

*Supplementary information*

**Accessing outdoor photochemical stability of conjugated polymers  
by EPR spectroscopy**

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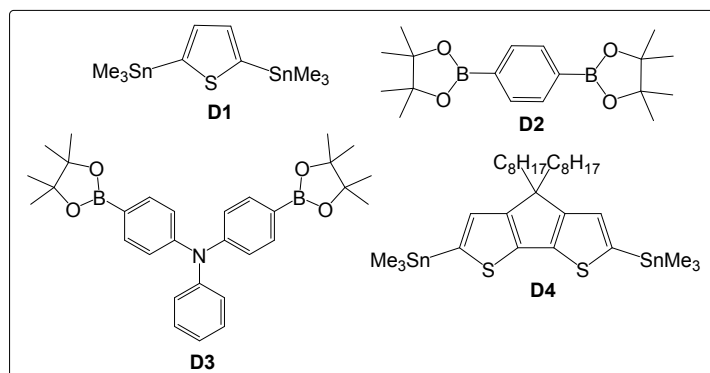
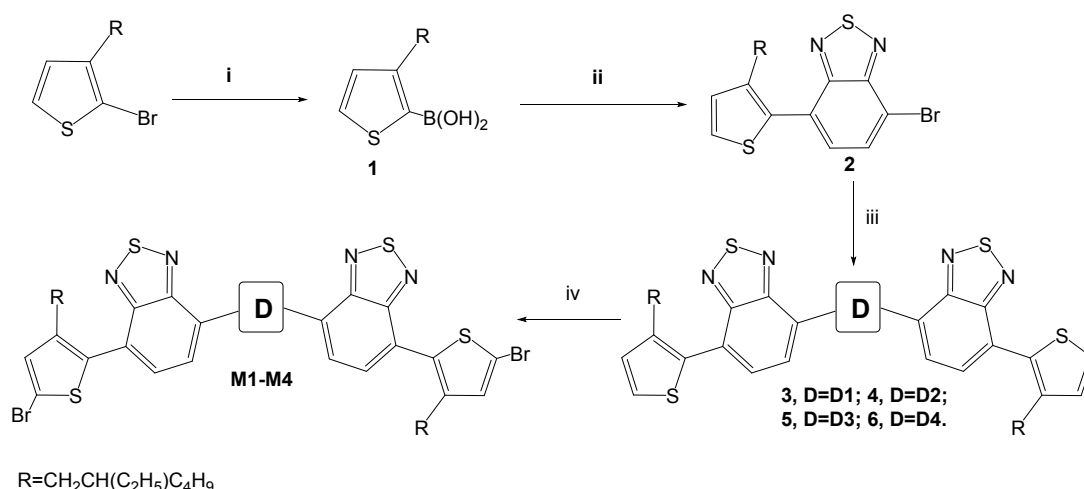
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## Synthesis of polymers P1-P4



Scheme S1. Synthesis of monomers **M1-M4**. Conditions: i – THF (-78°C), BuLi (1eq.), B(OMe)<sub>3</sub>, H<sup>+</sup>; ii – 4,7-dibromo-2,1,3-benzothiadiazole (1 eq.), Pd(PPh<sub>3</sub>)<sub>4</sub>, 2M K<sub>2</sub>CO<sub>3</sub> aq., aliquat 336, toluene, reflux 10h; iii – **D2** or **D3**, Pd(PPh<sub>3</sub>)<sub>4</sub>, 2M K<sub>2</sub>CO<sub>3</sub> aq., aliquat 336, toluene, reflux 10h; **D1** or **D4**, Pd(PPh<sub>3</sub>)<sub>4</sub>, toluene, reflux 12h; iv - NBS, 1,2-DCB.

### Compound 1

2-bromo-3-(2-ethylhexyl)thiophene (3.0 g, 11 mmol, 1.0 eq.), and THF (50 mL) were added to a 100 mL three-neck round-bottomed-flask, which was previously evacuated/backfilled with argon three times. The flask was then cooled to -78 °C in an acetone bath. Then 4.4 mL of n-BuLi (2.5 M) (11 mmol, 1.0 eq.) was added. Addition required 30 min to keep the temperature close -60°C. Then the reaction mixture was stirred at -60°C for 1 h. After 1 h, the trimethylborate (2.86 g, 27 mmol, 2.45 eq.) was added dropwise. The mixture was stirred while warming to RT over a period of 6 h. Then the reaction mixture was cooled again to 0°C in an ice bath and 6 M HCl (11 mL) was added dropwise keeping the temperature below 4°C. The mixture was extracted with diethyl ether (3 x 50 mL). Organic phase was separated, dried over magnesium sulfate, filtered, and concentrated under reduced pressure using a rotary evaporator. The (3-(2-ethylhexyl)thiophen-2-yl)boronic acid (**1**) was used without further purification. Yield: 2.23 g (84%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ (ppm) 7.63 (d, 1H), 7.09 (d, 1H), 2.55 (d, 2H), 1.86 (m, 1H), 1.24 (m, 8H), 0.86 (m, 6H).

### **Compound 2**

A mixture of 4,7-bromo-2,1,3-benzothiadiazole (10.0 g, 34.0 mmol) and compound **1** (8.16 g, 34.0 mmol) was dissolved in 50 mL of toluene. Tetrakis(triphenylphosphine)palladium(0) (0.026 g, 0.022 mmol), 2 M aqueous solution of K<sub>2</sub>CO<sub>3</sub> (0.5 mL), aliquat 336 (1 drop, ca. 80 mg) were added in the listed here sequence. The reaction mixture was deaerated using repeated cycles of freezing in liquid nitrogen, evacuation, filling with argon, and heating up to a room temperature. Then the mixture of reagents was heated at reflux and formation of the desired product (4-bromo-7-(3-(2-ethylhexyl)thiophen-2-yl)-2,1,3-benzothiadiazole, **2**) was controlled by HPLC. When the content of the product in the mixture exceeded 50%, the reaction was stopped. The mixture was poured into water and extracted with chloroform. The organic layers were separated, dried over MgSO<sub>4</sub>, and filtered. The residue formed after solvent evaporation was purified by distillation in vacuum (130°C, 10<sup>-2</sup> mm Hg) to give **2** as an orange oil (5.5 g, 40% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ (ppm) 7.92 (d, 1H), 7.50 (d, 1H), 7.45 (d, 1H), 7.07 (d, 1H), 2.57-2.59 (dd, 2H), 1.48 (m, 1H), 1.08-1.19 (m, 8H), 0.77 (t, 3H), 0.68 (t, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz): δ (ppm) 153.86, 153.48, 141.03, 131.93, 131.91, 130.74, 129.83, 128.13, 125.83, 113.59, 40.50, 33.31, 32.49, 28.65, 25.72, 22.89, 14.04, 10.75.

### **Compound 3**

Compound **2** (1 g, 2.4 mmol) and 2,5-bis(trimethylstannyl)thiophene **D1** (0.5 g, 1.2 mmol) were dissolved in anhydrous toluene (50 mL) in a three necked round-bottom flask. The mixture was deaerated and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.023 g, 0.02 mmol) was added under argon. Then the mixture was heated at reflux for 24 h and cooled afterwards to the room temperature, poured into deionized water (150 mL) and extracted by chloroform (3 x 50 mL). The combined organic phase was washed with deionized water and dried over anhydrous MgSO<sub>4</sub>. The crude product obtained after removal of the solvent was further purified by column chromatography (silica gel, 40–60 μm, 60°A). The title compound was eluted with toluene–hexane 3:7 v/v mixture. The yield of the dark red solid **3** was 35%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ (ppm) 8.18 (s, 2H), 7.92 (d, 2H), 7.57 (d, 2H), 7.34 (d, 2H), 6.98 (d, 2H), 2.55 (d, 4H), 1.45 (m, 2H), 0.92-1.13 (m, 16H), 0.66 (t, 6H), 0.59 (t, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz): δ (ppm) 154.76, 152.29, 140.89, 140.60, 132.90, 130.58, 129.86, 128.77, 127.26, 126.48, 125.64, 125.34, 40.54, 33.44, 32.55, 28.68, 25.78, 22.94, 14.09, 10.81.

### **Compound 4**

Compound **2** (1.1 g, 2.7 mmol) and 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (0.44 g, 1.3 mmol) **D2** were introduced into a 100 mL round-bottom three necked flask. Degassed toluene (50 mL), 2 M aqueous solution of K<sub>2</sub>CO<sub>3</sub> (0.5 mL), aliquat 336 (1 drop, ca. 80 mg) and tetrakis(triphenylphosphine)palladium(0) (20 mg) were added in the sequence listed here. The reaction mixture was vigorously stirred and heated at reflux 24h. Then the reaction mixture was cooled down to the room temperature and poured into 150 mL of deionized water. The organic layer was separated, while the aqueous layer was extracted three times with toluene (45 mL). The combined organic layers were dried over anhydrous MgSO<sub>4</sub>. Then the solvent was removed at the rotary evaporator and the obtained crude product was purified by column chromatography (silica gel, 40–60 μm, 60°A). The title compound was eluted with toluene–hexane 3:7 v/v mixture. The yield of the yellow solid **4** was 40%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ

(ppm) 8.17 (s, 4H), 7.86 (d, 2H), 7.72 (d, 2H), 7.42 (d, 2H), 7.06 (d, 2H), 2.63 (m, 4H), 1.47 (m, 2H), 0.95-1.19 (m, 16H), 0.72 (t, 6H), 0.66 (t, 6H).

#### **Compound 5**

Compound **5** was prepared using compound **2** (0.67 g, 1.6 mmol) and *N*-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline **D3** (0.42 g, 0.8 mmol) following the procedure given for compound **4**. The yield of **5** was 50%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ (ppm) 7.94 (d, 4H), 7.75 (d, 2H), 7.67(d, 2H), 7.40 (d, 2H), 7.31-7.35 (m, 6H), 7.25-7.29 (m, 3H), 7.05 (d, 2H), 2.60 (m, 4H), 1.46 (m, 2H), 0.95-1.20 (m, 16H), 0.71 (t, 6H), 0.64 (t, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz): δ (ppm) 154.96, 153.57, 147.79, 140.67, 147.13, 133.12, 133.06, 131.45, 130.8, 130.14, 129.80, 129.58, 126.98, 126.82, 125.63, 125.36, 124.01, 123.74, 40.53, 33.32, 32.51, 28.65, 25.75, 22.91, 14.08, 10.78.

#### **Compound 6**

Compound **6** was prepared using compound **2** (1.14 g, 2.8 mmol) and (4,4-dioctyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2,6-diyl)bis(trimethylstannane) **D4** (1 g, 1.4 mmol) following the procedure given for compound **3**. The yield of **6** was 44%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ (ppm) 8.16 (s, 2H), 7.96 (d, 2H), 7.65 (d, 2H), 7.45 (d, 2H), 7.09 (d, 2H), 2.65 (m, 4H), 2.06 (m, 4H), 1.53 (m, 2H), 1.06-1.23 (m, 40H), 0.83 (t, 6H), 0.78 (t, 6H), 0.71 (t, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz): δ (ppm) 159.78, 154.86, 152.06, 140.72, 140.52, 138.91, 133.08, 130.76, 129.79, 127.59, 126.06, 125.44, 123.85, 122.39, 54.40, 40.51, 37.96, 33.47, 32.57, 31.84, 30.08, 29.37, 29.29, 28.71, 25.77, 24.69, 22.95, 22.63, 14.07, 10.78.

#### **Compound M1**

Monomer **M1** was synthesized using compound **3** (0.6 g, 0.8 mmol) and *N*-bromosuccinimide (0.288 g, 1.6 mmol) following the previously reported procedure.<sup>1</sup> The yield of **M1** was 93%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ (ppm) 8.21 (s, 2H), 7.94 (d, 2H), 7.58 (d, 2H), 7.01 (s, 2H), 2.56 (m, 4H), 1.47 (m, 2H), 0.98-1.21 (m, 16H), 0.74 (t, 6H), 0.67 (t, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz): δ (ppm) 154.40, 152.17, 141.57, 140.57, 134.49, 132.44, 130.47, 128.97, 126.75, 125.88, 125.16, 112.85, 40.43, 33.52, 32.49, 28.66, 25.72, 22.96, 14.12, 10.80.

#### **Compound M2**

Monomer **M2** was synthesized using compound **4** (0.55 g, 0.75 mmol) and *N*-bromosuccinimide (0.265 g, 1.5 mmol) following the previously reported procedure.<sup>1</sup> The yield of **M2** was 67%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ (ppm) 8.16 (s, 4H), 7.85 (d, 2H), 7.69 (d, 2H), 7.02 (d, 2H), 2.55 (m, 2H), 0.95-1.20 (m, 16H), 0.73 (t, 6H), 0.67 (t, 6H).

#### **Compound M3**

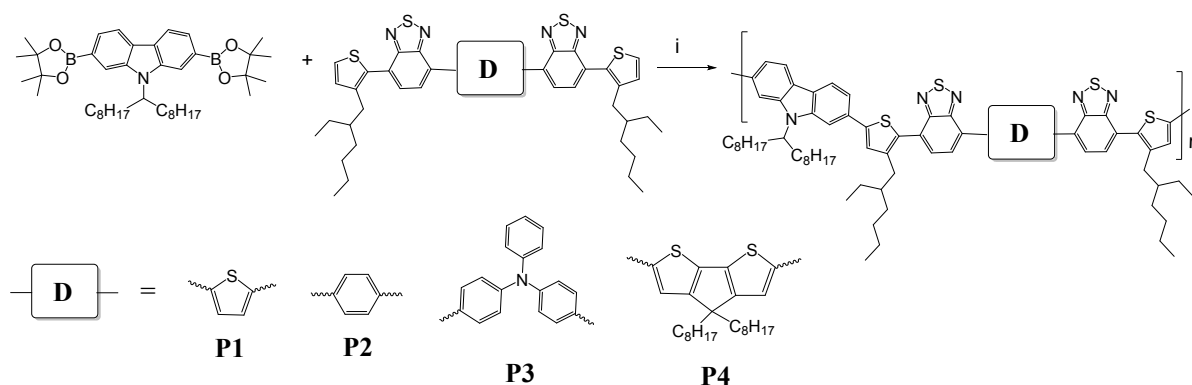
Monomer **M3** was synthesized using compound **5** (0.55 g, 0.75 mmol) and *N*-bromosuccinimide (0.266 g, 1.5 mmol) following the previously reported procedure.<sup>1</sup> The yield of **M3** was 67%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ (ppm) 7.94 (d, 4H), 7.74 (d, 2H), 7.64 (d, 2H), 7.43 (m, 3H), 7.31 (d, 4H), 7.15 (d, 2H), 7.0 (d, 2H), 2.54 (m, 4H), 1.44 (m, 2H), 0.91-1.20 (m, 16H), 0.72 (t, 6H), 0.65 (t, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz): δ (ppm) 155.10, 153.89, 147.88, 141.07, 146.73, 132.98, 132.87, 131.25, 130.60, 129.96, 129.94, 129.49, 127.00, 126.82, 125.42, 125.46, 123.81, 123.41, 40.52, 33.30, 32.50, 28.63, 25.75, 22.89, 14.07, 10.76.

### Compound **M4**

Monomer **M4** was synthesized using compound **6** (0.86 g, 0.81 mmol) and *N*-bromosuccinimide (0.29 g, 1.62 mmol) following the previously reported procedure.<sup>1</sup> The yield of **M4** was 86%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ (ppm) 8.17 (s, 2H), 7.94 (d, 2H), 7.62 (d, 2H), 7.05 (s, 2H), 2.59 (m, 4H), 2.05 (m, 4H), 1.51 (m, 2H), 1.02-1.23 (m, 40H), 0.80 (m, 12H), 0.71 (t, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz): δ (ppm) 159.92, 154.54, 151.97, 141.38, 140.49, 139.09, 134.65, 132.37, 130.73, 127.96, 124.64, 123.69, 122.60, 112.53, 54.41, 40.40, 37.96, 33.49, 32.47, 31.85, 30.09, 29.39, 29.31, 28.85, 25.67, 24.71, 22.95, 22.65, 14.10, 10.76.

### Polymers **P1-P4**

Polymers **P1-P4** were synthesized according to Scheme S2 and purified following the previously reported procedure.<sup>1</sup> The total yield of the purified polymers **P1-P4** varied between 40 and 80% depending on the initial molecular weight and number of the applied dissolving/precipitation cycles. Molecular weight characteristics for **P1**:  $M_w=79000$  g/mol, PDI =3.3; **P2**:  $M_w=13000$  g/mol, PDI =2.0; **P3**:  $M_w=59000$  g/mol, PDI =8.5; **P4**:  $M_w=28000$  g/mol, PDI =2.1.



Scheme S2. Synthesis of polymers **P1-P4**. i - Pd(PPh<sub>3</sub>)<sub>4</sub>, 2 M K<sub>2</sub>CO<sub>3</sub> aq., aliquat 336, toluene, reflux 8-20 h.



Fig. S1. Photograph of the setup used for outdoor aging studies. The EPR tubes with the polymer films inside are highlighted with a dashed red line.

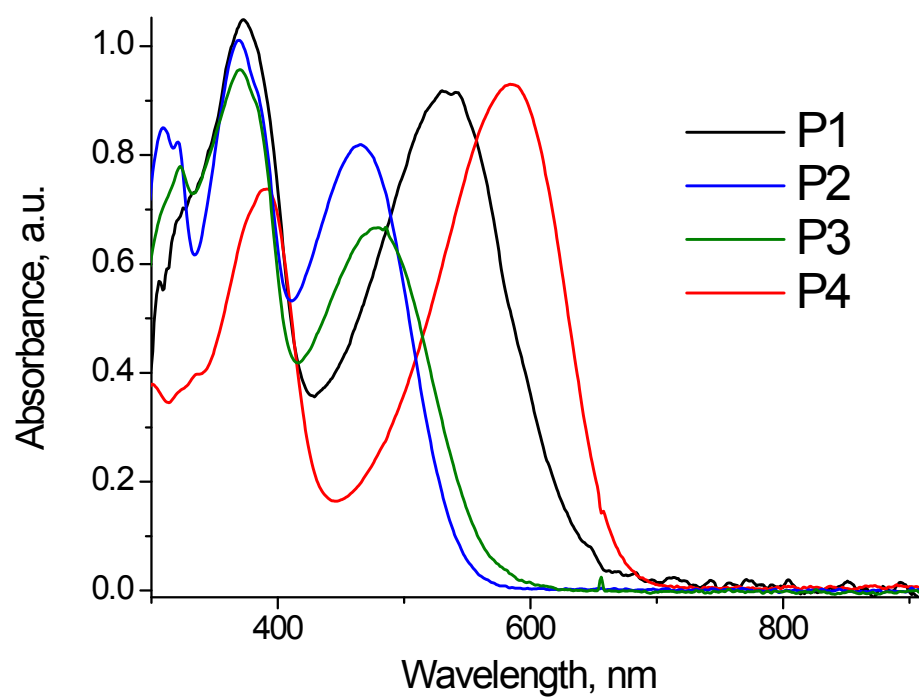


Fig. S2. Absorption spectra of **P1-P4**

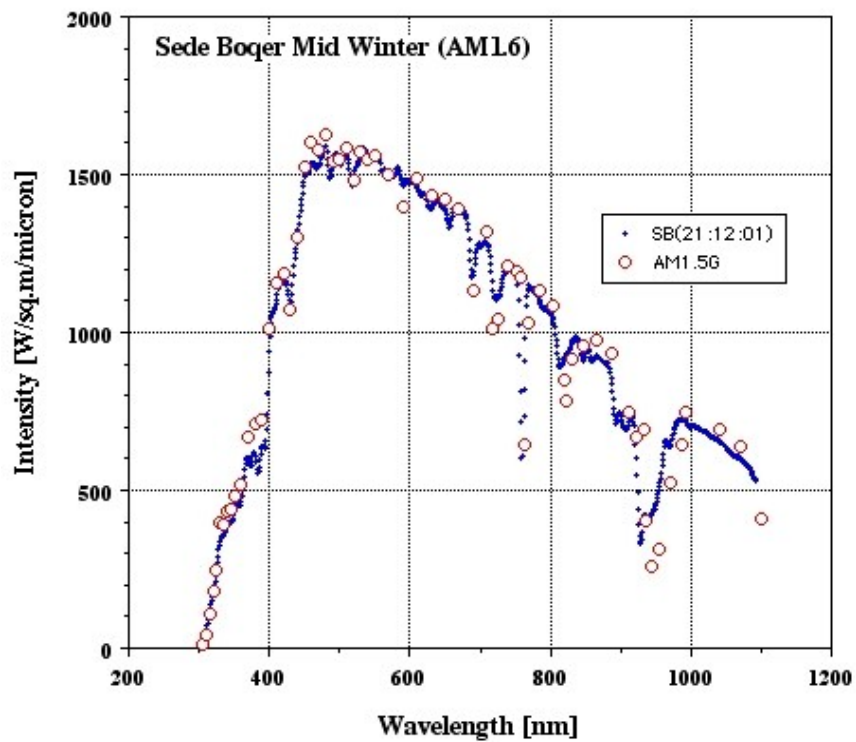
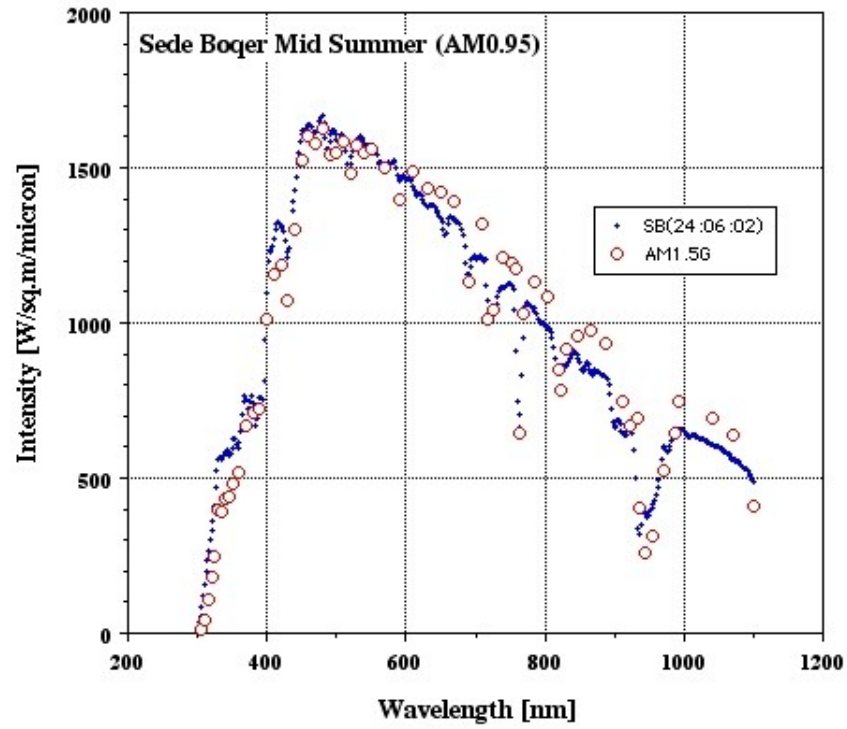


Fig. S2. Typical clear-day, noon-time, global spectra measured on a sun-tracking surface at Sede Boqer; ( a ) summer, (b) winter. The standard AM1.5G values are indicated by circles.



## References

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1. A. V. Akkuratov, D. K. Susarova, Y. L. Moskvina, D. V. Anokhin, A. V. Chernyak, F. A. Prudnov, D. V. Novikov, S. D. Babenko and P. A. Troshin. A strong influence of the positions of solubilizing alkyl side chains on optoelectronic and photovoltaic properties of TTBTBTT-based conjugated polymers. *J. Mater. Chem. C*, 2015, **3**, 1497-1506