*Electronic Supplementary Information*

# Double acceptors D-A copolymers containing benzotriazole and benzothiadiazole units: chemical tailoring towards efficient photovoltaic properties

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Content

## 1. Starting materials

Benzotriazole (Aldrich), 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-hexylthiophene (Aldrich), 9-heptadecanol (Rubipy), 4,8-di(2'-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene (Rubipy), 2-(tributystannyl)thiophene (Aldrich), 2-hexyldecan-1-ol (Aldrich), octyl bromide (Aldrich), diethyl malonate (Aldrich), (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (Aldrich), bromobenzene (Aldrich), tetrabromomethane (Aldrich), triphenylphosphine (Aldrich), potassium t-butoxide (Aldrich), bromine (Aldrich), N-bromosuccinimide (Aldrich), diisopropylazadicarboxylate (Aldrich), 1.6 M n-BuLi in hexane (Aldrich), lithium alluminium hydride (Aldrich), 60% sodium hydride in mineral oil (Aldrich), trimethyltinchloride (Aldrich), $Pd(PPh_3)_4$ (Aldrich), $Pd(PPh_3)_2Cl_2$

(Aldrich), $Pd(OCOCH_3)_2$ (Aldrich), potassium acetate (Aldrich), potassium hydroxide (Aldrich), 48% aqueous HBr (Carlo Erba), 30% aqueous $NH_3$ (Carlo Erba), tricaprylmethylammonium chloride (Aliquat® 336) (Aldrich), ethylenediaminetetraacetic acid disodium salt (EDTA) (Aldrich), sodium thiosulphate (Aldrich), sodium carbonate (Fluka) potassium carbonate (Fluka), sodium sulfate (Aldrich), silica gel 60A (Carlo Erba), acetone (Carlo Erba), methanol (Carlo Erba), n-propanol (Carlo Erba), i-propanol (Carlo Erba), ethyl acetate (Carlo Erba), diethyl ether (Carlo Erba), heptane (Carlo Erba), anhydrous N,N-dimethylformamide (Aldrich), N,N-dimethylacetamide (Aldrich), chloroform (Carlo Erba or Aldrich), chlorobenzene (Aldrich), ferrocene (Acros), tetrabutylammonium tetrafluoborate (electrochemical grade, Fluka), 1,2,4-trichlorobenzene (Aldrich) were used without further purification.

2,6-bis(trimethylstannyl)-4,8-di(2’-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene (Rubipy) was recrystallized from i-propanol. 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,1,3-benzothiadiazole (Aldrich) and 4,7-dibromo-2,1,3-benzothiadiazole (Aldrich) were purified by recrystallization from ethyl acetate.
Toluene (Carlo Erba) was distilled over sodium hydride. Tetrahydrofuran (Carlo Erba) was distilled over lithium aluminium hydride.

ITO-glass substrate, 15 Ω/☐, (KINTEC Company), PEDOT:PSS (H.C. Starck, Clevios P VP Al 4083), chlorobenzene, chloroform, orthodichlorobenzene, 1-chloronaphthalene, ethanol (Aldrich), $PC_{71}BM$ and $PC_{61}BM$ (Solenne BV).

## 2. Monomers and polymers synthesis

*2-Hexyldecyl bromide*. To a three-necked round bottom flask containing 48.4 g of triphenylphosphine (185.0 mmol) dissolved in 160 mL of dichloromethane, a solution of 32.0 g of 2-hexyldecanol (132.2 mmol) and 57.2 g of tetrabromomethane (172.0 mmol) in 280 mL of dichloromethane was added at 0°C under nitrogen atmosphere. After 2 hours of reaction at room temperature, the mixture was poured in 400 mL of heptane and 100 mL of diethyl ether. The triphenylphosphineoxide by-product was removed by filtration and the solution was concentrated under vacuum. The residue was purified by elution on a silica gel column. 40 g of 2-hexyldecyl bromide (99.9%) were obtained.
**$^1$H-NMR** (400 MHz, CDCl3): 3.45 ppm (d, CH2, 2H, J=4.5 Hz), 1.60 ppm (m, CH, 1H), 1.28 ppm (m,CH2, 24 H), 0.89 ppm (t, CH3, 6H, J= 6.6 Hz).

*2-(2-Hexyldecyl)benzotriazole (**1**).* To a three-necked round bottom flask containing 10.4 g of benzotriazole (87.0 mmol) dissolved in 100 mL of methanol, 10.4 g of potassium t-butoxide (92.8 mmol) have been added in small portions under nitrogen atmosphere. After 10 minutes of stirring, 31.8 g of 2-hexyldecyl bromide (104.4 mmol) dissolved in 50 ml of methanol have been added dropwise. The mixture was heated for 5 hours at 60°C. After removing the solvent under vacuum, the product was dissolved in ethyl acetate and extracted with water. The organic phase was dried over sodium sulfate and eluted on a silica gel column. 9.0 g of 2-(2-hexyldecyl)benzotriazole (**1**) (yield=30%) were obtained.
**$^1$H-NMR** (400 MHz, CDCl3): 7.89-7.80 ppm (AA’, 2H), 7.38-7.28 ppm (BB’, 2H), 4.60 ppm (d, CH2, 2 H, J= 6.8 Hz), 2.21 ppm (m, CH, 1H), 1.42 – 1.16 ppm (m, CH2, 24H), 0.90-0.84 ppm (t, CH3, 6H).

*4,7-Dibromo-2-(2-hexyldecyl)benzotriazole (**2**)*. 9.1 g of 2-(2-hexyldecyl)benzotriazole (**1**) (26.4 mmol) suspended in 54 mL of 48% aqueous HBr, were stirred for 1 hour in a three-necked round bottom flask at 100°C. 2.7 mL of bromine (52.8 mmol) were added dropwise at 110°C. The mixture was left to react for 24 hours; 2 ml of $Br_2$ were added, and the reaction continued for another 36 hours. The mixture was cooled to room temperature, 100 mL of water were added and the product was extracted with diethyl ether. The organic phase was washed with aqueous sodium thiosulphate, then with water, dried over sodium sulfate, concentrated, and the solid residue was eluted on a silica gel column (heptane/ethyl acetate 99:1). 8.0 g of 4,7-dibromo-2-(2-hexyldecyl)benzotriazole (**2**) (yield=65%) were obtained.
$^1$**H-NMR** (400 MHz, CDCl3): δ 7.44 ppm (s, CH, 2H), 4.67 ppm (d, CH2, *J* = 7.3 Hz, 2H), 2.34 ppm (m, CH, 1H), 1.44 –1.11 ppm (m, CH2, 24H), 0.87 ppm (t, CH3, 6H).

*4,7-Bis(3-hexylthien-2-yl)-2-(2-hexyldecyl)benzotriazole*. To a three-necked round bottom flask containing 2.0 g of 4,7-dibromo-2-(2-hexyldecyl)benzotriazole (**2**) (4.0 mmol) dissolved in 20 mL of N,N-dimethylformamide, 3.0 g 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-hexylthiophene (10.3 mmol) were added under nitrogen atmosphere, followed by 92 mg of $Pd(PPh_3)_4$ (0.08 mmol) and 40 mL of a 1M aqueous solution of sodium carbonate. The mixture was stirred for 9 hours at 100°C. After cooling and adding 100 ml of water, the product was extracted with diethyl ether, the organic phase was dried over sodium sulfate, concentrated, and the solid residue was eluted on a silica gel column (heptane/ethyl acetate 98:2). 2.1 g of 4,7-bis(3-hexylthien-2-yl)-2-(2-hexyldecyl)benzotriazole (yield=80%) were obtained.
$^1$**H-NMR** (400 MHz, CDCl3): δ 7.36 ppm (s, CH, 2H), 7.26 ppm (d, CH, J = 5.2 Hz, 2H), 7.01 ppm (d, CH, J = 5.2 Hz, 2H), 4.42 ppm (dd, CH2, J = 7.6 Hz, 2H), 2.79 – 2.68 ppm (m, CH2, 4H), 1.75 – 1.15 ppm (m, CH2, 44H), 0.97 ppm (t, CH3, J = 7.4 Hz, 3H), 0.87 ppm (t, CH3, J = 6.9 Hz, 3H), 0.84 ppm (t, CH3, J = 6.9 Hz, 6H).

*4,7-Bis(5-bromo-3-hexylthien-2-yl)-2-(2-hexyldecyl)benzotriazole (**3**)*. To a three-necked round bottom flask containing 2.1 g of 4,7-bis(3-hexylthien-2-yl)-2-(2-hexyldecyl)benzotriazole (3.1 mmol) dissolved in 10 mL of anydrous THF, 1.1 g of N-bromosuccinimide (6.2 mmol) were added under nitrogen atmosphere. The mixture was stirred for 24 hours under dark. 50 ml of water were added and the product was extracted with diethyl ether. The organic phase was washed with a solution of sodium thiosulphate, then with water, dried over sodium sulfate and concentrated. The solid residue was eluted on a silica gel column (eluent: heptane). 2.3 g of 4,7-bis(5-bromo-3-hexylthien-2-yl)-2-(2-hexyldecyl)benzotriazole (**3**) (yield=90%) were obtained.
$^1$**H-NMR** (400 MHz, CDCl3): δ 7.36 ppm (s, CH, 2H), 7.02 ppm (s, CH, 2H), 4.64 ppm (d, J = 7.0 Hz, 2H), 2.67 ppm (dd, CH2, 4H), 2.28 ppm (m, CH, 1H), 1.70 – 1.50 ppm (m, CH2, 4H), 1.43 – 1.11 ppm (m, 44H), 0.92 – 0.79 ppm (m, 12 H).

*Diethyl 2,2-dioctylmalonate.* To a solution of 15 g of diethyl malonate (0.1 mol) in 400 mL of dry tetrahydrofuran, 9.6 g of 60% sodium hydride (0.24 mol) were added in portions at 0°C under argon atmosphere. After 20 minutes, 38.6 g of octyl bromide (0.2 mol) were added dropwise. The mixture was heated at reflux for 5 hours. The reaction was cooled, carefully quenched with water and then diluted with 2M HCl. The reaction mixture was extracted with ethyl acetate, dried over sodium sulfate and evaporated. The residue was purified by flash chromatography eluting with 1:1 heptane/toluene to give 30.7 g of pure diethyl 2,2-dioctyl malonate (yield= 80%).
$^1$**H-NMR** (300 MHz, $CDCl_3$): δ 3.98 ppm (q, CH2, 4H), 1.70-1.60 ppm (m, CH2, 4H), 1.15-0.88 ppm (Cm, CH2, 30H), 0.69 ppm (t, CH3, 6H)

*2,2-Dioctylmalonic acid.* To a three-necked round bottom flask containing 26.8 g of potassium hydroxide (0.48 mol) in 48 mL of water, a solution of 30.7 g of 2,2-dioctyl malonate (0.08 mol) in 80 mL of ethanol was added dropwise. The mixture was heated to reflux for 8 hours. The ethanol was removed under reduced pressure and the residue was acidified to pH = 2 with 1M aqueous HCl. The solvent was evaporated under reduced pressure and the residue was extracted with ethyl acetate. The extracts were washed with brine, dried over sodium sulfate, filtered and evaporated in vacuo to give 25.6 g of 2,2-dioctylmalonic acid (yield= 96 %).
$^1$**H-NMR** (400 MHz, CDCl3): δ 12.65 ppm (s. br, COOH, 2H), 1.77 ppm (m, $CH_2$, 4H), 1.29 ppm (m, $CH_2$, 20 H), 1.15 ppm (m, $CH_2$, 4 H), 0.91 ppm (t, $CH_3$, 6H, J= 6.4 Hz).

*2-Octyldecanoic acid.* 25.6 g of 2,2-dioctylmalonic acid (0.078 mol) were heated in a two necked flask under argon at 200°C for 30 minutes. 21.3 g of 2-octyldecanoic acid (yield=96%) were obtained (y= 96%).
$^1$**H-NMR** (400 MHz, DMSO-$d_{12}$): δ 12.0 ppm (s. br, COOH, 1H), 2.22 ppm (m, CH, 1H), 1.60-1.40 ppm (m, $CH_2$, 4H), 1.30 ppm (m, $CH_2$, 24 H), 0.91 ppm (t, $CH_3$, 6H, J= 6.4 Hz)

*2-Octyldecan-1-ol.* To a three-necked bottom flask containing a suspension of 11.4 g of lithium aluminium hydride (0.3 mol) in 200 mL of anhydrous tetrahydrofuran, a solution of 21.3 g of 2-octyldecanoic acid (0.075 mol ) was added dropwise at 0 °C under gentle stirring. After 4 hours the reaction was quenched with 50 mL of ethyl acetate and the solvent was evaporated under reduced pressure. The residue was taken up in 50 mL of water and the resulting gel was vigorously shaken up with ethyl acetate. The extracts were washed with brine, dried over sodium sulfate, filtered and evaporated under reduced pressure. The residue was purified by column chromatography (eluent: hexane/ethyl acetate 20:1) to give 19.4 g of 2-octyldecan-1-ol (yield=96%) .
$^1$**H-NMR** (400 MHz, CDCl3): δ 3.53 ppm (d, $CH_2$, 2H, J= 5.6 Hz), 1.45 ppm (m, CH, 1 H), 1.27 ppm (m, $CH_2$, 28 H), 0.88 ppm (t, $CH_3$, 6H, J= 6.9 Hz).

*2-(2-Octyldecyl)benzotriazole (**4**).* To a three-necked round bottom flask containing 13.5 g of benzotriazole (42.0 mmol) dissolved in 100 mL of anhydrous THF, 17.9 g of 2-octyldecan-1-ol (50.0 mmol) and 13.2 g of $PPh_3$ (50.5 mmol) were added under nitrogen atmosphere. The mixture was cooled to 0°C and 9.87 mL of diisopropylazadicarboxylate (50.4 mmol) were added dropwise. The temperature was slowly brougth to 20°C and the reaction was continued for 12 hours. 100 mL of water were added and the product was extracted with diethyl ether. The organic phase was dried over sodium sulfate, concentrated, and the solid residue was eluted on a silica gel column (heptane/ethyl acetate 99:1). 10.9 g of 2-(2-octyldecyl)benzotriazole (**4**) (yield=70%) were obtained.
$^1$**H-NMR** (400 MHz, CDCl3): δ 7.92 – 7.83 ppm (m, AA', 2H), 7.43 – 7.34 ppm (m, BB', 2H), 4.61 ppm (d, CH2, J = 6.9 Hz, 2H), 2.27 ppm (m, CH, 1H), 1.22 ppm (m, CH2, 28H), 0.88 ppm (t, $CH_3$ J = 6.7 Hz, 6H).
*4,7-Dibromo-2-(2-octyldecyl)benzotriazole (**5**).* 9.8 g of 2-(2-octyldecyl)benzotriazole (**4**) (26.4 mmol) suspended in 54 mL of 48% aqueous HBr, were stirred for 1 hour in a three-necked round bottom flask at 100°C. 2.7 mL of bromine (52.8 mmol) were added dropwise at 110°C. The mixture was left to react for 24 hours; 2 ml of $Br_2$ were added, and the reaction continued for another 36 hours. The mixture was cooled to room temperature, 100 mL of water were added and the product was extracted with diethyl ether. The organic phase was washed with aqueous sodium thiosulphate, then with water, dried over sodium sulfate, concentrated, and the solid residue was

eluted on a silica gel column (heptane/ethyl acetate 99:1). 9.5 g of 4,7-dibromo-2-(2-octyldecyl)benzotriazole (**5**) (yield=65%) were obtained.
**$^1$H-NMR** (400 MHz, CDCl3): δ 7.44 ppm (s,CH, 2H), 4.67ppm (d, CH2, J = 7.3 Hz, 2H), 2.34 ppm (m, CH, 1H), 1.23 ppm (m, CH2, 28H), 0.88 ppm (t, CH3, J = 6.7 Hz, 6H).

*4,7-(Dithien-2-yl)bromo-2-(2-octyldecyl)benzotriazole.* To a three-necked round bottom flask containing 9.5 g of 4,7-dibromo-2-(2-octyldecyl)benzotriazole (17.9 mmol) dissolved in 34 mL of anhydrous N,N-dimethylformamide, 14.0 g of 2-(tributystannyl)thiophene (37.6 mmol) were added under nitrogen atmosphere, followed by 256 mg of $Pd(PPh_3)_2Cl_2$ (0.35 mmol). The mixture was stirred for 10 hours at 80°C. After cooling and adding 100 ml of water, the product was extracted with diethyl ether, the organic phase was dried over sodium sulfate, concentrated, and the solid residue was eluted on a silica gel column (heptane/ethyl acetate 99:1). 8.4 g of 4,7-(dithien-2-yl)bromo-2-(2-octyldecyl)benzotriazole (yield=88%) were obtained.
**$^1$H-NMR** (400 MHz, CDCl3): δ 8.09 ppm (dd, CH, J = 3.8, 1.2 Hz, 2H), 7.63 ppm (s, CH, 2H), 7.39 ppm (dd, CH, J = 5.1, 1.1 Hz, 2H), 7.17 ppm (dd, CH, J = 5.1, 3.6 Hz, 2H), 4.74 ppm (d, J = 6.6 Hz, 2H), 2.30 ppm (m, CH, 1H), 1.46 – 1.15 ppm (m, CH2, 28H), 0.85 ppm (t, CH3, J = 6.9, 6H).

*4,7-Bis(5-bromothien-2-yl)bromo-2-(2-octyldecyl)benzotriazole (**6**).* To a three-necked round bottom flask containing 8.4 g of 4,7-(dithien-2-yl)bromo-2-(2-octyldecyl)benzotriazole (15.8 mmol) dissolved in 30 mL of anydrous THF, 5.6 g of N-bromosuccinimide (31.6 mmol) were added under nitrogen atmosphere. The mixture was stirred for 24 hours under dark. 100 ml of water were added and the product was extracted with diethyl ether. The organic phase was washed with a solution of sodium thiosulphate, then with water, dried over sodium sulfate and concentrated. The solid residue was eluted on a silica gel column (eluent: heptane). 9.8 g of 4,7-bis(5-bromothien-2-yl)bromo-2-(2-octyldecyl)benzotriazole (**6**) (yield=90%) were obtained.
**$^1$H-NMR** (400 MHz, CDCl3): δ 7.79 ppm (d, CH, J = 3.9 Hz, 2H), 7.54 ppm (s, CH, 2H), 7.13 ppm (d, CH, J = 4.0 Hz, 2H), 4.73 ppm (d, CH2, J = 6.5 Hz, 2H), 2.34 – 2.23 ppm (m, CH, 1H), 1.45 – 1.16 ppm (m, CH2, 28H), 0.86 ppm (t, CH3, J = 6.9, 6H).

*2-(1-Octylnonyl)benzotriazole (**7**).* To a three-necked round bottom flask containing 5.0 g of benzotriazole (42.0 mmol) dissolved in 100 mL of anhydrous THF, 12.8 g of 9-heptadecanol (50.0 mmol) and 13.2 g of $PPh_3$ (50.5 mmol) were added under nitrogen atmosphere. The mixture was cooled to 0°C and 9.87 mL of diisopropylazadicarboxylate (50.4 mmol) were added dropwise. The temperature was slowly brought to 20°C and the reaction was continued for 12 hours. 100 mL of water were added and the product was extracted with diethyl ether. The organic phase was dried over sodium sulfate, concentrated, and the solid residue was eluted on a silica gel column (heptane/ethyl acetate 99:1). 10.4 g of 2-(1-octylnonyl)benzotriazole (**7**) (yield=70%) were obtained.
**$^1$H-NMR** (400 MHz, CDCl3): 7.91-7.85 ppm (m, AA', 2H), 7.40-7.34 ppm(m, BB',2H), 4.80 ppm (m, CH, 1H), 2.15 ppm (m, CH2, 2H), 1.93 ppm (m, CH2, 2H), 1.18 ppm (m, CH2, 24H), 0.84 ppm (t, CH3, 6H).

*4,7-Dibromo-2-(1-octylnonyl)benzotriazole (**8**).* 9.4 g of 2-(1-octylnonyl)benzotriazole (**7**) (26.4 mmol) suspended in 54 mL of 48% aqueous HBr, were stirred for 1 hour in a three-necked round bottom flask at 100°C. 2.7 mL of bromine (52.8 mmol) were added dropwise at 110°C. The mixture was left to react for 24 hours; 2 ml of $Br_2$ were added, and the reaction continued for another 36 hours. The mixture was cooled to room temperature, 100 mL of water were added and the product was extracted with diethyl ether. The organic phase was washed with aqueous sodium thiosulphate, then with water, dried over sodium sulfate, concentrated, and the solid residue was eluted on a silica gel column (heptane/ethyl acetate 99:1). 8.9 g of 4,7-dibromo-2-(1-octylnonyl)benzotriazole (**8**) (yield=65%) were obtained.

$^1$**H-NMR** (400 MHz, CDCl3): 7.43 ppm (s, 2H), 4.88 ppm (m, CH, 1H), 2.18 ppm (m, CH2, 2H), 1.95 ppm (m, CH2, 2H), 1.20 ppm (m, CH2, 24H), 0.85 ppm (t, CH3, 6H).

*2-(Trimethylstannyl)-4,8-di(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene*. To a three-necked round bottom flask containing 4.0 g of 4,8-di(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene (9.0 mmol) dissolved in 100 mL of anhydrous THF at -78°C, 5.6 mL of 1.6M n-BuLi in hexane (9.0 mmol) were added dropwise under argon. The mixture was left to react 0.5 hours at -78°C, 0.5 hours at 0°C and cooled again at -78°C. 13.5 mL of trimethyltinchloride (13.5 mmol) were added dropwise under gentle stirring. The temperature was slowly brougth to 20°C and the reaction was continued for 16 hours. 100 mL of water were slowly added and the product was extracted with diethyl ether. The organic phase was dried over sodium sulfate, concentrated, and the solid residue was used without further purification.

$^1$**H-NMR** (400 MHz, CD2Cl2): δ 7.52 ppm (s, CH, 1H), 7.45-7.36 ppm (AB, CH, 1H, J =5.6 Hz), 7.64 – 7.16 ppm (AB, 1H, JAB = 5.6 Hz), 4.17 ppm (d, CH2, 2H, J=5.4), 4.16 ppm (d, CH2, 2H, J=5.3), 1.91 – 1.52 ppm (m, CH2, 10H), 1.48-1.30 ppm (m, CH2, 8 H), 1.01 ppm (t, CH3, 3H, J=7.5 Hz), 1.00 ppm (t, CH3, 3H, J= 7.5 Hz), 0.93 ppm (t, CH3, 3H, *J* = 6.7 Hz), 0.92 ppm (t, CH3, 3H, J= 6.6 Hz), 0.43 ppm (s, Sn-CH3, 9H).

*4,7-Bis-(4,8-di(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophen-2-yl)-2-(1-octylnonyl)benzotriazole (**9**)*. To a three-necked round bottom flask containing 15.1 g of 4,7-dibromo-2-(1-octylnonyl)benzotriazole (**8**) (2.9 mmol) dissolved in 10 mL of anhydrous DMF, 3.75 g of 2-(trimethylstannyl)-4,8-di(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene (6.1 mmol) and 41 mg of $Pd(PPh_3)_2Cl_2$ (0.058 mmol) were added under nitrogen atmosphere. The mixture was heated at 80°C for 6 hours. After cooling at room temperature, 100 mL of water were added and the product was extracted with diethyl ether. The organic phase was dried over sodium sulfate, concentrated, and the solid residue was purified by flash chromatography (heptane/dicloromethane 99:1). 2.99 g of *4,7-bis-(4,8-di(2*-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophen-2-yl)-2-(1-octylnonyl)benzotriazole (**9**) (yield=82%) were obtained.

$^1$**H-NMR** (400 MHz, CD2Cl2): δ 8.83 ppm (s, CH, 2H), 7.78 ppm (s, CH, 2H), 7.64 – 7.16 ppm (AB, 4H, JAB =5.6 Hz), 5.01 ppm (m, CH, 1H), 4.42 – 4.31 ppm (m, OCH2, 4H), 4.31 – 4.22 ppm (m, OCH2, 4H), 2.35 ppm (m,CH2, 2H), 2.10 ppm (m, CH2, 2H), 1.98 – 1.56 ppm (m, CH2, 12H), 1.52 – 1.15 ppm (m, CH2, 32 H), 1.11 ppm (t, CH3, 6H, J=7.4 Hz), 1.08 ppm (t, CH3, 6H, J= 7 Hz), 0.99 ppm (t, CH3, 6H, *J* = 7 Hz), 0.96 ppm (t, CH3, 6H, J= 7 Hz), 0.79 ppm (t, CH3, 6H, J = 6.7 Hz).

*Poly{[2-(2-hexyldecyl)benzotriazole]-alt-[5,5-(4',7'-bis(4-hexylthien-2-yl)-2',1',3'-benzothiadiazole)]} (**P1**)*. 519 mg of 4,7-bis(5-bromo-3-hexylthien-2-yl)-2-(2-hexyldecyl)benzotriazole (**3**) (0.62 mmol) and 242 mg of 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)- 2,1,3-benzothiadiazole (0.62 mmol) were added under nitrogen atmosphere to a three-necked round bottom flask equipped with a mechanical stirrer containing 6 mL of deareated toluene, 2 mL of n-propanol 5 drops of Aliquat 336 and 1 mL of 4M $K_2CO_3$. The mixture is heated at 70°C and 7 mg of $Pd(PPh_3)_4$ (0.006 mmol) were added. The mixture is heated at 70°C for 40 hours. 14 mg of (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene and the heating was continued for 6 hours. 0.5 mL of bromobenzene were added and the heating was continued for 4 hours. After cooling to room temperature, the mixture is concentrated under vacuum and poured into 250 mL of methanol; the precipitate is collected, washed with water and methanol, and dissolved in 500 mL of chloroform. 400 ml of 30% aqueous $NH_3$ were added to the solution, and the mixture was refluxed for 3 hours under vigorous stirring. The organic phase was separated, 900 g of EDTA were added and the mixture was stirred overnight. The solution was extracted with water, concentrated to small volume and added to an excess of methanol. The solid was filtered and dried under vacumm at 50°C. 350 g of a red polymer (**P1**) were obtained. Mw=13800 Da, Mw/Mn=1.84.

*Poly{[2-(2-octyldecyl)benzotriazole]-alt-[5,5-(4',7'-di-2-thienyl)-2',1',3'-benzothiadiazole)]}* (***P2***). 1.234 g of 4,7-bis(5-bromothien-2-yl)bromo-2-(2-octyldecyl)benzotriazole (**6**) (1.78 mmol) and 691 mg of 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)- 2,1,3-benzothiadiazole (1.78 mmol) were added under nitrogen atmosphere to a three-necked round bottom flask equipped with a mechanical stirrer containing 4 mL of deareated toluene, 2 mL of n-propanol 10 drops of Aliquat 336 and 2 mL of 4M $K_2CO_3$. The mixture is heated at 70°C and 13.4 mg of $Pd(PPh_3)_4$ (0.011 mmol) were added. The mixture is heated at 70°C for 40 hours. 96 mg of (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene and the heating was continued for 6 hours. 1 mL of bromobenzene was added and the heating was continued for 4 hours. After cooling to room temperature, the mixture is concentrated under vacuum, the solid is dissolved in a chloroform/chlorobenzene mxture and poured into 250 mL of methanol; the precipitate is collected, washed with water and methanol, and dissolved in 500 mL of chloroform. 400 ml of 30% aqueous $NH_3$ were added to the solution, and the mixture was refluxed for 3 hours under vigorous stirring. The organic phase was extracted with water and concentrated to dryness. The solid was dissolved in the minimum amount of chloroform/chlorobenzene and added to an excess of methanol. The solid was filtered and dried under vacumm at 50°C. 1.046 g of a dark-brown polymer (**P2**) were obtained. Mw=7000 Da, Mw/Mn=1.46.

*Poly{[2-(1-octylnonyl)benzotriazole]-alt-[2,2-(4',7'-bis[4,8-di(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophen-6-yl]-2',1',3'-benzothiadiazole)]}* (***P3***). 240 mg of 4,7-dibromo-2,1,3-benzothiadiazole (0.80 mmol), 1.01 g of 4,7-bis-(4,8-di(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophen-2-yl)-2-(1-octylnonyl)benzotriazole (**9**) (0.80 mmol), 200 mg of $CH_3COOK$ (2.1 mmol), 2 mg of $Pd(OCOCH_3)$ (0.008 mmol) were added under nitrogen atmosphere to a pyrex glass reactor equipped with a mechanical stirrer containing 10 mL of N,N-dimethylacetamide. The mixture is heated at 120°C for 48 hours. After cooling to room temperature, the solution is poured into methanol; the precipitate is collected and dissolved in 80 ml of chloroform. 80 ml of 30% aqueous $NH_3$ were added to the solution, and the mixture was refluxed for 4 hours under vigorous stirring. The organic phase was separated, extracted with water, concentrated to small volume and added to an excess of methanol. The precipitate was collected, extracted in a Soxhlet apparatus with methanol, heptane, and chloroform. The chloroform soluble fraction was concentrated and precipitated into methanol. The solid was filtered and dried under vacumm at 50°C. 383 g of a dark purple polymer (**P3**) were obtained. Mw=7200 Da, Mw/Mn=1.20.

*Poly{[4’-(4,8-di(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophen-2-yl)-2’,1’,3’-benzothiadiazole-6,7’-diyl]-co-[4’-(4,8-di(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophen-2-yl)-(1-octylnonyl)-benzotriazole-6,7’-diyl]}* (***P4***). 787 mg of 2,6-bis(trimethylstannyl)-4,8-di(2’-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene (1.02 mmol), 149 mg of 4,7-dibromo-2,1,3-benzothiadiazole (0.51 mmol), 262 mg of 4,7-dibromo-2-(1-octylnonyl)benzotriazole (**8**) (0.508 mmol) were added under nitrogen atmosphere to a three-necked round bottom flask equipped with a mechanical stirrer containing 5 mL of anhydrous toluene. The mixture is heated at 70°C and 11 mg of $Pd(PPh_3)_4$ (0.0095 mmol) were added. The mixture is heated at 70°C for 40 hours. 1 mL of bromobenzene was added and the heating was continued for 3 hours. 1 mL of 2-(tributystannyl)thiophene was added and the heating was continued for 3 hours. After cooling to room temperature, the viscous product is poured into methanol; the precipitate is collected and extracted in a Soxhlet apparatus with methanol, acetone and heptane. The solid residue was dissolved in 120 mL of chloroform. 120 mL of 30% aqueous $NH_3$ were added to the solution, and the mixture was refluxed for 4 hours under vigorous stirring. The organic phase was separated, extracted with water, concentrated to small volume and added to an excess of methanol. The precipitate was collected and dried under vacumm at 50°C. 601 g of a blue polymer (**P4**) were obtained. Mw=61300 Da, Mw/Mn=3.21.

## 3. Analytical methods and spectroscopical characterizations

1H-NMR spectra were recorded with a Bruker Avance 400 spectrometer (Bruker Corp., Madison, WI, USA). The low molecular weight compounds were dissolved in $CDCl_3$ or $CD_2Cl_2$ (reference: 7.26 ppm or 5.30 ppm, respectively); the polymers were dissolved in $C_2D_2Cl_2$ (reference: 6.00 ppm).

Molecular weight determinations were made using a Agilent 220 chromatograph (Agilent Technologies Inc., Santa Clara, CA, USA) equipped with a refractive index detector on 1,2,4-trichlorobenzene solutions at 80°C. Molecular weight calibration was performed using monodisperse polystyrene standards.

Electrochemical measurements were performed with an Autolab PGSTAT30 potentiostat/galvanostat (EcoChemie, The Netherlands) run by a PC with GPES software, in a one-compartment three-electrode cell in argon-purged acetonitrile with 0.1 M $Bu_4NBF_4$ as supporting electrolyte. A $CHCl_3$ solution 1mg/ml of the compound was coated on the Glassy Carbon working electrode (Amel Electrochemistry, Milano, Italy) having a surface of 0.071 $cm^2$. A platinum counterelectrode and an aqueous saturated calomel (SCE) reference electrode were used. The film formed on the electrode was analysed at a scan rate of 200 mV/s. The data (Figure S1, Table S1) have been referred to the $Fc^+/Fc$ redox couple (ferricenium/ferrocene), according to IUPAC [1].

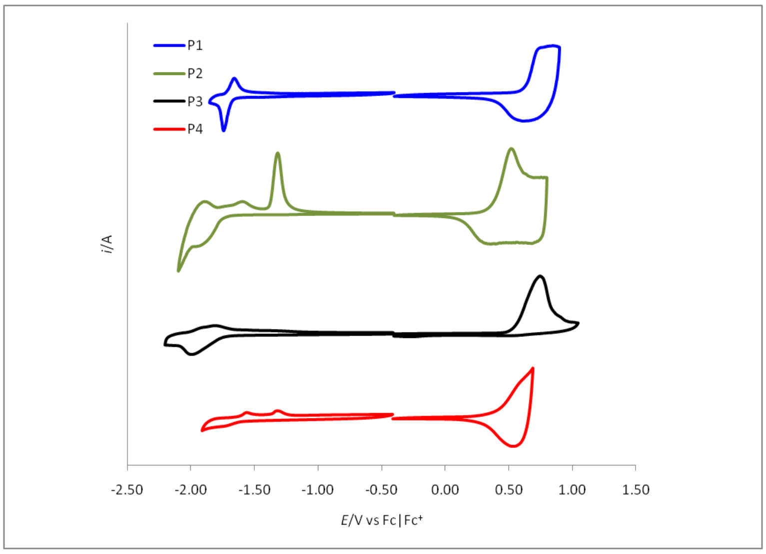


**Figure S1**. Cyclic voltammograms of polymers **P1**-**P4**.

TABLE S1. Oxidation and reduction potentials of **P1**-**P4** polymers.

| | $E_{onset}$ ox (V vs SCE) | $E_{onset}$ red (V vs SCE) | $E_{onset}$ ox (V vs Fc\|Fc$^+$) | $E_{onset}$ red (V vs Fc\|Fc$^+$) |
|---|---|---|---|---|
| **P1** | 0.99 | -1.25 | 0.59 | -1.65 |
| **P2** | 0.71 | -1.28 | 0.31 | -1.68 |
| **P3** | 0.92 | -1.30 | 0.51 | -1.71 |
| **P4** | 0.78 | -1.20 | 0.37 | -1.61 |

The HOMO and LUMO energies were calculated from the onsets of oxidation and reduction potentials according to the semiempirical equations [2]:
$E_{HOMO/LUMO} = [-e\ (E_{onset(vs.SCE)} - E_{onset(Fc/Fc+\ vs\ SCE)})]-4.8$ eV.

The PIA spectra were measured with a FTIR spectrometer (Bruker IFS66) in the MIR region. The fractional changes in transmission were measured at 80 ° K, in response to a 514 nm laser line incident on the sample, by the subsequent accumulation of scans with laser on and laser off for 4 sec, driven by a mechanical shutter. The samples were prepared by solution drop cast deposition on KBr windows. The film thickness were adjusted in order to obtain full absorbance at the laser excitation wavelength.

The UV-Vis absorption spectra were measured with a Perkin Elmer Lambda 9 spectrophotometer.

The Photoluminescence (PL) spectra were recorded with a flat field monochromator (270 M Spex) coupled to a $N_2$ cooled CCD detector (ISA Spectrum One), using excitation. The spectra were corrected for the instrument's response.

## 4. Solar cells devices fabrication and optimisation

### 4a. Device assembling

Typical sandwich geometry glass/ITO/PEDOT:PSS/active layer/cathode was used for the devices preparation. Each ITO-glass substrate, 15 Ω/☐, was washed in ultrasonic bath at 55 °C, sequentially with water, acetone and isopropanol. PEDOT:PSS was then spin coated (60 nm thick) and dried on a 100 °C hot plate for 5 min. The substrates were then inserted into a glove box where the device assembling was completed. The devices area were 0.06 $cm^2$ , as defined from the cathode electrodes, evaporated through a shadow mask in a vacuum chamber at a pressure of 2x10-6 mbar. The active layers were deposited by spin coating. To find the optimal deposition conditions for each copolymers, the copolymers and $PC_{71}BM$ were dissolved at different weight ratios in various solvents (chlorobenzene (CB), chloroform (CF), orthodichlorobenzene (oDCB)) ( see (4c). Different types of cathodes were used ( LiF/Al, Ca/Al, Al) ( see 4c).
The final optimised devices were prepared as follows. The copolymers and $PC_{71}BM$ were dissolved at 1 :3 weight ratio in CB, 24 mg/ml solute concentration. The solutions were stirred for 15 hours at 50 ° C, prior to spin coating deposition. For **P4** and **P3** based devices, the active layers were also prepared adding to the CB solution 2 % in volume of 1-chloronaphtalene (CN). The spin coater parameters were adjusted to obtain active layers with thicknesses in the range 70-80 nm. For P1:$PC_{71}BM$active layers, thermal annealing at 150 °C for 5 min on a hot plate was done. For P3:$PC_{71}BM$ and P4:$PC_{71}BM$ active layers, a mild thermal treatment of 90 °C for 5 min has been

done to remove the residual solvent. For the P2:$PC_{71}BM$ blend deposition, it was necessary to heat both, the solution and the substrates to 80 °C, due to a strong tendency to phase segregation.
After thermal annealing, the devices were completed by evaporating the following cathodes: Ca (15 nm)/Al (100 nm) for P1:$PC_{71}BM$ and P2:$PC_{71}BM$ devices, LiF (1.5 nm)/Al (100 nm) for P3:$PC_{71}BM$ devices and Al (100 nm) for P4:$PC_{71}BM$ devices.
The active film of devices prepared with the CN additive were also treated with ethanol prior to cathode deposition (i.e. EtOH is not in the solvent mixture), following the literature [3].

### 4b. Photovoltaic characterization.

The current density–voltage measurements were performed directly in the glove box where the solar cells were assembled, with a Keithley 2602 source meter, under AM1.5 G solar simulation ( ABET 2000). The incident power, measured with a calibrated (SI cell+ KG5 filter), was 100 mW/cm$^2$.

The EQE spectral responses were recorded by dispersing a Xe lamp through a monochromator, using a Si solar cell with calibrated spectral response to measure the incident light power intensity at each wavelength. The devices were taken outside the glove box for the EQE measurements, after mounting them on a sealed cell to avoid moisture and oxygen exposure.

### 4c. Device optimization

#### 1. P4:$PC_{71}BM$ – polymer/fullerene ratio

TABLE S2. Average photovoltaic parameters of P4:$PC_{71}BM$ solar cells with different blend ratio, from CB solvent, annealed 90 °C for 5 min, cathode LiF/Al, under illumination of standard AM1.5G 100 mW/cm$^2$

| blend ratio w:w | Voc (V) | FF | Jsc (mA/cm²) | PCE (%) |
|---|---|---|---|---|
| 1:2 | 0.87 | 0.55 | 4.28 | 2.05 |
| 1:3 | 0.86 | 0.6 | 4.57 | 2.36 |
| 1:4 | 0.85 | 0.61 | 4.34 | 2.25 |

#### 2. P4:$PC_{71}BM$ – cathode

TABLE S3. Average photovoltaic parameters of P4:$PC_{71}BM$, 1:3 w:w, solar cells with different cathodes type, from CB solvent, annealed 90 °C for 5 min, under illumination of standard AM1.5G 100 mW/cm$^2$

| cathode type | Voc (V) | FF | Jsc (mA/cm²) | PCE (%) |
|---|---|---|---|---|
| Ca/Al | 0.86 | 0.6 | 4.32 | 2.23 |
| LiF/Al | 0.86 | 0.6 | 4.57 | 2.36 |
| Al | 0.87 | 0.61 | 4.95 | 2.63 |

### 3. P4:PC$_{71}$BM – solvent

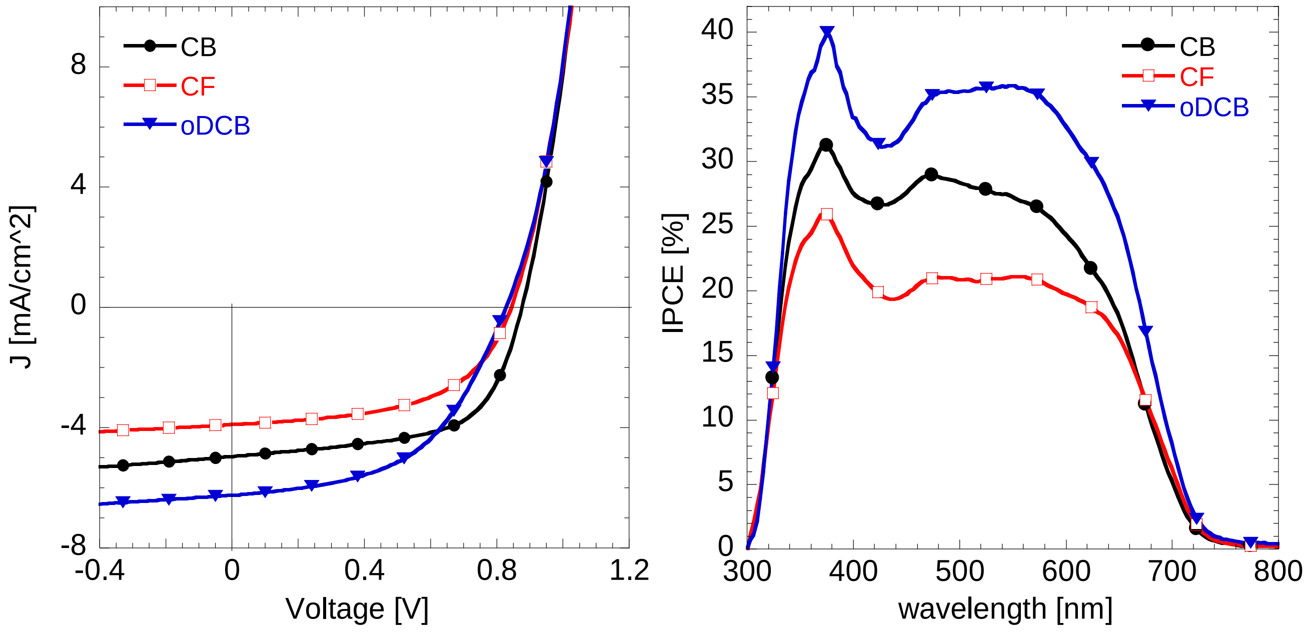


**Figure S2**. J-V (left) and EQE (right) characteristics of P4:PC$_{71}$BM, 1:3 w:w, from chlorobenzene (CB), chloroform (CF) and orthodichlorobenzene (oDCB) solvent, annealed 90 °C for 5 min, cathode Al, under illumination of standard AM1.5G 100 mW/cm$^2$

TABLE S4. Average photovoltaic parameters of P4:PC$_{71}$BM solar cells, presented on figure S2.

| solvent | Voc (V) | FF | Jsc (mA/cm²) | PCE (%) |
|---|---|---|---|---|
| CB | 0.87 | 0.61 | 4.95 | 2.63 |
| CF | 0.84 | 0.55 | 3.87 | 1.79 |
| oDCB | 0.83 | 0.51 | 6.23 | 2.64 |

## 4. P4:$PC_{71}$BM – CN additive & post deposition surface treatment with ethanol

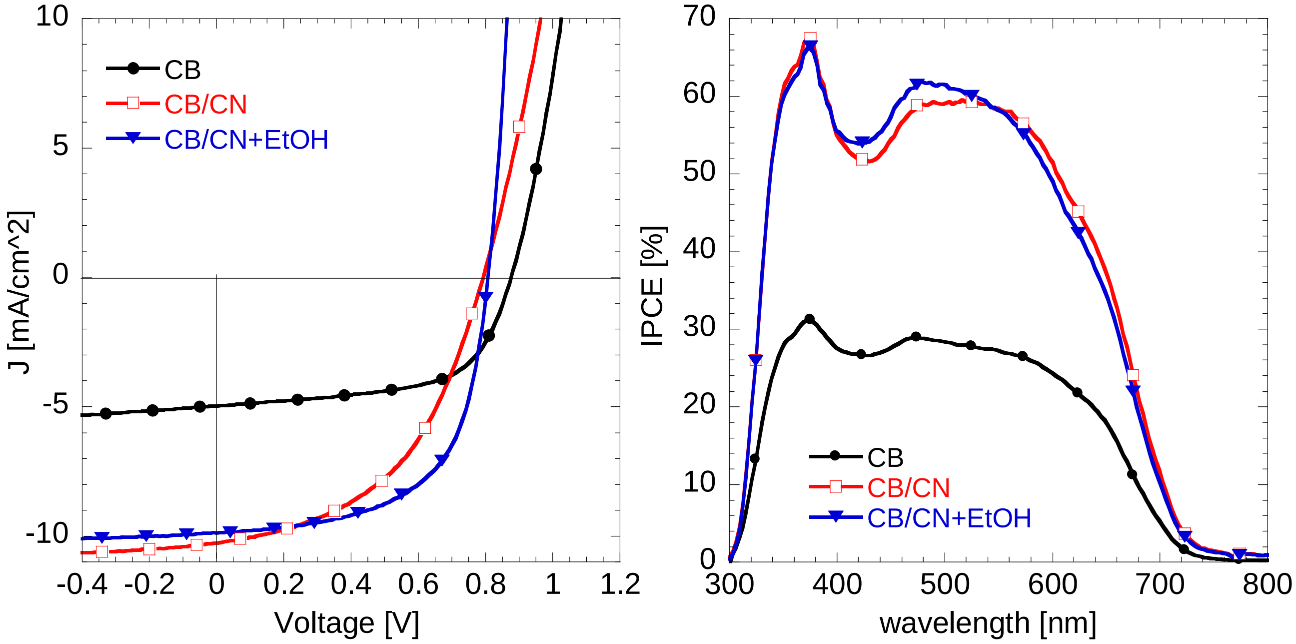


**Figure S3**. J-V (left) and EQE (right) characteristics of P4:$PC_{71}$BM, 1:3 from CB, CB/CN (98%/2% v/v) and CB/CN (98%/2% v/v)+post deposition surface treatment with EtOH, annealed 90 °C for 5 min, cathode Al, under illumination of standard AM1.5G 100 mW/$cm^2$

TABLE S5. Average photovoltaic parameters of P4:$PC_{71}$BM solar cells, presented on figure S3.

| solvent | Voc (V) | FF | Jsc (mA/cm²) | PCE (%) |
|---|---|---|---|---|
| CB | 0.87 | 0.61 | 4.96 | 2.63 |
| CB/CN | 0.79 | 0.48 | 10.3 | 3.94 |
| CB/CN+EtOH | 0.81 | 0.6 | 10.2 | 5 |

The deposition of the active layer with a CN additive reduces phase segregation, being responsible for a doubling of the Jsc and EQE max and of some reduction of the FF. The FF factor, then recovers to the previous values after an EtOH treatment. Note that the active blend optical absorption and PL spectra prior and after EtOH treatments are identical. Therefore the changes of the FF with EtOH treatments are not related to a variation of the nano-morphology. As a result, the FF enhancement can be interpreted according to the literature, by an improvement of the anode and/or cathode contact [3].

## 5. P3:PC$_{71}$BM – CN additive & post deposition surface treatment with ethanol

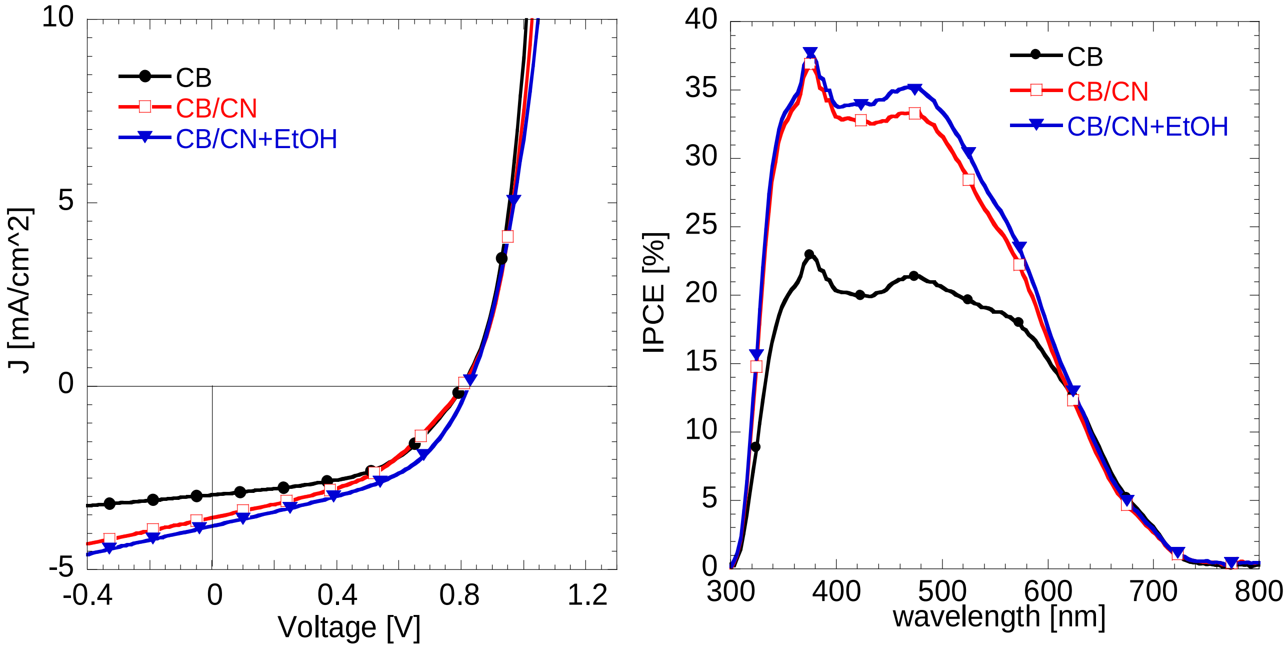


**Figure S4**. J-V (left) and EQE (right) characteristics of P3:PC$_{71}$BM, 1:3 from CB, CB/CN (98%/2% v/v) and CB/CN (98%/2% v/v)+post deposition surface treatment with EtOH, annealed 90 °C for 5 min, cathode LiF/Al, under illumination of standard AM1.5G 100 mW/cm$^2$

TABLE S6. Average photovoltaic parameters of P3:PC$_{71}$BM solar cells, presented on figure S4.

| solvent | Voc (V) | FF | Jsc (mA/cm²) | PCE (%) |
|---|---|---|---|---|
| CB | 0.8 | 0.50 | 2.94 | 1.23 |
| CB/CN | 0.8 | 0.43 | 3.57 | 1.27 |
| CB/CN+EtOH | 0.82 | 0.46 | 3.79 | 1.48 |

## 6. P2:PC$_{71}$BM vs P2:PC$_{61}$BM

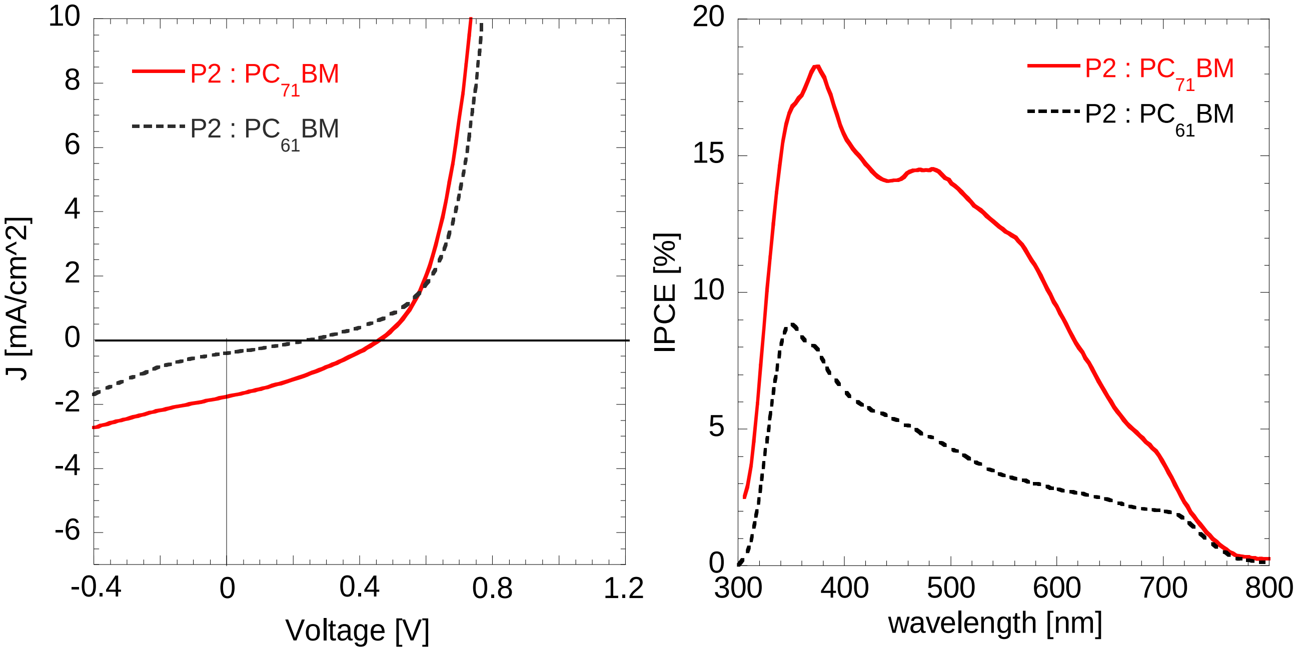
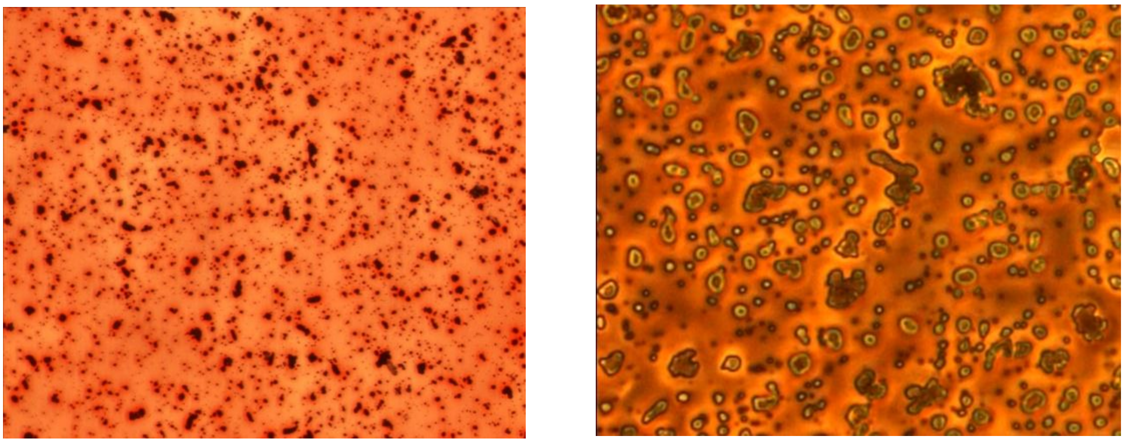


**Figure S5**. J-V (left) and EQE (right) characteristics of P2:PC$_{71}$BM (solid line) and P2:PC$_{61}$BM (dotted line), 1:3 from CB solvent, deposited on hot substrate (80 °C), cathode Ca/Al, under illumination of standard AM1.5G 100 mW/cm$^2$

TABLE S7. Photovoltaic parameters of P2:PC$_{71}$BM and P2:PC$_{61}$BM solar cells, presented on figure S5.

| sample | Voc (V) | FF | Jsc (mA/cm²) | PCE (%) |
|---|---|---|---|---|
| P2:PC$_{71}$BM | 0,46 | 0,32 | 1,76 | 0,26 |
| P2:PC$_{61}$BM | 0,25 | 0,27 | 0,41 | 0,03 |

Photo S1. Optical microscopy images of P2:PC$_{71}$BM (left) and P2:PC$_{61}$BM (right) film, from CB solvent.



## 7. P4:PC$_{61}$BM – polymer/fullerene ratio, CN additive & post deposition surface treatment with ethanol

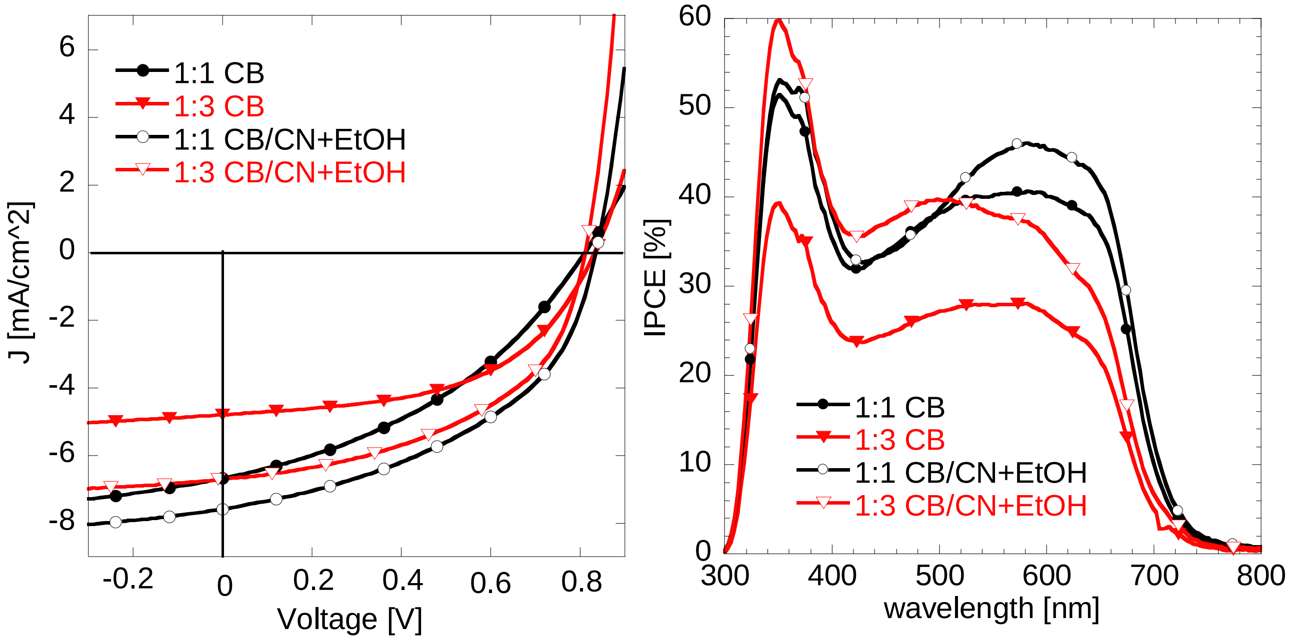


**Figure S6**. J-V (left) and EQE (right) characteristics of P4:PC$_{61}$BM, 1:1 and 1:3 w:w, from CB and CB/CN (98%/2% v/v)+post deposition surface treatment with EtOH, annealed 90 °C for 5 min, cathode Al, under illumination of standard AM1.5G 100 mW/cm$^2$

TABLE S8. Photovoltaic parameters of P4:PC$_{61}$BM, 1:1 and 1:3 solar cells, presented on figure S6.

| blend ratio w:w &solvent | Voc (V) | FF | Jsc (mA/cm²) | PCE (%) |
|---|---|---|---|---|
| 1:1 CB | 0.81 | 0.39 | 6.74 | 2.13 |
| 1:3 CB | 0.83 | 0.53 | 4.84 | 2.13 |
| 1:1 CB/CN+EtOH | 0.84 | 0.46 | 7.68 | 2.97 |
| 1:3 CB/CN+EtOH | 0.81 | 0.5 | 6.81 | 2.76 |

## 8. P1:PC$_{71}$BM – optimization

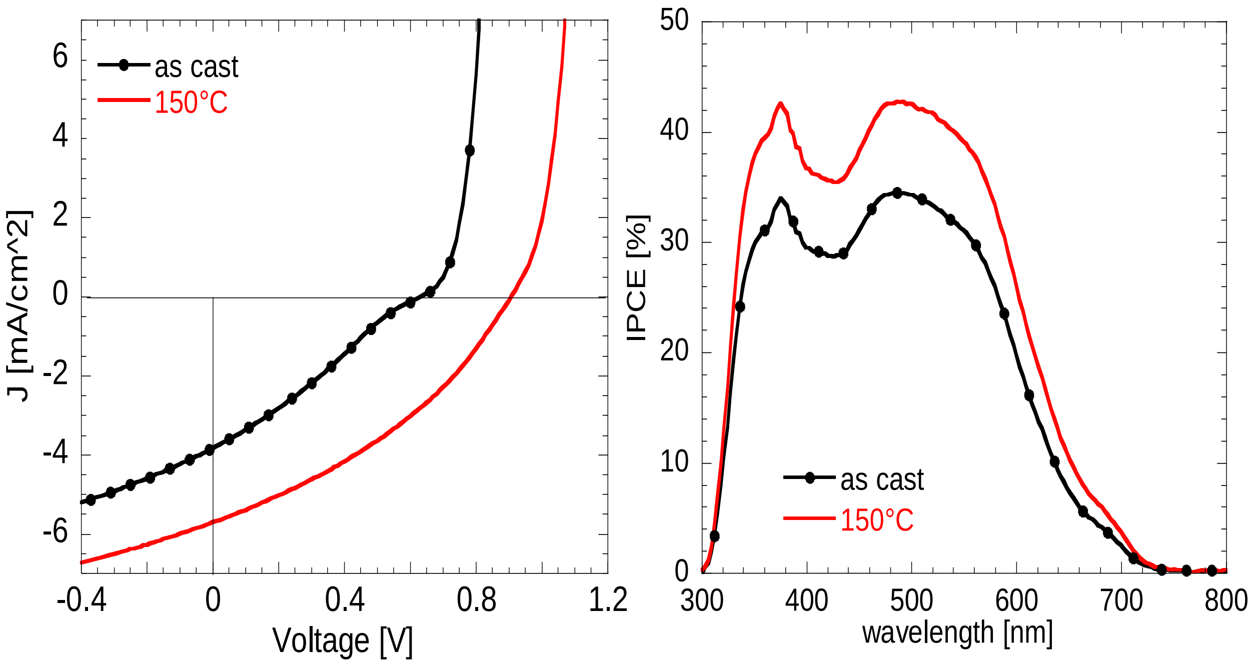


**Figure S7**. J-V (left) and EQE (right) characteristics of P1:PC$_{71}$BM 1:3 w:w, from CB solvent, as cast and annealed 150 °C for 5 min, cathode Ca/Al, under illumination of standard AM1.5G 100 mW/cm$^2$

TABLE S9. Photovoltaic parameters of P1:PC$_{71}$BM 1:3 w:w solar cells with different blend ratio, presented on figure S7.

| thermal treatment | Voc (V) | FF | Jsc (mA/cm²) | PCE (%) |
|---|---|---|---|---|
| as cast | 0.63 | 0.27 | 3.83 | 0.67 |
| 150°C | 0.91 | 0.35 | 5.70 | 1.88 |

## 9. P1:PC$_{61}$BM – polymer/fullerene ratio

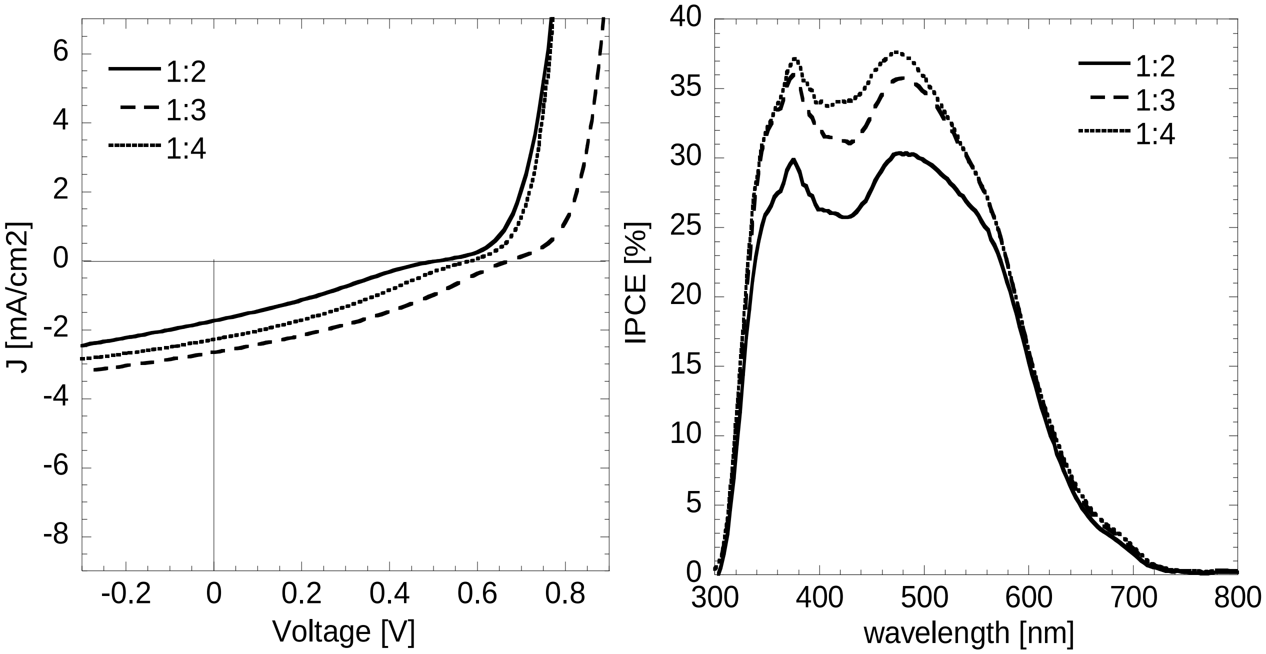


**Figure S8**. J-V (left) and EQE ( right) characteristics with different ratios of P1:PC$_{61}$BM from CB solvent, cathode LiF/Al, under illumination of standard AM1.5G 100 mW/cm$^2$

TABLE S10. Photovoltaic parameters of P1:PC$_{61}$BM solar cells with different blend ratio, presented on figure S8.

| blend ratio w:w | Voc (V) | FF | Jsc (mA/cm²) | PCE (%) |
|---|---|---|---|---|
| 1:2 | 0.51 | 0.27 | 1.83 | 0.25 |
| 1:3 | 0.67 | 0.33 | 2.79 | 0.62 |
| 1:4 | 0.73 | 0.33 | 3.03 | 0.73 |

*The J-V curve of solar cells based on P1 blends display an S-shape unlike P3 and P4 OPV devices is often interpreted by a non-optimal interface between the active material and the electrode. This probably correlates to relatively poorer film forming properties of P1blends, in particular with PC$_{61}$BM .*

## 5. SCLC hole mobility

In order to evaluate the copolymers hole transport properties under conditions that approach those of the operational solar cells, the dark current-voltage were measured in hole-only diodes, choosing suitable electrodes to block the electrons and measure the hole current. The hole transport through the device was modeled with a space charge limited current (SCLC) using a field dependent mobility [4]. The hole-only diodes were assembled with the following architecture: glass/ITO/PEDOT:PSS/polymer/Pd (10 nm)/Au (80 nm) [5].

To achieve a SCLC behavior in a polymer based diode, the polymer film should be thicker than 100-150 nm. Unfortunately it was not possible to obtain uniform polymer films of such thickness for copolymer P1. Therefore we focused on P3 and P4.

The dark current-voltage curves of copolymers P3 and P4, with film thicknesses respectively of 140 nm and 160nm, are reported in fig. S9a. It can be seen that a series of spikes are appearing in the curves and it is not possible to find a region of these curves with the typical SCLC $\propto V^2$ dependence. These spikes could possibly originate from the presence of pin-holes in the films that may disappear by increasing the thickness. While it was easy to prepare thicker P4 films, P3 does not show suitable film forming properties to make thicker films. The current-voltage characteristics of two diodes made with P4 films of different thicknesses are compared in fig. S9b. The current spikes are indeed disappearing in a thick films but, in any case, the curves do not follow the SCLC $\propto V^2$ dependence. Therefore, also for P4, it is not possible to assess the SCLC hole mobility.

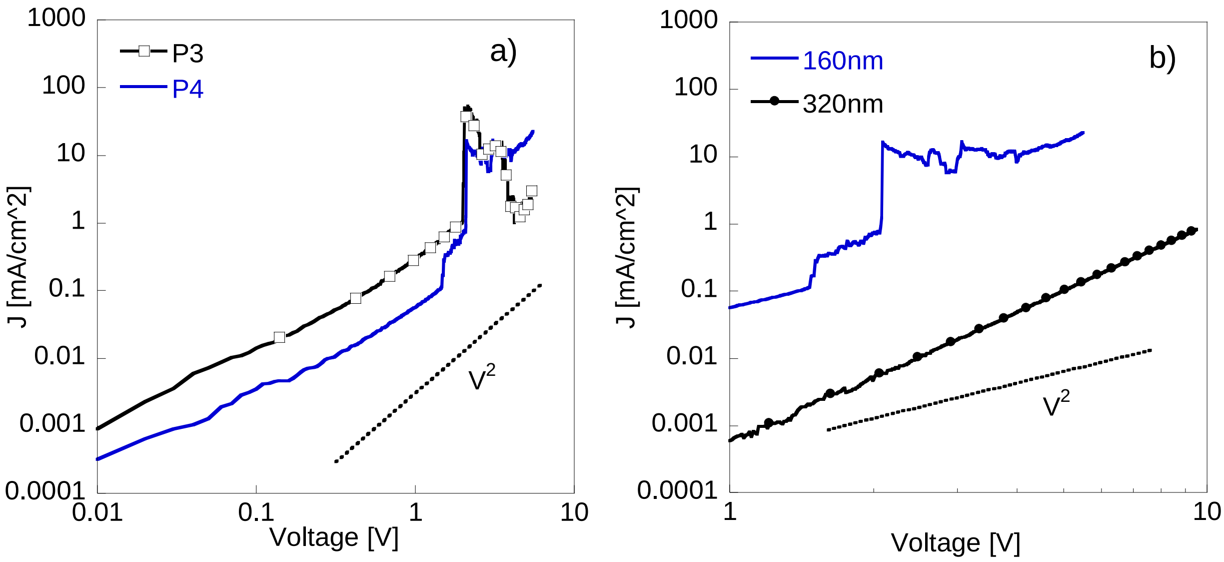


**Figure S9**. Dark J-V curves of hole only diodes; a) P3 (140 nm) and P4 (160 nm) films; b) P4 (160 nm) and P4 (320 nm ). The films are spin coated from chloroform solutions. Dotted lines : guideline for SCLC dependence

As a reference, we have also prepared an hole-only diode made with the same architecture, using a commercial OPV grade P3HT. From the current-voltage characteristics shown in fig. S10, an hole mobility of 3.6x10-8 $m^2$/Vs is found, which is in accordance to the literature [6].

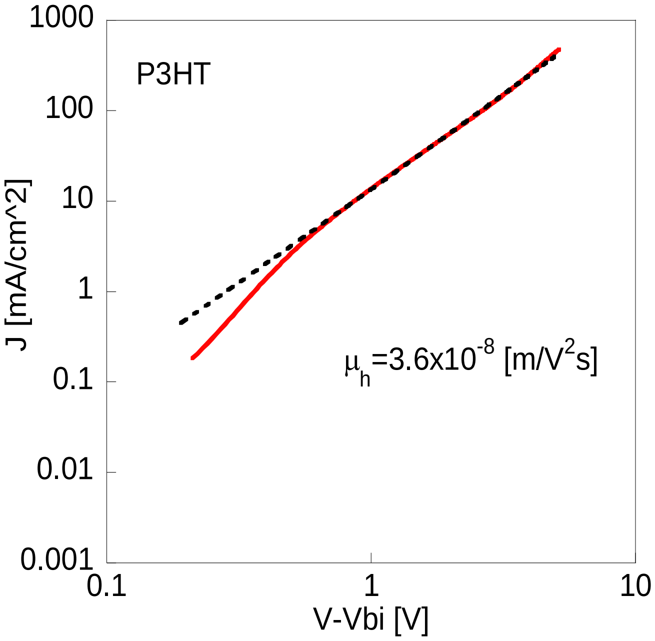
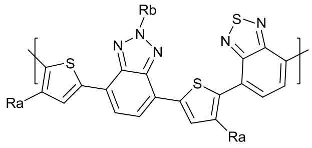
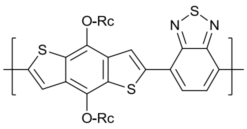


**Figure S10** Dark J-V curves of P3HT hole only diode (continuous line). The P3HT film (210 nm thick) is spin coated from chlorobenzene. Dotted line represents SCLC fit

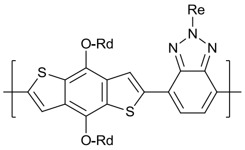
## 5. References



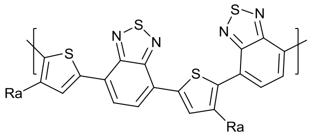
**L1** (R$_a$=H; R$_b$=dodecyl)[7]
**L2** (R$_a$=hexyl; R$_b$=dodecyl)[7]
**L3** (R$_a$=dodecyl; R$_b$=2-ethylhexyl)[8]



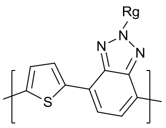
**L4** (R$_c$=dodecyl)[9]



**L5** (R$_d$=2-ethylhexyl; R$_e$=octyl)[10]
**L6** (R$_d$=2-ethylhexyl; R$_e$=1-octylnonyl)[10]



**L7** (R$_f$=dodecyl)[11]



**L8** (R$_g$=hexyl)[12]
**L9** (R$_g$=dodecyl)[12]

Chart S1. Chemical structure of selected polymers containing BDT, BT and/or BTz units reported in the literature

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