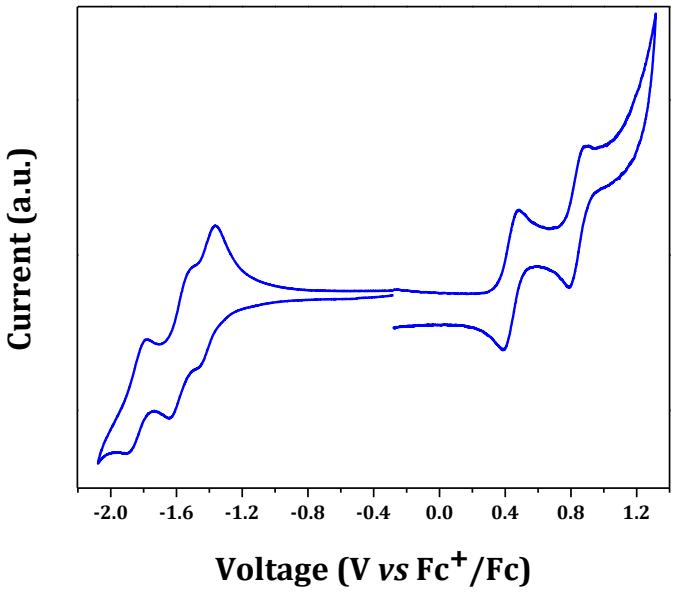
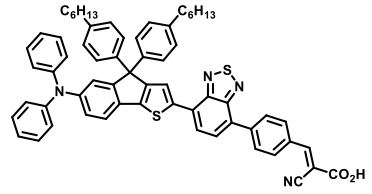
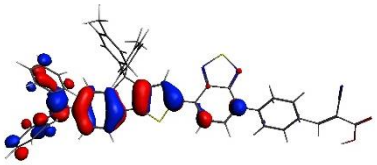
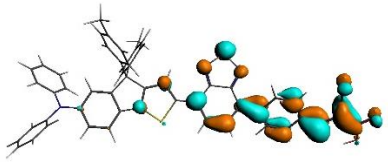
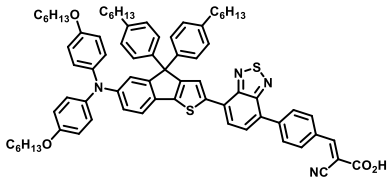
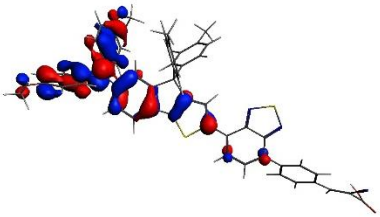
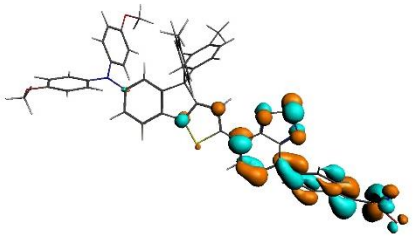
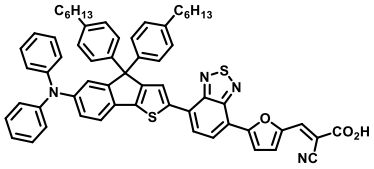
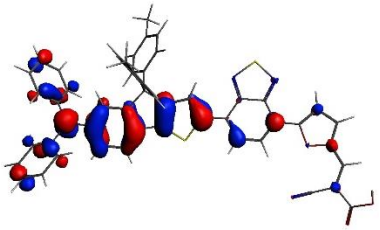
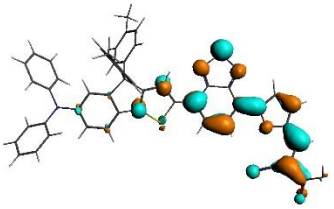
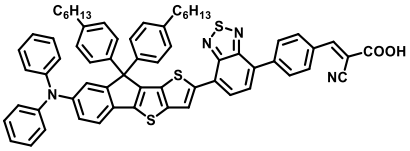
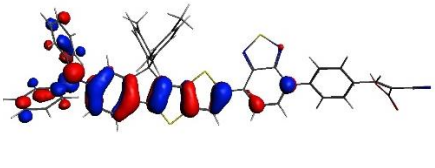
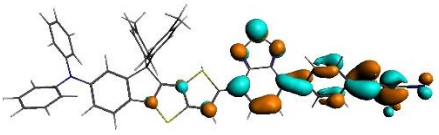
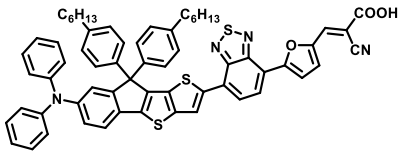
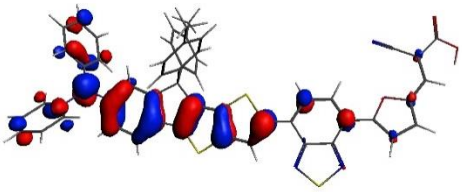
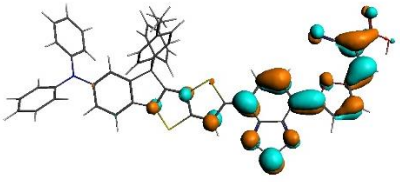


Figure S16: Cyclic voltammogram of compound **MG-214** (2.10^{-3} M in deoxygenated and anhydrous DCM, $TBAPF_6$ 0.1M).

3. DFT calculations

All DFT calculations were carried out in the Kohn-Sham framework, using the Amsterdam Density Functional package (ADF 2016).[3] Geometry optimizations were done using the revPBE functional with van der Waals interactions modelled using the Grimme D3 correction.[4] Optimizations were carried out in a continuum polarizable medium (COSMO) for dichloromethane (ε = 8.9). Then the analysis of Kohn-Sham orbitals (eigenvalues and spatial localization) is based on a single-point on the optimized geometry using the B3LYP hybrid functional in the same solvent medium. All calculations were made using triple zeta + 2 polarization functions on all atoms (named TZ2P set in ADF[3a]). For geometry optimizations a small frozen core was used (1s orbital) while single points were run with all electron basis sets. Such methodology allows i) to yield reliable calculated geometries useable for large molecules thanks to the revPBE-D3 combination[5] and ii) to obtain relevant orbital analysis getting rid of the usual errors given by GGA functionals in eigenvalues. Such approach proved to be successful in previous studies on DSSC dyes.[6] The graphical analysis of orbital localizations and dipole moments was realized using the ADF GUI module.[3b]

Table S3: HOMO and LUMO localization for the selected dyes from the B3LYP single-points after geometry optimisation with RevPBE functional.

Structure	HOMO	LUMO
		
		
		
		
		

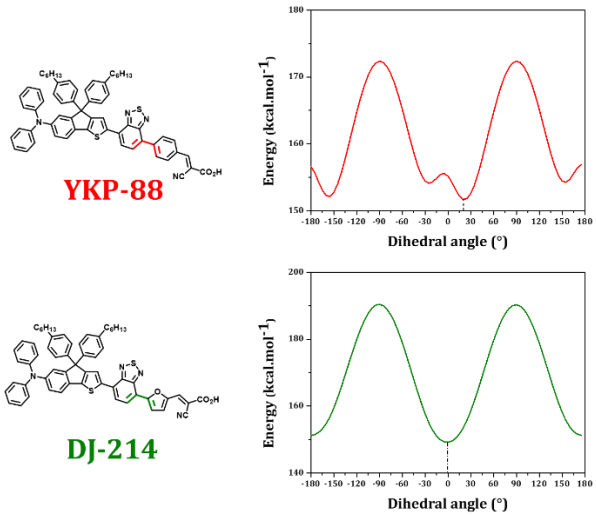


Figure S17: Influence of the torsion angle (bold line on the chemical structure) on the overall energy of the material.

III. DSSC Devices

1. Device fabrication

The devices reported in this paper were prepared using the following procedure.

TiO_2 thin films with specific thickness and a total area of 0.36 cm² were screen printed in Solaronix (Switzerland) using a TiO_2 nanoparticles paste (Ti-Nanoxide HT/SP). All along the manuscript, "opaque device" refers to a device that includes an additional TiO_2 layer of about 3 to 4 µm thick above the mesoporous TiO_2, (Solaronix, Ti-Nanoxide R/SP).

Beforehand, the electrodes are cleaned with absolute ethanol and dried under an argon flux. These photoanodes are then treated by immersion into a freshly prepared 4.1 $mmol.L^{-1}$ TiO_2 aqueous suspension at 70°C for 20 minutes. The electrodes are then cooled to room temperature, rinsed with distilled water then absolute ethanol followed by drying under an argon flux. The electrodes are then sintered under air at 500°C for 20 minutes, following the following heating procedure:

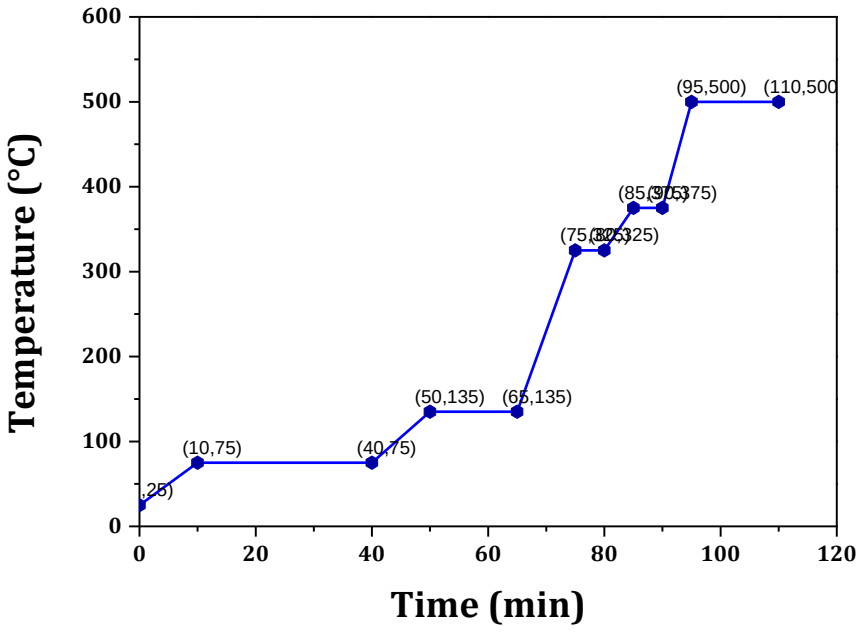


Figure S18: Temperature evolution for the electrodes thermal annealing process.

The photoanodes are then cooled down to 80°C, and sensitized through immersion in the dyeing solution for 16 hours at room temperature in the dark ([Dye] = 0.2 M, [CDCA] as indicated, CH_3CN/*t*BuOH 1/1, v/v). The dyeing bath solutions are stable for a few days under our storage conditions (in the dark at 25°C). However, to warrant a good reproducibility of our results, it should be noted that we prepare fresh dyeing baths every two batches of cells to guarantee that the dye concentration on the electrodes does not vary significantly from batch to batch.

The drilled counter electrodes are coated with a thin layer of platisol (Solaronix, Switzerland) and charred under air at 500^0C. The sensitized photoanode is rinsed with DCM, absolute ethanol and dried with an argon flux. Both electrodes are then sealed together using a surlyn thermoglueing polymer (60 µm thick) using a heating press at 105°C for 16 seconds.

The cell was then filled with an appropriate acetonitrile-based electrolyte (Solaronix Iodolyte HI-30 or our optimized composition) *via* the pre-drilled hole using a vacuum pump. The electrolyte injection

hole on the counter electrode was then sealed with the aid of surlyn® underneath the thin glass cover using heat. A contact along the cell edges was created.

Before measurements, the AM1.5G simulator was calibrated using a reference silicon photodiode equipped with an IR-cutoff filter (KG-3, Schott). The current-voltage characteristics of the cells were measured under dark and under AM 1.5G (1000 $W.m^{-2}$)irradiation condition, achieved by applying an external potential bias to the cell while measuring the generated photocurrent with a Keithley model 2400 digital source meter (Keithley, USA). The devices were masked prior to measurements to attain an illuminated active area of 0.36 cm^2.

2. J(V) and IPCE characteristics of the solar cells

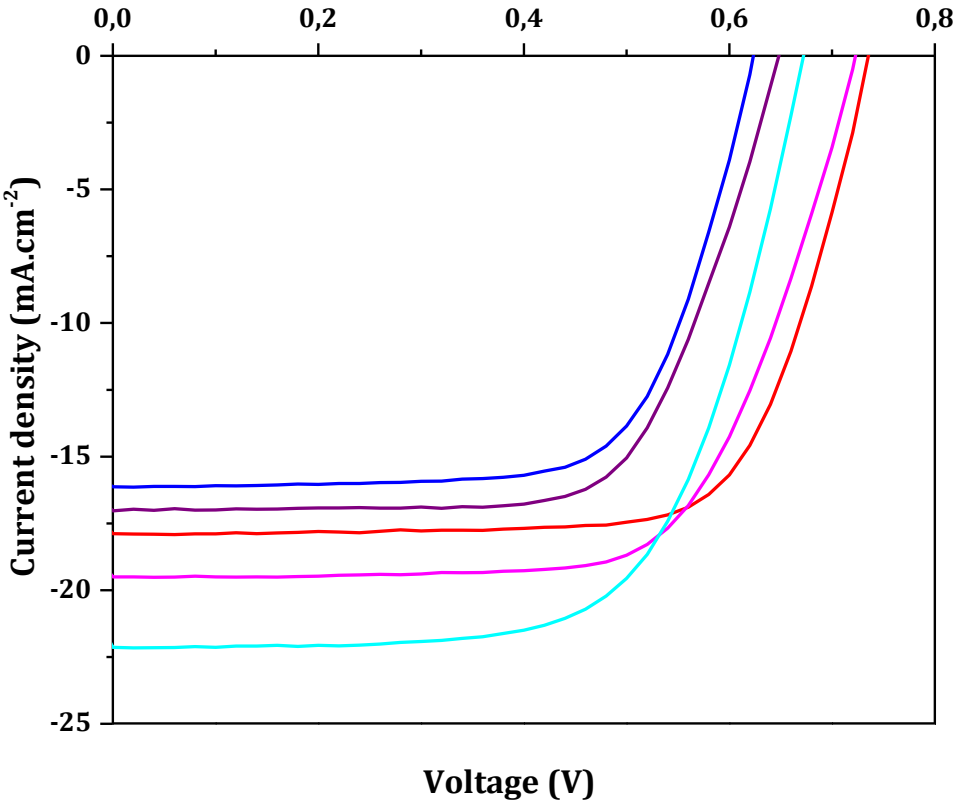


Figure S19 . J(V) curves of solar cells fabricated with **YKP-88**, **YKP-137**, **DJ-214**, **MG-207** and **MG-214**.

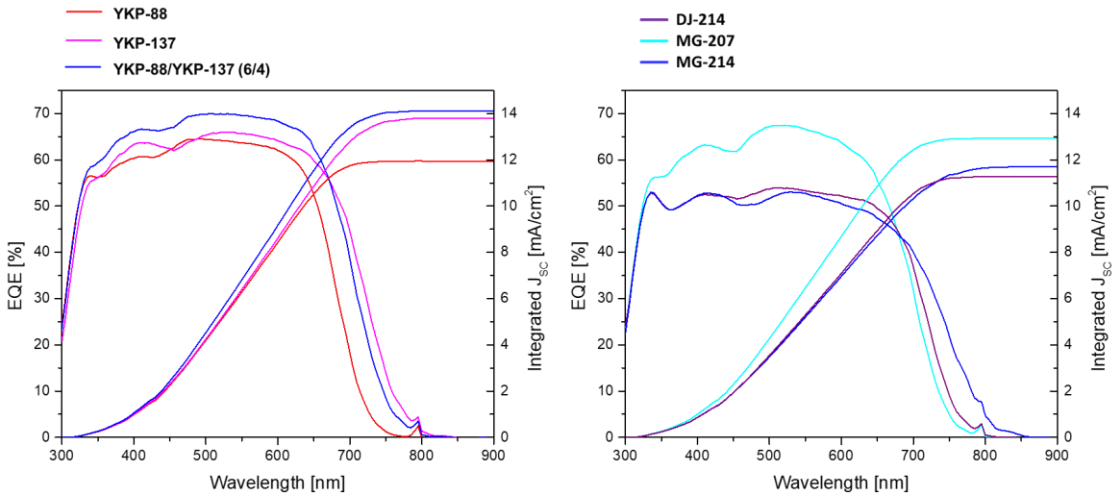


Figure S20 : IPCE curves and integrated currents of DSSCs based on YKP-88, YKP-137, YKP-88 and YKP137 (6/4), MG-207, MG-214, DJ-214 with the Iodolyte electrolyte.

Samples	J_{sc} [mA/cm^2] (under light soaking)	Integrated J_{IPCE} [mA/cm^2]
YKP-88	17.6	13.1
YKP-137	16.6	13.8
YKP-88/YKP-137 (6/4)	19.1	14.1
MG-207	18.3	14.4
MG-214	14.3	11.7
DJ-214	15.6	11.7

Table S4: Values of the IPCE integrated currents and Jsc of DSSCs based on YKP-88, YKP-137, YKP-88 and YKP137 (6/4), MG-207, MG-214, DJ-214 with the Iodolyte electrolyte.

We found that the variations of the current between the two techniques are comprised between 16% and 26 %, which remain acceptable taking into account the differences in the experimental conditions and set-ups.

Dyes	Electrolyte	TiO_2 Electrode (µm)	Jsc ($mA.cm^{-2}$)	Voc (mV)	FF (%)	PCE (%)
YKP-88	Iodolyte	13+3 [a]	18.98 (18.71)	705 (704)	71 (70)	9.41 (9.40)
YKP-137	Iodolyte	13+3 [a]	19.07 (19.04)	715 (714)	65 (64)	8.87 (8.79)
DJ-214	Iodolyte	13+3 [a]	16.53 (16.45)	680 (678)	69 (68)	7.76 (7.71)
MG-207	Iodolyte	13+3 [a]	18.94 (18.54)	687 (685)	67 (67)	8.77 (8.65)
MG-214	Iodolyte	13+3 [a]	14.07 (13.99)	640 (640)	67 (66)	6.03 (6.02)

Table S5: Photovoltaic parameters of compounds YKP-88, YKP-137, DJ-214, MG-207 and MG-214, under irradiation AM1.5G at 1000 W.m-2; Electrodes: TiO2 mesoporous anatase + scattering layer. (a) Fabricated and tested at CEA. Highest value and mean-values in parenthesis. Dyeing bath: [Dye] = 0.2 mM, in MeCN:tBuOH 1:1, (v:v) except for MG-207 and MG-214 Dyeing bath: [Dye] = 0.2 mM, in CHCl3:EtOH 1:1, (v:v).

3. Stability test of YKP-88 compared to RK1

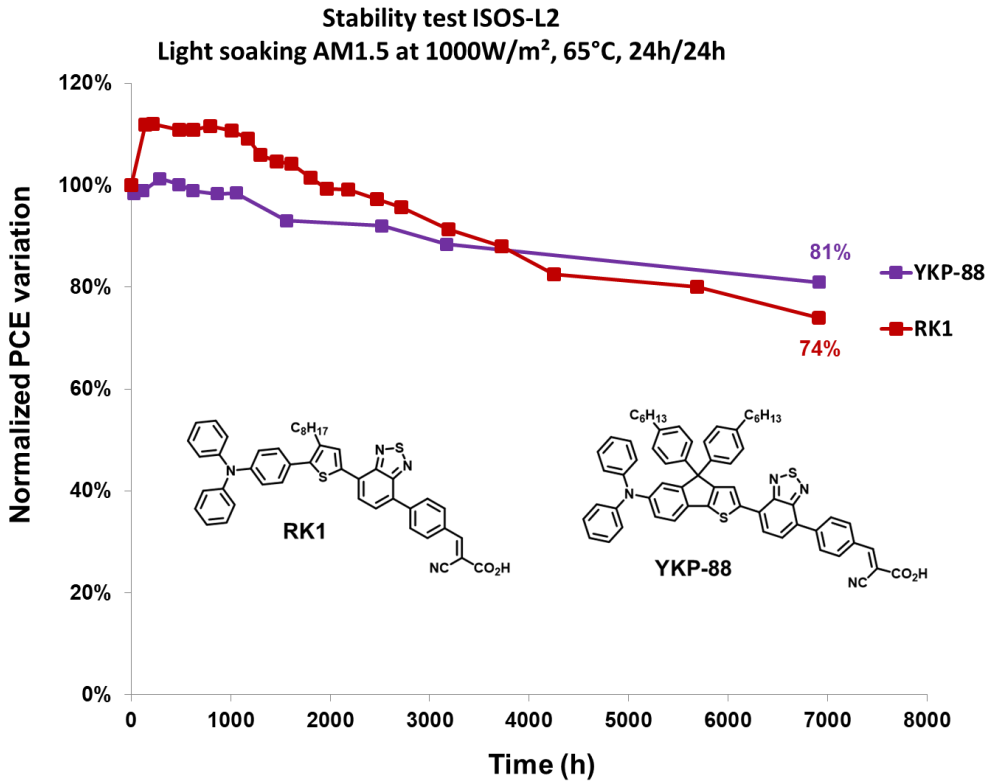


Figure S21. Stability measurements of YKP-88 and RK1 solar cells under ISOS-L2 ageing test

4. Co-sensitization approach

Table S6: Electrical parameters of the devices realized with a mixture of **YKP-88** and **YKP-137** (0.5 mM of ratio **YKP-88 :YKP-137** 5 mM of CDCA in a 1:1 mixture of CH_3CN/t-BuOH, 0.36 cm^2 TiO_2 electrodes, 13 µm + 4 µm, electrolyte: 0.5 M 1-butyl-3-methylimidazolium iodide (BMII), 0.03 M of I_2, 0.5 M of 4-tertbutylpyridine, 0.1 M lithium iodine and 0.1 M guanidinium thiocyanate in HPLC grade acetonitrile).

Molar ratio YKP-88 :YKP-137	**V_{oc} (mV)**	**J_{sc} ($mA.cm^{-2}$)**	**FF (%)**	**η (%)**
1:0	735	17.89	72	9.52
8:2	733	19.76	73	10.51
6:4	**745**	**20.66**	**71**	**10.90**
1:1	742	19.38	73	10.48
4:6	723	20.54	70	10.40
2:8	722	19.59	72	10.20
0:1	723	19.50	68	9.55

5. Mini-modules fabrication

First, the electrodes of the DSSC sub-modules were fabricated on F-doped tin oxide (FTO) coated glass with a conductivity of 7 Ω/sq. A LASER scribing machine was used to remove the FTO layer on the photoelectrode side following the W-module design. All the FTO glass substrates were cleaned by ultra-sonicating consecutively in soap water, acetone and isopropanol for 20 min. The TiO2 paste (Solaronix Ti-Nanoxide T/SP) was deposited on the electrodes in two steps via screen printing to obtain TiO2 films with a thickness of 7-8 µm. All samples were dried on a hot plate at 120 °C for 10 min in between depositions. Then they were annealed at 485 °C for 30 min. All samples received a TiCl4 post-treatment by heating in 40 mM TiCl4 solution at 70 °C for 30 min. The W-module design was chosen, so the counter electrode is on the same electrode. The FTO was drilled where the counter electrode is and the Pt solution painted (Platisol T solution), followed by another calcination at 485 °C for 30 min. After cooling, the TiO2 film coated FTO were soaked in the YKP-88 or N-719 (reference) dyeing solution with CDCA overnight. Before cell construction, the sensitized electrodes were rinsed in ethanol to remove excess dye and then dried. The sealing lamination was done with a dual hot-press, using Surlyn® film as sealant material. Both heating sides were set up to 125 °C, the pressure was set to 1.5 bars for 10 s and increased to 4 bars for 45 s more. The module was filled with electrolyte using vacuum and closed with a piece of glass glued with Surlyn®. Contacts were ultrasonically soldered. The pictures of the YKP-88 and N-719 (reference) mini-modules are shown in Figure 6 of the manuscript.

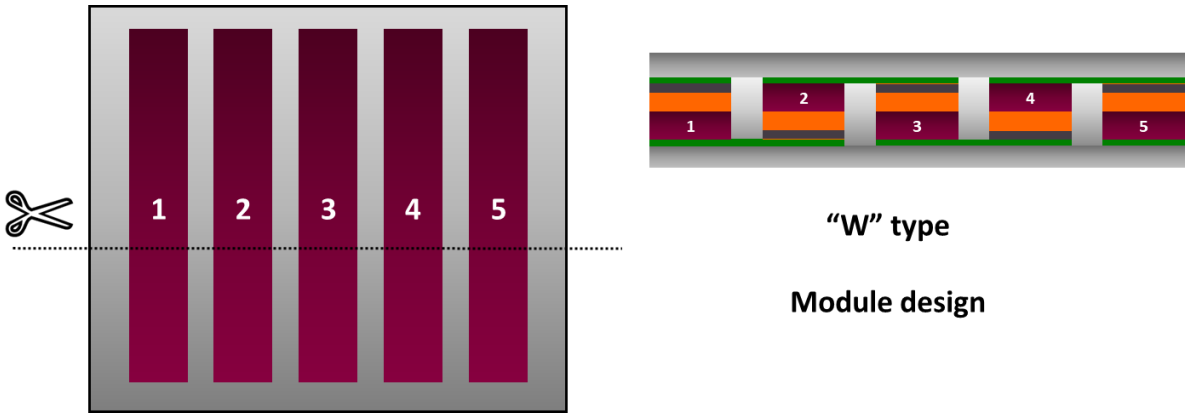


Figure S22: Side view of a five stripes mini-module.

IV. References

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