Supplementary Information

Design and Synthesis of novel N-substituted perylene diimide based low band gap polymers for organic photovoltaic application

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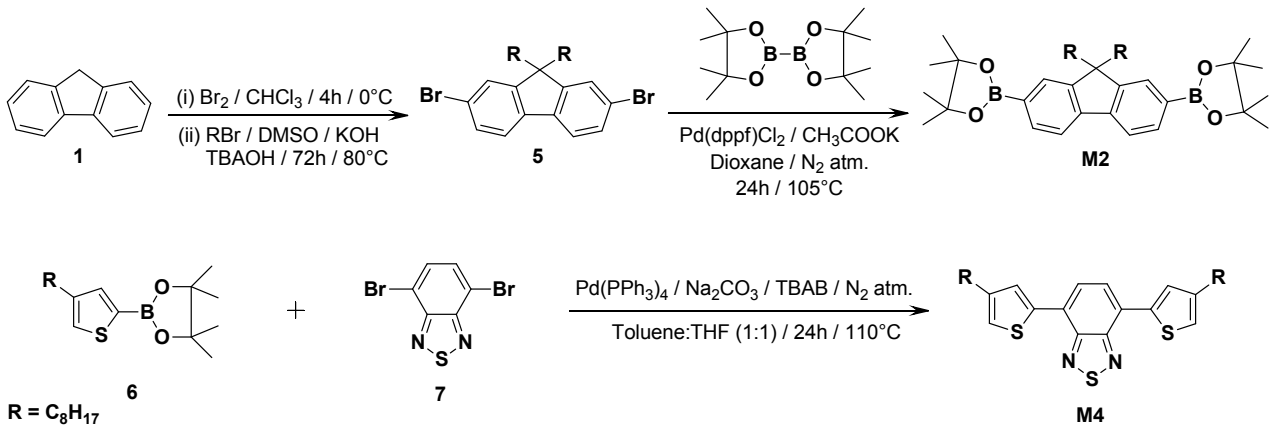
Contents

1. Synthesis of 2,2′-(9,9-Dioctyl-9H-fluoren-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (M2). Bromination of **1** (2.0 g, 12.03 mmol) in presence of bromine (1.48 mL, 27.67 mmol; added dropwise at 0 °C) with 10 mL of chloroform at room temperature for overnight stirring in dark was resulted in dibromo fluorene. This was alkylated with n-octyl bromide (5.36 mL, 30.0 mmol) in DMSO (40 mL) using tetrabutylammonium hydroxide (0.09 g) and KOH (5.49 g dissolved in 5.5 mL of distilled water) at 80 °C for 72 h yielded in 2,7-dibromo-9,9-dioctyl-9*H*-fluorene **5** (5.26 g, 80%). A mixture of **5** (2.0 g, 3.64 mmol), bis(pinacolato)diboron (2.14 g, 8.40 mmol), potassium acetate (2.14 g, 21.84 mmol) and Pd(dppf)Cl_2 (0.05 g, 0.06 mmol) were dissolved in dry 1,4-dioxane (20 mL, 3.64 mmol) under N_2 atmosphere for 36 h at 105 °C with continuous stirring. The reaction was monitored using TLC with 2% ethyl acetate in hexane. The reaction was cooled to room temperature and the crude product was extracted with ethyl acetate, washed with 2 × 30 mL of distilled water and dried over anhydrous Na_2SO_4. The solvent was evaporated and residue was purified using column chromatography over silica gel with 3.5% ethyl acetate in hexane as the eluent to isolate **M2** as a creamy white solid. Yield: 1.71 g, 70%. Anal. Calc. for $C_{41}H_{64}B_2O_4$: C, 76.64%; H, 10.04%. Found: C, 76.55%; H, 9.96%. ^{1}H NMR (400.13 MHz, $CDCl_3$, 25 °C *vs* TMS) δ: 7.81(d, 2H, J = 7.6 Hz), 7.75(s, 2H), 7.72(d, 2H, J = 7.6 Hz), 2.00(t, 4H, J = 6.8 Hz), 1.39(s, 24H), 1.18-1.01(m, 20H), 0.81(t, 6H, J = 7.2 Hz), 0.55(m, 4H). ^{13}C NMR (100.61 MHz, $CDCl_3$, 25 °C *vs* TMS) δ: 150.4, 143.8, 133.6, 128.8, 119.3, 83.6, 55.1, 40.0, 31.7, 29.8, 29.2, 29.1, 24.9, 23.5, 22.5, 14.0.

***2*. Synthesis of 4,7-bis(4-octylthiophen-2-yl)benzo[c]-1,2,5-thiadiazole (M4).**

7 (1.0 g, 3.40 mmol) and **6** (3.29 g, 10.20 mmol) were dissolved in a mixture of toluene and THF under N_2 atmosphere followed by the addition of sodium carbonate (1.08 g dissolved in 2 mL of distilled water) and tetrabutylammonium hydroxide (0.1 g). After purging the reaction mixture with N_2 for another 20 minutes, Pd(PPh_3)$_4$ (0.18 g, 0.16 mmol)

was added. The reaction was carried out for 24 h at 110 °C. The reaction was monitored using TLC with 2% ethyl acetate in hexane. The reaction was cooled to room temperature and the crude product was extracted with chloroform, washed with 30 mL of distilled water and dried over anhydrous Na_2SO_4. The solvent was evaporated and residue was purified using column chromatography over silica gel with 2.5% ethyl acetate in hexane as the eluent to obtain **M4** as a bright orange solid. Yield: 1.43 g, 80%. Anal. Calc. for $C_{30}H_{40}N_2S_3$: C, 68.65%; H, 7.68%; N, 5.34%. Found: C, 68.56%; H, 7.59%; N, 5.25%. ^{1}H NMR (400.13 MHz, $CDCl_3$, 25 °C *vs* TMS) δ: 7.97(s, 2H), 7.80(s, 2H), 7.04(s, 2H), 2.69(t, 4H, J = 7.6 Hz), 1.71(quint, 4H, J = 7.6 Hz), 1.41-1.29(m, 20H), 0.89(t, 6H, J = 6.9 Hz). ^{13}C NMR (100.61 MHz, $CDCl_3$, 25 °C *vs* TMS) δ: 152.4, 144.2, 138.9, 128.9, 125.8, 125.3, 121.4, 31.8, 30.6, 30.4, 29.4, 29.3, 29.2, 22.6, 14.1.



Scheme S1 Synthesis of Monomers **M2** and **M4.**

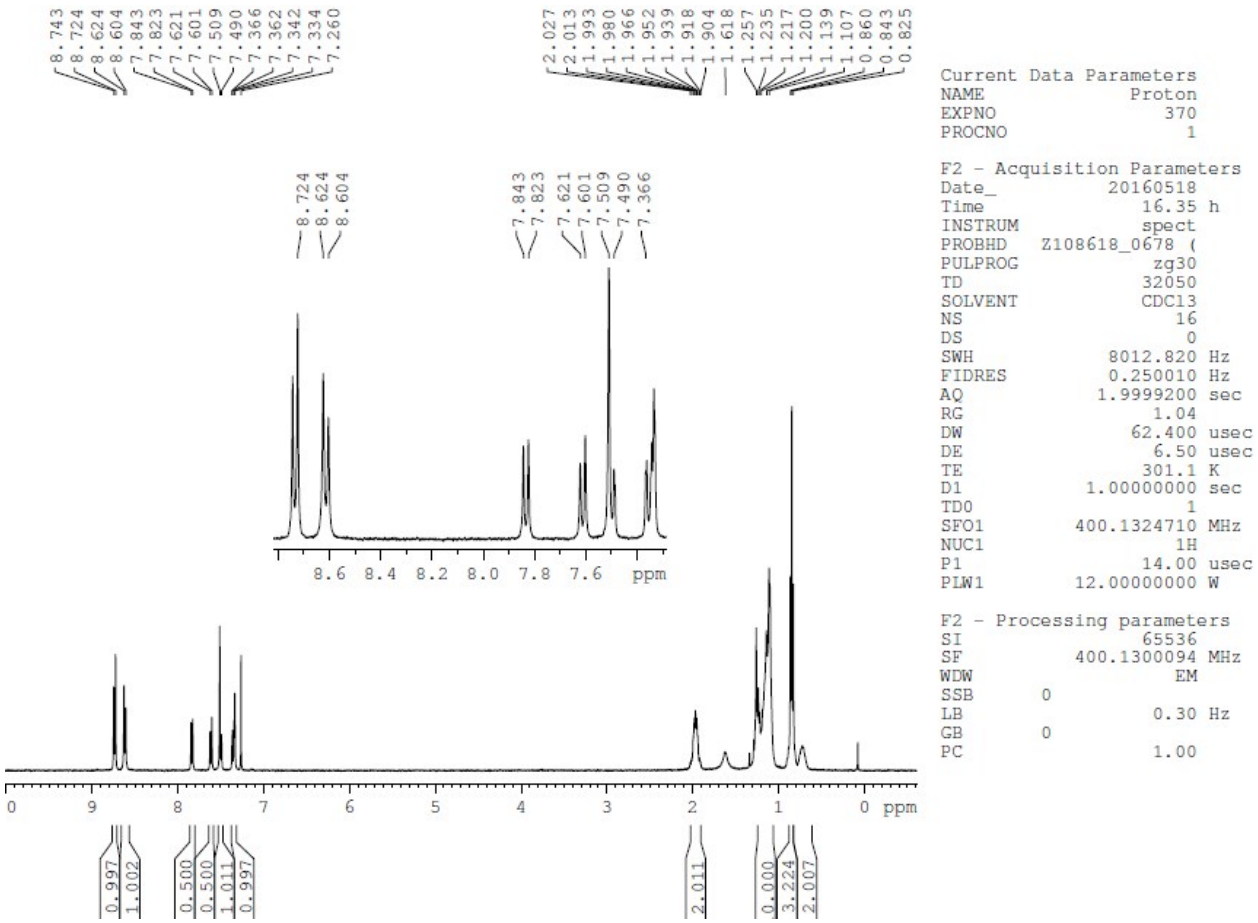


Fig. S1 ^{1}H NMR spectrum of **M1**

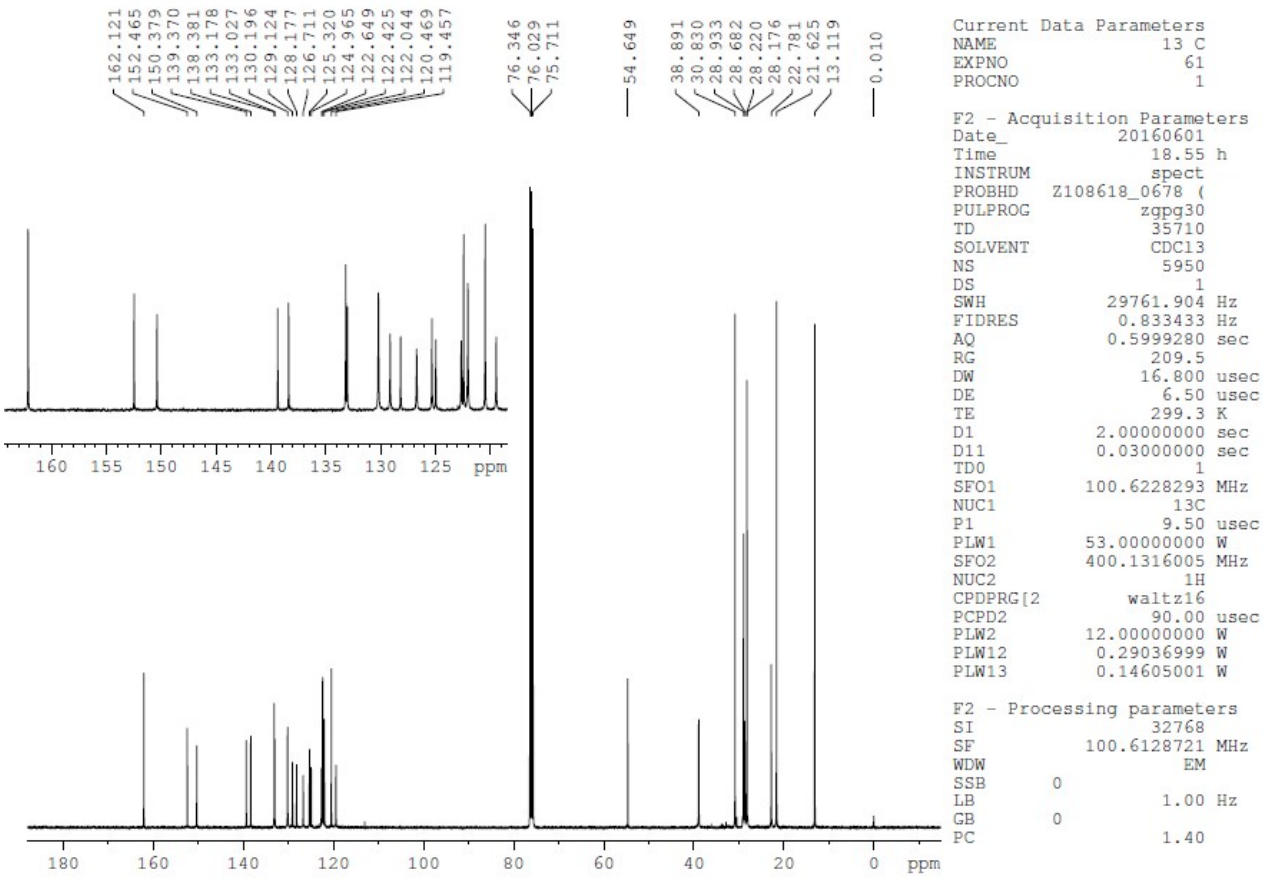


Fig. S2 ^{13}C NMR spectrum of **M1**

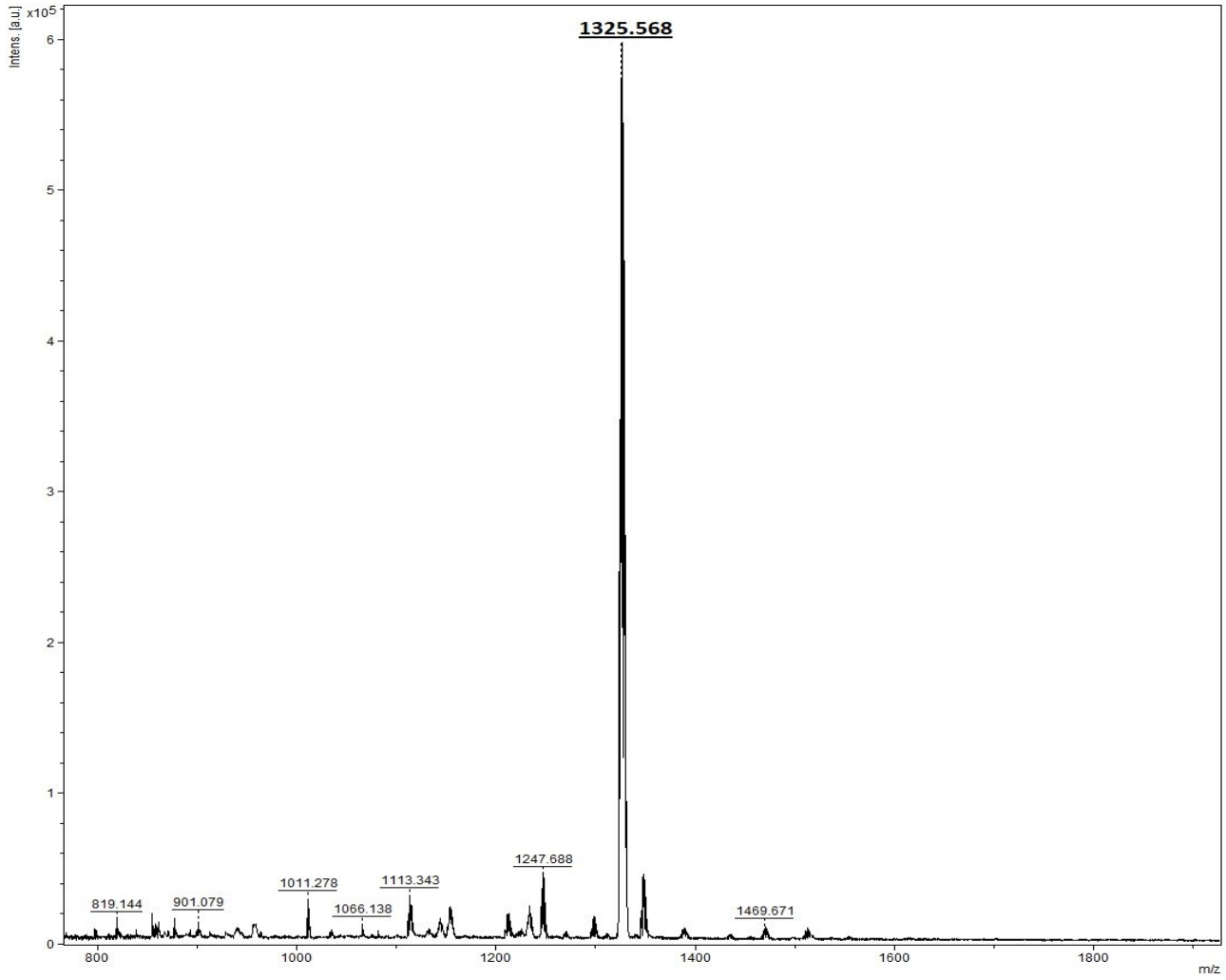


Fig. S3 MALDI-TOF MS spectrum of **M1**

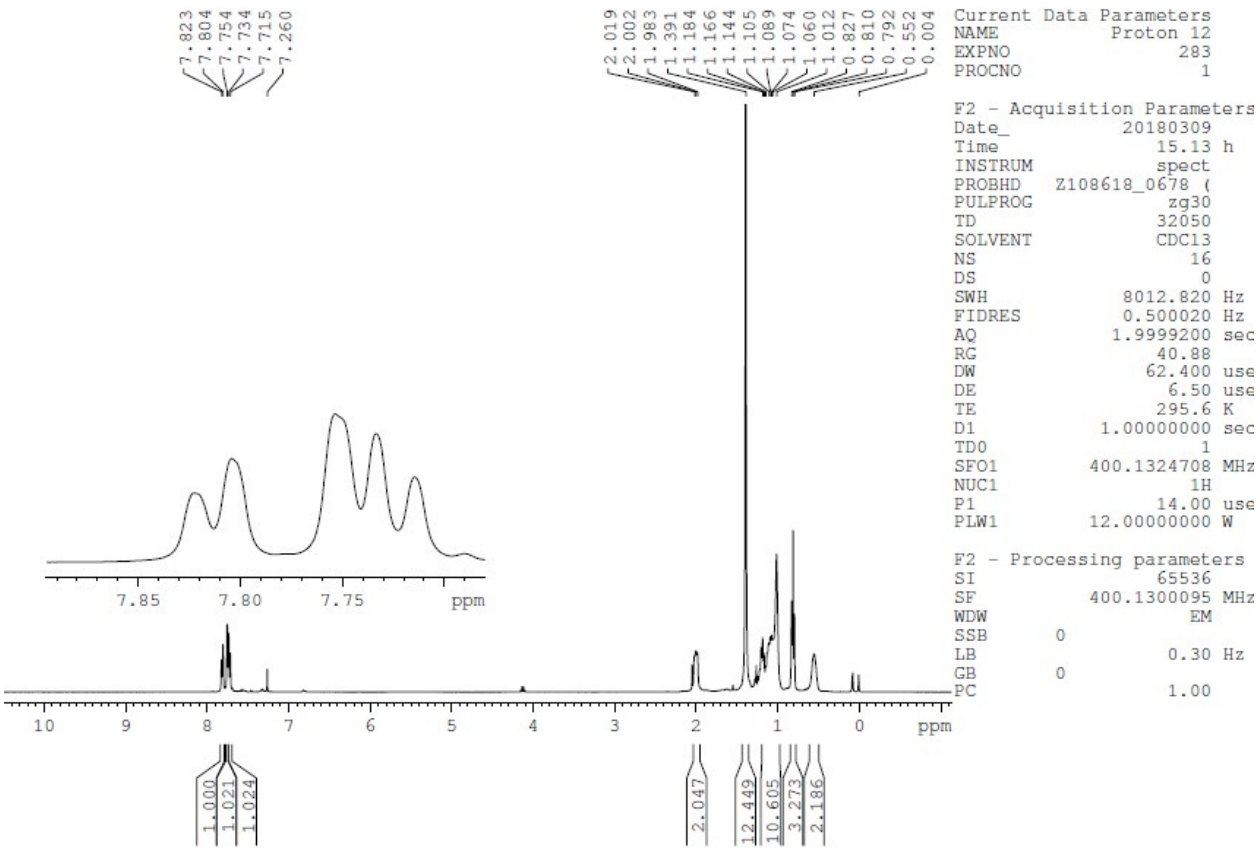


Fig. S4 ^{1}H NMR spectrum of **M2**

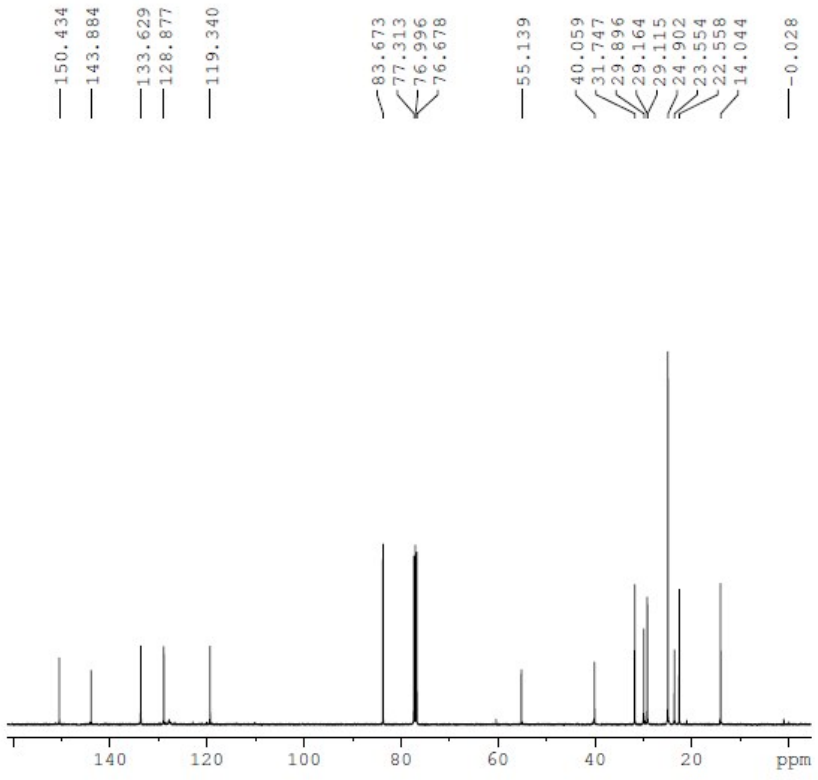



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Fig. S5 ^{13}C NMR spectrum of **M2**

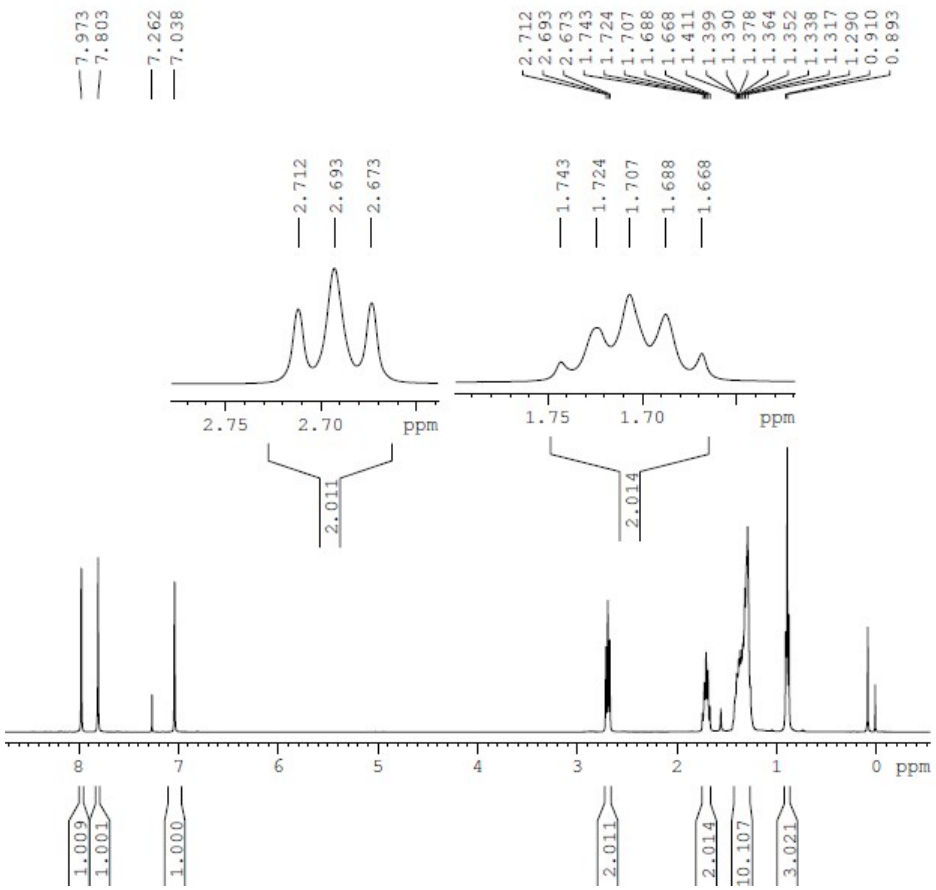


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Fig. S6 ^{1}H NMR spectrum of **M4**

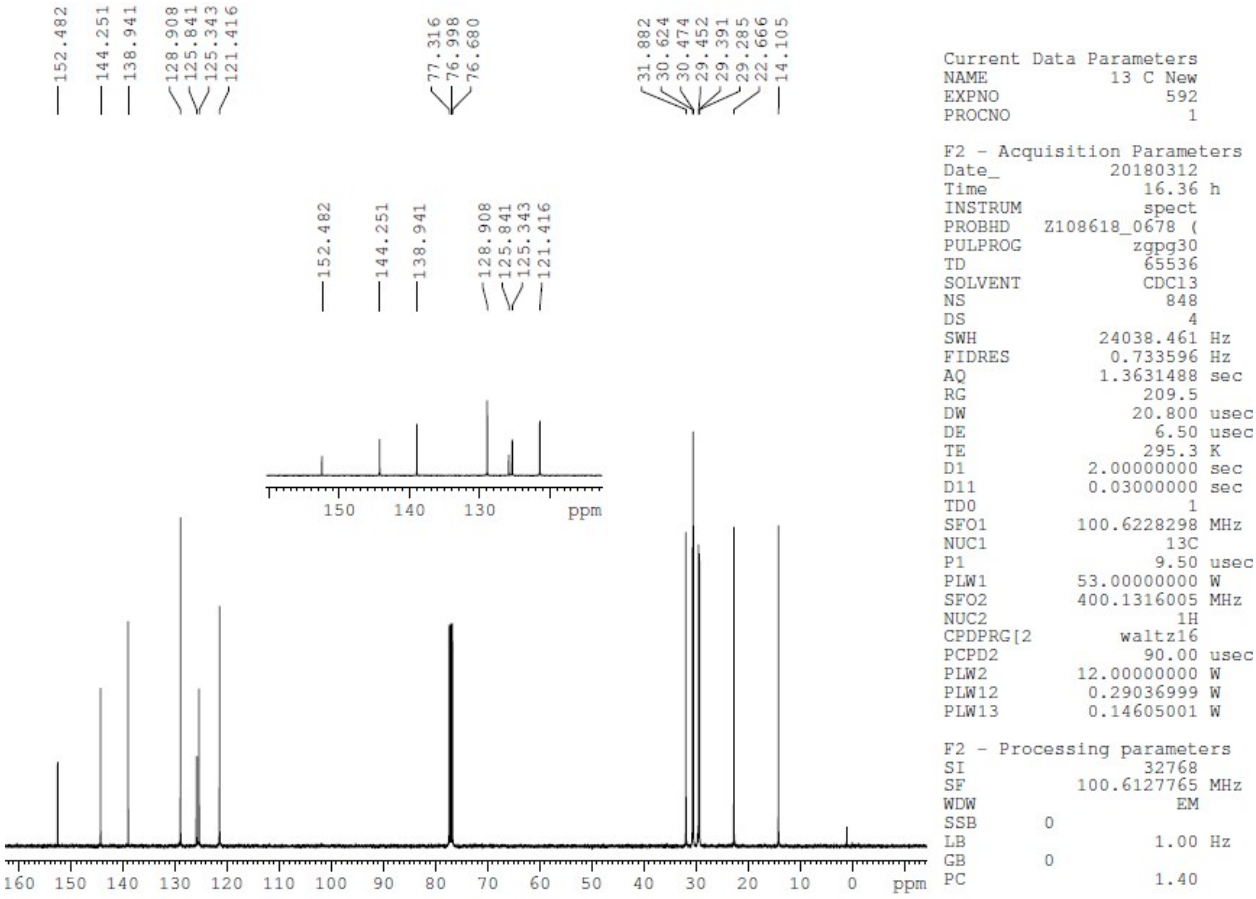


Fig. S7 ^{13}C NMR spectrum of **M4**

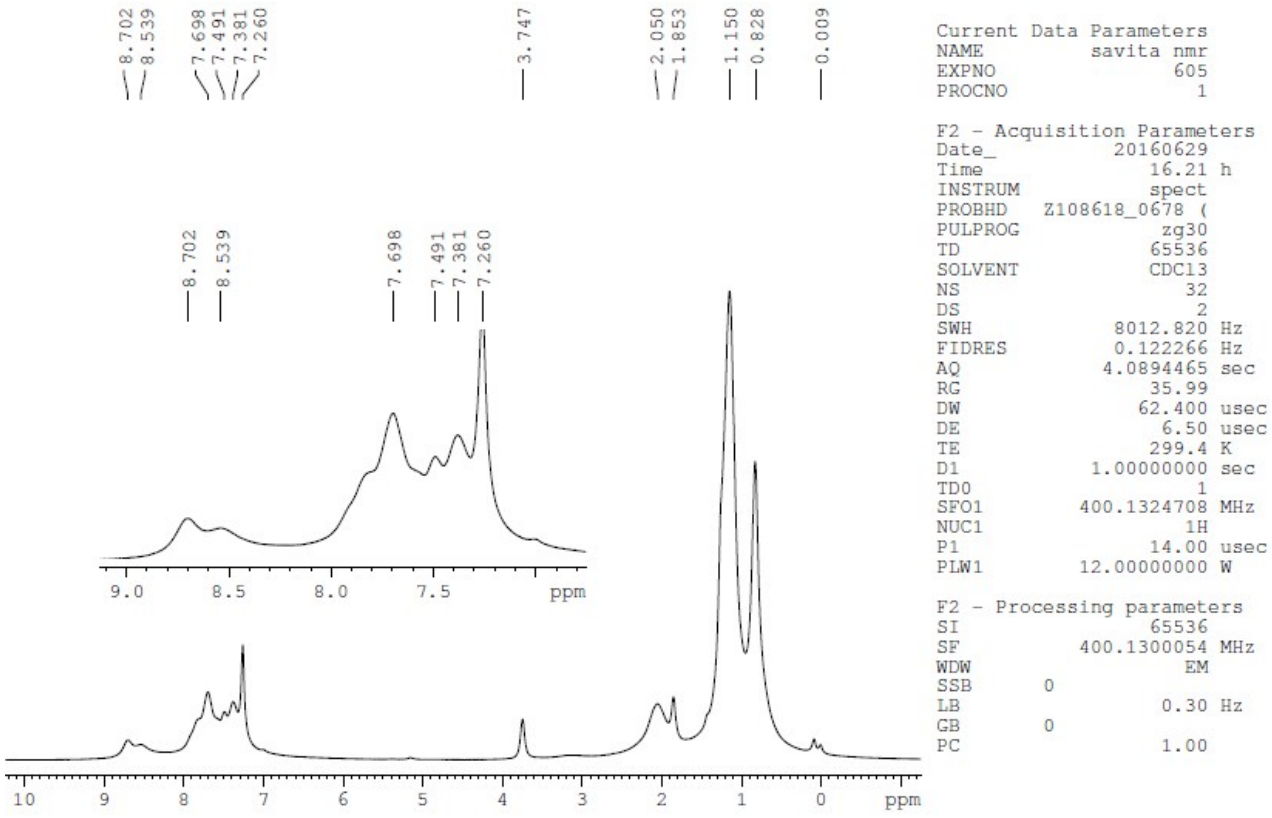


Fig. S8 ^{1}H NMR spectrum of **P1**

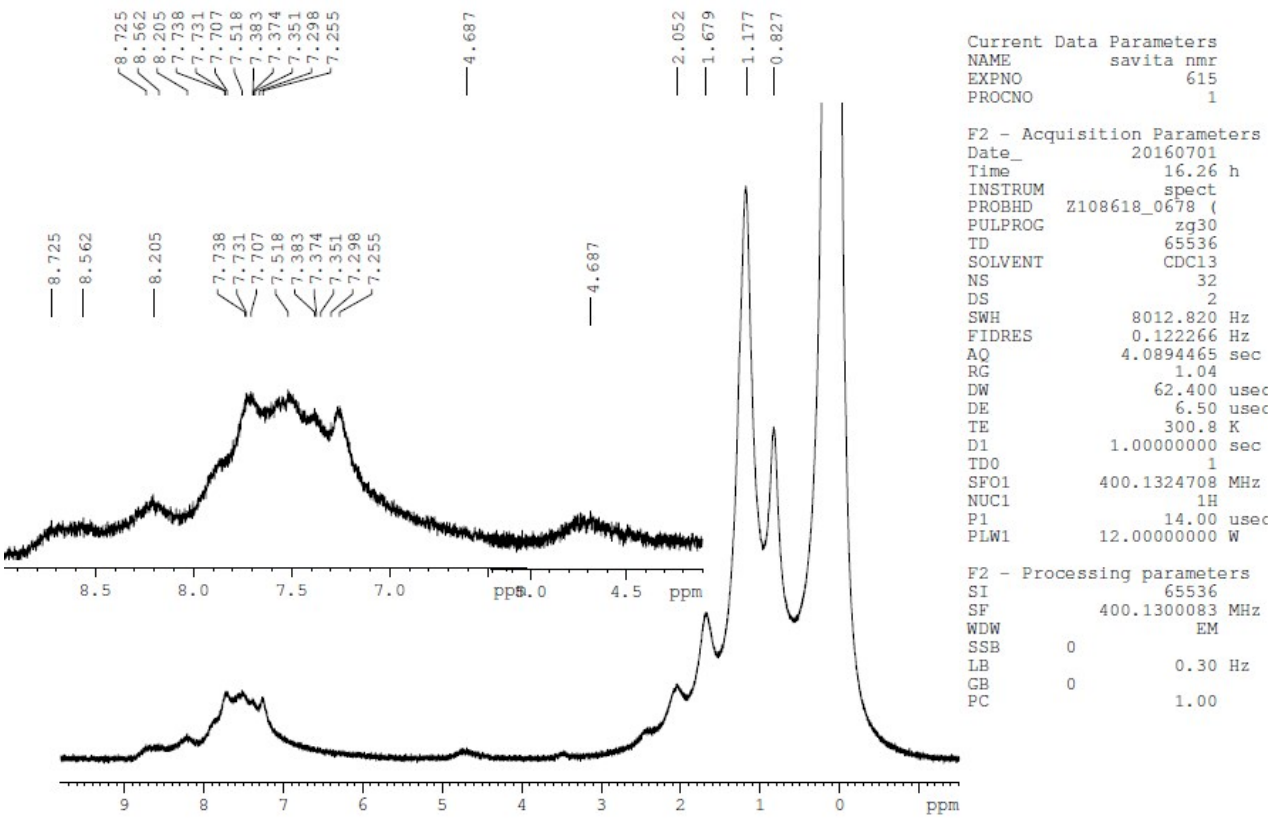


Fig. S9 ^{1}H NMR spectrum of **P2**

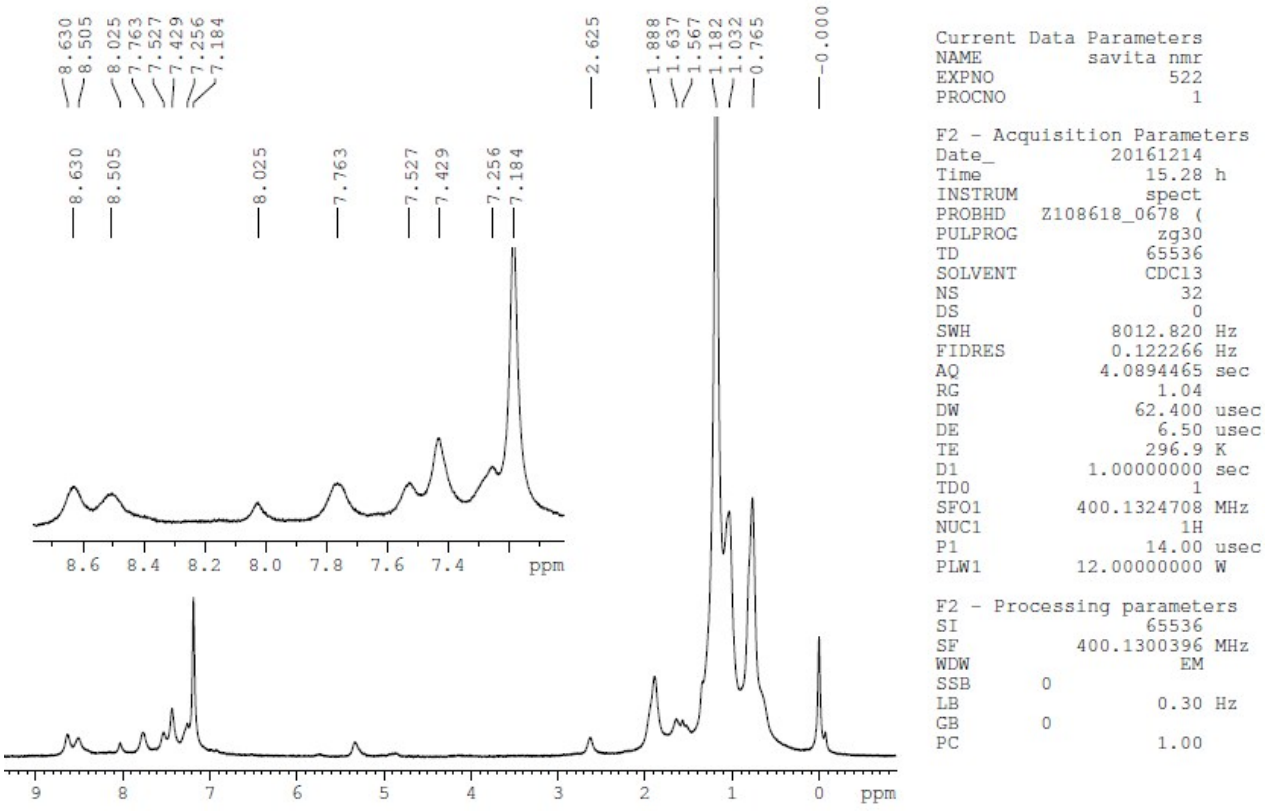


Fig. S10 ^{1}H NMR spectrum of **P3**

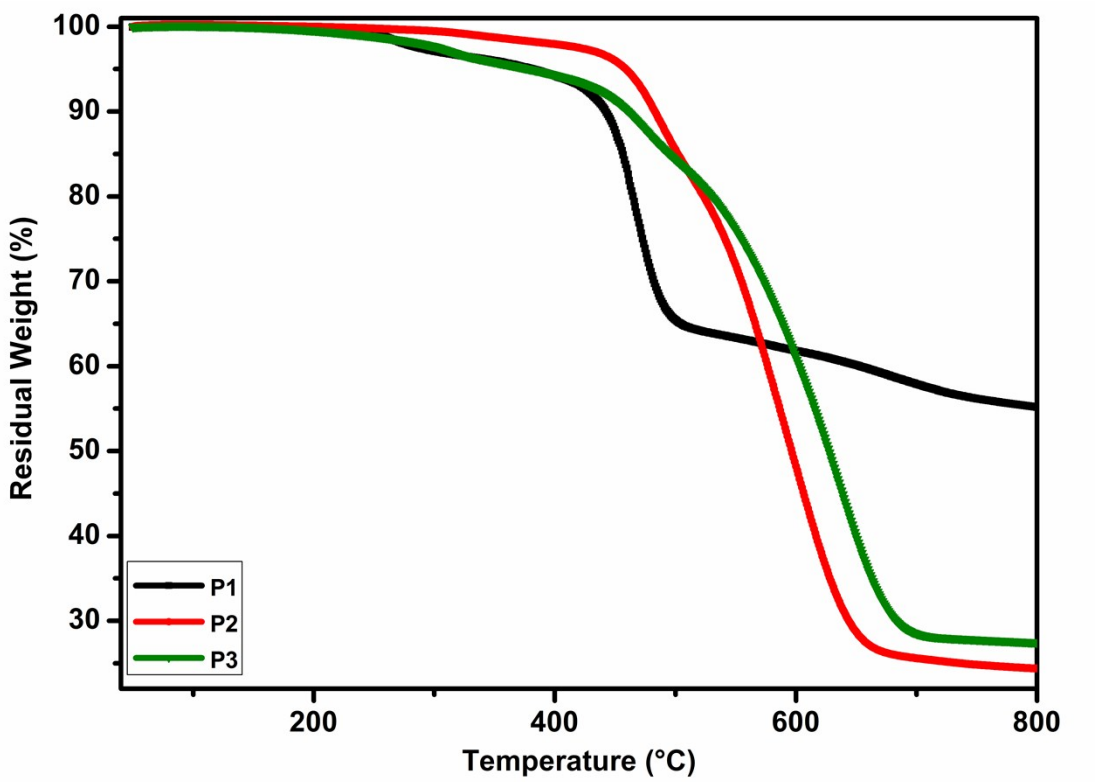
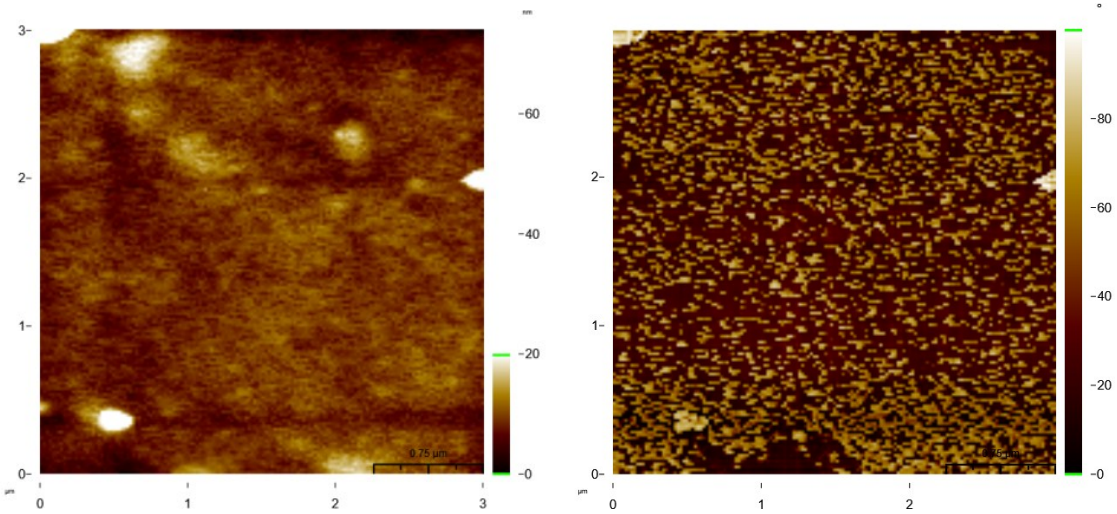


Fig.S11 TGA Graph for polymers **P1-P3**



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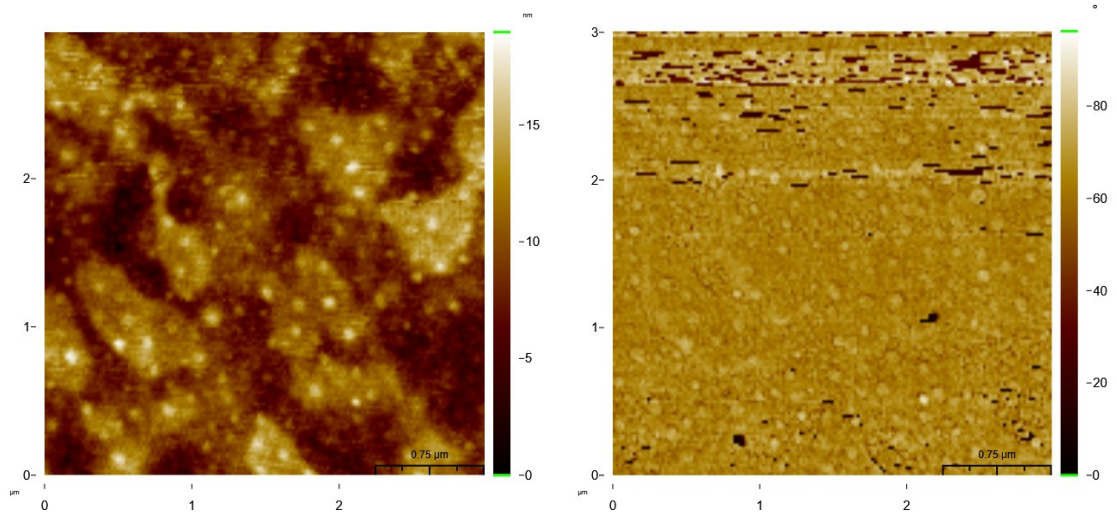
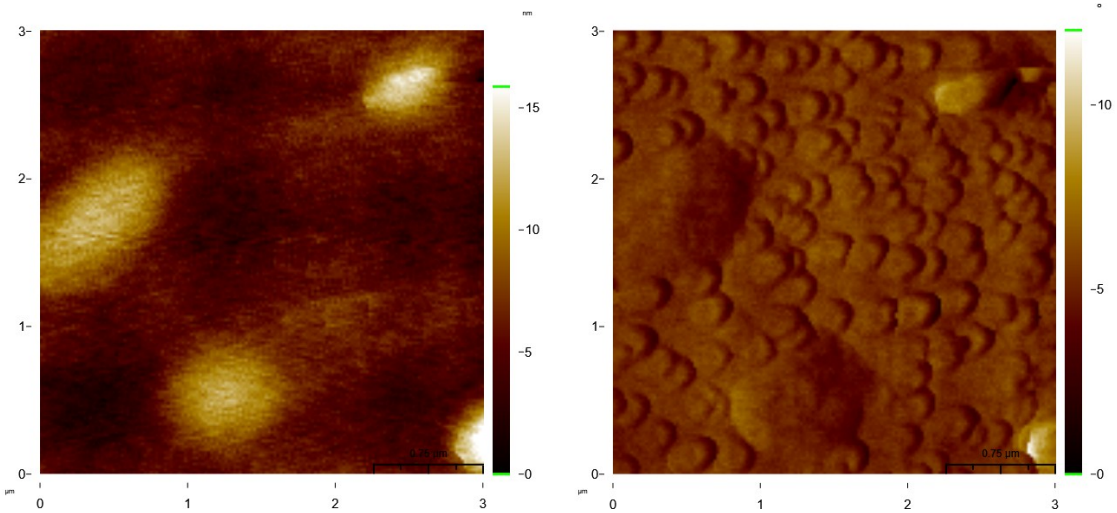
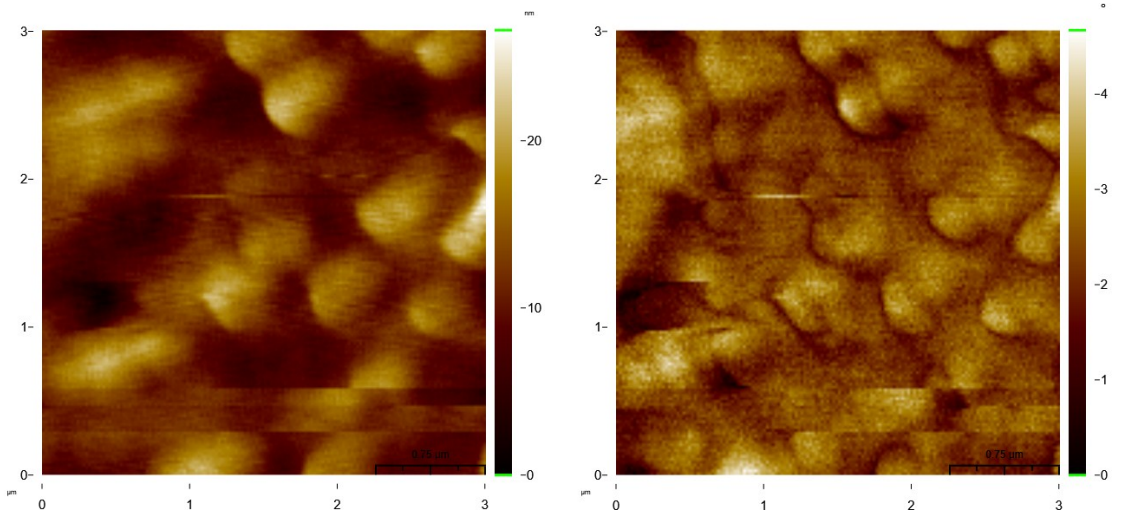


P1:P3HT (2:1) blend



P2:P3HT (1.5: 1) blend



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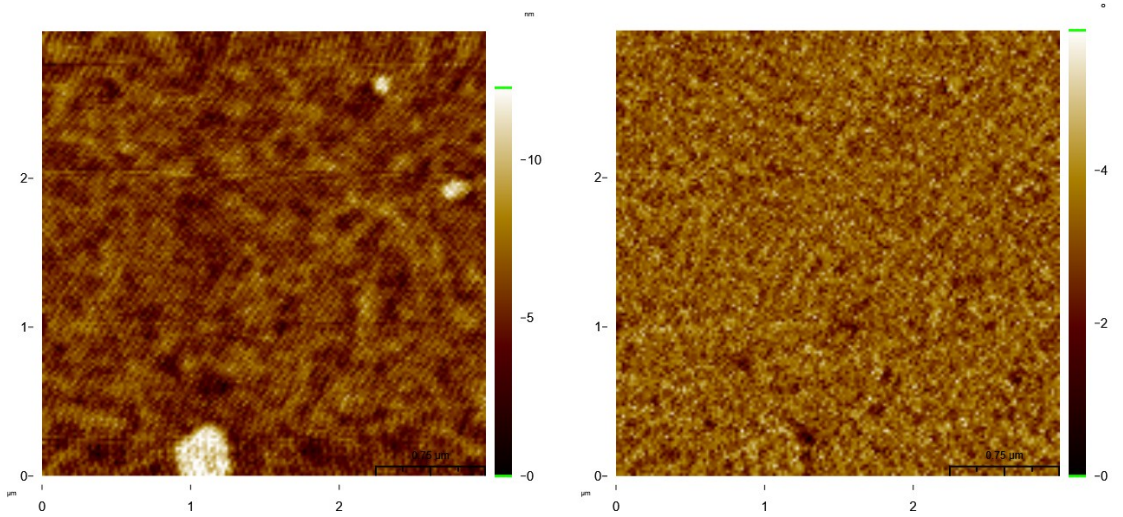
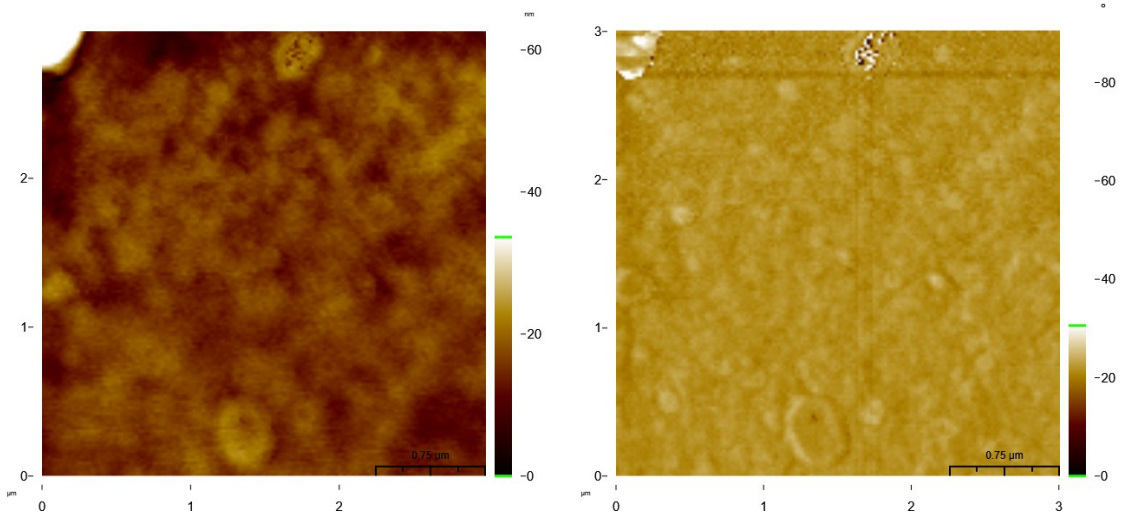


P3:P3HT (1.5:1) blend



P3:P3HT (2:1) blend

Fig. S12 AFM topographic (left) and phase (right) images of **P1**:P3HT, **P2**:P3HT and **P3**:P3HT blend films.