

## Supporting Information

### I. Synthetic procedures for F8T2Ox1

#### Materials and characterization methods

The palladium(0) tetrakis(triphenylphosphine) catalyst used in the polymerization reactions was purchased from Aldrich and handled under inert atmosphere. The tetraethylammonium hydroxide (Et<sub>4</sub>NOH) was purchased from Aldrich as aqueous solution (20 %). 3-(6-bromo-2-oxaheptyl)-3-methyloxetane was prepared according to reported procedures.<sup>1</sup> 2,7-dibromofluorene (**1**) and 5,5'-dibromo-2,2'-bithiophene (**6**) were purchased from Aldrich and used as received. All the solvents used for synthesis were purified according to standard methods and were degassed prior to use. All the reactions proceeded under inert atmosphere (N<sub>2</sub>). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian spectrometer (300 MHz and 75 MHz, respectively) in CDCl<sub>3</sub> with tetramethylsilane as internal reference. FT-IR spectra were recorded using a Mattson 1000 spectrophotometer, dispersing the samples in KBr. Average number-average (*M<sub>n</sub>*) and average weight-average (*M<sub>w</sub>*) molecular weights were estimated by gel permeation chromatography (GPC) in a Waters 51 chromatograph equipped with two Waters UltraStyragel columns (1000 Å-500 Å) in series and with two detectors (a Water 410 Differential Refractometer and a Scanning Fluorescence Detector) at a flux rate of 1 ml/min. GPC analyses were performed on filtered solutions (0.45 μm, Millipore Millex HV) of the copolymers in tetrahydrofuran (THF) and using polystyrene standards.

**9-octylfluorene (2)** To a solution of 10.18 g (60 mmol) of fluorene (Aldrich) in dry Et<sub>2</sub>O and 7.0 g of N,N,N',N'-tetramethyl-ethylenediamine (TMEDA), at -78 °C, under stirring, 41.5 ml of *n*-BuLi (1.6 M in hexanes, Aldrich) were added dropwise for 30 minutes, under N<sub>2</sub>. The mixture stirred for 1 hour at -78 °C and 11.59 g (60 mmol) of 1-bromo-octane (Aldrich) in 20 ml of Et<sub>2</sub>O were added dropwise. The mixture was allowed to stir overnight at room temperature and 40 ml of water were added. The phases were separated and the aqueous phase was extracted with Et<sub>2</sub>O. The organic extracts were collected, washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The pure product (colourless oil) was obtained by chromatography on silica using *n*-hexane as eluent. Yield: 99 %. Elemental analysis for C<sub>21</sub>H<sub>26</sub>: calc. (%) C 91.59; H 9.41; found C 91.20; H 9.00. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ (ppm): 7.76-7.74 (2H, d, *J* = 6.9 Hz); 7.52-7.50 (2H, d, *J* = 7.2 Hz); 7.38-7.25 (4H, m); 3.99-3.95 (1H, t, *J* = 5.7 Hz); 2.02-1.95 (2H, q, *J* = 6.9 Hz); 1.20 (12H, m); 0.88-0.83 (3H, t, *J* = 6.8 Hz); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 147.60; 141.06; 126.78; 126.74; 124.32; 119.73; 47.45; 33.06; 31.82; 29.95; 29.36; 29.27; 25.66; 22.62; 14.09.

**2,7-dibromo-9-octylfluorene (3)** 3.45 g (21.6 mmol) of Br<sub>2</sub> were added to a solution of 2.86 g (10.3 mmol) of 9-octylfluorene (**2**) in 24 ml of CHCl<sub>3</sub> containing 12 mg of Fe(0), under stirring, at 0 °C, protected from light. The solution was allowed to warm until room temperature and after stirring for 24 hours, an aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was added to eliminate non-reacted bromine. The aqueous phase was extracted with CHCl<sub>3</sub>. The organic extracts were collected, washed with water and dried over Na<sub>2</sub>SO<sub>4</sub>. Recrystallization in *n*-hexane yielded 3.51 g of pure product as white needles. Yield: 78 %. Elemental analysis for C<sub>21</sub>H<sub>24</sub>Br<sub>2</sub>: calc. (%) C 57.82; H 5.54; found C 58.02; H 6.02. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ (ppm): 7.62-7.47 (6H, m); 3.96-3.93 (1H, t, *J* = 5.7 Hz); 2.00-1.92 (2H, m); 1.20 (12H, m); 0.88-0.83 (3H, *J* = 5.8 Hz). <sup>13</sup>C NMR (75 MHz,

CDCl<sub>3</sub>): 149.25; 139.06; 130.18; 127.61; 121.13; 121.08; 47.45; 32.60; 31.78; 29.80; 29.27; 29.24; 25.33; 22.63; 14.10.

**2,7-dibromo-9-(methyl-4'-(6-(3-methyloxetan-3-yl)methoxy)hexyl)-9-octylfluorene**

**(4)** 1.74 g (4 mmol) of 2,7-dibromo-9-octylfluorene (**3**) were added to a solution of 9 ml of NaOH aq. (50 %) and 0.43 g (1.3 mmol) of tetrabutylammonium bromide, under stirring, at room temperature. The red suspension was heated to 60 °C for 15 minutes and 3-(6-bromo-2-oxahexyl)-3-methyloxetane (1.32 g, 5 mmol) was added drop wise. After stirring for 24 h at 60 °C, the product was extracted with a mixture of THF/Et<sub>2</sub>O (50:50, v/v) and the organic phase was washed with H<sub>2</sub>O until neutral pH, and dried over Na<sub>2</sub>SO<sub>4</sub>. After evaporating the solvent, an yellowish oil was obtained and this was submitted to chromatography on silica using Pet. Ether/EtOAc (7/3, v/v) as eluent yielding 4.35 g of pure product as a pale yellow oil. Yield: 88 %. Elemental analysis for C<sub>32</sub>H<sub>44</sub>Br<sub>2</sub>O<sub>2</sub>: calc. (%) C 61.94; H 7.15; found C 61.85; H 7.05. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ (ppm): 7.55-7.43 (6H, m); 4.48-4.46 (2H, d, *J* = 5.4 Hz); 4.34-4.32 (2H, d, *J* = 5.4 Hz); 3.41 (2H, s); 3.36-3.32 (2H, t, *J* = 6.6 Hz); 1.94-1.89 (4H, m); 1.42-1.04 (21H, br + 3H (1.27), s); 0.85-0.80 (3H, t, *J* = 7.1 Hz); 0.59 (2H, m). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 152.41; 139.02; 130.13; 126.08; 121.44; 121.12; 80.20; 75.97; 71.45; 55.60; 40.08; 39.80; 31.72; 29.80; 29.63; 29.35; 29.14; 29.11; 25.70; 23.55; 22.56; 21.34; 14.06.

**2,7-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-(methyl-4'-(6-(3-**

**methyloxetan-3-yl)methoxy)hexyl)-9-octylfluorene (5)** To a solution of 1.32 g (1.9 mmol) of 2,7-dibromo-9-(methyl-4'-(6-(3-methyloxetan-3-yl)methoxy)hexyl)-9-octylfluorene (**4**) in 15 ml of THF, under stirring, at -78 °C, 4.9 ml of *tert*-BuLi (1.7 M in pentane) were added drop wise, under N<sub>2</sub>. After 2 hours at -78 °C, the reddish suspension was warmed to 0 °C for 15 minutes and then it was cooled again to -78 °C. At this temperature, 1.44 g (7.6 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolan (Aldrich) were added under N<sub>2</sub> and the reaction was allowed to warm until room temperature and stirred for 24 hours. After this period, 10 ml of water were added and the phases were separated. The aqueous phase was extracted with Et<sub>2</sub>O and the organic phase was washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. After evaporating the solvent a viscous colourless oil was obtained which yielded a white solid (pure product) in *n*-pentane. Yield: 80 %. Elemental analysis for C<sub>44</sub>H<sub>68</sub>B<sub>2</sub>O<sub>6</sub>: calc. (%) C 73.95; H 9.59; found C 73.56; H 10.07. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ (ppm): 7.82-7.79 (2H, d, *J* = 7.5 Hz); 7.73-7.71 (2H, d, *J* = 7.5 Hz + 2H (7.73), s); 4.46-4.44 (2H, d, *J* = 5.7 Hz); 4.32-4.30 (2H, d, *J* = 5.7 Hz); 3.38 (2H, s); 3.32-3.28 (2H, t, *J* = 6.6 Hz); 2.02-1.97 (4H, m); 1.43-1.00 (21H, br, (1.27), s); 0.83-0.78 (3H, t, *J* = 7.1 Hz); 0.54 (2H, m). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 150.35; 143.88; 133.65; 128.82; 119.39; 83.72; 80.26; 76.00; 71.55; 55.12; 40.11; 39.81; 31.76; 29.91; 29.82; 29.43; 29.19; 29.13; 25.75; 24.92; 23.64; 23.53; 22.58; 21.34; 14.07.

**F8T2Ox1** The polymerization reaction was carried out in a refluxing toluene/aqueous Et<sub>4</sub>NOH (20%) medium (30 ml of toluene/15 ml of Et<sub>4</sub>NOH aq.) containing 2.4 mmol of (**6**), 2.4 mmol of (**5**), and a catalytic amount of Pd(PPh<sub>3</sub>)<sub>4</sub> (1-2 % mol), for 48 hours, in the dark, under N<sub>2</sub> and vigorous stirring. The polymer was precipitated by addition of the reaction mixture to 250 ml of methanol under stirring. The collected solid was dissolved in toluene and the solution was filtered and stirred with aqueous NaCN solution (1 %) overnight. The phases were separated; the organic phase was washed with water, concentrated by removing the solvent under reduced pressure and

precipitated again in methanol. The solid was collected, washed with methanol in a soxhlet extractor and dried overnight under vacuum. Yield: 64 %. Elemental analysis for  $C_{40}H_{42}O_2S_2$  calc. (%) C 77.63; H 8.02; S 11.60; found C 76.70; H 8.89; S 12.09.  $M_n = 7700$ ,  $M_w = 12000$ ,  $M_w/M_n = 1.6$ . IR (KBr pellet,  $cm^{-1}$ ): 2920 (CH<sub>2</sub>, CH<sub>3</sub>), 2850 (CH), 1465 (C=C), 1110 (C-O-C acyclic), 980 (C-O-C oxetane), 790 (C-S). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$ (ppm): 7.70-7.57 (6H, m); 7.34-7.23 (4H, m); 4.45-4.43 (2H, d,  $J = 5.7$  Hz); 4.31-4.29 (2H, d,  $J = 5.7$  Hz); 3.37 (2H, s) 3.32 (2H, br), 2.04 (4H, br); 1.39 (2H, m); 1.25 (3H, s); 1.10 (18H, br); 0.78 (5H, m); 0.69 (2H, m). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 151.70; 143.73; 140.32; 136.50; 132.94; 127.90; 124.65; 124.48; 123.72; 123.56; 120.23; 119.68; 80.20; 75.95; 71.51; 55.30; 40.41; 39.79; 31.78; 31.42; 29.95; 29.78; 29.69; 29.38; 29.20; 25.71; 23.71; 22.60; 21.32; 14.07.

## References

1 – Motoi, M.; Suda, H.; Shimamura, K.; Nagahara, S.; Takei, M.; Kanoh, S. Bull. Chem. Soc. Jpn. 1988, **61**, 1653.

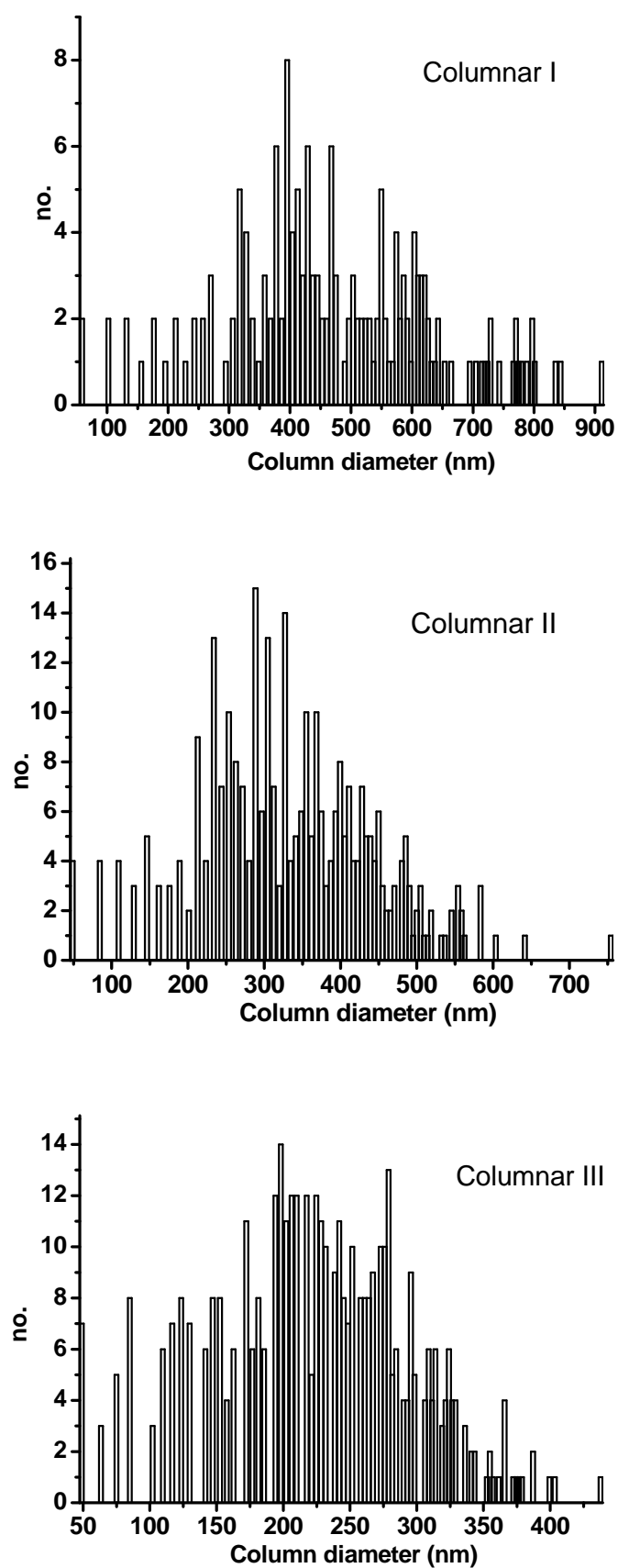


Figure I. Histograms of column diameters obtained from AFM imaging of “Columnar I” (a), “Columnar II” (b), and “Columnar-III” (c) films of r-F8T2Ox1.

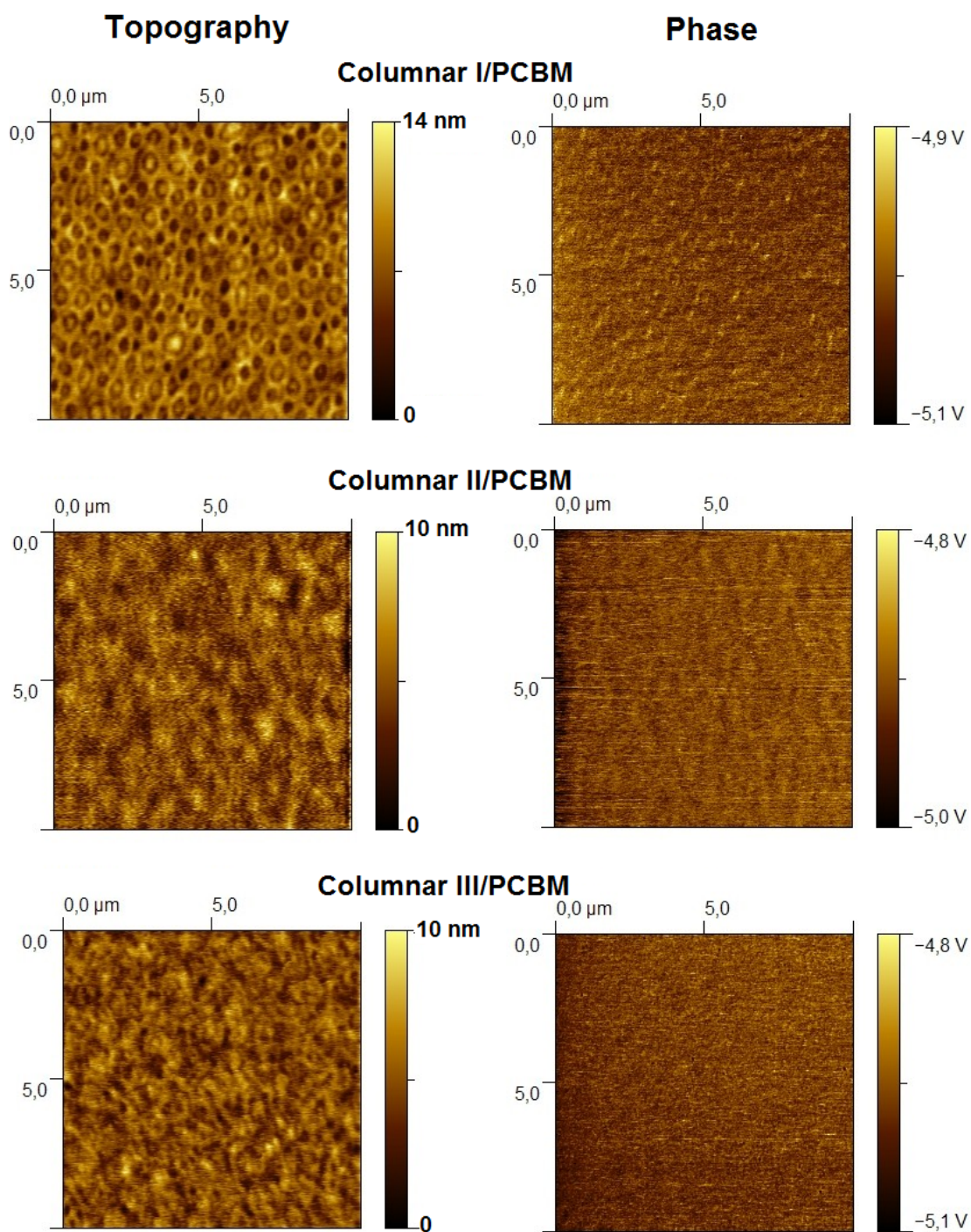


Figure II. AFM topography and phase images ( $10 \mu\text{m} \times 10 \mu\text{m}$ ) of the composite films Columnar I/PCBM, Columnar II/PCBM, and Columnar III/PCBM evidencing that one single material (PCBM) is present at the surface.



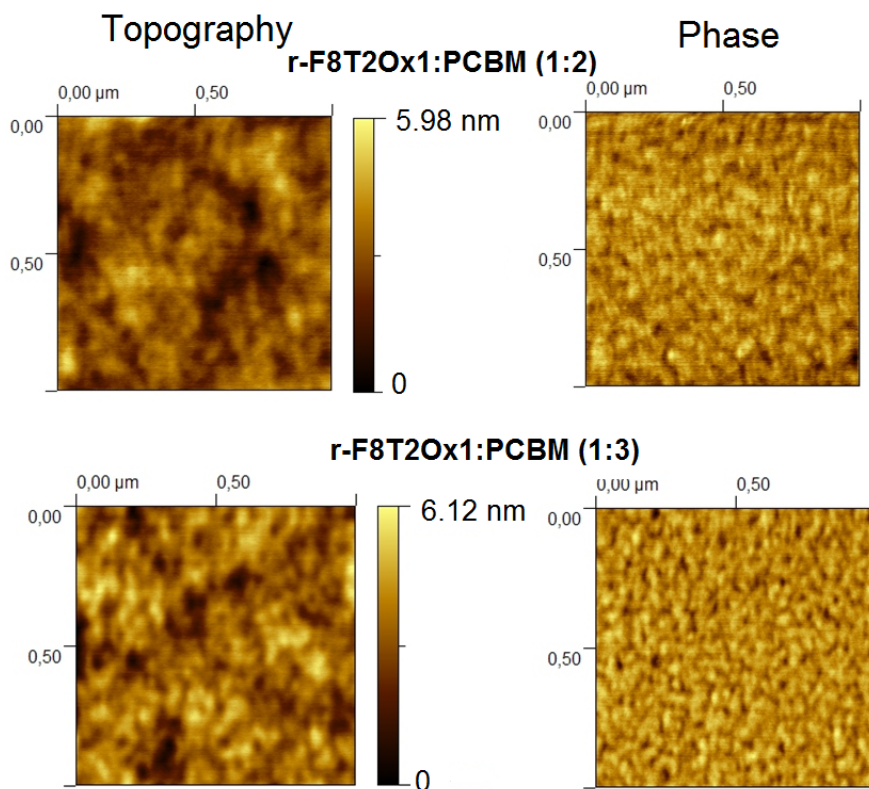


Figure III. AFM topography and phase images ( $1 \mu\text{m} \times 1 \mu\text{m}$ ) of the films prepared from 1:2 and 1:3 r-F8T2Ox1:PCBM blends (% wt) ( $R_{\text{rms}}$  for the film of 1:2 blend is 0.774 nm and for the film of 1:3 blend is 0.872 nm).