

Supporting Information

Effect of ambient environment on light-induced degradation of organic solar cells based on a benzodithiophene-quinoxaline copolymer in air

Kidan G. Gebremariam,^{1,2} Fikadu G. Hone,¹ Jane Dai,³ Genene T. Mola,^{1,4} Wendimagegn Mammo,⁵ Newayemedhin A. Tegegne*¹

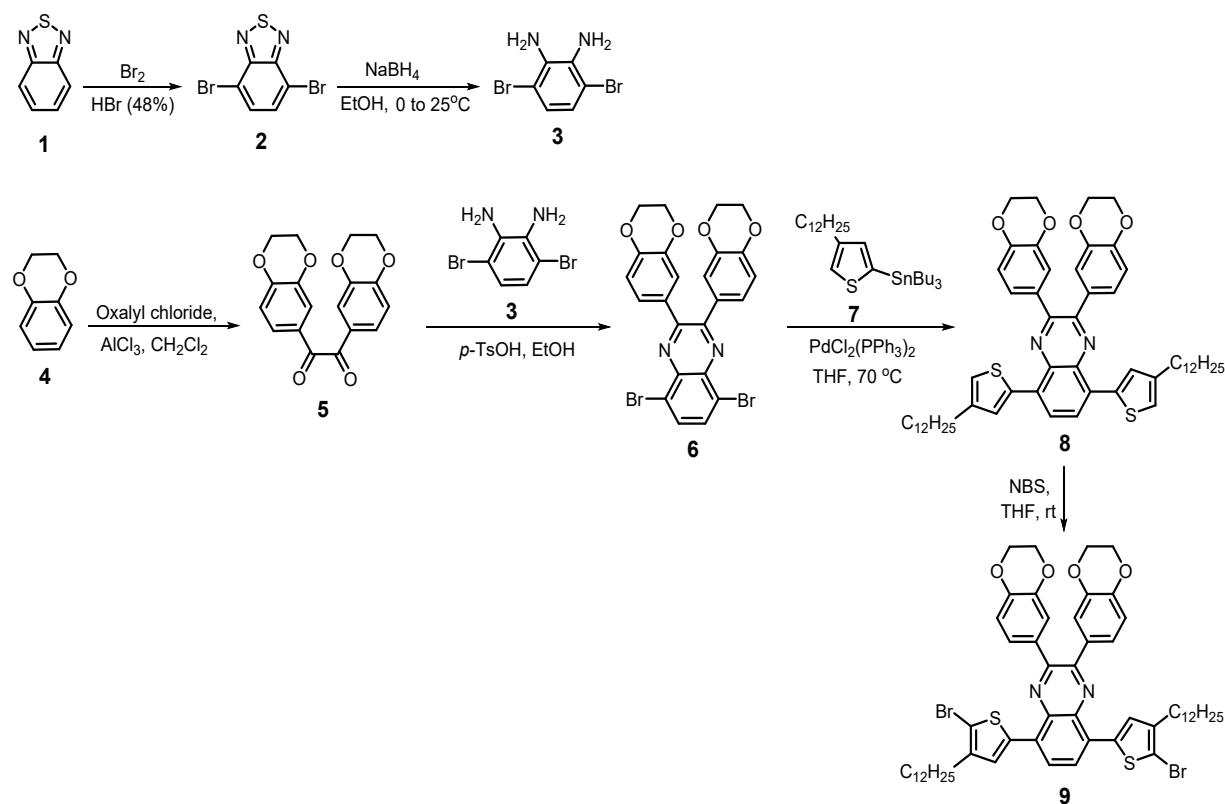
¹ Department of Physics, Addis Ababa University, 1176 Addis Ababa, Ethiopia

² Department of Physics, Kotebe University of Education, 31248 Addis Ababa, Ethiopia

³ Department of Physics, Laser research Institute, Stellenbosch University, Private Bag X1, 7602, South Africa

⁴ School of Chemistry and Physics, University of Kwazulu Natal, Pietermaritzburg Campus, Private Bag X01, Scottsville 3209, South Africa

⁵ Department of Chemistry, Addis Ababa University, 33658, Addis Ababa, Ethiopia



Scheme S1. Synthesis of monomer 6

Synthetic Procedures

Synthesis of 4,7-dibromobenzo[c][1,2,5]thiadiazole (2)

Bromine (6.40 g, 40 mmol) was slowly added to a mixture of benzo[*c*][1,2,5]thiadiazole (**1**, 2.72 g, 20 mmol) and aqueous HBr (48%, 40 mL) and the mixture was heated under reflux for 2 h. The needle-like precipitate was separated by filtration of the hot mixture. The supernatant was cooled to room temperature to form more needle-like precipitate, which was collected by filtration. The combined solid product was washed with water, and recrystallized from EtOAc to afford compound **2** (5.1 g, 86.9%) as white needle-shaped crystals.

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.73 (*s*, 2H).

¹³C-NMR (400 MHz, CDCl₃) δ (ppm): 152.9, 132.3, 113.9.

Synthesis of 3,6-dibromobenzene-1,2-diamine (**3**)

4,7-Dibromobenzo[*c*][1,2,5]thiadiazole (**2**) (2.0 g, 6.8 mmol) was dissolved in EtOH (40 mL) and cooled in an ice bath. To this solution, sodium borohydride (10 g, 0.264 mol) was added and the mixture was stirred at this temperature for 30 min. and at ambient temperature for 40 h. The mixture was quenched with water and extracted with diethyl ether. The organic layer was dried over anhydrous MgSO₄, filtered and the solvent was removed. The residue was purified by silica gel column chromatography using CH₂Cl₂ as eluent to afford **3** (1.3 g, 72.2%) as off-white fluffy solid.

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 6.84 (*s*, 2H), 3.89 (*bs*, 4H).

¹³C-NMR (400 MHz, CDCl₃) δ (ppm): 133.7, 123.2, 109.6.

Synthesis of 1,2-bis(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)ethane-1,2-dione (**5**)

To a suspension of AlCl₃ (0.98 g, 7.4 mmol) in CH₂Cl₂ (15 mL), a light-yellow solution of benzo-1,4-dioxane (**4**, 1 g, 7.4 mmol) and oxalyl chloride (0.47 g, 3.7 mmol) in CH₂Cl₂ (15 mL) was added dropwise over 15 min at 25 °C. The solution turned violet immediately after addition of a few drops of this mixture. The resulting mixture was stirred at room temperature for 4 h and then poured into 100 mL ice-cold water. The organic layer was separated and was washed with a saturated solution of NaHCO₃ and brine, dried over anhydrous Na₂SO₄ and filtered. The solvent was removed by rotary evaporation to give a pale-colored liquid which was purified by silica gel column chromatography using pet. ether:EtOAc (1:1 v/v) to give **5** (0.44 g, 18.4%) as a yellow solid.

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.43 (*d*, *J* = 2 Hz, 2H), 7.38 (*dd*, *J* = 8.4 Hz, *J* = 2 Hz, 2H), 6.86 (*d*, *J* = 8.4 Hz, 2H), 4.27- 4.19 (*m*, 8H).

¹³C-NMR (400 MHz, CDCl₃) δ (ppm): 193.4, 149.6, 143.7, 126.7, 124.3, 118.8, 117.7, 64.8, 64.0.

Synthesis of 5,8-dibromo-2,3-bis(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)quinoxaline (6)

To a solution of 3,6-dibromobenzene-1,2-diamine (**3**) (346 mg, 1.3 mmol) in EtOH (60 mL) at room temperature, 1,2-bis(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)ethane-1,2-dione (**5**) (425 mg, 1.3 mmol) and a catalytic amount of *p*-toluenesulfonic acid were added. The temperature was raised to 75 °C and the mixture was stirred for 4 h. It was then cooled to room temperature and the precipitate was collected by filtration, washed with cold EtOH, and dried to give **6** (495 mg, 68.7%).

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.86 (*s*, 2H), 7.41 (*d*, *J* = 1.2 Hz, 2H), 7.10 (*dd*, *J* = 8.4 Hz, *J* = 1.2 Hz, 2H), 6.82 (*d*, *J* = 8.4 Hz, 2H), 4.33-4.30 (*m*, 8H).

¹³C-NMR (400 MHz, CDCl₃) δ (ppm): 153.1, 145.1, 143.6, 139.0, 132.6, 131.3, 123.8, 123.4, 119.1, 117.0, 64.5, 65.2.

Synthesis of 2,3-bis(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-5,8-bis(4-dodecylthiophen-2-yl)quinoxaline (8)

5,8-Dibromo-2,3-bis(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)quinoxaline (**6**) (440 mg, 0.79 mmol) and 4-dodecylthiophen-2-yl)trimethylstannane (**7**) (722 mg, 1.74 mmol) were dissolved in dry THF (35 mL) and nitrogen was bubbled into the mixture for 20 min. Pd₂(dba)₃ (30 mg, 0.03 mmol) and P(*o*-tol)₃ (60 mg, 0.2 mmol) were added to the solution and the mixture was heated at 80 °C overnight. It was then cooled to room temperature, quenched with water and extracted with CH₂Cl₂. The combined organic extract was washed with brine, dried over MgSO₄ and the solvent was removed by rotary evaporation. The crude product was purified by silica gel column chromatography using CHCl₃:hexane (2:3) as eluent to give **8** (0.53 g, 74.6%) as sticky orange solid.

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 8.03 (*s*, 2H), 7.70 (*d*, *J* = 1.6 Hz, 2H), 7.46 (*d*, *J* = 2 Hz, 2H), 7.20 (*dd*, *J* = 8.4 Hz, *J* = 2.4 Hz, 2H), 7.10 (*d*, *J* = 1.2 Hz, 2H), 6.84 (*d*, *J* = 8.4 Hz, 2H), 4.30-4.26 (*m*, 8H), 2.68 (*t*, 4H), 1.72 (*m*, 4H), 1.44-1.26 (*m*, 36H), 0.89 (*t*, 6H).

^{13}C -NMR (400 MHz, CDCl_3) δ (ppm): 150.5, 144.5, 143.4, 142.7, 138.5, 136.9, 132.2, 131.0, 127.8, 126.5, 124.0, 123.7, 119.3, 116.9, 64.5, 64.2, 31.9, 30.6, 30.5, 29.7, 29.7, 29.6, 29.6, 29.5, 29.4, 29.3, 22.7, 14.1.

Synthesis of 5,8-bis(5-bromo-4-dodecylthiophen-2-yl)-2,3-bis(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)quinoxaline (9)

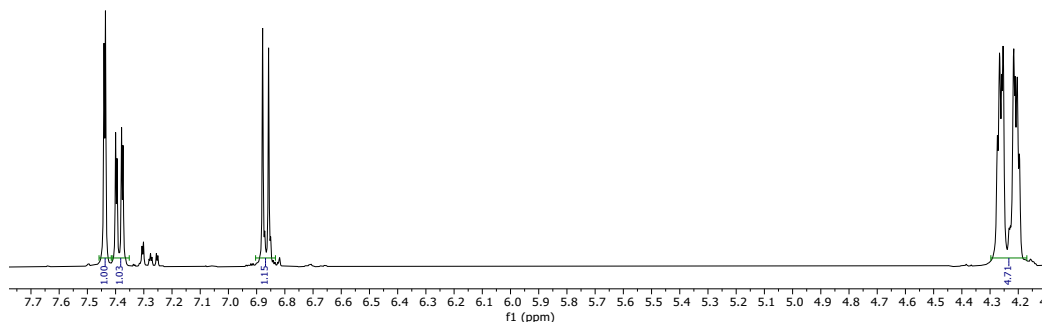
2,3-Bis(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-5,8-bis(4-dodecylthiophen-2-yl)quinoxaline (8) (0.4 g, 0.45 mmol) was dissolved in THF (15 mL) and NBS (158 mg, 0.89 mmol) was added in one portion. The mixture was stirred for 5 h at room temperature in the dark and the solvent was removed by rotary evaporation. The residue was dissolved in water and extracted with CH_2Cl_2 . The combined CH_2Cl_2 extract was dried over MgSO_4 , the solvent was removed and the crude product was purified by silica gel column chromatography using CHCl_3 :hexane (2:3) as eluent to give **9** (0.45 g, 95.7%) as orange solid.

^1H -NMR (400 MHz, CDCl_3) δ (ppm): 7.97 (*s*, 2H), 7.51 (*s*, 2H), 7.35 (*d*, $J = 2.4$ Hz, 2H), 7.19 (*dd*, $J = 8.4$ Hz, 2 Hz, 2H), 6.87 (*d*, $J = 8.4$ Hz, 2H), 4.31 (*m*, 8H), 2.62 (*t*, 4H), 1.66 (*m*, 4H), 1.41-1.25 (*m*, 36H), 0.88 (*t*, 6H).

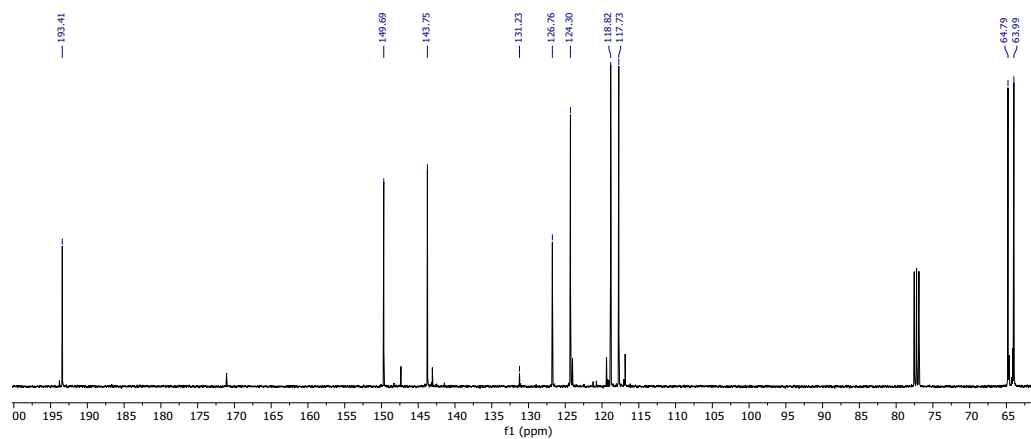
^{13}C -NMR (400 MHz, CDCl_3) δ (ppm): 151.1, 144.7, 143.4, 141.2, 137.7, 136.5, 131.8, 130.3, 126.4, 125.3, 123.9, 119.3, 117.1, 113.9, 64.5, 64.2, 31.9, 29.8, 29.6, 29.6, 29.6, 29.6, 29.5, 29.4, 29.3, 29.3, 22.6, 14.1.

The NMR spectra of each of the components synthesized is given below

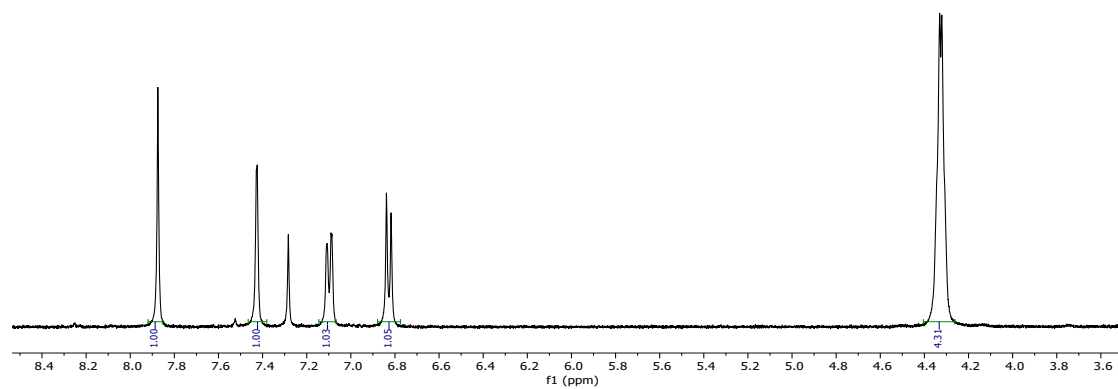
^1H and ^{13}C NMR spectra of compounds



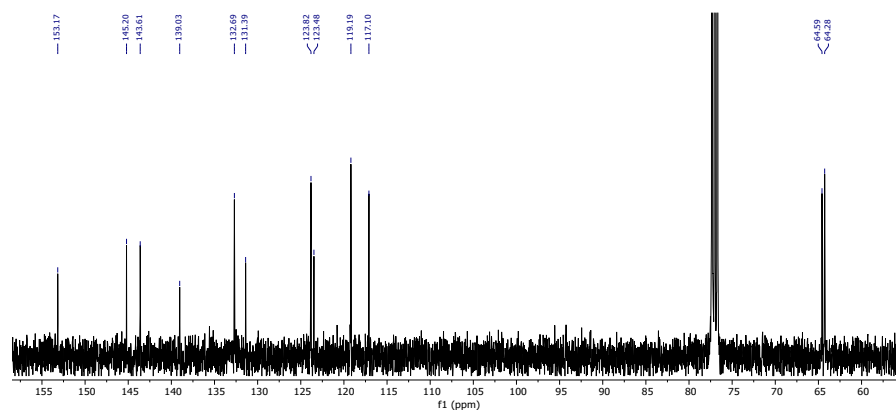
^1H NMR spectrum (400.13 MHz, CDCl_3) of 1,2-bis(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)ethane-1,2-dione (**5**).

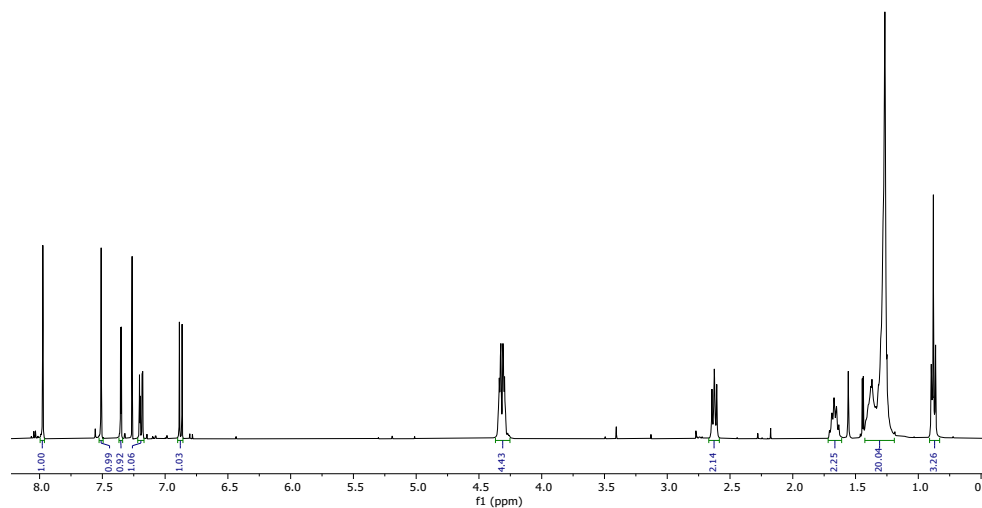


^{13}C NMR spectrum (100.6 MHz, CDCl_3) of 1,2-bis(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)ethane-1,2-dione (**5**).

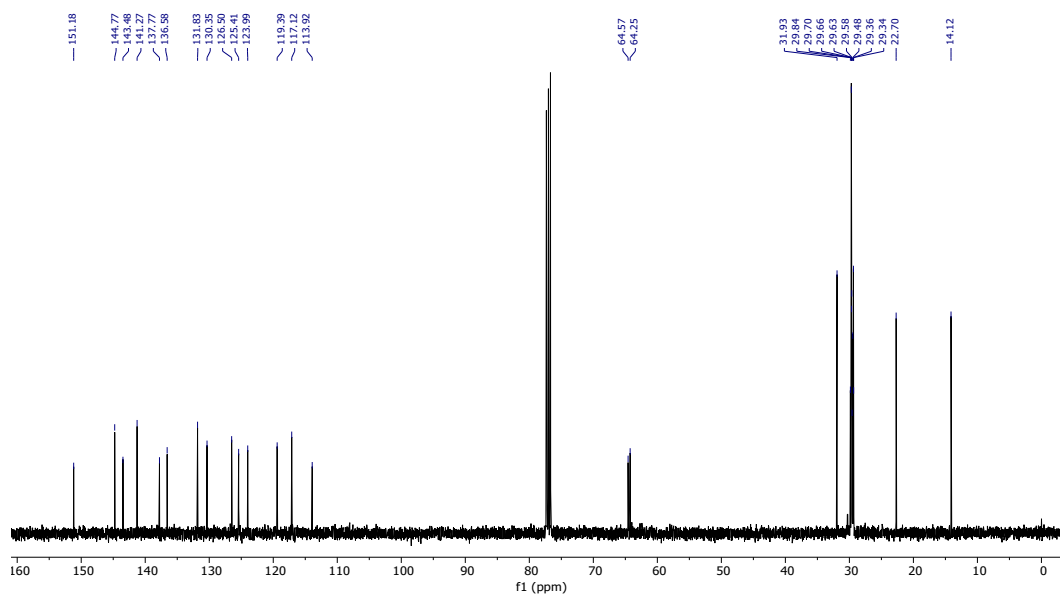


^1H NMR spectrum (400.13 MHz, CDCl_3) of 5,8-dibromo-2,3-bis(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)quinoxaline (**6**).





^1H NMR spectrum (400.13 MHz, CDCl_3) of 5,8-bis(5-bromo-4-dodecylthiophen-2-yl)-2,3-bis(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)quinoxaline (**9**).



^{13}C NMR spectrum (100.6 MHz, CDCl_3) of 5,8-bis(5-bromo-4-dodecylthiophen-2-yl)-2,3-bis(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)quinoxaline (**9**).

Synthesis of PBDTQ-4O

A round-bottomed flask (25 mL) was charged with 5,8-bis(5-bromo-4-dodecylthiophen-2-yl)-2,3-bis(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)quinoxaline (**9**) (0.15 g, 0.14 mmol) and 2,6-bis(trimethylstannyl)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*;4,5-*b'*]dithiophene (**10**) (0.11 g, 0.14

mmol) and kept under nitrogen atmosphere. Toluene (4 mL), Pd₂(dba)₃ (6 mg, 0.01 mmol) and P(*o*-tol)₃ (10 mg, 0.03 mmol) were added and the flask was purged again with successive vacuum/nitrogen cycles (3 times). The reaction mixture was heated at 100 °C for 24 h and the resulting polymer was first end-capped with 2-bromothiophene (26.1 mg, 0.16 mmol) and then with 2-(tributylstannyl)thiophene (67.1 mg, 0.18 mmol) at 2.5 h interval. After cooling to room temperature, the polymer was precipitated from acetone, separated by filtration and the crude polymer was dissolved in CHCl₃ and washed with sodium diethyldithiocarbamate trihydrate overnight. The organic layer was separated and washed with water three times, concentrated and then the polymer was precipitated from MeOH, filtered and purified by Soxhlet extraction with hexane, diethyl ether and CHCl₃. The CHCl₃ extract was concentrated, precipitated from MeOH, filtered and dried in vacuum oven at 40 °C for 16 h to give **PBDTQ-4O** (0.17 g, 89.4%) as dark-brown solid. *Mn* = 47,800 g/mol, *Mw* = 147,300 g/mol.

Table S1. Photovoltaic parameters under 1-sun condition with time of irradiation

	Time (min)	Voc (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
Light stressed	Fresh	0.76	14.9	42	4.8
Unstressed		0.76	14.7	42	4.2
Light stressed	120	0.76	13.0	40	4.0
Unstressed		0.76	13.7	40	4.0
Light stressed	240	0.77	12.9	40	3.9
Unstressed		0.76	13.5	42	3.9
Light stressed	360	0.76	12.3	41	3.8
Unstressed		0.78	13.2	39	3.8
Light stressed	480	0.76	11.7	40	3.5
Unstressed		0.77	12.7	39	3.6
Light stressed	600	0.75	11.0	40	3.2

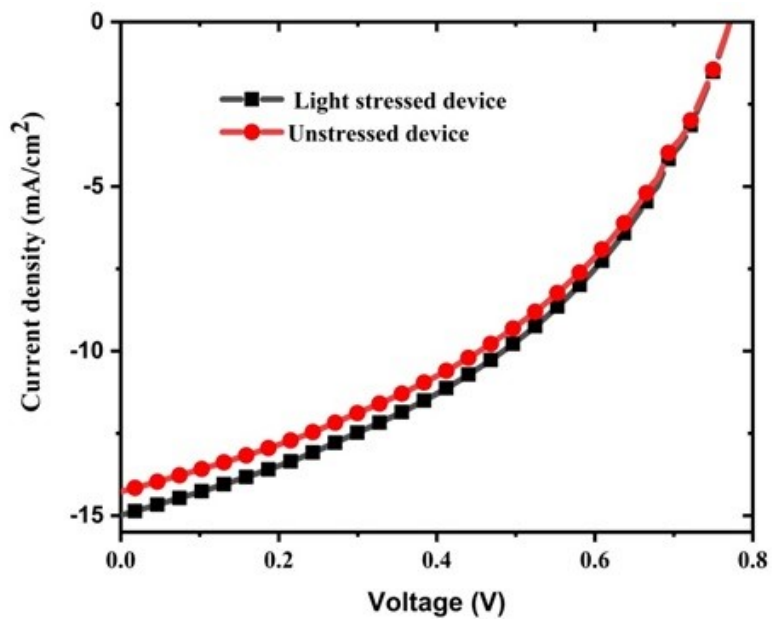


Fig. S1 J-V characteristics of devices used for the light stressed and unstressed measurements

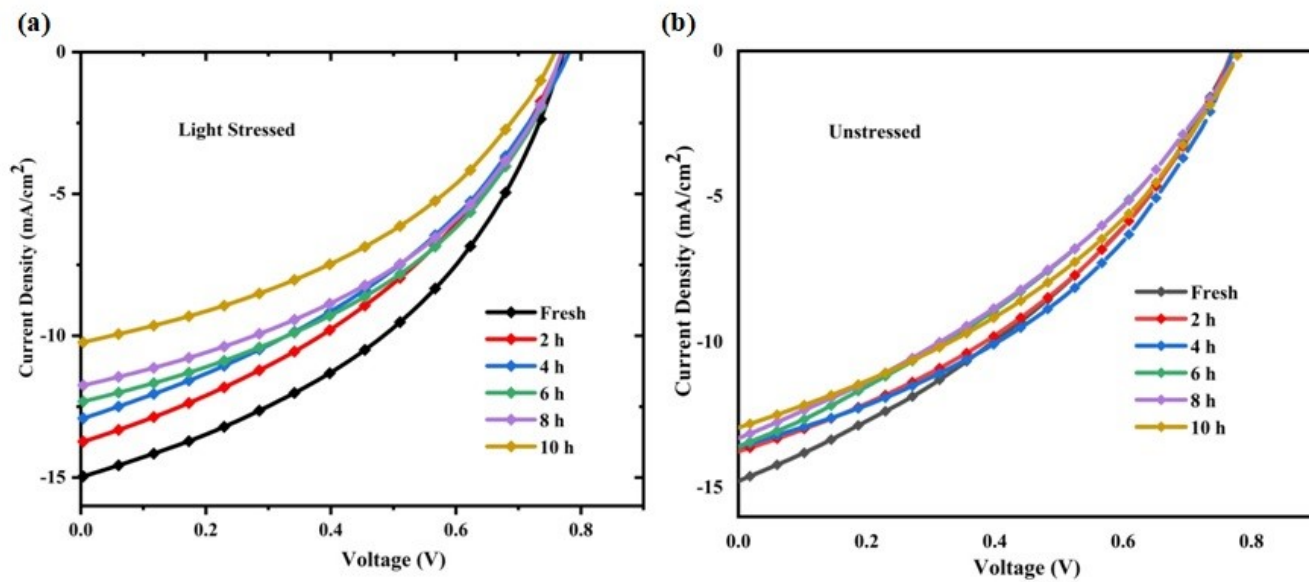


Fig. S2 J-V degradation of PBBDTQ based devices under (a) light stress (b) unstressed

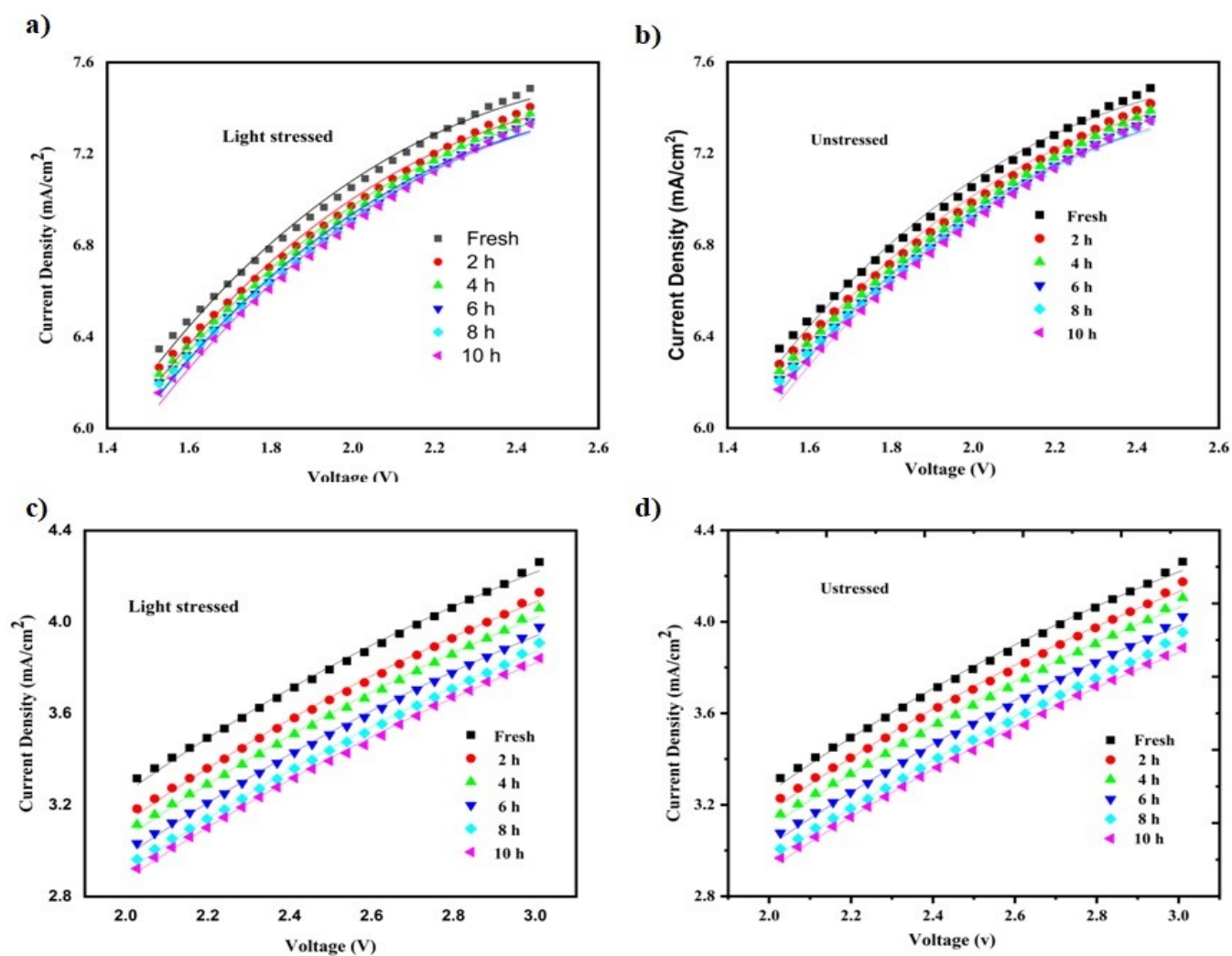


Fig. S3 Mobility kinetics fitting a) light stressed hole only b) unstressed hole only c) light stressed electron only d) unstressed electron only