Energy & Environmental Science

Electronic Supplementary Information (ESI) for

Metal-free organic sensitizers with narrow absorption in the visible for solar cells exceeding 10% efficiency

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Synthesis

2-bromo-3-octylthiophene, 2-bromo-3(2-ethylhexyl)thiophene, 4-(N,N-diphenylamine)phenylboronic acid, N,N-diphenylamine, 4-formylphenylboronic acid, tri-tert-butyl phosphonium tetrafluoroborate mixture, tri(o-tolyl)phosphine, palladium tetratkis (0), tris(dibenzylideneacetone)dipalladium(0), 2-cyanoacetic acid, piperidine, n-BuLi [2.5 M solution in Tetrahydrofuran (THF)], trimethyl tin chloride solution [1 M solution in n-hexane] were purchased from Aldrich or TCI chemicals and used as received. N-Bromo-Succinimide (NBS) was purchased from Fisher Chemicals, 4,7-dibromo-2,1,3-benzothiadiazole and 4,7-dibromo-2,1,3-benzoselenadiazole from Orgalight. The solvents, such as anhydrous toluene, chloroform and acetonitrile from Aldrich were used as received. THF was used after distillation under sodium and benzophenone. Spectroscopic grade solvents from Aldrich were used for spectral measurements. 6-Bromo-4H-indeno[1,2-b]thiophene [1] 4-bromo-7-(4-formylbenzyl)-2,1,3-benzothiadiazole,[2] 4-(N,N-di((4-hexyl)phenyl)amine)phenyl-(4,4,5,5-tetramethyl-1,3,2-dioxa)-borolane,[3] 4-(N,N-di((4-hexyloxy)phenyl)amine)phenyl-(4,4,5,5-tetramethyl-1,3,2-dioxa)-borolane,[4] **RK1** and its precursors [5] were synthesised according to literature.

Synthesis of **1**:

Under argon 6-bromo-4*H*-indeno[1,2-*b*]thiophene (255 mg, 1.02 mmol), octyl bromide (490 mg, 2.54 mmol, 2.5 eq), potassium iodide (15 mg, 90 μmol, 0.09 eq) was dissolved in DMSO (50mL) at room temperature. After added KOH (170.90 mg, 3 mmol, 3 eq), the mixture was stirred for 48h at room temperature before being poured water. The organic phase was extracted with Et_2O, dried on Na_2SO_4 and concentrated. The crude oil was chromatographed on silica using *n*-hexane as eluent and the result was distillated by kugelrohr to afford colorless oil (355 mg, 0.75 mmol, 73.5 %). ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.42-7.38 (m, 2H, H_{ar}), 7.34 (d, 1H, J=4.8Hz, H_{ar}), 7.27 (d, 1H, J=8.6Hz, H_{ar}), 6.96 (d, 1H, J=4.8Hz), 1.99-1.88 (m, 2H, CH_2),1.88-78 (m, 2H, CH_2), 1.34-1.12 (m, 16H, CH_2), 0.86 (t, 6H, J=7.1Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ =156.10, 155.56, 140.14, 137.26, 129.75, 127.86, 125.92, 121.53, 119.80, 118.79, 54.27, 38.85, 31.78, 29.93, 29.25, 29.20, 24.06, 22.60, 14.07. HRMS (ESI): $[M]^{+\cdot}$= 474.1967 (calcd. for $C_{27}H_{39}{}^{79}BrS$: 474.19558), $[M+H]^+$= 475.2036 (calcd. for $C_{27}H_{40}{}^{79}BrS$: 475.20341).

Synthesis of **2**:

Under argon, Pd_2dba_3 (3.85 mg, 4.2 μmol) and tri-*tert*-butylphosphine tetrafluoroborate (2.44 mg, 8.4 μmol) were dissolved with anhydrous toluene (10mL). After stirred for 15min, a solution of 6-bromo-4,4-dioctyl-4*H*-indeno[1,2-*b*]thiophene [**1**] (200 mg, 420.5 μmol) and diphenylamine (78.3 mg, 462.65 μmol) in anhydrous toluene (10mL) was added. Before refluxed for 48h, the resulting mixture was stirred for 30min at room temperature. The melt was filtered through celite and poured into HCl (2M). The organic phase was extracted with Et_2O, washed with water, dried over Na_2SO_4 and concentrated. The crude oil was chromatographed on silica using n-hexane/DCM 9:1 as eluent to afford colorless oil (215 mg, 381.3 μmol, 90.7%). ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.30-7.22 (m, 6H, H_{ar}), 7.12 (d, 4H, J=7.8Hz, H_{ar}), 7.10 (d, 1H, J=1.9Hz, H_{ar}), 7.02-6.92 (m, 4H, H_{ar}), 1.92-1.83 (m, 2H, CH_2), 1.80-1.72 (m, 2H, CH_2) 1.30-1.10 (m, 16H, CH_2), 0.83 (t, 6H, J=7.1Hz, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 155.37, 148.05, 145.20, 140.89, 133.80, 129.10, 126.37, 123.62, 123.54, 122.25, 121.49, 119.92, 119.12, 53.93, 38.92, 31.81, 29.99, 29.33, 29.23, 24.19, 22.62, 14.09. HRMS (ESI): $[M]^{+\cdot}$= 563.3585 (calcd. for $C_{39}H_{49}NS$: 563.35857).

Synthesis of **4** :

Under argon, 4-(diphenylamino)phenylboronic acid (315 mg, 1.09 mmol), 2-bromo-3-(2-ethylhexyl)thiophene (300 mg, 1.09 mmol), Pd(PPh_3)$_4$ (25 mg, 22 μmol) were dissolved in degassed toluene, aqueous solution of K_2CO_3 (2.2 mL, 4.36 mmol) was added and the mixture was heated at 100°C overnight before being poured into water. The organic phase was extracted with Et_2O, dried on Na_2SO_4 and concentrated. The crude oil was chromatographed on silica using *n*-hexane/DCM 9:1 as eluent to afford pale yellow oil **4** (360 mg, 0.81 mmol, 75 %). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.49 (d, 2H, J=7.8Hz, H_{ar}), 7.31 (t, 4H, J=7.7Hz, H_{ar}), 7.20-7.00 (m, 9H, H_{ar}), 6.75 (d, 1H, J=3.0Hz, H_{ar}), 2.80 (d, 2H, J=6.6Hz, CH_2), 1.75-1.55 (m, 1H, CH), 1.52-1.25 (m, 8H, CH_2), 0.95 (t, 6H, J=7.0Hz, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ =147.68, 146.80, 143.55, 141.72, 129.33, 129.27, 126.30, 126.12, 124.35, 124.13, 122.94, 121.84, 41.50, 34.31, 32.47, 28.98, 25.63, 23.10, 14.24, 10.96. HRMS (ESI): [M]$^+$= 439.2332 (calcd. for $C_{30}H_{33}NS$: 439.23337), [M+Na]$^+$= 462.2245 (calcd. for $C_{30}H_{33}NNaS$: 462.22314). Anal. Calcd for $C_{30}H_{33}NS$: C, 81.96; H, 7.57; N, 3.19; S, 7.29,. Found: C, 82.31; H, 7.41; N, 3.25; S, 6.80

Synthesis of **5** :

Under argon, 4-(N,N-di((4-hexyl)phenyl)amine)phenyl-(4,4,5,5-tetramethyl-1,3,2-dioxa)-borolane (200 mg, 0.37 mmol), 2-bromo-3-octylthiophene (118 mg, 0.41 mmol), Pd(PPh_3)$_4$ (17 mg, 16 μmol) were dissolved in degassed toluene, aqueous solution of K_2CO_3 (3.0 mL, 1.48 mmol) was added and the mixture was heated at 100°C overnight before being poured into water. The organic phase was extracted with Et_2O, dried on Na_2SO_4 and concentrated. The crude oil was chromatographed on silica using *n*-hexane as eluent to afford pale yellow oil **5** (150 mg, 0.24 mmol, 67 %). ^{1}H NMR (CD_2Cl_2, 200 MHz): δ = 7.35 (d, 2H, J=8.5Hz, H_{ar}), 7.23-6.72 (m, 12H, H_{ar}), 2.65-2.35 (m, 6H, CH_2), 1.65-1.40 (m, 6H, CH_2), 1.35-1.10 (m, 20H, CH_2), 0.92-0.66 (m, 9H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 147.48, 145.31, 138.04, 137.89, 129.91, 129.52, 129.24, 127.69, 124.82, 123.85, 122.92, 122.05, 35.49, 31.97, 31.84, 31.57, 31.13, 29.59, 29.49, 29.34, 29.17, 28.78, 22.76, 22.71, 14.19. HRMS (ESI): [M]$^{+\cdot}$= 607.4208 (calcd. for $C_{42}H_{57}NS$: 607.42117), [M+Na]$^+$= 630.4125 (calcd. for $C_{42}H_{57}NNaS$: 630.41094.

Synthesis of **6** :

Under argon, 4-(N,N-di((4-hexyloxy)phenyl)amine)phenyl-(4,4,5,5-tetramethyl-1,3,2-dioxa)-borolane (1.75 g, 3.05 mmol), 2-bromo-3-octylthiophene (746 mg, 2.78 mmol), Pd(PPh_3)$_4$ (128 mg, 0.11 mmol) were dissolved in degassed toluene, aqueous solution of K_2CO_3 (4.16 mL, 8.32 mmol) was added and the mixture was heated at 100°C overnight before being poured into water. The organic phase was extracted with Et_2O, dried on Na_2SO_4 and concentrated. The crude oil was chromatographed on silica using *n*-hexane/DCM 8:2 as eluent to afford pale yellow oil **6** (750 mg, 1.17 mmol, 47 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.10 (ABq, 4H, Δνab=114.0Hz, J=8.5Hz, H_{ar}), 7.07 (ABq, 2H, Δνab=80.3Hz, J=5.0Hz, H_{ar}), 6.99 (ABq, 8H, Δνab=98.4Hz, J=8.8Hz, H_{ar}), 3.97 (t, 4H, J=6.5Hz, OCH_2), 2.67 (t, 2H, J=7.8Hz, CH_2), 1.90-1.70 (m, 4H, CH_2), 1.64-1.20 (m, 24, CH_2), 0.99-0.83 (m, 9H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): 155.60, 148.01, 140.57, 138.08, 137.86, 129.79, 129.45, 126.81, 126.357, 122.69, 119.78, 115.31, 68.28, 31.91, 31.63, 31.08, 29.54, 29.43, 29.35, 29.27, 28.71, 25.781, 22.69, 22.63, 14.13, 14.06.

Synthesis of **8** :

Under argon, 4,7-dibromo-2,1,3-benzoselenadiazole (300 mg, 0.88 mmol), 4-formylphenylboronic acid (66 mg, 0.44 mmol),palladium tetrakis (10.2 mg, 2% mol) potassium carbonate (300 mg, 2.2 mmol) were dissolved in toluene (15 mL), water (2.2 mL) and THF (3 mL). The solution was vigorously stirred and heated at 70°C overnight. The reaction was quenched with water and the organic phase was extracted with diethylether and washed with brine, dried over sodium sulphate, filtered and concentrated under vacuum. The crude solid was chromatographed on silica gel using chloroform as eluent to afford yellow solid **8** (105 mg, 0.29 mmol, 65%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 10.14(s, 1H, CHO), 8.05 (ABq, 4H, Δνab=12.2Hz, J=8.4Hz, H_{ar}), 7.72 (ABq, 2H, Δνab=79.1Hz, J=7.4Hz, H_{ar}). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 192.215, 143.527, 136.408, 134.683, 132.523, 130.509, 130.272, 129.563, 119.268, 117.627, 116.429. HRMS (ESI): $[M+Na]^+$= 388.8800 (calcd. for $C_{13}H_7N_2O^{79}BrNa^{80}Se$: 388.88046).

General procedure for Stille coupling.

Under argon, triarylamine-thiophene precursor (0.34 mmol) was dissolved in distilled THF (5 mL) then n-BuLi (0.15 mL, 0.37 mmol) was added at -78 °C. The solution was stirred for an hour at -50 °C before adding a n-hexane solution of Me_3SnCl (0.38 mL, 0.38 mmol) at -78 °C. The solution was allowed to reach room temperature and stirred for 2 hours. The reaction was quenched with water and the organic phase was extracted with n-hexane, dried on Na_2SO_4, filtered and concentrated under vacuum. The resulting oil was engaged without any further purification in a Stille coupling with **7** or **8**. Under argon, stannic, solid **7** or **8** (0.34 mmol), Pd_2dba_3 (5.2 mg, 6 μmol) and P(o-tolyl)3 (3.5 mg, 11 μmol) were dissolved in anhydrous toluene (8 mL) and refluxed for 24 hours. The mixture was then poured into HCl (2M). The organic phase was extracted with Et_2O, washed with HCl (2M), dried over Na_2SO_4 and concentrated. The crude solid was chromatographed on silica using DCM/n-hexane 6:4 as eluent to afford corresponding aldehyde.

10: (0.22 mmol, 65%). ^{1}H NMR (CD_2Cl_2, 200 MHz): δ = 10.15 (s, 1H, CHO), 8.16 (ABq, 4H, Δνab =31.4Hz, J=8.3Hz, H_{ar}), 8.13 (s, 1H, H_{ar}), 7.90 (ABq, 2H, Δνab =25.9Hz, J=7.6Hz, H_{ar}), 7.42 (d, 2H, J=8.6Hz,H_{ar}), 7.23-7.05 (m, 10H, H_{ar}), 2.78 (d, 2H, J=7.1Hz, CH_2), 1.85-1.65 (m, 1H, CH), 1.45-1.25 (m, 8H, CH_2), 1.00-0.80 (m, 6H, CH_3). ^{13}C NMR (CD_2Cl_2, 50 MHz): δ = 192.09, 154.11, 153.03, 147.88, 147.82, 143.53, 141.27, 139.16, 136.37, 136.14, 131.87, 130.86, 130.50, 129.71, 129.34, 128.51, 127.89, 125.10, 125.04, 123.615, 123.36, 40.97, 33.14, 32.92, 29.04, 26.15, 23.47, 14.34, 10.98. HRMS (ESI): $[M+H]^+$= 678.2604 (calcd. for $C_{43}H_{40}N_3OS$: 678.26073), $M^{+\cdot}$= 677.2517 (calcd. for $C_{43}H_{39}N_3OS$: 677.25346). Anal Calcd for $C_{43}H_{39}N_3OS_2$: C, 76.18; H, 5.80; N, 6.20; S, 9.46. Found: C, 75.75; H, 5.74; N, 5.93; S, 9.25.

11: (0.21 mmol, 61%). ^{1}H NMR (CD_2Cl_2, 200 MHz): δ = 10.15 (s, 1H, CHO), 8.15 (s, 1H, H_{ar}), 8.14 (ABq, 4H, Δνab =31.0Hz, J=8.2Hz, H_{ar}), 7.90 (ABq, 2H, Δνab =24.6Hz, J=7.6Hz, H_{ar}), 7.42 (d, 2H, J=8.6Hz,H_{ar}), 7.23-7.05 (m, 10H, H_{ar}), 2.81 (t, 2H, J=7.8Hz, CH_2), 2.81 (t, 4H, J=7.8Hz, CH_2), 1.90-1.55 (m, 6H, CH_2), 1.55-1.25 (m, 22H, CH_2), 0.93 (m, 9H, CH_3). ^{13}C NMR (CD_2Cl_2, 50 MHz): δ = 192.09, 154.13, 153.02, 148.31, 145.46, 143.54, 140.83, 139.77, 138.79, 136.36, 136.15, 131.57, 130.77, 130.09, 130.02, 129.70, 129.36, 127.90, 127.24, 125.366, 125.05, 121.98, 35.79, 32.34, 32.19, 32.01, 31.47, 30.138, 30.00, 29.85, 29.74, 29.52, 29.380, 23.14, 23.08, 14.34. HRMS (ESI): [M]$^+$= 845.4405 (calcd. for $C_{55}H_{63}N_3OS_2$: 845.44071), [M+Na]$^+$= 868.4302 (calcd. for C $C_{55}H_{63}N_3ONaS_2$: 868.43103).

12 : (0.14 mmol, 40%). ^{1}H NMR ($CDCl_3$, 200 MHz): 10.15 (s, 1H, CHO), 8.15 (ABq, 4H, Δνab =23.8Hz, J=8.3Hz, $_{Har)}$, 8.12 (s, 1H, H_{ar}), 7.90 (ABq, 4H, Δνab =25.3Hz, J=7.5Hz, H_{ar}), 7.18 (ABq, 4H, Δνab =69.5Hz, J=8.7Hz, H_{ar}), 7.03 (ABq, 8H, Δνab =50.3Hz, J=8.9Hz, H_{ar}), 3.99 (t, 4H, J=6.5Hz, OCH_2), 2.79 (t, 2H, J=7.5Hz, CH_2), 1.96-1.68 (m, 4H, CH_2), 1.60-1.20 (m, 24, CH_2), 0.96 (t, 9H, J=7.2Hz, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 191.84, 155.78, 153.78, 152.75, 148.46, 143.35, 140.85, 140.38, 139.21, 135.79, 135.71, 131.19, 130.43, 129.96, 129.71, 129.00, 127.93, 126.97, 126.73, 125.684, 124.72, 119.59, 115.38, 68.32, 31.92, 31.63, 31.08, 29.61, 29.46, 29.36, 29.31, 29.03, 25.79, 22.70, 22.64, 14.14, 14.06. HRMS (ESI): [M+H]$^+$= 878.4385 (calcd. for $C_{55}H_{64}N_3O_3S_2$: 878.43891), M$^{+\cdot}$= 877.4300 (calcd. for $C_{55}H_{63}N_3O_3S_2$: 877.43109)

13 : (0.31 mmol, 90%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 10.14(s, 1H, CHO), 8.10 (ABq, 4H, Δνab =8.8Hz, J=8.6Hz, H_{ar}), 8.02 (s, 1H, $H_{ar)}$, 7.79 (ABq, 2H, Δνab =38.4Hz, J=7.4Hz, H_{ar}), 7.50-7.32 (m, 6H, H_{ar}), 7.26-7.06 (m, 8H, H_{ar}), 2.81 (t, 2H, J=7.8Hz, CH_2), 1.87-1.67 (m, 2H, CH_2), 1.50-1.20 (m, 10H, CH_2), 0.93 (t, 3H, J=6.7Hz, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 192.07, 159.35, 158.53, 147.71, 147.56, 144.16, 143.53, 140.87, 139.41, 136.77, 135.85, 132.60, 131.09, 130.72, 130.26, 130.05, 130.04, 129.58, 129.36, 129.19, 128.62, 128.28, 125.65, 125.12, 124.97, 123.47, 123.19, 32.13, 31.29, 29.82, 29.67, 29.53, 29.21, 22.92, 14.38. HRMS (ESI): [M+H]$^+$= 726.2051 (calcd. for $C_{43}H_{40}N_3OS^{80}Se$: 726.20518).

14: (0.14 mmol, 40%). %). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 10.14(s, 1H, CHO), 8.16 (s, 1H, $H_{ar)}$, 8.14 (ABq, 4H, Δνab =50.8Hz, J=8.2Hz, H_{ar}), 7.93 (ABq, 2H, Δνab =70.9Hz, J=7.6Hz, H_{ar}), 7.38 (d, 1H, J=8.1Hz, H_{ar}), 7.32-7.26 (m, 4H, H_{ar}), 7.19-7.12 (m, 5H, H_{ar}), 7.08-7.00 (m, 3H, H_{ar}), 2.00 (dt, 2H, J=5.0Hz, J=12.9Hz, CH_2), 1.84 (dt, 2H, J=5.0Hz, J=12.9Hz, CH_2), 1.30-1.10 (m, 16H, CH_2), 0.85 (t, 6H, J=6.9Hz, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 191.83, 155.85, 155.43, 153.81, 152.54, 147.89, 146.16, 143.67, 143.32, 140.45, 135.65, 133.08, 130.07, 129.96, 129.65, 129.20, 129.03, 128.69, 124.09, 123.91, 123.34, 122.83, 122.63, 119.77, 119.28, 54.48, 38.97, 31.81, 30.01, 29.34, 29.25, 24.28, 22.61, 14.07.). HRMS (ESI): M$^{+\cdot}$= 801.3778 (calcd. for $C_{52}H_{55}N_3OS_2$: 801.37811). Anal Calcd for $C_{52}H_{55}N_3OS_2$: C, 77.86; H, 6.91 N, 5.24; S, 7.99. Found: C, 77.42; H, 6.82; N, 5.03, S, 7.63.

General procedure for knoevenagel condensation.

Under argon, aldehyde (0.35 mmol), cyanoacetic acid (148 mg, 1.72 mmol), were dissolved in a mixture of acetonitrile (6 mL) and chloroform (4 mL). A catalytic amounf of piperidine was added and the solution was refluxed for 3 hours. Solvent was removed under reduced pressure and the solid redissolved in chloroform. The organic phase was washed with HCl solution (1.5 M), dried on Na_2SO_4 and concentrated. The crude solid was chromatographed on silica using DCM first then DCM/MeOH/Acetic acid 90/5/5 as eluent to afford the corresponding dye.

RK2: (0.31 mmol, 91%). ^{1}H NMR (dmso-d6, 400MHz): δ = 8.14 (d, 2H, J=8.0Hz, H_{ar}), 8.08-7.98 (m, 5H, H_{ar}), 7.95 (d, 1H, J=7.5Hz, H_{ar}), 7.20 (d, 2H, J=8.5Hz, H_{ar}), 7.37-7.30 (m, 4H, H_{ar}), 7.12-7.02 (m, 8H, H_{ar}), 2.68 (d, 2H, J=6.9Hz, CH_2), 1.68-1.58 (m, 1H, CH), 1.32-1.16 (m, 8H, CH_2), 0.80 (t, 3H, J=6.5Hz, CH_3), 0.79 (t, 3H, J=7.4Hz, CH_3). ^{13}C NMR (dmso-d_6, 100 MHz): δ = 162.80, 152.74, 151.59, 146.58, 146.24, 139.72, 138.19, 137.70, 135.19, 132.82, 130.56, 129.88, 129.53, 129.12, 129.00, 128.82, 128.41, 128.20, 127.37, 125.684, 124.72, 123.97, 123.07, 122.21, 118.60, 113.66, 32.02, 31.76, 27.712, 25.94, 25.09, 21.91, 13.32, 10.13. HRMS (ESI): $M^{+\cdot}$= 744.2587 (calcd. for $C_{46}H_{39}N_4O_2S_2$: 744.25927).

6RK1: (0.31 mmol, 90%). ^{1}H NMR (THF-d_8, 500MHz): δ = 8.38 (s broad, 1H, Har), 8.14 (s broad, 5H, H_{ar}), 7.31 (d, 2H, J=7.2Hz, H_{ar}), 7.22-6.80 (m, 10H, H_{ar}), 2.71 (s broad, 2H, CH_2), 2.57 (t, 4H, J=7.1Hz, CH_2), 1.80-1.52 (m, 6H, CH_2), 1.50-1.20 (m, 22H, CH_2), 1.00-0.78 (m, 9H, CH_3). ^{13}C NMR (THF-d_8, 50 MHz): δ = 155.45, 153.42, 152.52, 147.70, 145.01, 142.32, 140.64, 139.20, 138.00, 135.80, 131.62, 131.13, 130.61, 129.59, 129.18, 128.95, 128.76, 127.77, 126.84, 124.85, 124.48, 122.73, 121.68, 115.54, 102.26, 35.41, 31.89, 31.74, 31.50, 31.02, 29.61, 29.434, 29.30, 29.10, 29.05, 29.001, 22.677, 22.62, 14.11.

6ORK1: (0.31 mmol, 90%). ^{1}H NMR (THF-d_8, 400MHz): δ = 8.32 (s, 1H, CH=),8.27 (d, 2H, J=8.1Hz, H_{ar}), 8.22-8.16 (m, 3H, H_{ar}), 7.90 (ABq, 4H, Δνab =23.0Hz, J=7.4Hz, H_{ar}), 7.12 (ABq, 4H, Δνab =154.5Hz, J=8.6Hz, H_{ar}), 6.97 (ABq, 8H, Δνab =85.3Hz, J=8.8Hz, H_{ar}), 3.95 (t, 4H, J=6.3Hz, OCH_2), 2.75 (t, 2H, J=7.5Hz, CH_2), 1.54-1.44 (m, 4H, CH_2), 1.40-1.16 (m, 24, CH_2), 0.96-0.80 (m 9H, CH_3). ^{13}C NMR (THF-d_8, 100 MHz): δ = 156.16, 153.75, 152.74, 152.31, 148.71, 141.28, 140.70, 140.41, 138.77, 136.01, 131.77, 131.00, 130.68, 130.16, 129.55, 129.45, 129.37, 128.64, 127.61, 126.840, 126.51, 126.04, 125.78, 124.51, 119.34, 115.22, 67.94, 31.82, 31.54, 30.87, 29.43, 29.35, 29.31, 29.18, 28.80, 25.70, 22.49, 22.45, 13.36, 13.27.

RKSe: (0.30 mmol, 87%). ^{1}H NMR (THF-d_8, 500MHz): δ = 8.37 (s, 1H, H_{ar}), 8.29-8.17 (m, 4H, $H_{ar)}$, 8.15 (s, 1H, $H_{ar)}$, 7.95 (s, 1H, H_{ar}), 7.81 (s, 1H, H_{ar}), 7.45 (d, 2H, J=8.2Hz, H_{ar}), 7.31 (t, 4H, J=7.8Hz, H_{ar}), 7.19-7.11 (m, 6H, H_{ar}), 7.07 (t, 2H, J=7.3Hz, H_{ar}), 2.80 (t, 2H, =7.4Hz, CH_2), 1.50-1.25 (m, 12H, CH_2), 0.92 (t, 3H, J=6.8Hz, CH_3) ^{13}C NMR (THF-d_8, 50 MHz): δ = 159.56, 158.77, 153.51, 153.48, 148.36, 148.14, 143.00, 141.02, 139.41, 137.80, 132.67, 132.21, 132.17, 131.39, 131.33, 130.70, 130.34, 129.97, 129.48, 129.12, 125.38, 125.03, 123.88, 123.56, 32.69, 31.79, 30.34, 30.24, 30.09, 29.63, 23.38, 14.28. HRMS (ESI): $[M-CO_2]^-$= 748.2157 (calcd. for $C_{45}H_{40}N_4S^{80}Se$: 748.21444).

RKF: (0.28 mmol, 80%). ^{1}H NMR (THF-d_8, 400MHz): δ = 8.35-8.30 (m, 3H, $H_{ar)}$, 8.28 (s, 1H), 8.22 (d, 2H, J=8.5Hz, H_{ar}), 8.06 (ABq, 2H, Δνab =44.0Hz, J=7.6Hz, H_{ar}), 7.39 (d, 1H, J=8.1Hz, H_{ar}), 7.27-7.20 (m, 4H, H_{ar}), 7,17 (d, 1H, J=1,9Hz, H_{ar}), 7.12-7.07 (m, 4H, H_{ar}), 7.01-6.96 (m, 3H, H_{ar}), 2.01 (dt, 2H, J=5.2Hz, J=13.0Hz, CH_2), 1.87 (dt, 2H, J=5.2Hz, J=13.0Hz, CH_2), 1.29-1.14 (m, 16H, CH_2), 0.82 (t, 6H, J=6.9Hz, CH_3). ^{13}C NMR (THF-d_8, 100 MHz): δ = 172.011, 164.042, 156.790, 156.455, 154.837, 154.111, 153.644, 149.148, 147.471, 144.829, 142.642, 142.105, 134.419, 132.675, 132.054, 130.873, 130.660, 130.185, 129.982, 129.500, 125.275, 124.908, 124.521, 123.774, 123.650, 120.783, 120.434, 116.603, 55.518, 40.027, 32.995, 31.196, 30.444, 23.706, 20.520, 14.629. HRMS (ESI): $M^{+\cdot}$= 868.3835 (calcd. for $C_{55}H_{56}N_4O_2S_2$: 868.38447).

Photophysical properties and DFT calculations

UV-vis absorption spectra were recorded in solution on a Perkin-Elmer Lambda 2 spectrometer (wavelength range: 180-820 nm; resolution: 2 nm). Electrochemical studies of the synthesized molecules were carried out in a one compartment, three-electrode electrochemical cell equipped with a planar platinum working electrode (7 mm^2), a Pt wire counter electrode, and a Ag wire pseudo-reference electrode, whose potential was checked using the Fc/Fc$^+$ couple as an internal standard. The electrolyte consisted of 0.1 M tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) solution in dichloromethane containing 2 x 10^{-3} M of the dye. The experiments were carried out in a glove box.

The density functional theory (DFT) calculations were performed on the two organic sensitizers by using the Amsterdam Density Functional package (ADF 2010.01).[6] The structures of the dyes have been fully optimized at a GGA level using the Perdew-Burke-Ernzerhof (PBE) functional and triple zeta plus 2 polarization Slater functions (TZ2P set in ADF) basis sets for all atoms, with 1s orbitals frozen for C, N and O atoms. On these optimized geometries, B3LYP hybrid functional calculations with TZ2P all electron basis sets were then performed to yield more reliable frontier orbital energies. Acetonitrile solvent was taken into account using a polarizable continuum model (COSMO in ADF)[7] for all geometry optimizations and B3LYP single point calculations. Orbitals were drawn using the graphical interface of ADF (ADF-GUI).

Figure S1: Cyclic voltammograms of RK derivatives in CH_2Cl_2, NBu_4PF_6 (0.1 M), [c] = 2 mM, 295 K, scan rate = 200 mV.s^{-1}, vs. Fc$^+$/Fc.

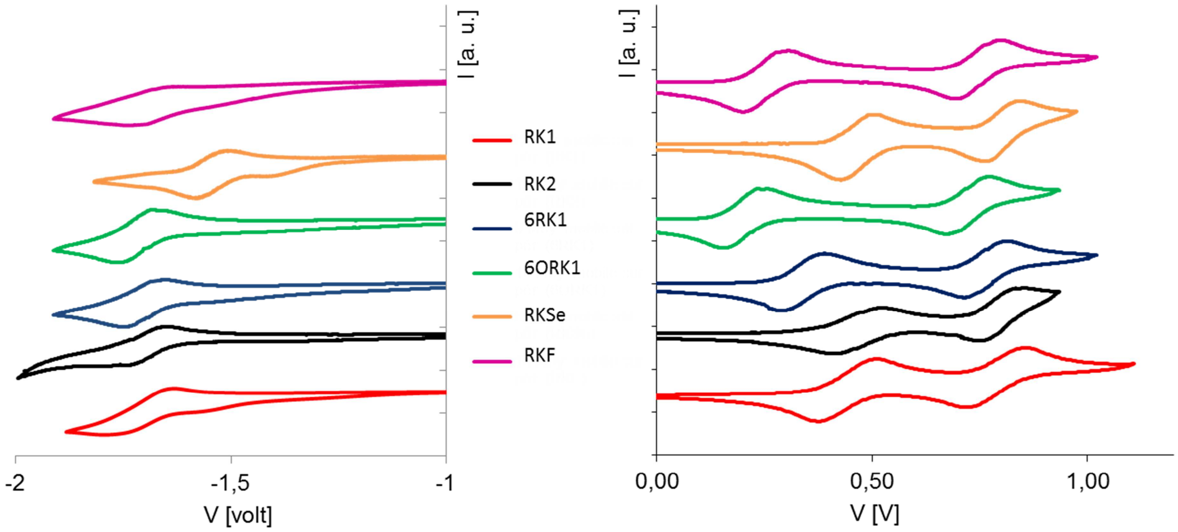


Figure S2. Modelling of frontier orbitals of dyes with calculated HOMO and LUMO level.

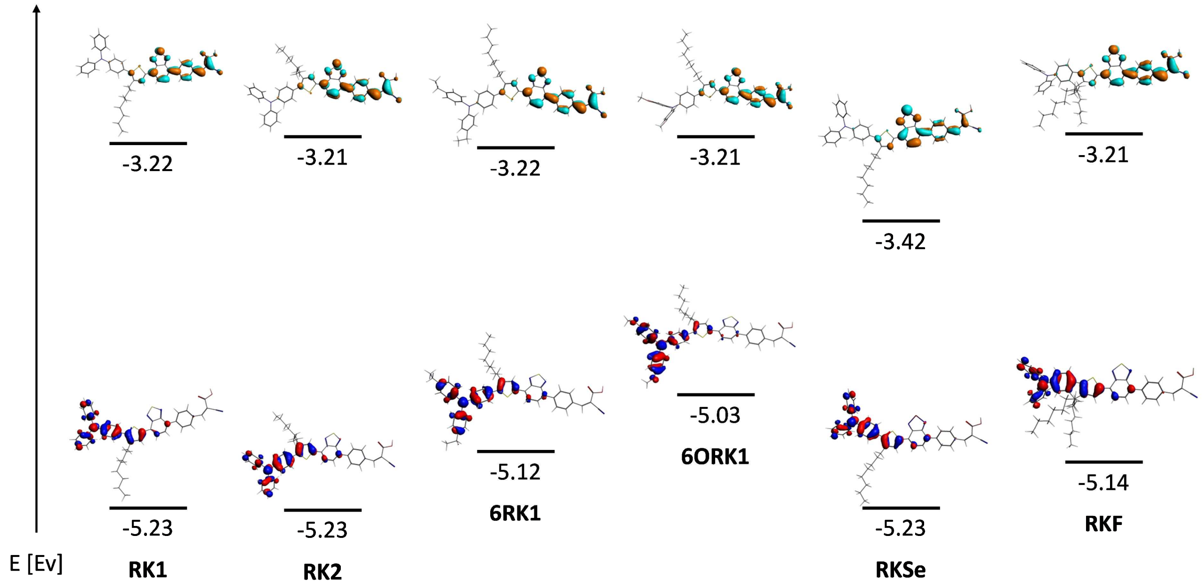
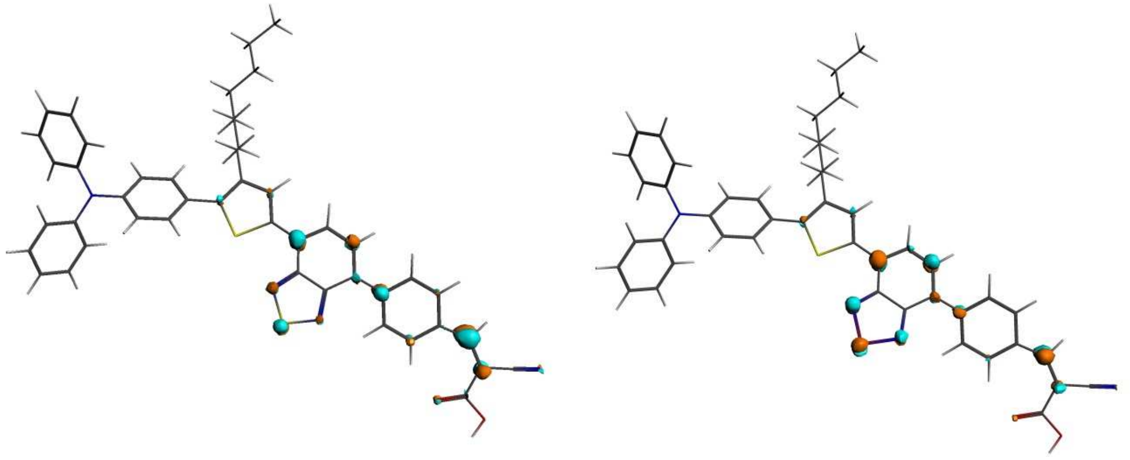


Figure S3. Modelling of frontier orbitals of RK1 and RKSe dyes with calculated HOMO and LUMO level.

RK1 **RKSe**



Contribution of the S and Se atoms in benzothiadiazole/benzoselenadiazole to the LUMO energy level :

RK1

S : 7.4 %, C : 21.7 %, N : 7.6 %

Total contribution to the LUMO: 36.7 %.

RKSe

Se : 9.9 %, C : 24.5 %, N : 11.1 %

Total contribution to the LUMO: 45.5 %.

Device Fabrication and characterization

The devices were prepared as followed: the various layers of TiO_2 films were screen printed. The electrode total active area was 0.36 cm^2. Several layers of transparent titania were deposited using a TiO_2 nanoparticles paste (Ti-Nanoxide HT/SP) obtained from Solaronix, Switzerland. On top of that, to further increase the light-harvesting capacity of these devices, a reflective layer (Solaronix' Ti-Nanoxide R/SP) of about 3 to 4 µm was added. The total thickness of the titania working electrode is expressed in **Table S3** and was optimized for each dye. In order to maximize adhesion, titania layer porosity and specific area a pre and post $TiCl_4$ treatment was performed. After sintering at 500°C and cooling down to 80°C, the sintered TiO_2 electrodes were sensitized by immersion in a solution of the dye in indicated solvent with or without chenodeoxycholic acid (CDCA) for 18 h, and then assembled using a thermally platinized FTO/glass (TCO 22-7, Solaronix) counter electrode. The working and counter electrodes were separated by a 25 µm thick hot melt gasket (Meltonix 1170-25, Solaronix) and sealed by heating. The heating was minimized to avoid dye thermal degradation. The cell was then filled with a volatile electrolyte (Solaronix Iodolyte HI-30) through a pre-drilled hole using a vacuum pump. The electrolyte injection hole on the thermally platinized FTO glass counter electrode was finally sealed with a thin glass cover. Devices using a non-volatile ionic liquid based electrolyte (Solaronix Mosalyte TDE-250) were prepared following the previously described procedure except that the titania layer was reduced to 12 µm in total using 8µm of Ti-Nanoxide HT/SP and 4 µm of scattering particules. The devices were characterized using a Solaronix SolarSim 150 previously calibrated. The current–voltage characteristics of the cell measured under AM 1.5G, 100% sun, were obtained by applying external potential bias to the cell and by measuring the generated photocurrent with a Keithley model 2400 digital source meter (Keithley, USA). The devices were masked prior to measurement according to a procedure previously described to attain an illuminated active area of 0.36 cm^2 [8]

Table S1: Photovoltaic parameters of liquid electrolyte based DSCs using optimized parameters.

	Adsorbing solution	TiO_2 thickness	Surface area [mm²]	J_{sc} [mA.cm^{-2}]	V_{oc} [V]	FF [%]	η [%]
RK1	0.2 mM EtOH, 2 mM CDCA	6 + 4 [a]	36 [b]	14.28	0.74	74	7.75
	0.2 mM EtOH-$CHCl_3$, 2 mM CDCA	6 + 4 [a]	36 [b]	13.80	0.71	75	7.42
6ORK1	0.2 mM ACN-^{t}BuOH, 2 mM CDCA	12 + 4 [a]	36 [b]	17.87	0.75	70	9.41
	0.2 mM EtOH-$CHCl_3$, 2 mM CDCA	12 +4 [a]	36 [b]	17.87	0.73	68	8.88

a TiO_2 Solaronix (HT/SP 1 R/SP), *b* fabrication and measurement performed at Solaronix

Table S2: Photovoltaic parameters of liquid electrolyte based DSCs using RK1 and various amount of CDCA.

Adsorbing solution	$TiO_{2thickness}$ [µm]	J_{sc} [mA.cm^{-2}]	V_{oc} [V]	FF [%]	η [%]
MeOH without Cheno	13+3.5	20.25	0.691	64	8.89
MeOH/Cheno (2mM)	13+3.5	19.50	0,713	72	10.00
EtOH/Cheno (5mM)	13+4	18.26	0.759	74	10.20

Figure S4: Variation of the PCE of the solar cells measured under the irradiance of AM1.5G sunlight during successive full-sun visible-light soaking (1 Sun 1000 W/m^2) at 65°C.

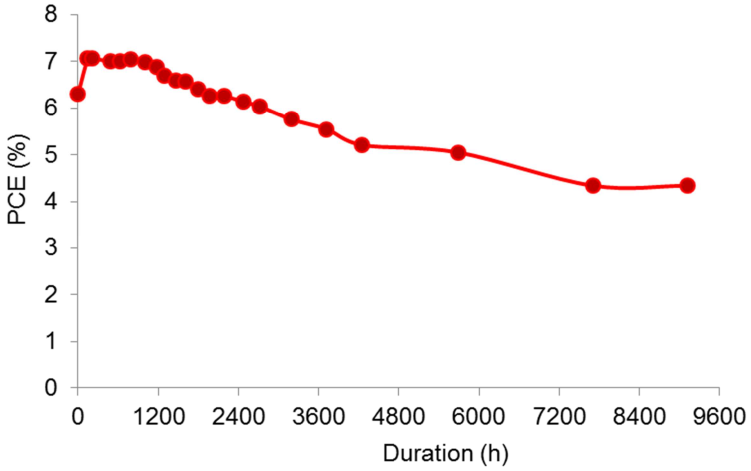
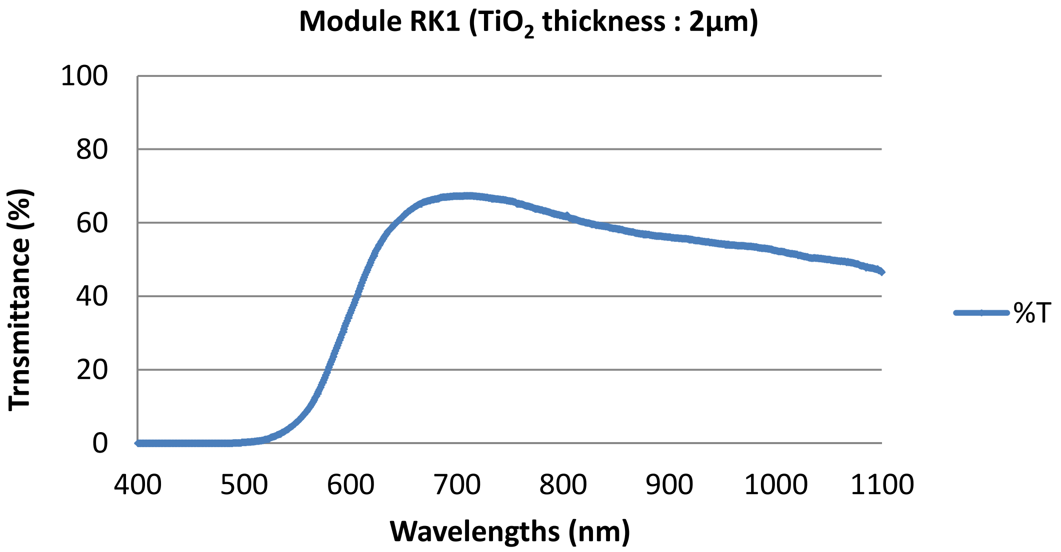


Figure S5. Transmission curve of a RK1 module based on 2µm thick TiO_2 electrodes.



References

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[1] K. Lim, C. Kim, J. Song, T. Yu, W. Lim, K. Song, P. Wang, N. Zu, J. Ko, *J. Phys. Chem. C* **2011**, *115*, 22640

[2] A. D. S. Sandanayaka, Y. Taguri, Y. Araki, T. Ishi-i, S. Mataka, O. Ito, *J. Phys. Chem. B* **2005,** *109*, 22502

[3] a) K. T. Kamtekar, K. Dahms, A. S. Batsanov, V. Jankus, H. L. Vaughan, A. P. Monkman, M. R. Bryce, *J. Polym. Sci. A Polym. Chem.* **2011**, *49*, 1129; b) Q. Luo, S. Sheng, S. Cheng, H. Tian, *Australian Journal of Chemistry* **2005**, *58*, 321

[4] a) J.-H. Yum, D. P. Hagberg, S.-J. Moon, K. Karlsson, T. Marinado, L. Sun, A. Hagfeldt, M. K. Nazeeruddin, M. Grätzel, *Angew. Chem. Int. Ed.* **2009**, *48*, 1576; b) Q. Liu, Q.-Y. Feng, H. Yamada, Z.-S. Wang, N. Ono, X.-Z. You, Z. Shen, *Chem. Asian J.* **2012**, *7*, 1312

[5] D. Joly, L. Pellejà, S. Narbey, F. Oswald, J. Chiron, J. N. Clifford, E. Palomares, R. Demadrille, *Scientific Report* **2014**, 4, 4033

[6] a)ADF2010, SCM, Theoretical Chemistry, Vrije Universiteit, The Netherlands Amsterdam, http://www.scm.com; b) G. te Velde, F.M. Bickelhaupt, S. J. A. van Gisbergen, C. Fonseca Guerra, E. J. Baerends, J. G. Snijders, T. Ziegler, J. Comput. Chem. 2001, 22, 931. c) C. Fonseca Guerra, J.G. Snijders, G. te Velde, E.J. Baerends, Theor. Chem. Acc. 1998, 99, 391

[7] C.C. Pye, T. Ziegler, Theor. Chem. Acc. 1999, 101, 396

[8] S. Ito, Md. K. Nazeeruddin, P. Liska, P. L. Comte, R. Charvet, P. Péchy, M. Jirousek, A. Kay, S. M. Zakeeruddin, M. Grätzel, *Prog. Photovolt: Res. Appl.* **2006**; 14, 589