

## SUPPORTING INFORMATION

### Photochemical stability and Photovoltaic Performance of Low-Bandgap polymers based on Dithiophene with Different Bridging Atoms

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## General experimental details

**General methods, instrumentation and materials.** Molecular weights were determined using size exclusion chromatography in HPLC-grade chloroform against polystyrene standards on a KNAUER chromatograph with a refractive index detector and a diode array UV-vis detector. UV-vis absorption spectra were measured with a Perkin-Elmer Lambda 900 spectrometer. AFM images were taken on a Nanos multimode AFM (Bruker). Unless stated otherwise all reagents and solvents were obtained from Aldrich and used without further purification. Dichloromethane, THF and toluene were dried with molecular sieves (3 Å) and used directly without filtration or distillation. NBS was recrystallized from water and dried at 70 °C in vacuum. Evaporation was performed on a rotary evaporator at 40 °C. NMR spectra were obtained on a Bruker 250 MHz spectrometer. 4,7-bis(5-bromothiophen-2-yl)-5,6-bis(tetradecyloxy)benzo[c][1,2,5]thiadiazole,<sup>1</sup> 4,7-bis(5-bromo-4-dodecylthiophen-2-yl)benzo[c][1,2,5]thia-diazole,<sup>2</sup> (4,4-bis(2-ethylhexyl)-4H-cyclopenta[1,2-b:5,4-b']dithiophene-2,6-diyl)-bis(trimethylstannane)<sup>3</sup> and 4,4-dihexyl-2,6-bis(trimethylstannyl)-4H-silolo[3,2-b:4,5-b']dithiophene<sup>4</sup> were prepared according to literature procedures or slight modifications thereof.

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<sup>1</sup> Helgesen, M.; Gevorgyan, S. A.; Krebs, F. C.; Janssen, R. A. *J. Chem. Mater.* **2009**, *21* (19), 4669-4675.

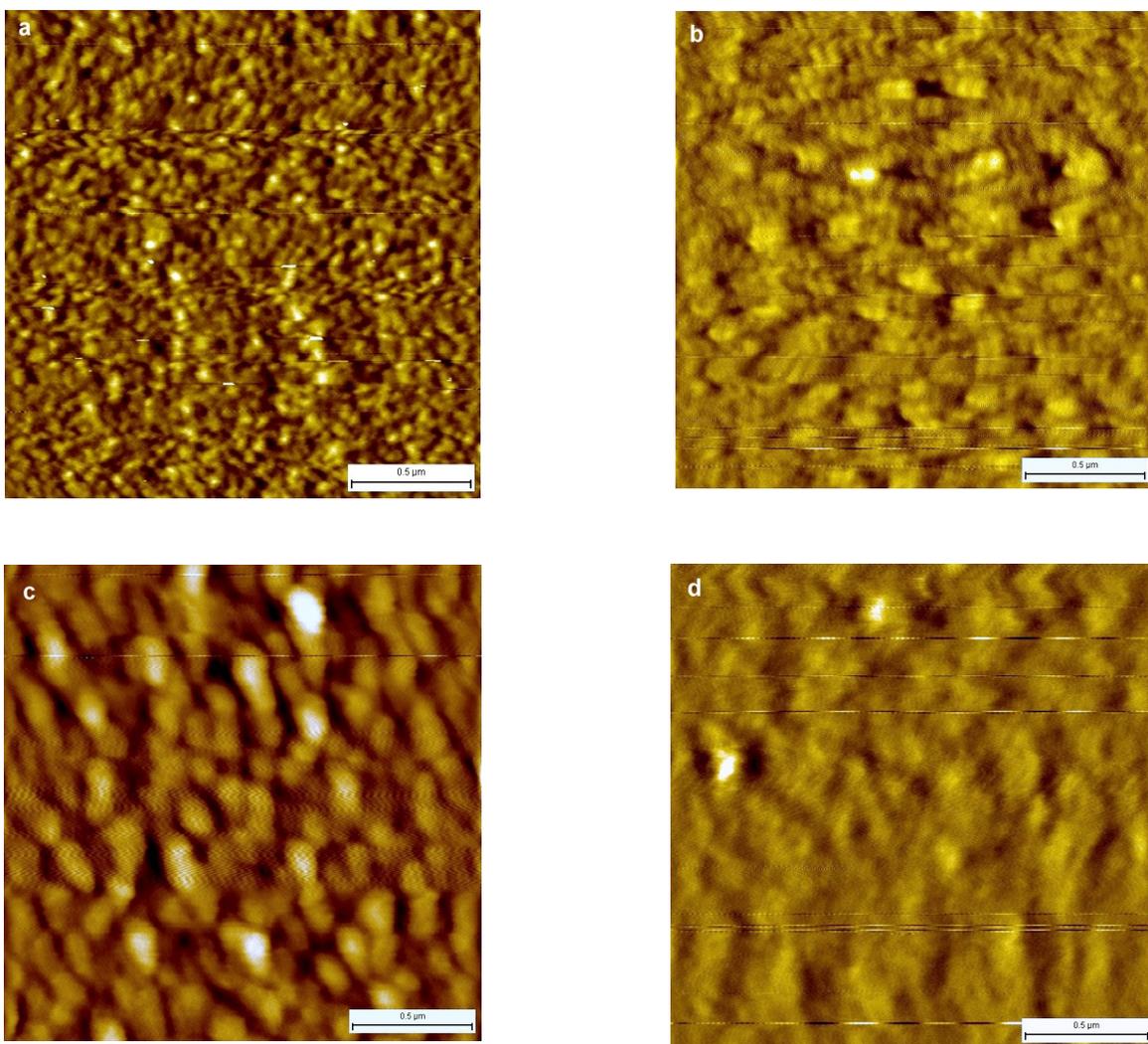
<sup>2</sup> Zhou, H.; Yang, L.; Xiao, S.; Liu, S.; You, W. *Macromolecules* **2010**, *43*, 811–820

<sup>3</sup> Helgesen, M.; Krebs, F. C. *Macromolecules* **2010**, *43*, 1253-1260

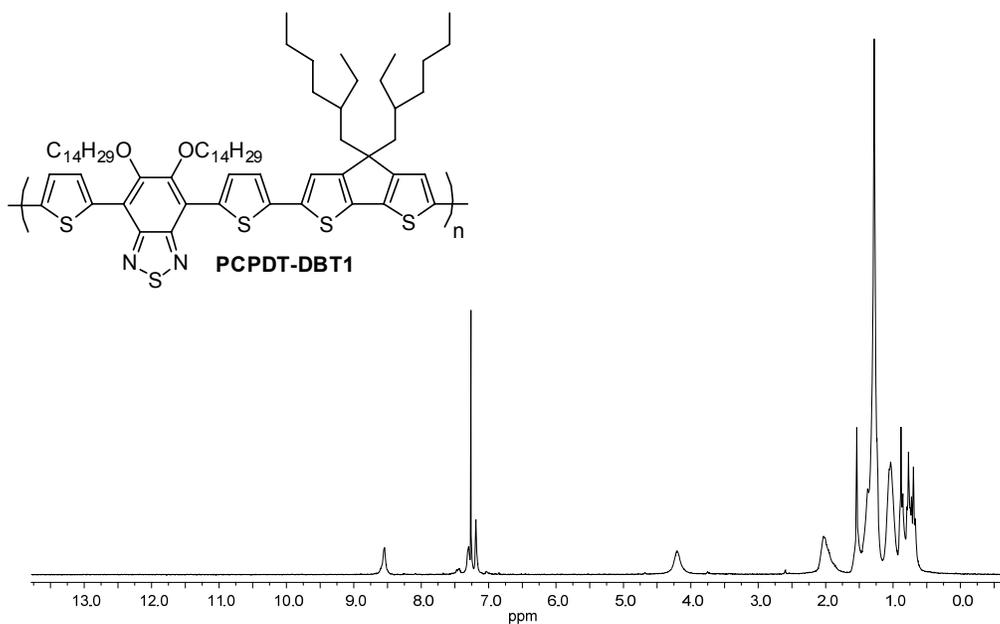
<sup>4</sup> Usta, H.; Lu, G.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 9034-9035

## Atomic force microscopy (AFM)

**Figure S1.** AFM topography images ( $2\ \mu\text{m} \times 2\ \mu\text{m}$ ) of solar cells based on blends of PCBM and (a) **PCPDT-DBT1**,  $S_q = 0.86\ \text{nm}$  (b) **PCPDT-DBT2**,  $S_q = 0.59\ \text{nm}$  (c) **PSDT-DBT1**,  $S_q = 1.13\ \text{nm}$  (d) **PSDT-DBT2**,  $S_q = 0.35\ \text{nm}$ .



**Figure S2.**  $^1\text{H-NMR}$  Spectrum of **PCPDT-DBT1** in  $\text{CDCl}_3$



**Figure S3.**  $^1\text{H-NMR}$  Spectrum of **PCPDT-DBT2** in  $\text{CDCl}_3$

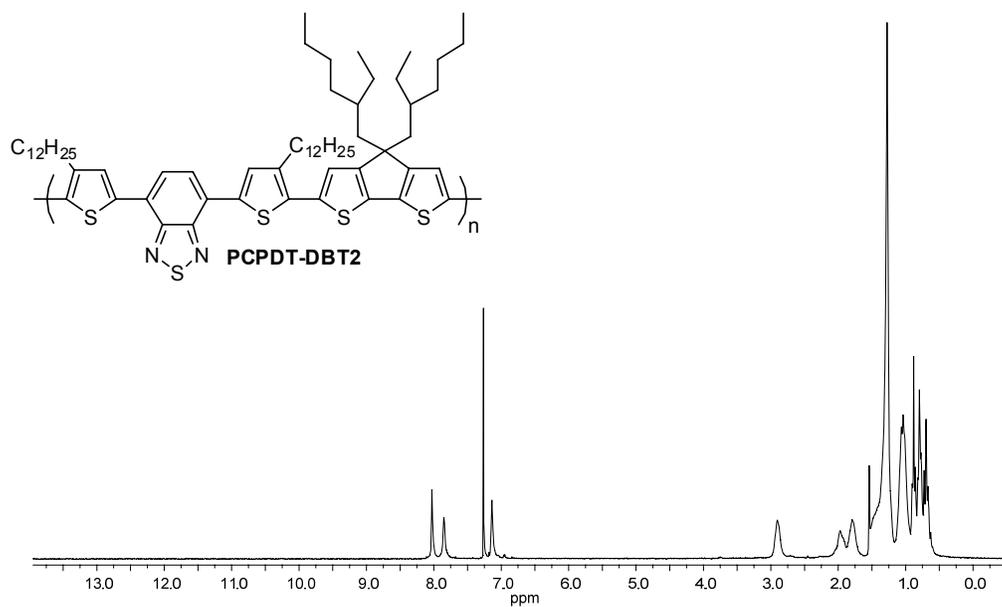


Figure S4. <sup>1</sup>H-NMR Spectrum of PSDT-DBT1 in CDCl<sub>3</sub>

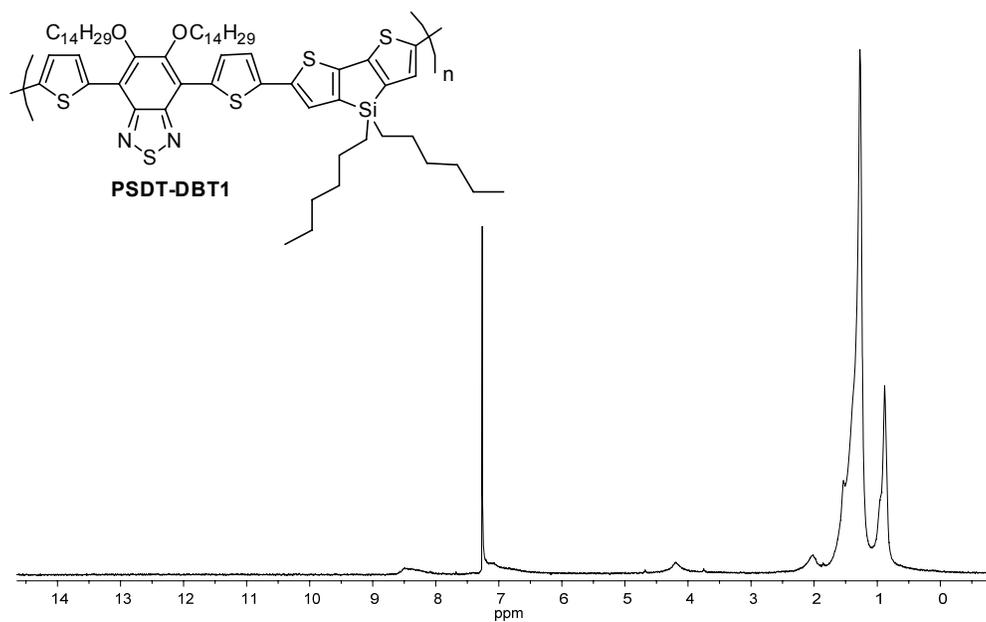


Figure S5. <sup>1</sup>H-NMR Spectrum of PSDT-DBT2 in CDCl<sub>3</sub>

