

Electronic Supplementary Information (ESI)

Relating polymer chemical structure to the stability of polymer:fullerene solar cells

Nutifafa Y. Doumon,^a G. Wang,^b Ryan C. Chiechi,^{a,b} and L. Jan Anton Koster^{†a}

^a Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, NL-9747 AG, Groningen-The Netherlands.

^b Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, NL-9747 AG, Groningen-The Netherlands

Contents:

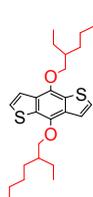
1. Synthesis of BDT-Unit Monomers
2. Figure s1: Absorption Spectra of Films of blends of Polymers
3. Effects of DIO
 - Table s1: Effect of DIO on PCE of the Solar Cells
 - Figure s2: J-V and PCE Curves of Devices with and without DIO
4. Figure S3: PCE Degradation Curves of Solar Cells with ITO and pH-neutral PEDOT:PSS Interfaces
5. Figure S4: Details of ¹HNMR Spectra of the Monomers
6. Figure S5: Charge transport (R-O₂ and R-T₂ polymer based devices)
7. Light Intensity Measurements
 - Table s2: Summary of Values of the Slopes of V_{oc} vs. Light Intensity of all Polymers Solar Cells Under Study for Different UV-exposure Times
 - Figure S6: Graphical Representation of the Values for R-O Devices Compared to R-T Devices
8. Lamp
9. AFM images

[†] E-mail: l.j.a.koster@rug.nl

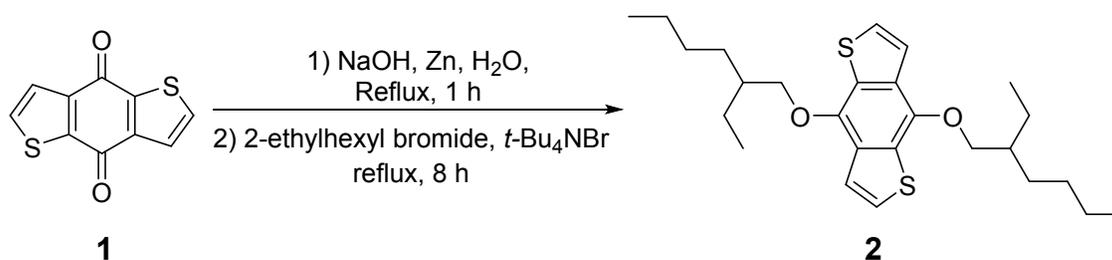
1. Synthesis of BDT-monomers

All reactions were performed using oven-dried glassware and dry solvents unless otherwise specified. THF was taken from an MBraun solvent purification system (SPS-800). All other reagents were purchased from Sigma–Aldrich, TCI Europe, or Acros Organics and were used without further purification unless noted otherwise. ¹H NMR spectra were recorded on a Varian AMX600 (600MHz). Chemical shift values are reported in ppm with the solvent resonance as the internal standard. Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, dq = double quartet, qd = quarter doublet, m = multiplet, br = broad), coupling constants (Hz), and integration. Flash chromatography: Merck silica gel type 9385 230–400 mesh. TLC: Merck silica gel 60, 0.25 mm. Compounds were visualised by UV.

1.1. Synthetic Procedures of M_{R-O}:



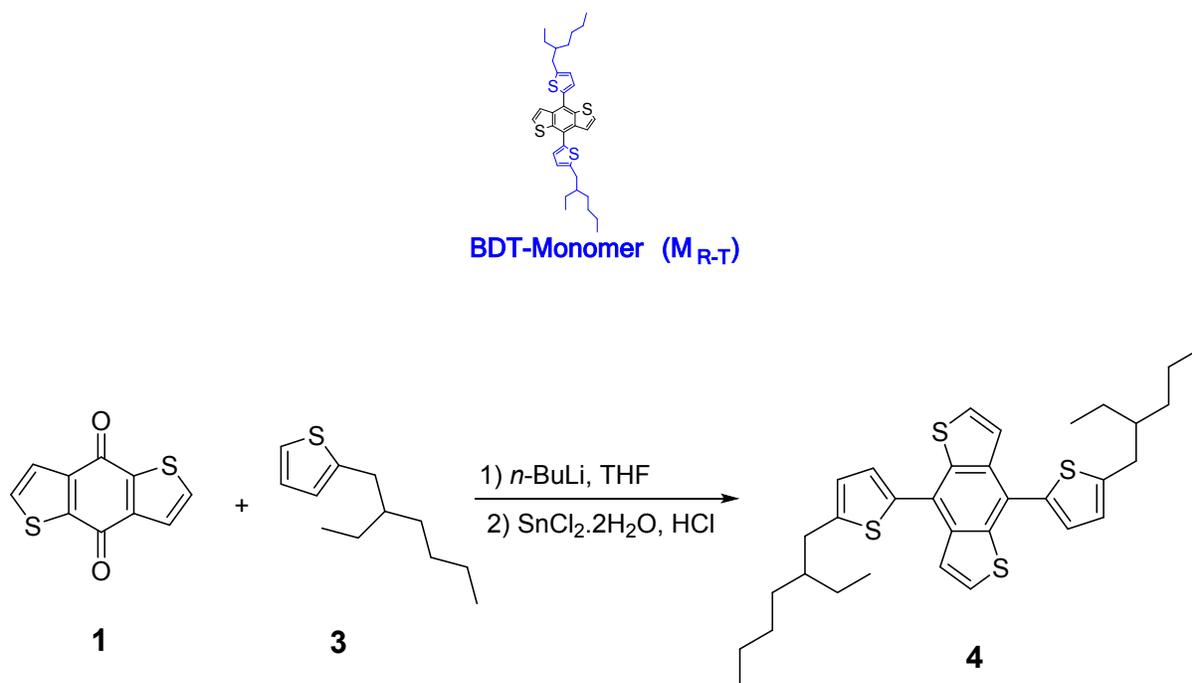
BDT-monomer (M_{R-O})



1 **Benzo[1,2-b:4,5-b']dithiophene-4,8-dione** was synthesized according to previously reported methods.¹

2 **4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene:** 4,8-dihydrobenzo[1,2-b:4,5-b']dithiophen-4,8-dione (0.22 g, 1.0 mmol), zinc powder (0.16 g, 2.5 mmol), and water (6 mL) were put into a 25 mL flask, then NaOH (0.6 g, 15.0 mmol) was added into the mixture. After the mixture was stirred and refluxed for 1 hour, 1-bromioctane (0.58 g, 3.0 mmol) and a catalytic amount of tetrabutylammonium bromide (0.06 g, 0.2 mmol) were added into the flask. The reactant was refluxed for 8 hours and then was poured into cold water and extracted by diethyl ether three times. The organic layer was dried over anhydrous MgSO₄. After the solvent had been removed, the crude product was purified by column chromatography (hexane/DCM: 8/2). Compound **2** (0.28 g, yield 62%) was obtained as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, *J* = 5.2 Hz, 2H), 7.37 (d, *J* = 5.6 Hz, 2H), 4.18 (d, *J* = 5.6 Hz, 4H), 1.85–1.75 (m, 2H), 1.73–1.49 (br, 8H), 1.46–1.37 (br, 8H), 1.01 (t, *J* = 7.4 Hz, 6H), 0.94 (t, *J* = 7.2 Hz, 6H).

1.2. Synthetic Procedures of M_{R-T} :



2-(2-ethylhexyl)thiophene (3) was synthesized according to previously reported methods.²

4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (4): 3.0 mL of *n*-Butyllithium (4.8 mmol, 1.6 M) was added dropwise to the solution of 2-(2-ethylhexyl)thiophene (0.79 g, 4.0 mmol) in 12 mL of anhydrous THF at -30°C under nitrogen atmosphere. The mixture was heated up to 50°C for 2 hours. Then the solvent was cooled in ice-water bath, subsequently, 4,8-dihydrobenzo[1,2-b:4,5-b']dithiophen-4,8-dione (0.22 g, 1.0 mmol) was added in one portion, and the mixture was heated at 50°C for another 2 hours. After cooling the mixture down to RT, a mixture of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (1.81 g, 8.0 mmol) in 5 mL of aqueous HCl (10%) was added, and the mixture was stirred overnight. The reaction mixture was poured into cold water and extracted by diethyl ether three times. The combined organic layer was washed with water and brine, dried with MgSO_4 , filtered, concentrated via rotary evaporation. Further purification was carried out by column chromatography on silica gel eluting with petroleum ether to obtain pure compound **4** as a yellow liquid (0.44 g, 77%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.65 (d, $J = 6.0$ Hz, 2H), 7.46 (d, $J = 5.6$ Hz, 2H), 7.30 (d, $J = 3.2$ Hz, 2H), 6.89 (d, $J = 3.2$ Hz, 2H), 2.86 (d, $J = 6.8$ Hz, 4H), 1.72–1.65 (m, 2H), 1.47–1.26 (br, 16H), 0.97–0.89 (m, 12H).

2. Absorption

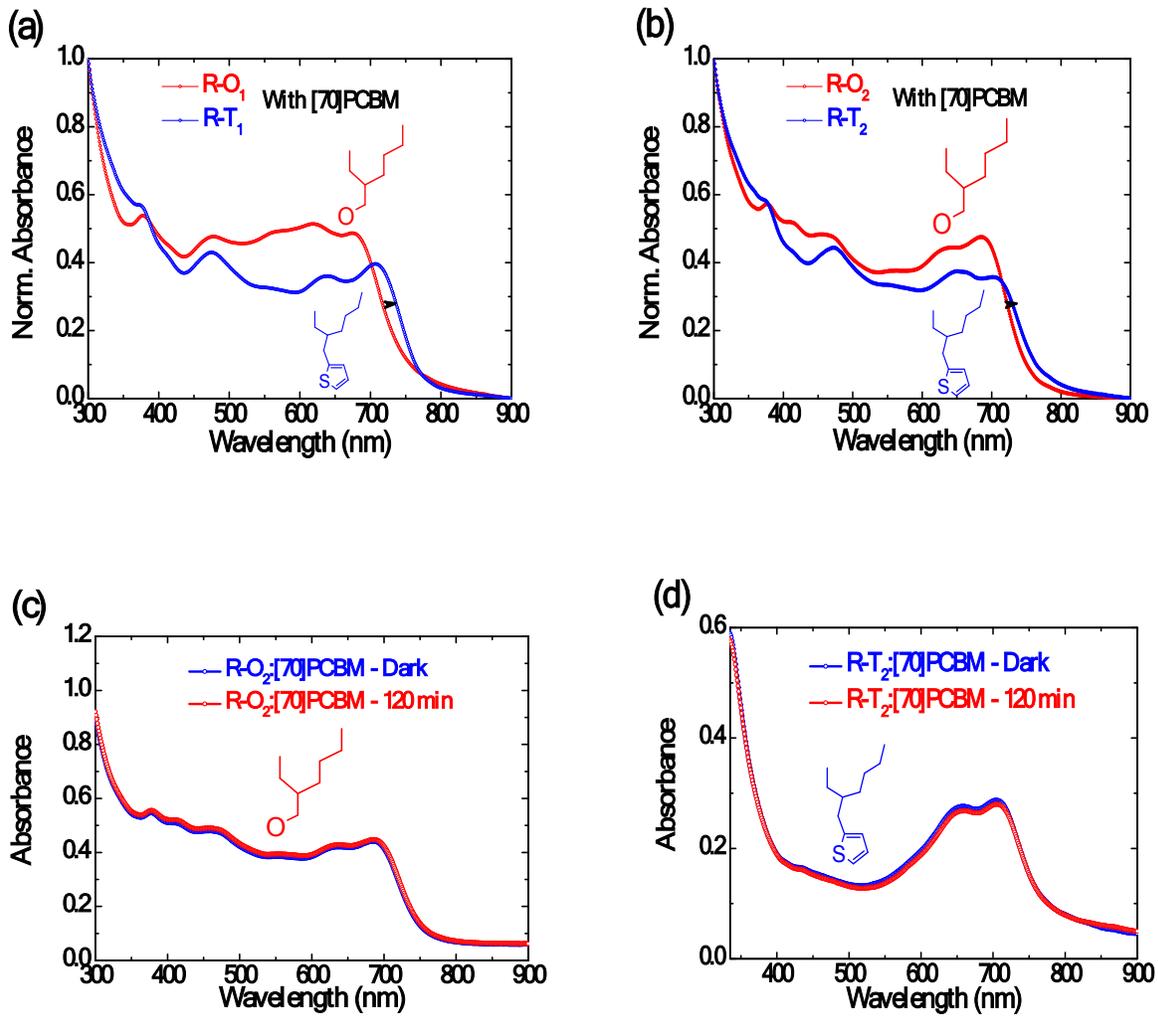


Fig. S1: Absorption spectra of (a,b) R-T devices with onset Red-shifted compared to R-O devices; and of unexposed (Blue) and exposed (Red) films of (c) R-O₂ and (d) R-T₂.

3. Effects of DIO

Table S1: Photovoltaic performances of conventional PSCs of the different blends with and without DIO under same conditions. Average values are for at least 20 selected devices without DIO, and for a lesser number of devices with DIO.

Devices	L. (nm)	J_{sc} (mA.cm ⁻²)	V_{oc} (mV)	FF (%)	PCE (%)	Average PCE (%)
PTB7	~100	10.10	798	56.4	4.54	4.22±0.51
DIO		14.00	740	68.3	7.07	6.34±0.64
PTB7-Th	~110	15.60	804	68.7	8.62	8.67±0.40
DIO		16.07	785	66.4	8.37	8.24±0.22
PBDTTT-C	~130	12.33	743	45.5	4.17	3.78±0.20
DIO		14.06	696	58.4	5.72	5.26±0.38
PBDTTT-C-T	~110	11.32	839	54.8	5.21	5.27±0.28
DIO		14.62	755	67.6	7.46	6.97±0.38

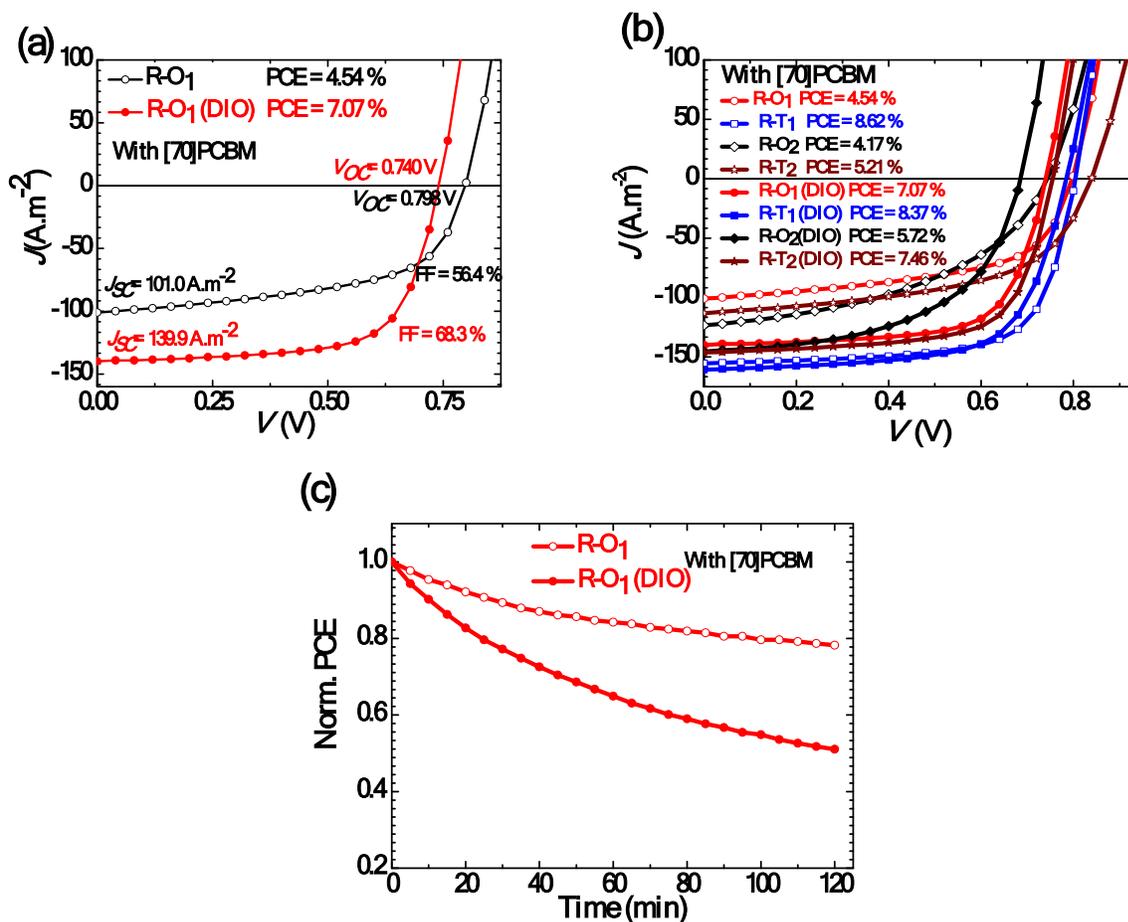


Fig. S2: Current-Voltage characteristics of blend devices with and without DIO of (a) R-O₁, and (b) all polymers; (c) PCE degradation curves of blend R-O₁ devices with and without DIO.

4. PCE Degradation Curves for Different Interfaces

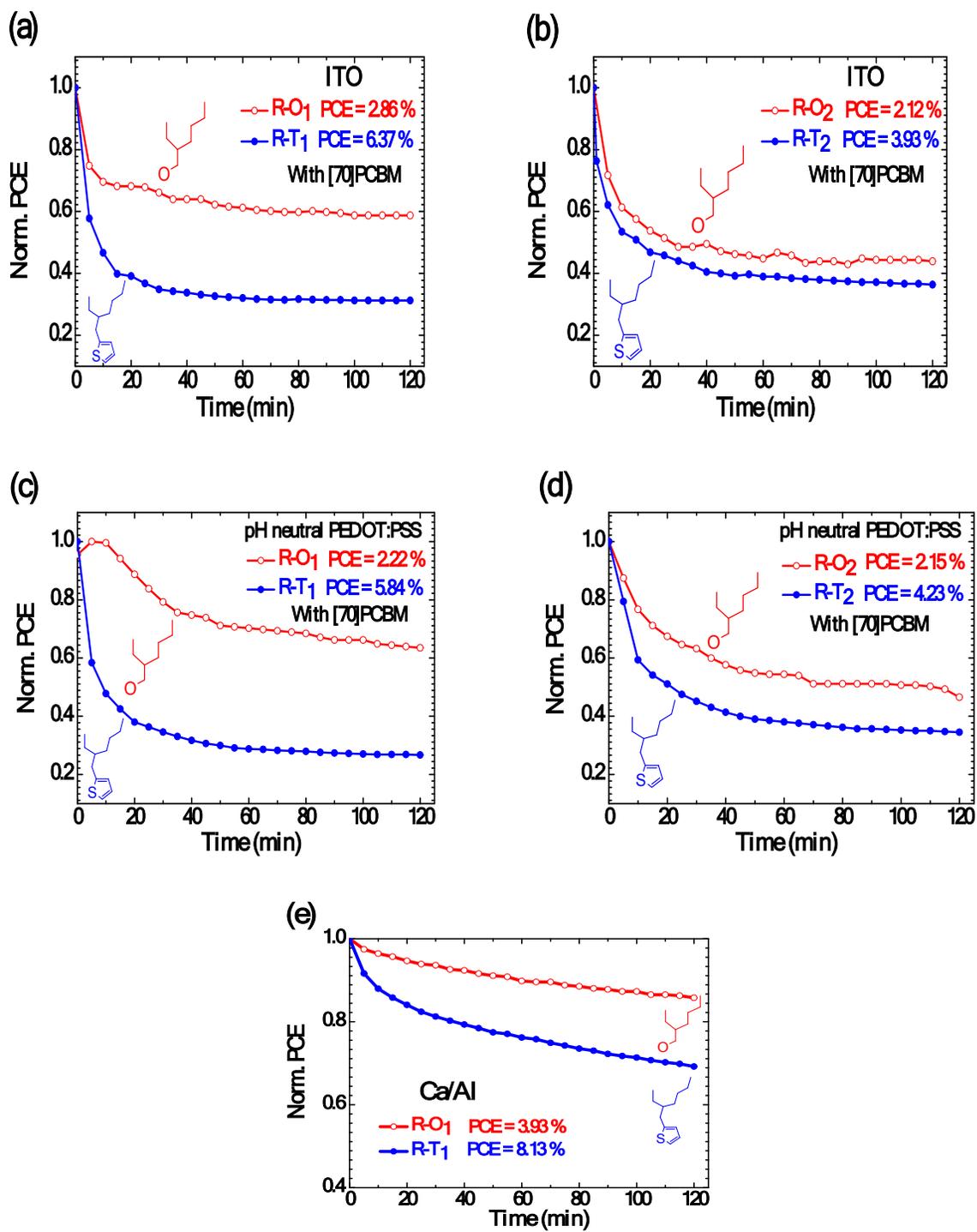
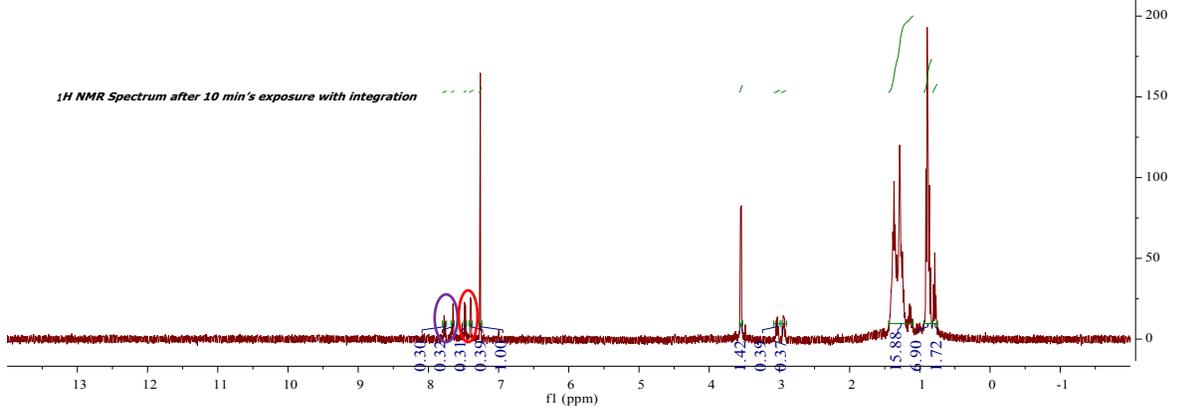
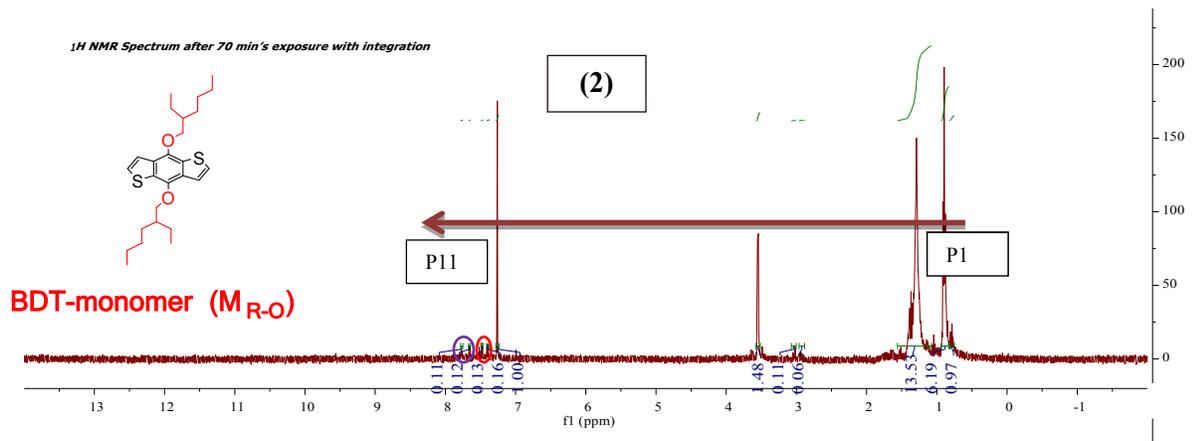
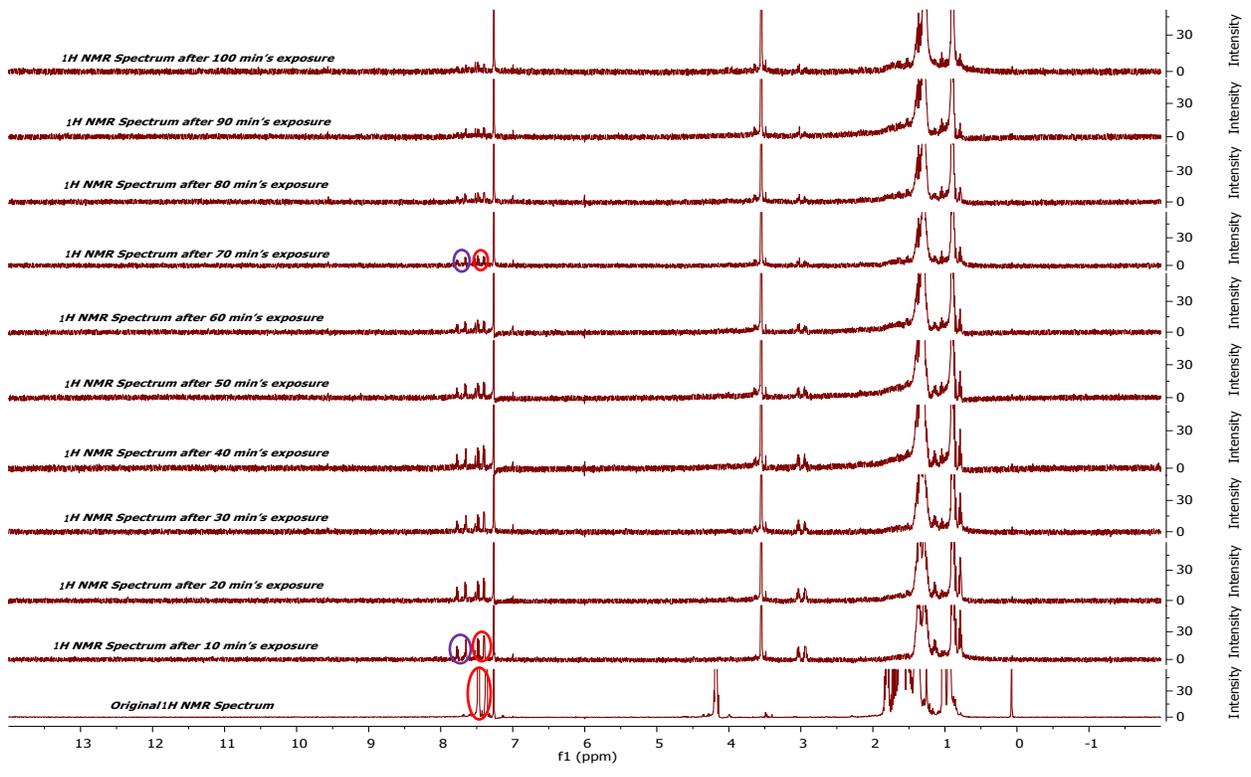


Fig. s3: Current-Voltage characteristics PCE degradation curves: of devices (just with ITO) without PEDOT:PSS (a) R-O₁ and R-T₁ and (b) R-O₂ and R-T₂; of devices with pH-neutral PEDOT:PSS (c) R-O₁ and R-T₁ and (d) R-O₂ and R-T₂; and of devices with (e) Ca/Al as top electrodes.

5. ¹HNMR Spectrum

(a)

(1)



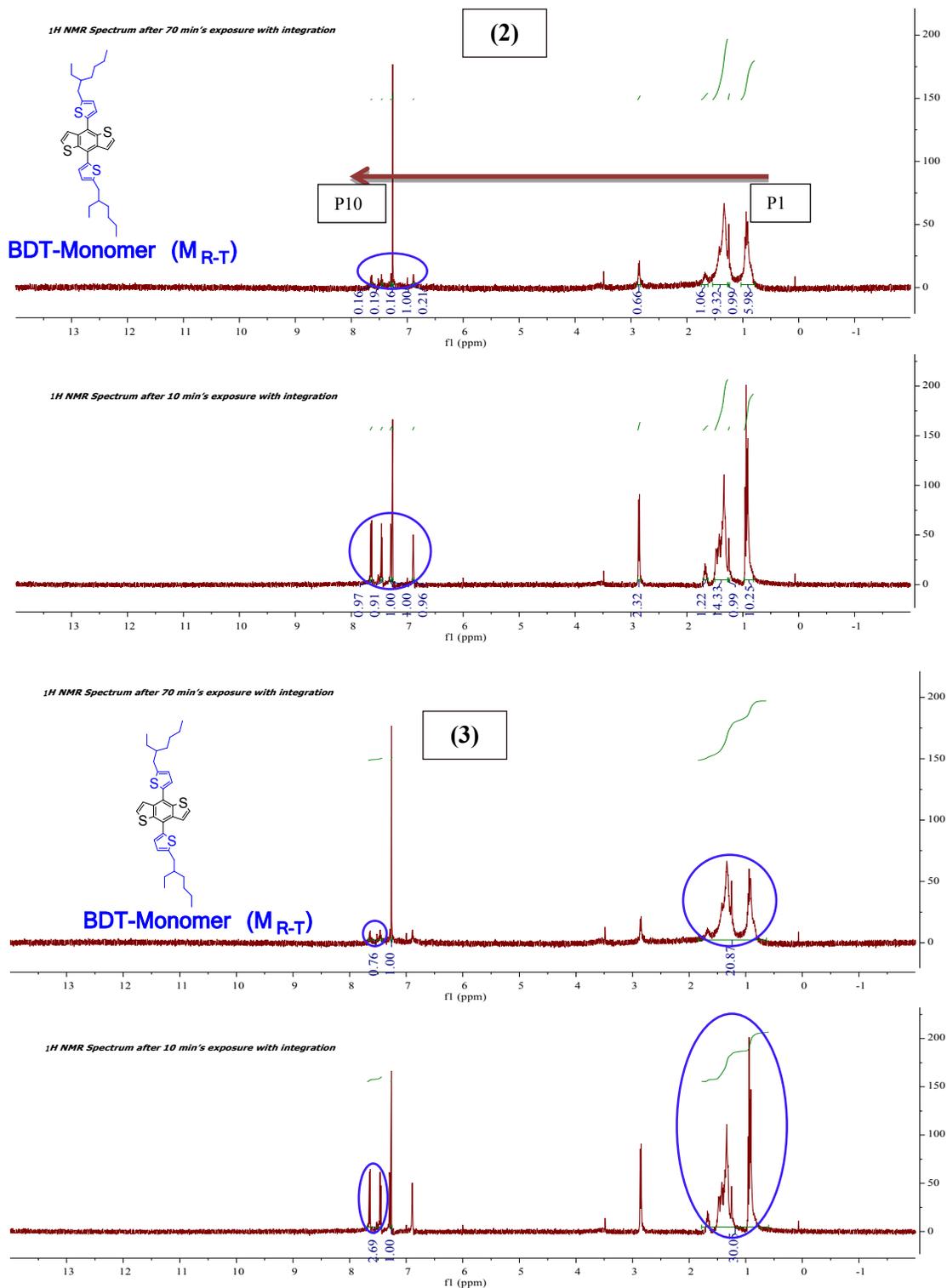


Fig. s4: ^1H NMR spectra (initial and after exposure to a shuttered UV flood light in steps of 10 mins for 100 mins) of monomer solutions of (a) R-O (P1 ~ 1st peak to P10 ~ 10th peak) and (b) R-T (P1 ~ 1st peak to P11 ~ 11th peak). Normal (1) and relative integrated peaks to: (2) solvent (CDCl_3) and (3) for peaks >7.3 ppm and between 0.5 and 2.25 ppm as used in fig. 2f,g.

6. Charge Transport

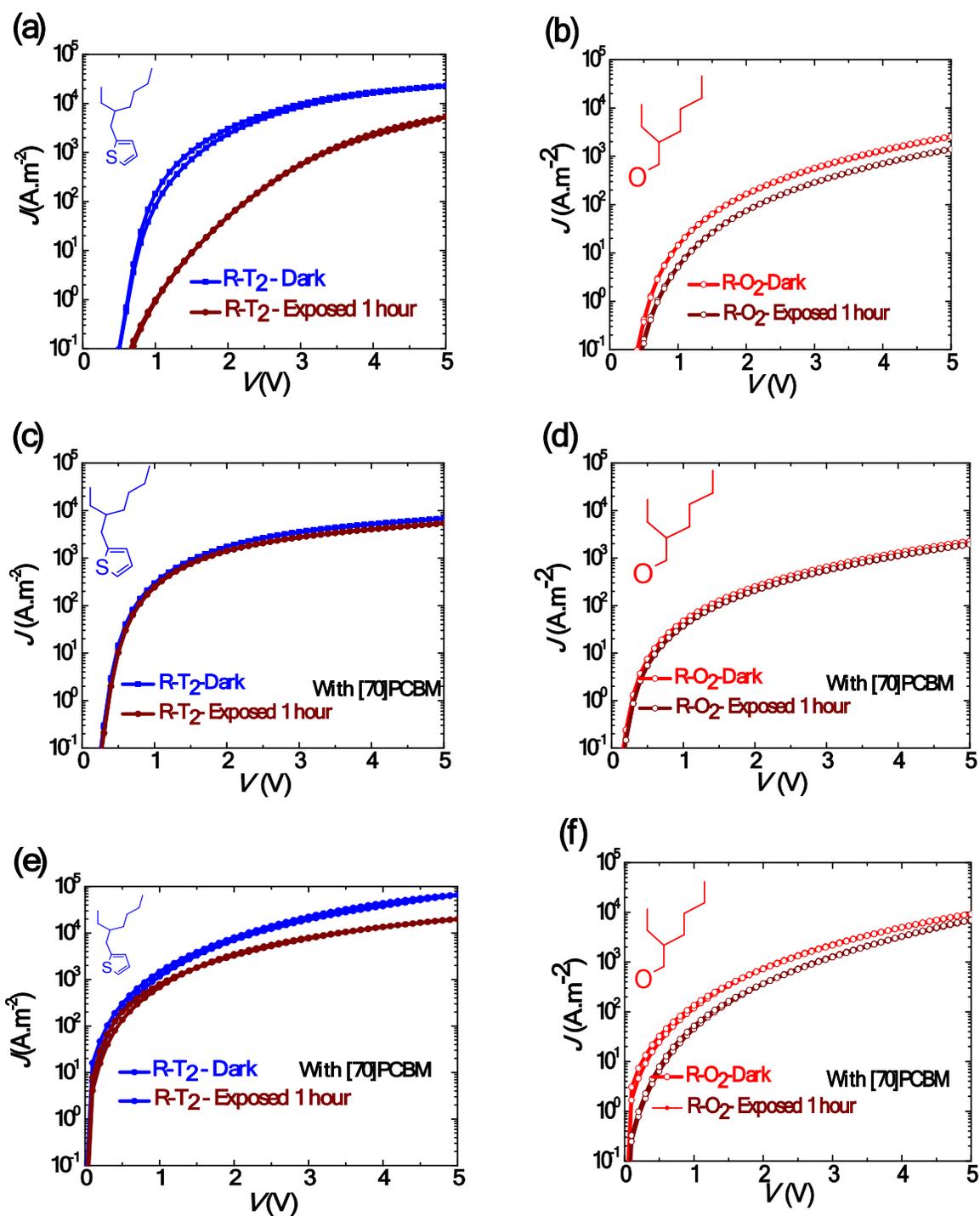


Fig. s5: Current-Voltage characteristics of unexposed (Blue if R-T, Red if R-O) and exposed (1 hour – Brown) (a) pristine R-T₂ polymer hole only device; (b) pristine R-O₂ polymer hole only device; (c) blend R-T₂ polymer hole only device; (d) blend R-O₂ polymer hole only device; (e) blend R-T₂ polymer electron only devices; and (f) blend R-O₂ polymer electron only device.

7. Light Intensity Measurements

Table s2: V_{OC} light intensity dependence of PSC of the different blends: Light exposure time dependent n values as a function of n -Fresh (i.e. n of unexposed devices).

Polymer	n -Fresh	n -1 hour	n -2 hours	n -3 hours
R-O ₁	~1.50	~1.16 n -Fresh	~1.18 n -Fresh	~1.20 n -Fresh
R-T ₁	~1.09	~1.19 n -Fresh	~1.23 n -Fresh	~1.24 n -Fresh
R-O ₂	~1.07	~1.13 n -Fresh	~1.20 n -Fresh	~1.24 n -Fresh
R-T ₂	~1.00	~1.20 n -Fresh	~1.26 n -Fresh	~1.28 n -Fresh

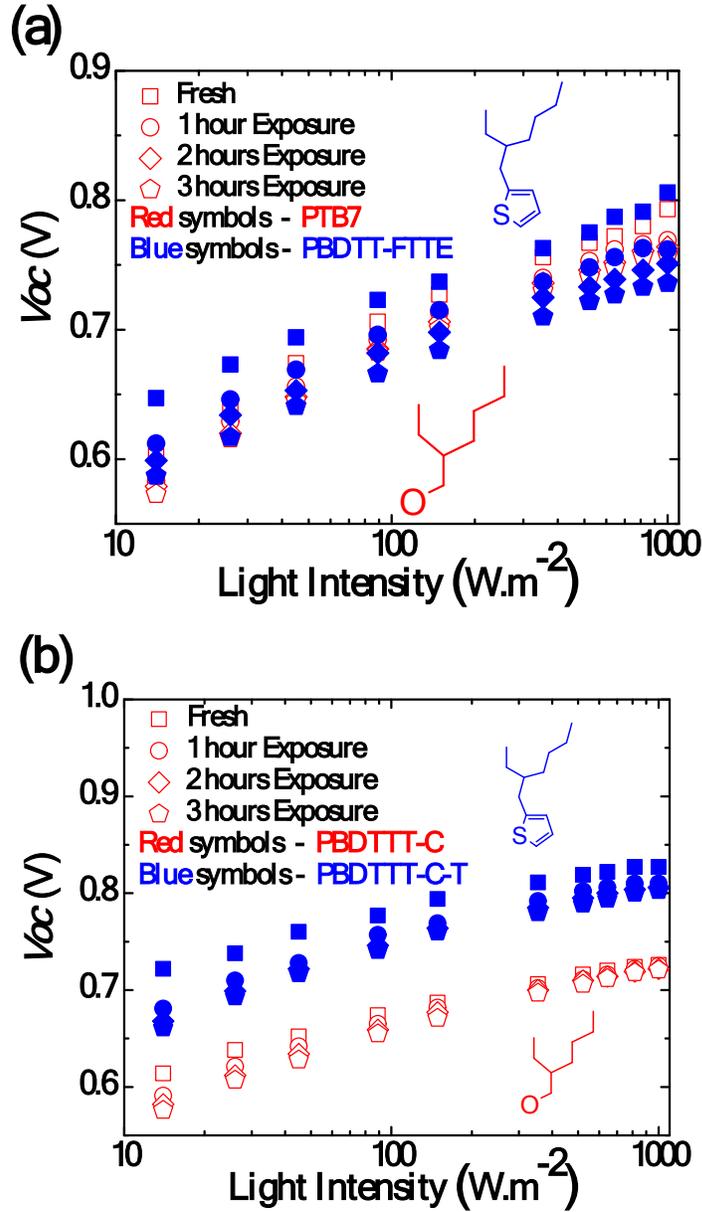


Fig. s6: Light Intensity dependence of V_{OC} of (a) R-O₁ (PTB7) and R-T₁ (PTB7-Th), and (b) R-O₂ (PBDTTT-C) and R-T₂ (PBDTTT-C-T) blended with [70]PCBM devices.

8. Lamp

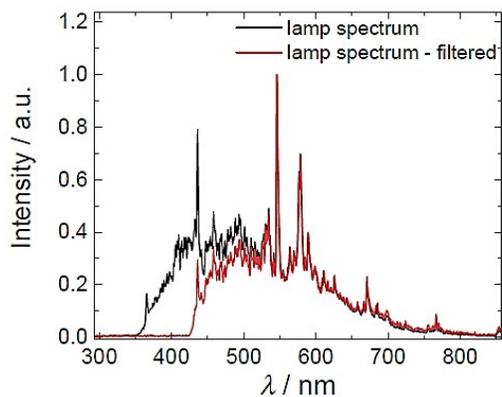
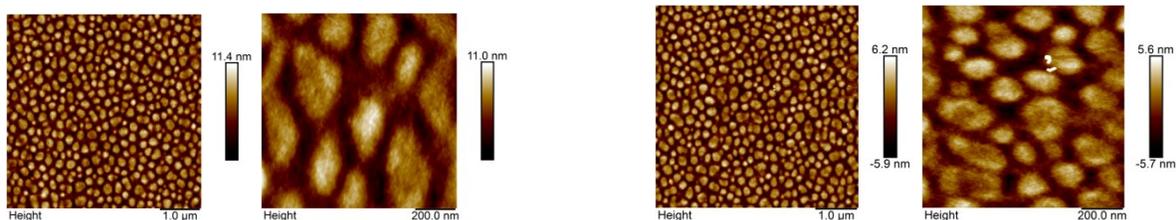


Fig. s7: Spectrum (black line) of lamp used during the (degradation) experiment.³

9. AFM images



(a) Film 1: as Cast

(b) Film 2: Exposed to light

Fig. s8: Two films of PTB7:[70]PCBM spin-coated on glass under the same conditions (a) as cast (1 micron and 200 nm) and (b) after 2 hours UV-exposure (1 micron and 200 nm)

References

- 1 J. Hou, M. Park, S. Zhang, Y. Yao, L.-M. Chen, J.-H. Li and Y. Yang, *Macromolecules*, 2008, **41**, 6012–6018.
- 2 L. Marin, L. Lutsen, D. Vanderzande and W. Maes, *Org. Biomol. Chem.*, 2013, **11**, 5866–76.
- 3 D. Bartesaghi, G. Ye, R. C. Chiechi and L. J. A. Koster, *Adv. Energy Mater.*, 2016, **6**, 1–9.