Side Chains Engineering of Organic Sensitizers for Dye-Sensitized Solar Cells: a Strategy to Improve Performances and Stability

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General methods for synthesis

4-(N,N-diphenylamine)phenylboronic acid, 4-formylphenylboronic acid, tri-*tert*-butylphosphonium tetrafluoroborate, 2-cyanoacetic acid, piperidine, *n*-BuLi [2.5 M solution in Tetrahydrofuran (THF)], trimethyl tin chloride solution [1 M solution in *n*-hexane] palladium acetate(II), magnesium sulfate, sodium sulfate, tri(*o*-tolyl)phosphine, tetrakis (triphenylphosphine) palladium (0), tris(dibenzylideneacetone)dipalladium(0) and trimethylborate were purchased from Aldrich or TCI chemicals and used as received. N-Bromo-Succinimide 4,7-dibromo-2,1,3-benzothiadiazole was purchased from Orgalight. Ethylene glycol, paratoluenesulfonic acid, 2,2-dimethyl-1,3-propanediol and potassium carbonate from Acros Organics. 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. Compounds **1**,[14] **2**,[15] 4-(N,N-di((4-hexyl)phenyl)amine)phenyl-(4,4,5,5-tetramethyl-1,3,2-dioxa)-borolane,[21] **8**,[15] **10**,[9] and **PK1**[14] were synthesized according to literature. The precursor **7** was synthesized in two steps starting from 4-(5-bromothiophen-2-yl)benzaldehyde (Scheme S1) which was synthesized according to previous literature.[S1]

Instruments

UV-vis absorption spectra were recorded in solution on a Perkin-Elmer Lambda 2 spectrometer (wavelength range: 180-820 nm; resolution: 2 nm).

Fluorescence spectra were carried out on a F-4500 fluorescence spectrophotometer Hitachi using a quartz cell of 1 cm width.

Electrochemical studies of the synthesized molecules were carried out in a one compartment, three-electrode electrochemical cell equipped with a flat platinum working electrode (7 mm^2), a platinum wire counter electrode, and a silver wire pseudo-reference electrode, whose potential was checked using the Fc^+/Fc couple as an internal standard. The potential of this reference was found at 0.62 V vs NHE in acetonitrile.[S2] As here, the electrolyte consisted of

0.2 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) solution in dichloromethane containing 2 x 10^{-3} M of the dye. A conversion between dichloromethane and acetonitrile had to be conducted according our experiments with a difference of 0.03 V between the two solvents with the dichloromethane the more positive one. So, the measured potentials of the dyes measured versus internal reference in dichloromethane were converted to NHE adding 0.59 V (0.62 – 0.03). Cyclic voltammetry measurements were conducted with a sweep rate of 200 $mV.s^{-1}$.

The luminescence quantum yields were determined at room temperature through an absolute method using an integrating sphere from GMP S.A. (Switzerland) coupled to a Fluorolog FL3-22 spectrometer from Horiba-Jobin Yvon-Spex. The spectrometer is equipped with a double grating excitation monochromator, an iHR320 imaging spectrometer and a Hamamatsu R928P photomultiplier. All spectra were corrected for detection and optical spectral response (instrumental functions) of the spectrofluorimeters.

Quartz capillaries 4 mm in diameter were used both in solution and solid state. The values reported are the average of three independent determinations for each sample. The absolute quantum yields were calculated using the following expressions:

$$\Phi = E_c/(L_a-L_c) = E_c/L_a \times \alpha \qquad \alpha = (L_a-L_c)/L_a$$

where Ec, Lc and La are the emission spectra of the sample, the excitation wavelength of the sample and the excitation wavelength of the reference, respectively. The excitation wavelength was 520nm for each sample.

Dye-Sensitized Solar Cells preparation

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. A first layer (13 µm) of transparent titania was deposited with 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 4 µm was added on top. The total thickness of the titania working electrode was around 17 µm. In order to optimize 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 12 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. 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 0.16 cm^2.[24]

Synthesis of dyes

Synthesis of **3**:

Under argon, **1** (150 mg, 0.18 mmol), triphenylamine-4-boronic acid (34 mg, 0.12 mmol), tetrakis (triphenylphosphine) palladium (5.5 mg, 4 mol%), potassium carbonate (25 mg, 0.47 mmol) were dissolved in toluene (10 mL) and water (0.25 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 diethyl ether and washed with brine, dried over sodium sulphate, filtered and concentrated under vacuum. The crude solid was chromatographed on silica gel using *n*-hexane/DCM 8:2 as eluent to afford orange solid **3** (85 mg, 0.08 mmol, 70%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 7.97 (s, 1 H), 7.93 (s, 1 H), 7.83 (s, 2 H), 7.52 (d, *J* = 8.5 Hz, 2 H), 7.52 (d, *J* = 8.5 Hz, 2 H), 7.30 (m, 3 H), 7.23 (ABq, *Δvab* = 0.9Hz, *J* = 3.6 Hz, 2 H), 7.20-7.05 (m, 10 H), 7.00 (d, *J* = 3.8 Hz, 2 H), 2.86 (d, *J* = 7.3 Hz, 2 H), 2.77 (d, *J* = 7.3 Hz, 2 H), 1.79 (m, 2 H), 1.50-1.20 (m, 16 H), 0.95-0.87 (m, 12 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ (ppm): 153.0, 147.9, 147.8, 144.7, 140.7, 140.0, 138.0, 137.8, 136.9, 135.0, 133.8, 132.2, 130.7, 129.8, 128.5, 127.7, 127.1, 126.9, 126.1, 125.8, 125.6, 125.5, 125.0, 124.1, 123.6, 123.0, 112.6, 40.7, 40.6, 34.0, 33.0, 33.0, 32.0, 29.2, 29.1, 26.2, 23.6, 23.5, 23.1, 14.6, 14.6, 11.2. HRMS (ESI): $[M]^+$= 1009.2262 (calcd. for $C_{56}H_{56}N_3{}^{79}BrS_5$: 1009.2257), $[M+Na]^+$= 1032.2148 (calcd. for $C_{65}H_{61}N_4NaS_5$: 1032.21534). Anal. Calcd for $C_{56}H_{56}BrN_3S_5$: C, 66.51; H, 5.58; N, 4.16; S, 15.85. Found: C, 66.26; H, 5.57; N, 4.15; S, 15.73.

Synthesis of **4**:

A mixture of 4-(N,N-di((4-hexyl)phenyl)amine)phenyl-(4,4,5,5-tetramethyl-1,3,2-dioxa)-borolane (13 mg, 0.03 mmol), **2** (31 mg, 0.04 mmol), $Pd(OAc)_2$ (1 mg, 0.01 mmol, 10 mol%), K_3PO_4 (11 mg, 0.05 mmol), ^{i}PrOH (2 mL) and distilled water (1 mL) was stirred at 80 °C for 30 min. The mixture was added to brine and extracted four times with ethyl acetate. Combined organic phases were filtered on celite pad, washed with ethyl acetate, dried over

Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (Hexane/CH_2Cl_2, 9:1 to 8:2) to obtain the desired product **7** (12 mg, r = 41 %) as a purple film. ^{1}H NMR (CD_2Cl_2, 200 MHz) δ (ppm): 7.96 (d, *J* = 6.4 Hz, 2 H), 7.81 (s, 2 H), 7.45 (d, *J* = 8.4 Hz, 2 H), 7.19 (s, 2 H), 7.15-6.92 (m, 2 H), 7.10 (d, *J* = 8.8 Hz, 4 H), 7.01 (d, *J* = 8.4 Hz, 4 H), 6.99 (d, *J* = 8.4 Hz, 2 H), 2.98-2.68 (m, 4 H), 2.68-2.45 (m, 4 H), 1.86-1.55 (m, 8 H), 1.50-1.08 (m, 32 H), 0.97-0.74 (m, 12 H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm): 152.6, 148.0, 145.2, 144.6, 141.1, 138.1, 137.7, 137.6, 136.7, 134.3, 133.1, 131.4, 131.0, 130.5, 129.4, 127.1, 127.0, 126.4, 126.3, 125.8, 125.5, 125.2, 124.8, 122.6, 122.5, 112.2, 35.6, 32.1, 32.0, 31.9, 31.7, 30.8, 30.8, 29.8, 29.7, 29.6, 29.6, 29.5, 29.4, 29.2, 22.9, 22.8, 14.3. HRMS (ESI): $[M]^{+\cdot}$= 1177.4134 (calcd. for $C_{68}H_{80}N_3{}^{79}BrS_5$: 1177.4134). Anal. Calcd for $C_{68}H_{80}N_3BrS_5$: C, 69.24; H, 6.84; N, 3.56; S, 13.59. Found: C, 69.83; H, 7.08; N, 3.51; S, 12.92.

Synthesis of **5**:

Under argon, **3** (100 mg, 99 µmol), 4-formylphenylboronic acid (23 mg, 148 µmol), tris(dibenzylideneacetone)dipalladium(0) (1.8 mg, 2% mol), Tri-*tert*-butylphosphonium tetrafluoroborate (2.3 mg, 8 mol%) potassium carbonate (27 mg, 0.2 mmol) were dissolved in toluene (5 mL) and water (50 µL). The solution was vigorously stirred and heated at 70°C overnight. The reaction was quenched with water and the organic phase was extracted with diethyl ether and washed with brine, dried over sodium sulphate, filtered and concentrated under vacuum. The crude solid was chromatographed on silica gel using *n*-hexane/DCM 1:1 as eluent to afford purple solid **5** (85 mg, 0.08 mmol, 70%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 10.01 (s, 1 H), 8.05-7.75 (m, 8 H), 7.62-7.47 (m, 4 H), 7.60-7.05 (m, 14 H), 2.95-2.75 (m, 4 H), 1.83 (s broad, 2 H), 1.50-1.20 (m, 16 H), 1.05-0.85 (m, 12 H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm): 191.4, 152.5, 147.4, 147.4, 146.8, 144.2, 142.1, 140.3, 139.7, 139.5, 137.9, 137.3, 136.4, 135.0, 134.5, 133.4, 132.4, 131.4, 131.2, 130.5, 129.3, 128.0, 127.3, 127.2,

126.4, 125.7, 125.6, 125.5, 125.3, 125.0, 125.0, 124.5, 123.6, 123.2, 122.5, 40.2, 40.1, 33.8, 33.8, 32.6, 32.6, 29.7, 28.8, 28.7, 25.83, 25.8, 23.1, 14.2, 10.8. HRMS (ESI): $[M]^{+\cdot}$= 1035.3406 (calcd. for $C_{63}H_{61}N_3OS_5$: 1035.3413).

Synthesis of **6**:

A mixture of **4** (150 mg, 0.13 mmol, 1 eq.), 4-formylphenylboronic acid (29 mg, 0.19 mmol, 2 eq.), $Pd(OAc)_2$ (1.0 mg, 3.0 µmol, 2 mol%), K_3PO_4 (54 mg, 0.25 mmol, 2 eq.), THF (5 mL), ^{i}PrOH (2 mL) and distilled water (1 mL) was stirred at 80 °C for 62 hours. The mixture was added to brine and extracted four times with ethyl acetate. Combined organic phases were filtered on celite pad, washed with ethyl acetate, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (Hexane/CH_2Cl_2, 6:4 to 1:1) to obtain the desired product **6** (126 mg, 82%) as a purple film. ^{1}H NMR (CD_2Cl_2, 200 MHz) δ (ppm): 9.99 (s, 1 H), 8.02 (s, 2 H), 7.90 (d, *J* = 9.0 Hz, 2 H), 7.88 (s, 2 H), 7.80 (d, *J* = 8.6 Hz, 2 H), 7.52 (s, 1 H), 7.47 (d, *J* = 9.2 Hz, 2 H), 7.28 (d, *J* = 4.0 Hz, 1 H), 7.25-7.17 (m, 2 H), 7.11 (d, *J* = 8.4 Hz, 4 H), 7.06-6.95 (m, 6 H), 2.97-2.82 (m, 4 H), 2.66-2.48 (m, 4 H), 1.86-1.69 (m, 4 H), 1.69-1.55 (m, 4 H), 1.49-1.20 (m, 32 H), 0.98-0.79 (m, 12 H). ^{13}C NMR (CD_2Cl_2, 100 MHz) δ (ppm): 152.9, 148.4, 145.4, 144.8, 142.4, 141.5, 140.7, 140.0, 138.7, 138.2, 137.8, 136.8, 135.7, 134.7, 133.3, 132.3, 131.2, 131.0, 130.7, 130.0, 127.3, 127.2, 126.6, 126.0, 125.6, 125.2, 123.2, 122.7, 122.5, 120.7, 35.8, 32.3, 32.2, 32.0, 31.0, 30.9, 30.1, 30.1, 29.9, 29.7, 29.5, 23.1, 23.1, 14.3, 14.3. HRMS (ESI): $[M]^{+\cdot}$= 1203.5287 (calcd. for $C_{75}H_{85}N_3OS_5$: 1203.5291). Anal. Calcd for $C_{75}H_{85}N_3OS_5$: C, 74.77; H, 7.11; N, 3.49; S, 13.31. Found: C, 75.09; H, 7.47; N, 3.12; S, 11.75.

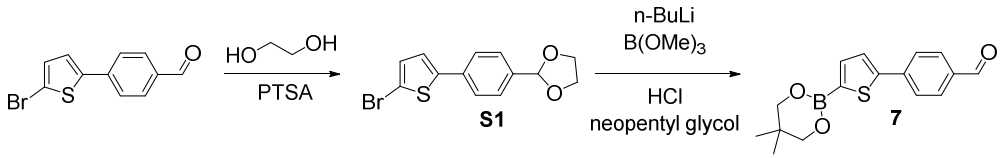
General procedure for dye synthesis by Knœvenagel condensation:

Under argon, aldehyde (0.10 mmol), cyanoacetic acid (78 mg, 0.48 mmol), were dissolved in a mixture of acetonitrile (6 mL) and chloroform (4 mL). A catalytic amount of piperidine was

added and the solution was refluxed for 3 hours. Solvent was removed under reduced pressure and the solid dissolved in chloroform. The organic phase was washed with an HCl solution (1.5 M), dried on $MgSO_4$ and concentrated. The crude solid was chromatographed on silica using DCM then DCM/MeOH/Acetic acid 90/5/5 as eluent to afford purple solid.

PK2: (70 mg, 0.07 mmol, 68%). ^{1}H NMR (THF-d_8, 500MHz) δ (ppm): 8.26 (s, 1 H), 8.20-7.40 (m, 11 H), 7.35-7.15 (m, 7 H), 7.15-6.95 (m, 8 H), 1.50-1.20 (m, 16 H), 1.00-0.75 (m, 12 H). ^{13}C NMR (THF-d_8, 100 MHz): δ (ppm): 153.4, 148.5, 145.2, 143.5, 140.9, 140.2, 138.8, 138.4, 137.6, 135.4, 133.6, 132.5, 132.4, 132.2, 130.1, 129.1, 128.4, 128.1, 127.2, 126.5, 126.4, 126.1, 126, 125.9, 125.4, 124.5, 124.0, 123.6, 41.2, 34.7, 34.6, 33.6, 33.6, 32.5, 30.6, 29.7, 29.7, 26.8, 26.7, 24.0, 23.5, 14.5, 11.2. HRMS (ESI): $[M-H]^-$= 1101.3409 (calcd. for $C_{66}H_{61}N_4O_2S_5$: 1101.34036), $[M-CO_2H]^-$= 1057.3510 (calcd. for $C_{65}H_{61}N_4S_5$: 1057.35053)

6PK1: (109 mg, 0.09 mmol 86%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ (ppm): 8.08 (m, 4 H), 7.97 (s, 1 H), 7.96 (d, *J* = 7.6 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2 H), 7.68 (d, *J* = 3.6 Hz, 1 H), 7.54 (d, *J* = 8.4 Hz, 2 H), 7.38 (d, *J* = 3.2 Hz, 1 H), 7.35 (d, *J* = 3.2 Hz, 1 H), 7.26 (d, *J* = 3.2 Hz, 1 H), 7.16 (d, *J* = 8.0 Hz, 4 H), 6.99 (d, *J* = 8.0 Hz, 4 H), 6.93 (d, *J* = 8.0 Hz, 2 H), 2.89 (m, 4 H), 2.57 (m, 4 H), 1.75 (m, 4 H), 1.60 (m, 4 H), 1.52-1.05 (m, 32 H), 0.87 (m, 12 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 152.7, 148.0, 147.9, 145.2, 144.7, 142.8, 141.2, 141.1, 140.0, 138.2, 137.4, 137.1, 136.6, 134.4, 133.1, 132.7, 132.2, 131.5, 131.0, 130.9, 130.8, 129.9, 129.3, 128.2, 127.2, 127.1, 127.0, 126.4, 125.8, 125.5, 125.3, 125.2, 124.9, 124.8, 122.6, 122.5, 117.7, 94.6, 58.6, 35.5, 32.0, 31.9, 31.6, 30.7, 30.7, 29.8, 29.8, 29.6, 29.4, 29.2, 22.8, 22.8, 18.6, 14.2. HRMS (ESI): $[M]^{+\cdot}$= 1270.5344 (calcd. for $C_{75}H_{85}N_3OS_5$: 1270.5349).



Scheme S1. Synthesis of precursor **7**

Synthesis of **7**: Using a Dean-Starck apparatus, 1-(5-bromothien-2-yl)-4-formaldehyde (600 mg, 2.25 mmol, 1.0 eq.) and *p*-toluenesulfonic acid (20 mg, 0.11 mmol, 5 mol%) were dissolved in toluene (25 mL) and ethylene glycol (12 mL). The mixture was refluxed for 6 hours before being poured into an aqueous solution of $NaHCO_3$ 1M. The organic phase was extracted with toluene, washed with $NaHCO_3$, dried on Na_2SO_4 and concentrated to get white solid **S1** (560 mg, 1.8 mmol, 80%).

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.58 (d, *J* = 8.8 Hz, 2 H), 7.53 (d, *J* = 8.8 Hz, 2 H), 7.10 (d, *J* = 3.9 Hz, 1 H), 7.07 (d, *J* = 3.9 Hz, 1 H) 5.87 (s, 1 H), 4.24-4.02 (m, 4 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 145.3, 137.5, 134.4, 130.9, 127.1, 125.5, 123.6, 111.7, 103.3, 65.3.

Under argon, **S1** (540 mg, 1.70 mmol, 1.0 eq.) was dissolved in distilled THF (10 mL). *n*-BuLi (0.83 mL, 2.10 mmol, 1.2 eq.) was added slowly at -78 °C, the reaction was allowed to reach room temperature. After 1 hour trimethylborate (0.23 mL, 2.1 mmol, 1.2 eq.) was added at -78 °C. The reaction was stirred for 1.5 hours while reaching room temperature. 10 mL of a 2 M HCl solution was added to the mixture and stirred for 30 minutes. The organic phase was then extracted with diethyl ether, dried over $MgSO_4$ and concentrated. The boronic acid derivative was dissolved in THF mixture, neopentyl glycol (203 mg, 2.0 mmol, 1.2 eq.) and $MgSO_4$ were added to the solution. After 2 hours at room $MgSO_4$ was filtered off and the solution concentrated to dryness. The crude solid was chromatographed on silica gel DCM first to remove excess of neopentyl glycol then the product was eluted with ethyl acetate as eluent to afford pale pink solid **7** (200 mg, 41%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 10.00 (s, 1 H), 8.06 (d, *J* = 3.5 Hz, 1 H), 7.99-7.85 (m, 4 H), 7.67 (d, J = 3.6 Hz, 1 H), 3.79 (s, 4 H), 1.05 (s, 6 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 191.5, 148.1, 140.1, 136.8, 135.2, 130.4, 126.3,

126.1, 72.4, 32.1, 21.9. HRMS (Q-TOF): $[M+H]^+$= 301.1071 (calcd. for $C_{16}H_{18}O_3{}^{11}BS$: 301.1070). Anal. Calcd for $C_{16}H_{17}BO_3S$: C, 64.02; H, 5.71; S, 10.68. Found: C, 64.29; H, 5.74; S, 10.44.

Synthesis of **9**: Under argon, **8** (646 mg, 0.94 mmol, 2.0 eq.), **7** (142 mg, 0.47 mmol, 1.0 eq.), tetrakis (triphenylphosphine) palladium (21 mg, 0.02 mmol, 4 mol%), potassium carbonate (261 mg, 1.89 mmol, 4.0 eq.) were dissolved in anhydrous toluene (5.0 mL) and heated at 80°C overnight. The reaction was quenched with water and the organic phase was extracted with diethyl ether and washed with brine, dried over magnesium sulphate, filtered and concentrated under vacuum. The crude solid was chromatographed on silica gel using DCM/*n*-hexane 1:1 as eluent to afford red solid **9** (181 mg, 50%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm): 10.05 (s, 1 H), 8.02 (s, 1 H), 8.00-7.90 (m, 2 H), 7.90-7.65 (m, 5 H), 7.50 (d, *J* = 3.9 Hz, 1 H), 7.30 (s, 1 H), 2.93 (t, *J* = 7.6 Hz, 2 H), 2.68 (t, *J* = 7.6 Hz, 2 H), 1.90-1.60 (m, 4 H), 1.45-1.25 (m, 20 H), 0.93 (t, *J* = 6.6 Hz, 6 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ =191.4, 152.4, 152.3, 143.0, 142.1, 141.07, 139.7, 138.5, 137.8, 137.2, 135.0, 132.0, 130.8, 130.5, 128.0, 127.0, 126.0, 125.6, 125.5, 125.4, 125.1, 124.8, 111.6, 31.9, 31.6, 30.5, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 22.7, 14.1. Anal. Calcd for $C_{41}H_{45}N_2OBrS_4$: C, 62.34; H, 5.74; N, 3.55; S, 16.24. Found: C, 62.69; H, 5.72; N, 3.45; S, 16.29.

Synthesis of **11**: Under argon, stannic **10** (66 mg, 0.11 mmol, 1.0 eq.), **9** (90 mg, 0.11 mmol, 1.0 eq.), Pd_2dba_3 (4 mg, 4.5 μmol, 4 mol%) and P(*o*-tolyl)$_3$ (11 mg, 8 mol%) were dissolved in anhydrous toluene (5.0 mL) and refluxed for 24 hours. The mixture was then poured into HCl (2 M). The organic phase was extracted with Et_2O, washed with HCl (2 M), dried over Na_2SO_4 and concentrated. The crude solid was chromatographed on silica using DCM/*n*-hexane 1:1 first then DCM/*n*-hexane 4:1 as eluent to afford purple solid **11** (105 mg, 80%). ^{1}H NMR (CD_2Cl_2, 200 MHz): δ = 9.98 (s, 1H), 7.95-7.82 (m, 4H), 7.80-7.64 (m, 4H) 7.45-7.27

(m, 7H) 7.25-7.06 (m, 10H), 2.83 (t, *J* = 7.1 Hz, 4 H), 2.72 (t, *J* = 7.9 Hz, 4H), 1.58-1.52 (m, 6 H), 1.36 (s, 30 H), 0.95 (s, 9 H). ^{13}C NMR (CD_2Cl_2, 50 MHz): δ = 191.5, 152.6, 147.9, 147.6, 142.1, 141.2, 140.3, 139.9, 139.2, 138.3, 138.2, 137.5, 136.5, 135.5, 133.9, 133.3, 132.6, 132.3, 131.1, 130.8, 130.7, 130.1, 129.8, 128.7, 128.4, 127.0, 125.9, 125.8, 125.6, 125.3, 125.1, 124.9, 123.7, 123.4, 32.4, 31.5, 31.0, 30.8, 30.2, 30.2, 30.1, 30.0, 29.9, 29.9, 29.8, 29.3, 23.2, 14.4. HRMS (ESI): $[M]^{+\cdot}$= 1147.4657 (calcd. for $C_{41}H_{45}N_2O^{79}BrS_4$: 1147.4665). Anal. Calcd for $C_{71}H_{77}N_3OS_5$: C, 74.24; H, 6.76; N, 3.66; S, 13.96. Found: C, 73.68; H, 6.67; N, 3.66; S, 13.66.

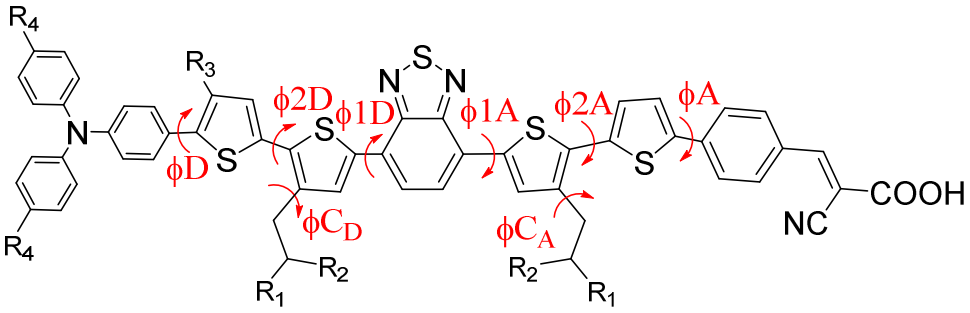
Synthesis of **PK3**: Under argon, the compound **11** (70 mg, 0.06 mmol, 1.0 eq.), cyanoacetic acid (49 mg, 0.30 mmol, 5.0 eq.), were dissolved in a mixture of acetonitrile (6 mL) and chloroform (4 mL). A catalytic amount of piperidine was added and the solution was refluxed for 3 hours. Solvent was removed under reduced pressure and the solid dissolved in chloroform. The organic phase was washed with an HCl solution (2 M), dried on $MgSO_4$ and concentrated. The crude solid was chromatographed on silica using DCM then DCM/MeOH/Acetic acid 90/5/5 as eluent to afford the purple solid **PK3** (51 mg, 70 %).^{1}H NMR (DMSO-d, 400 MHz): δ (ppm): 8.08-7.98 (m, 4 H), 7.96-7.87 (m, 3 H), 7.78 (d, *J* = 8.1 Hz, 2 H), 7.64 (d, *J* = 3.8 Hz, 1 H), 7.42-7.29 (m, 7 H), 7.18-7.07 (m, 5 H), 7.03 (d, *J* = 8.5 Hz, 2 H), 2.89 (t, *J* = 7.3 Hz, 2 H), 2.82 (t, *J* = 7.7 Hz, 2 H), 2.82 (t, *J* = 7.7 Hz, 2 H), 2.68 (t, *J* = 7.6 Hz, 2 H), 1.50-1.20 (m, 36 H), 0.90-0.80 (m, 9 H). ^{13}C NMR (DMSO-d, 100 MHz): δ (ppm): 159.5, 158.3, 153.9, 153.8, 143.1, 142.4, 140.2, 139.8, 139.2, 137.9, 137.0, 136.4, 136.1, 135.3, 133.7, 133.2, 132.9, 132.4, 131.1, 130.4, 130.1, 130.0, 129.0, 127.8, 127.7, 126.1, 125.9, 125.0, 124.0, 122.9, 119.9, 31.7, 30.4, 30.3, 30.3, 29.4, 29.3, 29.3, 29.1, 29.1, 29.1, 29.0, 29.0, 28.9, 28.6, 25.2, 22.4, 14.2. HRMS (ESI): $[M]^-$= 1214.4678 (calcd. for $C_{74}H_{78}N_4O_2S_5$: 1213.47339), $[M-H]^-$= 1213.4656 (calcd. for $C_{74}H_{77}N_4O_2S_5$: 1213.46556).

Computational details.

Density Functional Theory (DFT) as implemented in ADF 2014[S3-S4] has been used to examine the most stable conformations for molecules PK1, PK2 and PK3 as well as 6PK1. Considering the numerous possible conformations due to the various dihedral angles between the aromatic rings of the conjugated core, combined to the lateral aliphatic chain anchoring on the thiophene groups, it has been first necessary to carry out a screening of the conformations using firstly geometry optimizations with the PBE functional combined to double-zeta + polarization basis sets (DZP in ADF, Slater basis functions) in gas phase. The 6 lowest energy conformations were then chosen and submitted to a more accurate geometry optimization, with the PBE functional corrected for dispersion using Grimme methodology[S5] with larger basis sets (TZ2P : triple zeta + 2 polarization functions) and in a solvent phase modelled through the COSMO model set for dichloromethane. Single-point B3LYP + dispersion (Grimme 3) calculations with TZ2P sets in a solvent phase were then performed on the four most stable conformations to examine the HOMO and LUMO energies and their spatial localizations. Interestingly the energy ordering of the various conformations for a given molecule was not method-dependent, thus insuring that the initial screening to identify the most stable conformations - based on PBE in gas phase - was reliable and did not change with more accurate approaches.

For molecules PK1 to PK3, the four most stable conformations lie in an energy range of *ca* 3 kcal/mol at the B3LYP-D/TZ2P level.

For molecules PK1 to PK3, all dihedral angles between the various aromatic rings were examined and initial conformations with either cis or trans positions were examined (see scheme S2 for definitions of these geometrical parameters). The anchoring of the aliphatic chain was also varied with either an in plane (*vs* the thiophene plane) or an out-of-plane (*vs* the thiophene plane) conformation.



PK1: R_1 = n-C_6H_{13}, R_2 = R_3 = R_4 = H
PK2: R_1 = n-C_4H_9, R_2 = C_2H_5, R_3 = R_4 = H
PK3: R_1 = n-C_6H_{13}, R_2 = H, R_3 = n-C_8H_{17}, R_4 = H
6PK1: R_1 = n-C_6H_{13}, R_2 = R_3 = H, R_4 = n-C_6H_{13}

Scheme S2. Definitions of dihedral angles of the dyes

Table S1: Values of dihedral angles for the four most stable conformations of **PK1** at B3LYP level

	ϕD	ϕ2D	ϕCD	ϕ1D	ϕ1A	ϕCA	ϕ2A	ϕA
CC oop	9.2	5.9	73	-9.1	-5.3	71.3	10.2	1.7
CT ip2	6	177.8	172.7	-9.3	-8.1	172.1	178.3	-0.3
CT oop	8	174.2	80.9	-7.4	-5.5	79.7	175.7	1.4
TC oop	10.5	7.7	74.9	-170.4	-173.6	73.4	8.5	3.7

CC oop CT ip2 CT oop TC oop

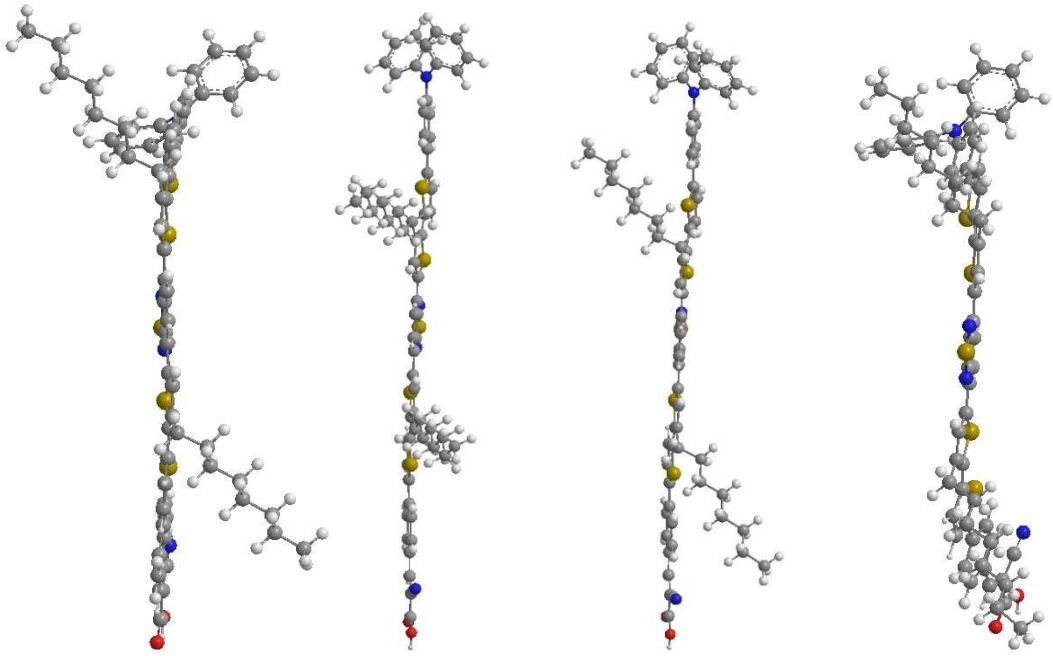


Figure S2. Geometry of the four most stable conformations of **PK1** at B3LYP level

CT oop HOMO = -4.87 ; LUMO = -3.12 eV

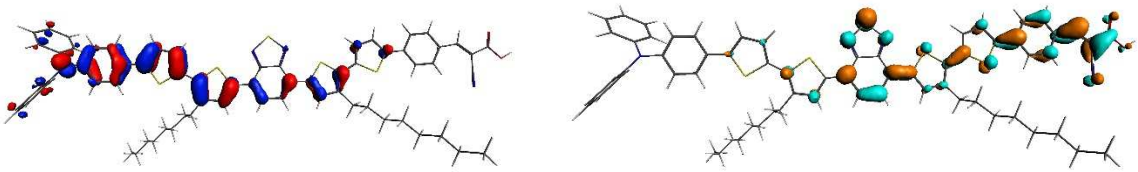


Figure S3. Energy levels of the most stable conformation of **PK1** at B3LYP level

Table S2: Values of dihedral angles for the four most stable conformations of **PK2** at B3LYP level

	ϕD	ϕ2D	ϕCD	ϕ1D	ϕ1A	ϕCA	ϕ2A	ϕA
TC oop1 t	31	38.6	79.5	-174.8	-167.9	65.4	47.1	-9.7
CC oop1 t	28.7	26.6	65.4	5.5	2.7	65.6	22.4	-16.4
CT oop2 t	26.4	165.7	99.3	14.5	17.8	99.4	161.7	-14.9
CT oop1 t	22.8	-172.7	76.3	0.2	0.8	80.7	170.7	-17.6

CT oop1 CT oop2 TC oop1 CC oop1

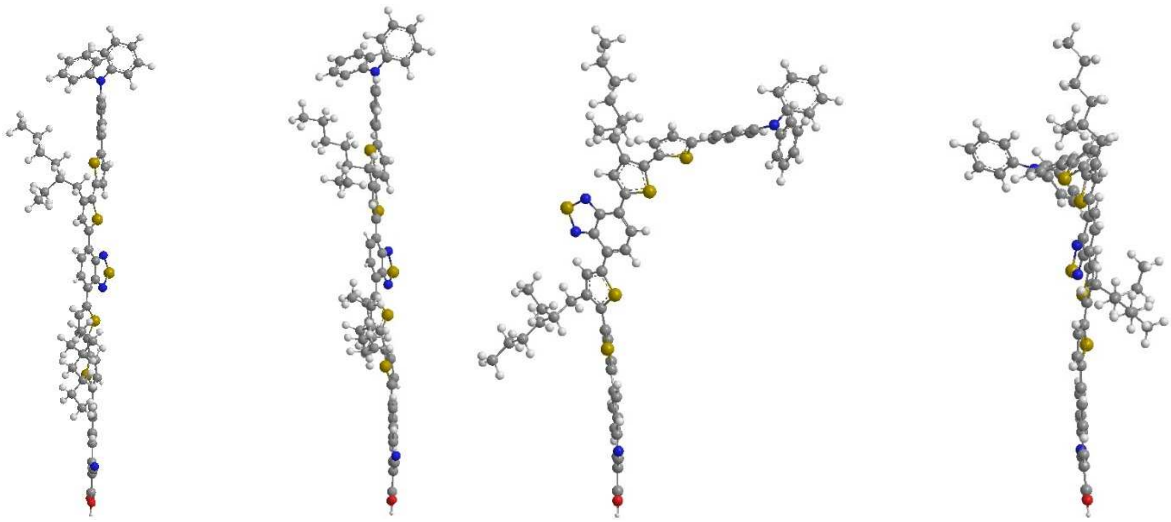


Figure S4. Geometry of the four most stable conformations of **PK2** at B3LYP level

CT oop1 HOMO = -4.93; LUMO = -3.13 eV

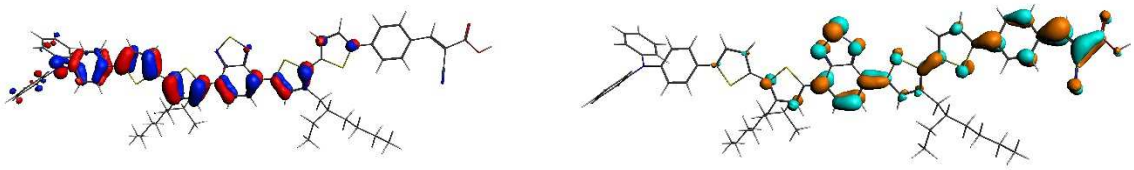


Figure S5. Energy levels of the most stable conformation of **PK2** at B3LYP level

Table S3: Values of dihedral angles for the four most stable conformations of **PK3** at B3LYP level

	ϕD	ϕ2D	ϕCD	ϕ1D	ϕ1A	ϕCA	ϕ2A	ϕA
TC oop ip	42.7	-19.6	89.7	-167.5	-174.4	74.6	33.1	7.8
CT oop ip	10.9	173.9	81.7	-12.7	6.9	87.9	168.6	4.3
CT oop oop	0.3	-178.9	80.9	-9.9	0.7	88	171.5	3.1
CC oop oop	-19.7	26.3	68.6	-6.4	-4.5	72.8	8	1.5

TC oop ip CT oop ip CT oop oop CC oop oop

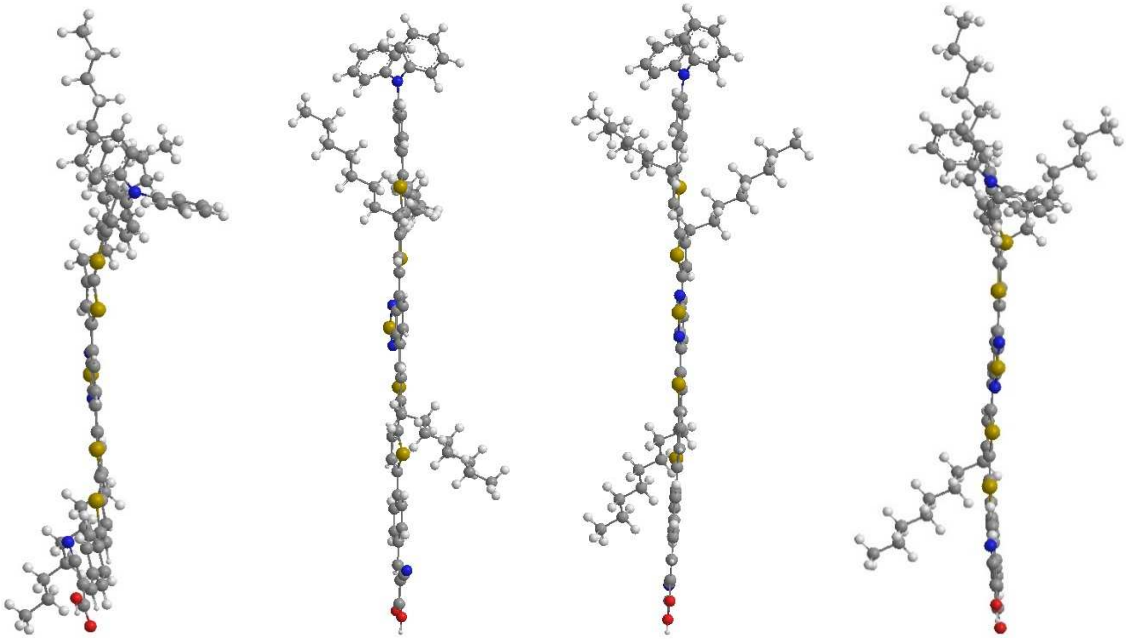


Figure S6. Geometry of the four most stable conformations of **PK3** at B3LYP level

CT oop oop HOMO = -4.86 ; LUMO = -3.11 eV

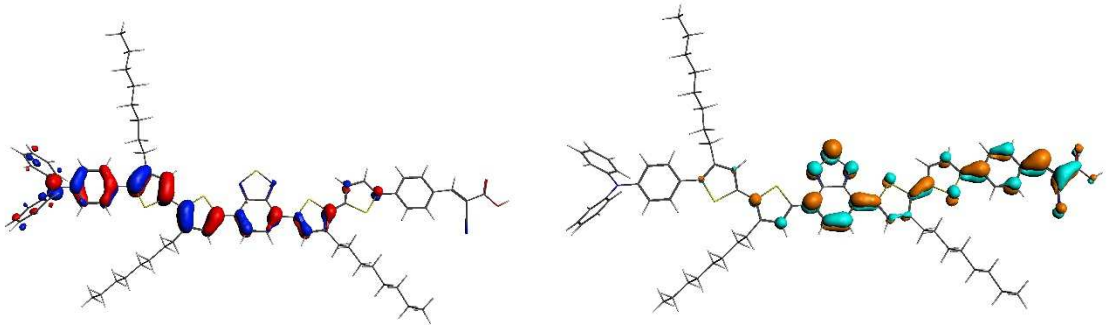


Figure S7. Energy levels of the most stable conformation of **PK3** at B3LYP level

Table S4 : Values of dihedral angles for the most stable conformation of **6PK1** at B3LYP level

	ϕD	ϕ2D	ϕCD	ϕ1D	ϕ1A	ϕCA	ϕ2A	ϕA
CT oop	8.1	174.7	80.9	-7.5	-5.2	79.8	176.3	1.0

HOMO = -4.85 ; LUMO = -3.15 eV

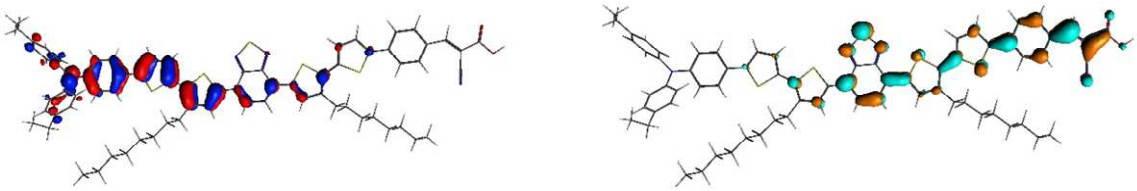


Figure S8. Energy levels of the most stable conformation of **6PK1** at B3LYP level

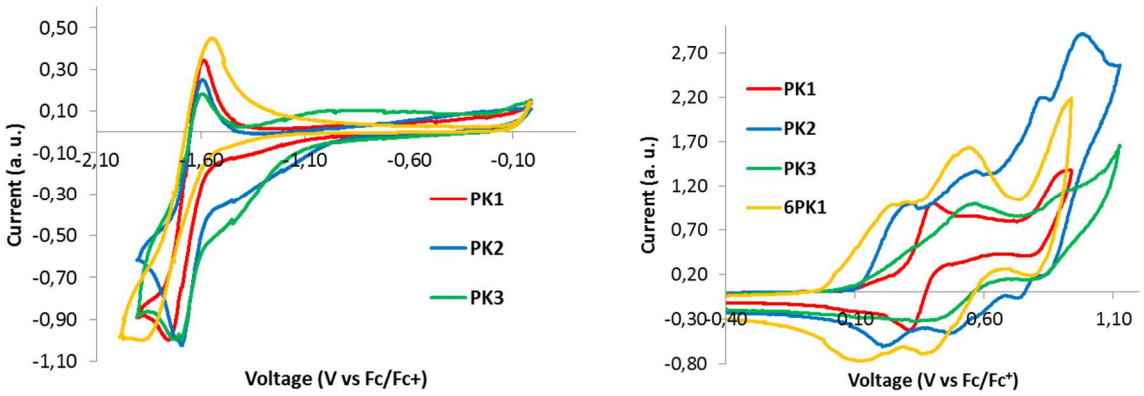


Figure S9: Cyclic voltammograms upon oxidation (right) and reduction (left) of **PK** dyes in dichloromethane solution (2 mM) with 0,1 M of Bu_4NPF_6 .

Dye 0.2 [mM]	Thickness TiO_2 [µm]	Ratio CDA [mM]	Electrolyte	J_{sc} [mA.cm^{-2}]	V_{oc} [mV]	FF [%]	η [%]
PK2	13+4	10	HI-30	18.08	704	71	9.05
PK2	13+3	2	HI-30	18.27	679	69	8.50
PK2	13+3	0	HI-30	15.27	655	72	7.24
PK1	13+4	10	HI-30	14.77	679	72	7.20
PK1	12+3	2	HI-30	14.70	682	70	6.87
PK1	12+3.5	0	HI-30	10.99	674	77	5.67

Table S5: Performances of solar cells fabricated with PK2 and various amount of CDCA (HI30 as electrolyte).

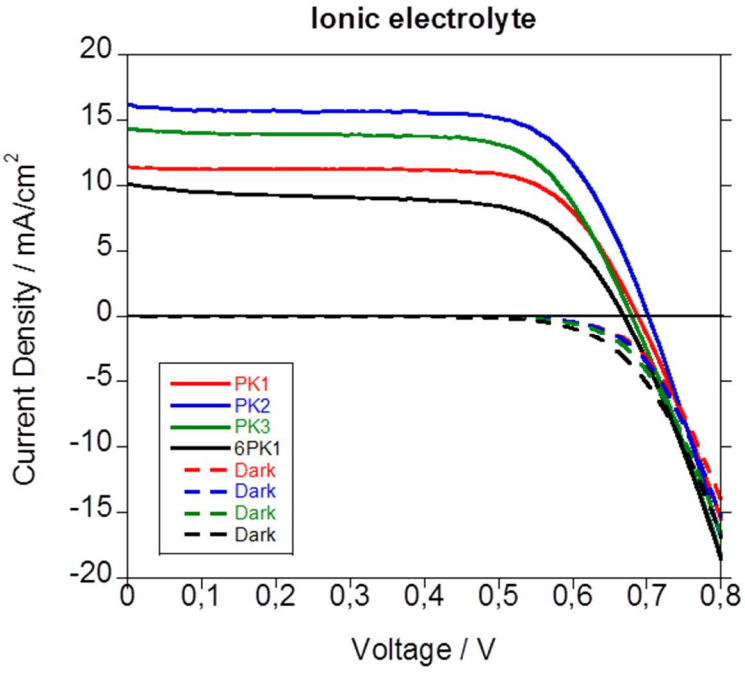


Figure S10. J-V curves of TDE-250 ionic electrolyte based DSSCs using optimized parameters

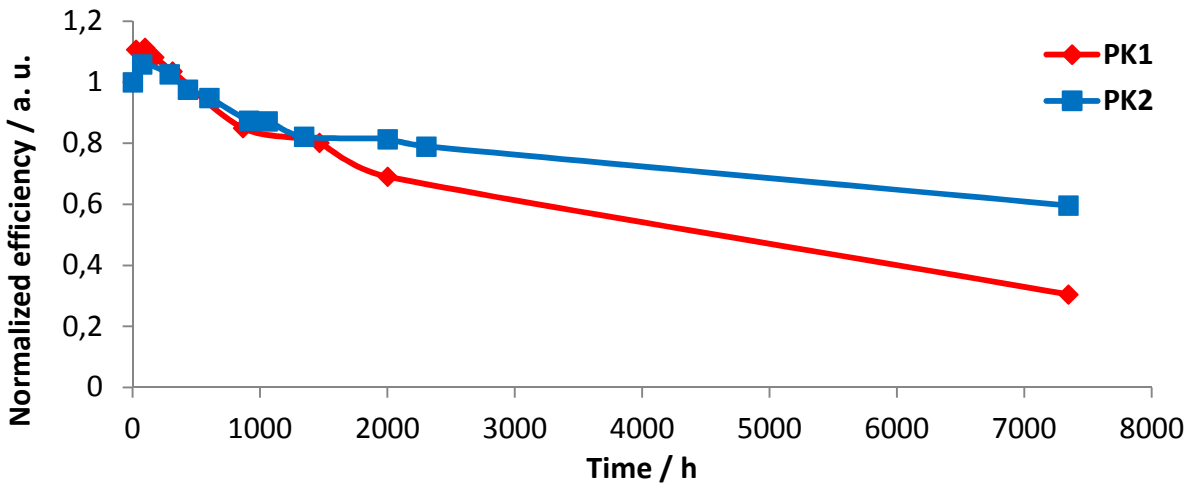


Figure S11. TDE-250 ionic electrolyte based DSSCs under irradiation of 1000 $W.m^{-2}$ at 65 °C. (ISOS-L2 test)

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