

Electronic Supplementary Information

Nitrogen containing graphene like structures from pyrolysis of pyrimidine polymers for polymer/graphene hybrid field effect transistors

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Experimental

Materials

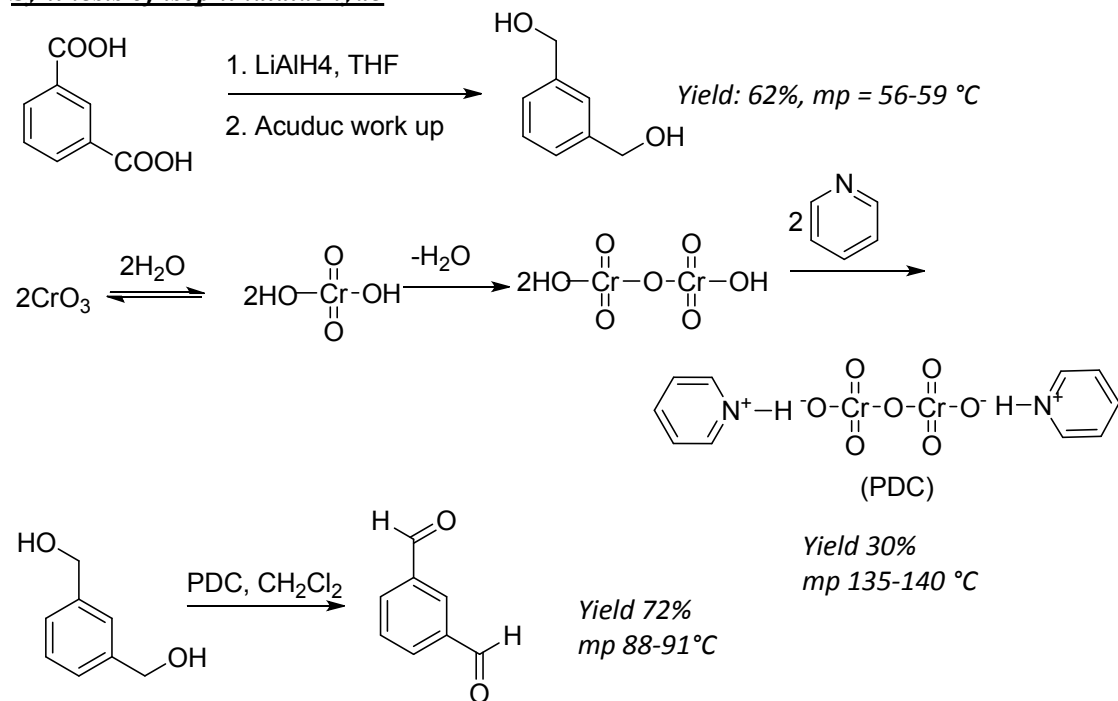
All the chemicals were purchased from Aldrich Chemical Co., Inc. and were used without further purification unless otherwise noted. All reactions were conducted under purified nitrogen. The polymerization glassware and syringes were dried at 120 °C for at least 24 hours before use and cooled under a nitrogen atmosphere. Tetrahydrofuran was dried over sodium/benzophenone ketyl and freshly distilled prior to use. Pyrimidine monomer, 2-decyloxy-4,6-dimethylpyrimidine and Poly[2-(decyloxy)-4-vinyl-6-(4-vinylstyryl)pyrimidine] (polymer **P1**) were prepared according the previously reported methods.¹

Instruments

¹H-NMR spectra were collected using Bruker Avance III 500 MHz NMR instrument. UV-visible spectra were collected using Agilent 8453 UV-visible spectrometer. The molecular weights of the polymers were measured by size exclusion chromatography (SEC) on a Viscotec VE 3580 system equipped with ViscoGEL™ columns connected to a refractive index detector. GPC solvent/sample module was used with HPLC-grade THF as the eluent and the calibration was based on polystyrene. Thermogravimetric analysis (TGA) was carried out on SDT Q600 instrument. Powder X-ray diffraction studies were carried out using Rigaku Ultima IV X-ray diffractometer with Cu-K α radiation and scan rate of 1 degree/min.

Monomer Synthesis

Synthesis of isophthalaldehyde



Scheme S1: Synthesis of isophthalaldehyde

Synthesis of 1,3-phenylenedimethanol

Isophthalic acid (2.000 g, 0.012 mol) and lithium aluminum hydride (1.142 g, 0.030 mol) were added to a three neck round bottom flask equipped with a reflux condenser. The flask was degassed with nitrogen for 15 minutes. The setup was kept in an ice bath and dry THF (~150 mL) was added while stirring. The reaction mixture was stirred at 0 °C for additional 30 minutes. After 30 minutes the ice bath was removed and the reaction mixture was warmed to room temperature. The reaction mixture was heated at reflux for overnight, cooled to room temperature, quenched in cold 1% HCl (~200 mL), extracted with diethyl ether (~200 mL), dried over anhydrous MgSO₄ and concentrated to yield an off white solid, which was purified by column chromatography on silica gel using hexane:ethyl acetate (1:1) as the eluent to obtain the pure product as a white solid. (1.00 g, 62%, mp 56-59 °C) ¹H-NMR (CDCl₃, 270 MHz): 7.25 (t, 1H), 7.16 (d, 2H), 7.13 (s, 1H), 5.14 (t, 2H), 4.47 (d, 4H) ¹³C-NMR (CDCl₃, 270 MHz): 142.83, 128.30, 125.29, 125.09, 63.49.

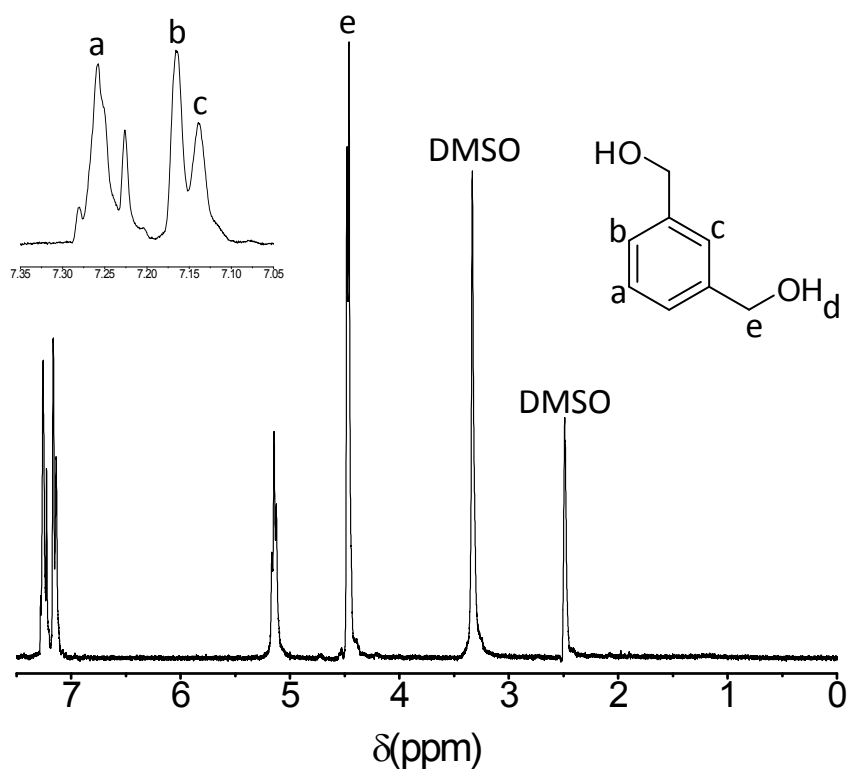


Figure S1: ¹H-NMR spectrum of 1,3-phenylenedimethanol

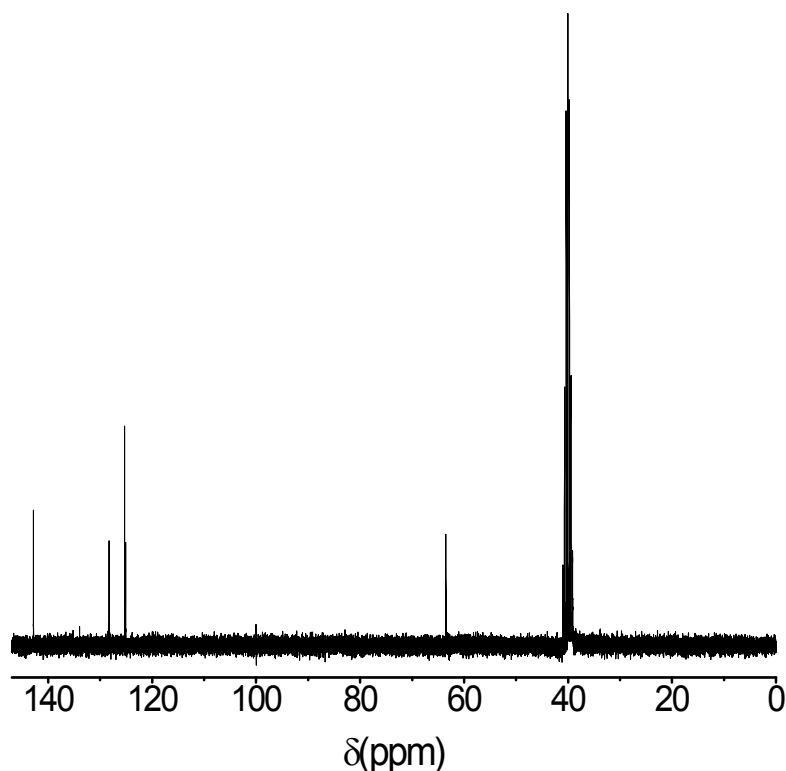


Figure S2: ^{13}C -NMR spectrum of 1,3-phenylenedimethanol

Synthesis of dipyridinium dichromate (PDC)

Chromium trioxide (12.500 g, 0.125 mol) was dissolved in water (~15 mL) and pyridine (10 mL, 0.125 mol) was added slowly over a period of 15 minutes. An ice bath was applied periodically to cool the solution below 30 °C. After stirring for 1.5 hours the solution was placed in a 250 mL beaker and placed in a freezer. After 3 hours the product was filtered and washed with acetone. The orange crystalline material was dried under vacuum. (11.51 g, 25%, mp 135-140 °C)

Synthesis of isophthalaldehyde

1,3-Phenylenedimethanol (0.979 g, 7.094 mmol) was added to a one neck round bottom flask and dissolved in dry THF (~10 mL). Dipyridinium dichromate (PDC) (5.879 g, 0.016 mol) and methylene chloride (~110 mL) were added and the reaction mixture was stirred at room temperature for 24 hours. The reaction mixture was quenched in water, extracted with diethyl ether (~200 mL), washed with water (3×100 mL), dried over anhydrous MgSO_4 and concentrated to yield a white solid. The product was purified by column chromatography on silica gel using hexane:ethyl acetate (7:3) as the eluent to obtain the pure product as a white solid. (0.68 g, 72%, mp 88-91 °C). ^1H NMR (CDCl_3 , 500 MHz): 10.14 (s, 2H), 8.40 (s, 1H), 8.18 (d, 2H), 7.75 (t, 1H) ^{13}C NMR (CDCl_3 , 500 MHz): 191.05, 137.02, 134.64, 131.00, 129.93.

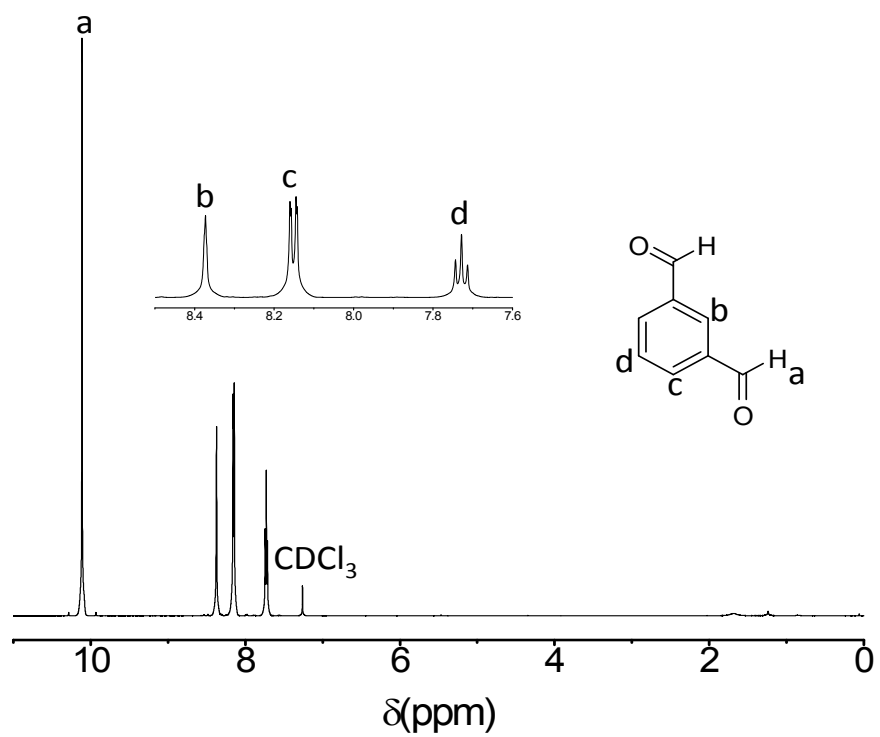


Figure S3: $^1\text{H-NMR}$ spectrum of isophthalaldehyde

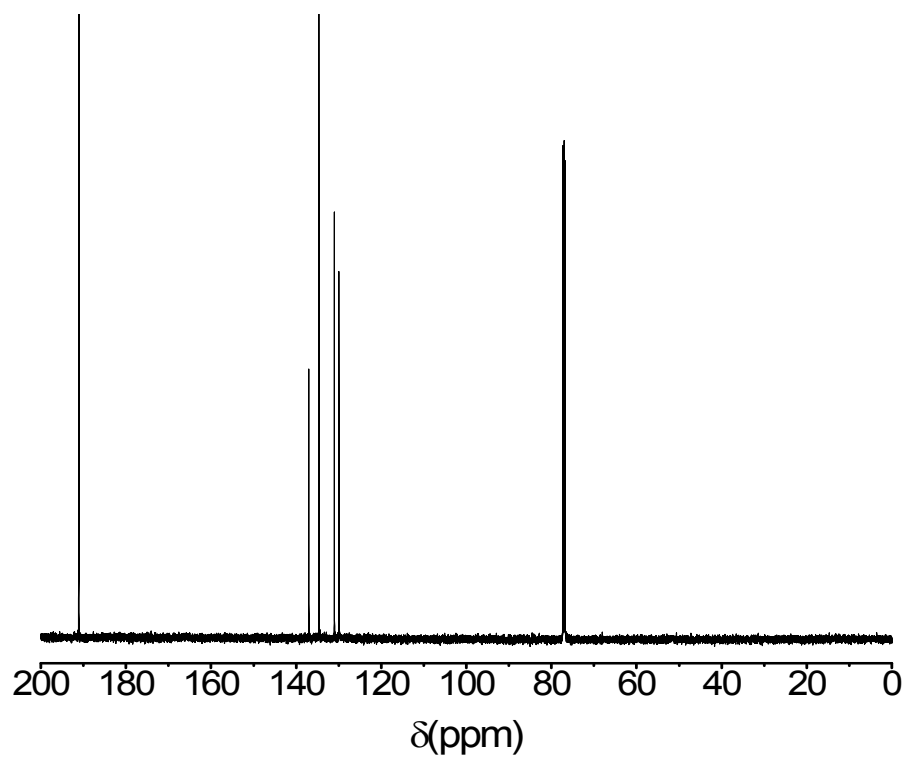


Figure S4: ^{13}C -NMR spectrum of isophthalaldehyde

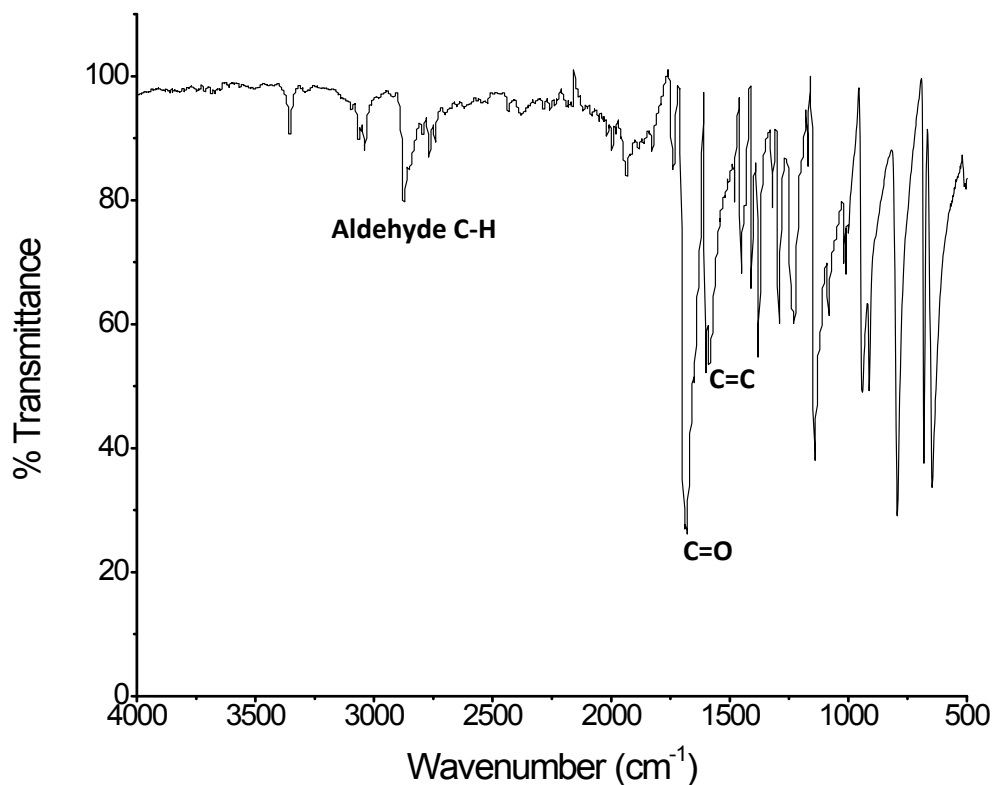
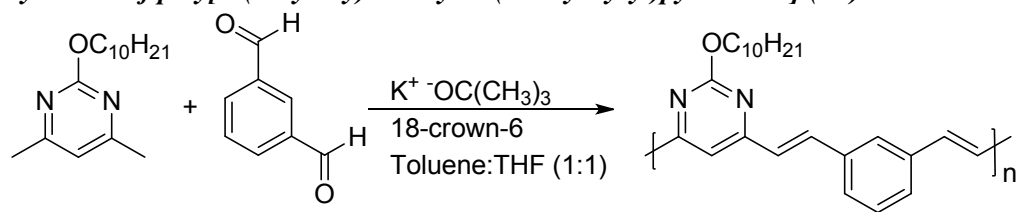


Figure S5: FT-IR spectrum of isophthalaldehyde

Synthesis of poly[2-(decyloxy)-4-vinyl-6-(3-vinylstyryl)pyrimidine] (P2)



Scheme S2: Synthesis of polymer **P2**

2-Decyloxy-4,6-dimethylpyrimidine (0.511 g, 1.938 mmol) was added to a three neck round bottom flask equipped with a reflux condenser and degassed with nitrogen for 15 minutes. Potassium t-butoxide (0.543 g, 4.844 mmol), 18-crown-6 (1.279 g, 4.844 mmol) dissolved in a mixture of dry THF (5 mL) and dry toluene (5 mL) was added to the reaction mixture under nitrogen while stirring. The reaction mixture was stirred for 15 minutes at room temperature. Isophthalaldehyde (0.511 g, 1.938mmol) dissolved in a mixture of dry THF (10 mL) and dry toluene (10 mL) was added to the reaction mixture and stirred under nitrogen at 60 °C for 20 minutes. The polymer was precipitated in methanol, filtered and was purified by Soxhlet extractions with methanol, hexane and chloroform. The polymer was obtained as a red solid by evaporating chloroform. Soluble fraction was used to characterize the polymer while the insoluble fraction was pyrolyzed at 600 °C for 3 hours under a nitrogen atmosphere.

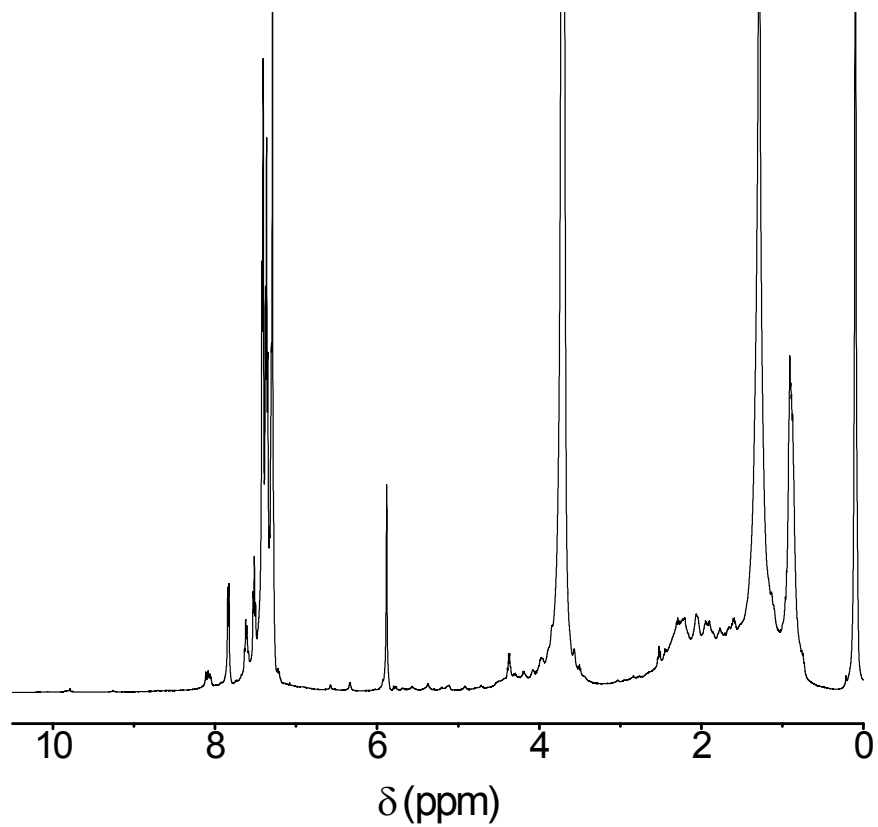


Figure S6: ¹H-NMR spectrum of *poly[2-(decyloxy)-4-vinyl-6-(3-vinylstyryl)pyrimidine]* (**P2**)

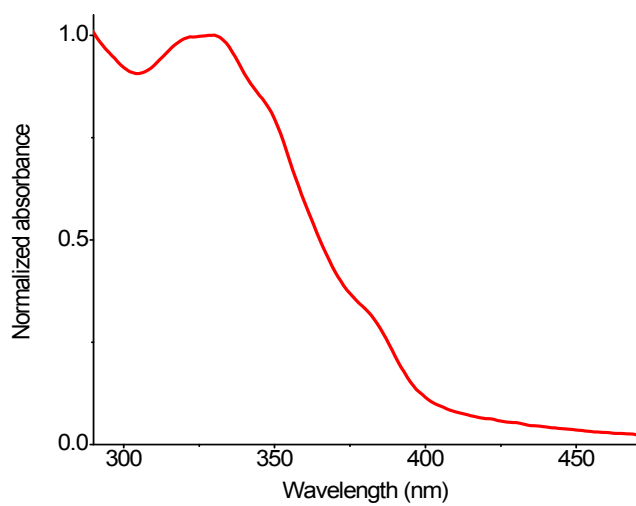


Figure S7: UV-visible spectrum of *poly[2-(decyloxy)-4-vinyl-6-(3-vinylstyryl)pyrimidine]* (**P2**) in chloroform solution

Pyrolysis of Polymer P1 and P2

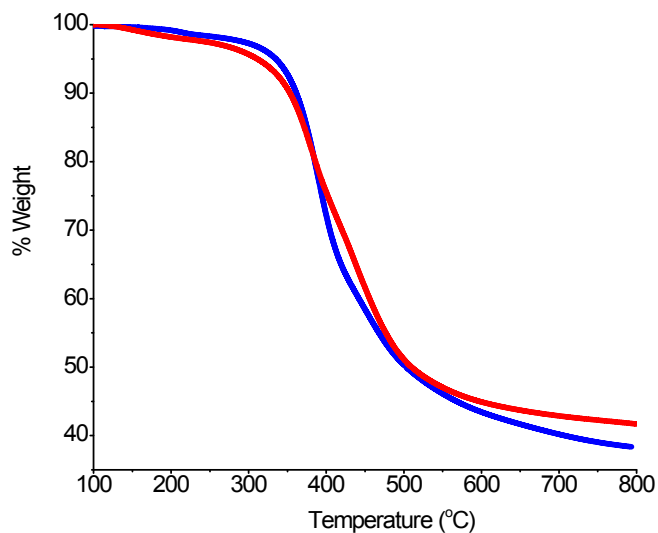


Figure S8: TGA thermograms of P1 (blue) and P2 (red)

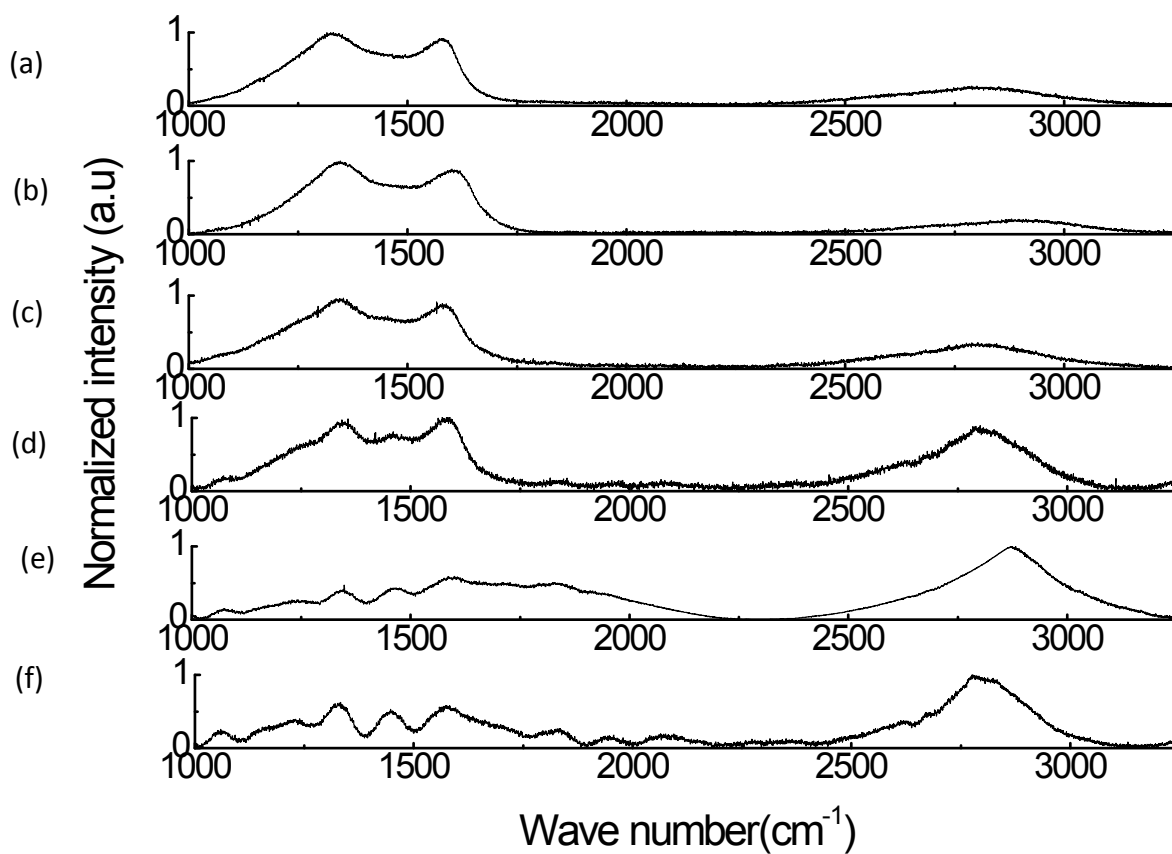


Figure S9: Temperature studies on pyrolysis for polymer P2: Raman spectra at (a) 600 °C, (b) 500 °C, (c) 450 °C, (d) 350 °C, (e) 300 °C, (f) room temperature (25 °C).

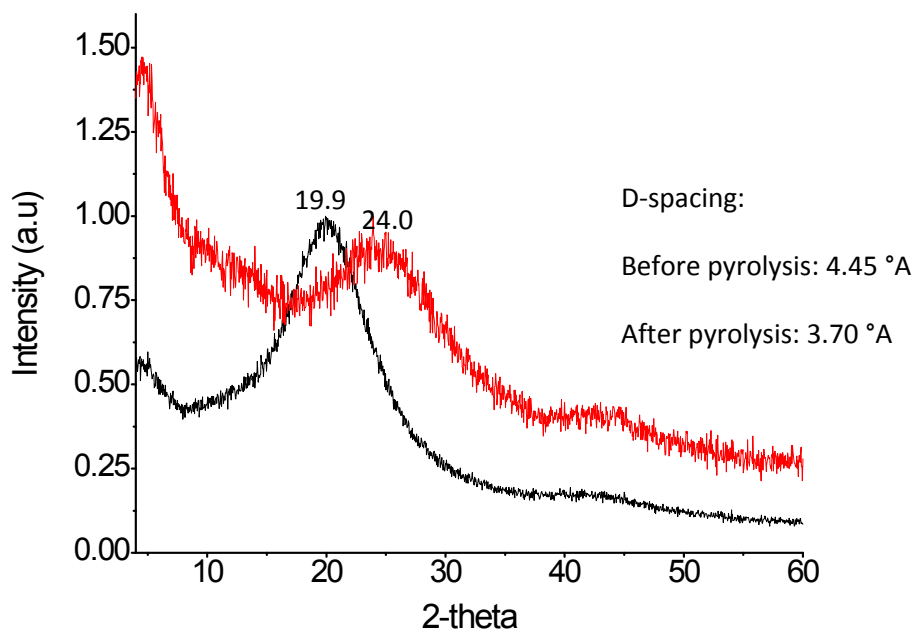


Figure S10: Powder XRD patterns of polymer **P1** before (black) and after (red) pyrolysis

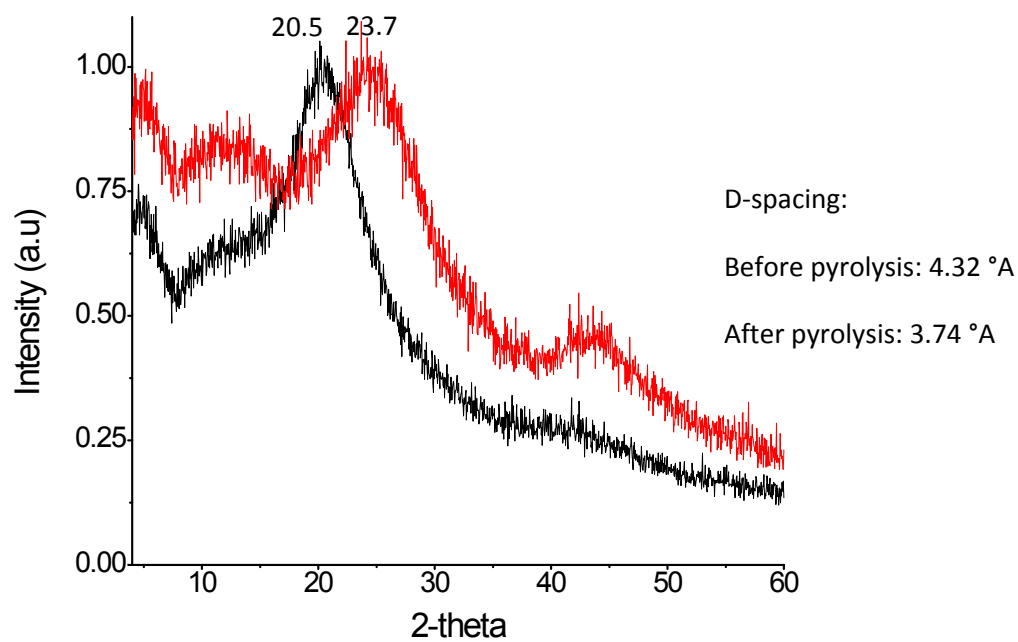


Figure S11: Powder XRD patterns of polymer **P2** before (black) and after (red) pyrolysis

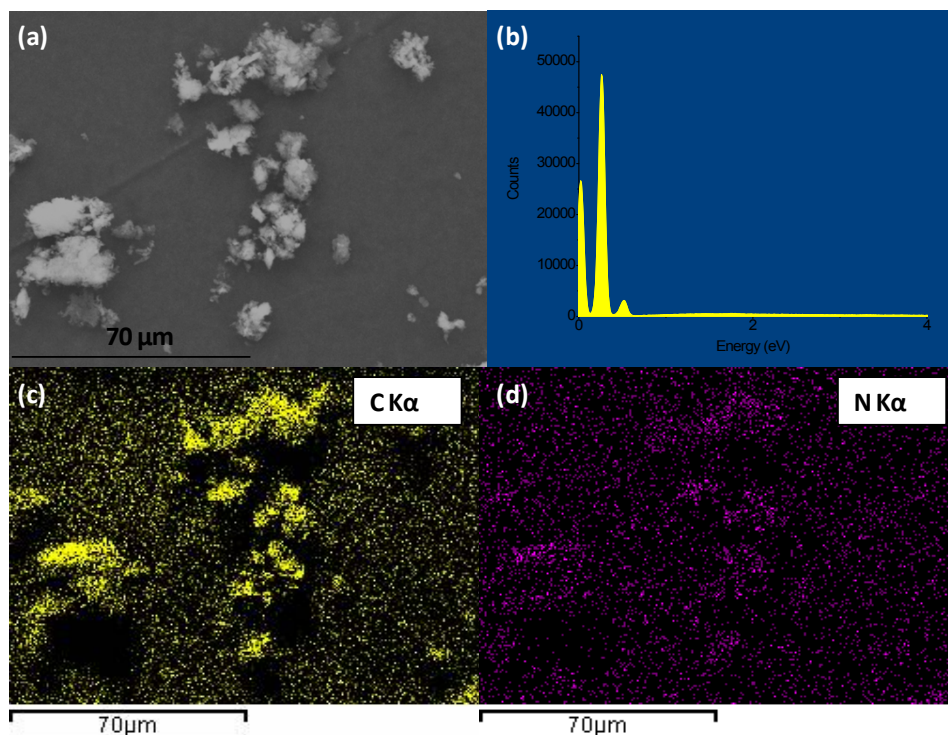


Figure S12: (a) SEM micrograph where EDS was performed, (b) EDS spectrum, (c) elemental mapping for carbon, (d) elemental mapping for nitrogen for polymer **P1** before pyrolysis

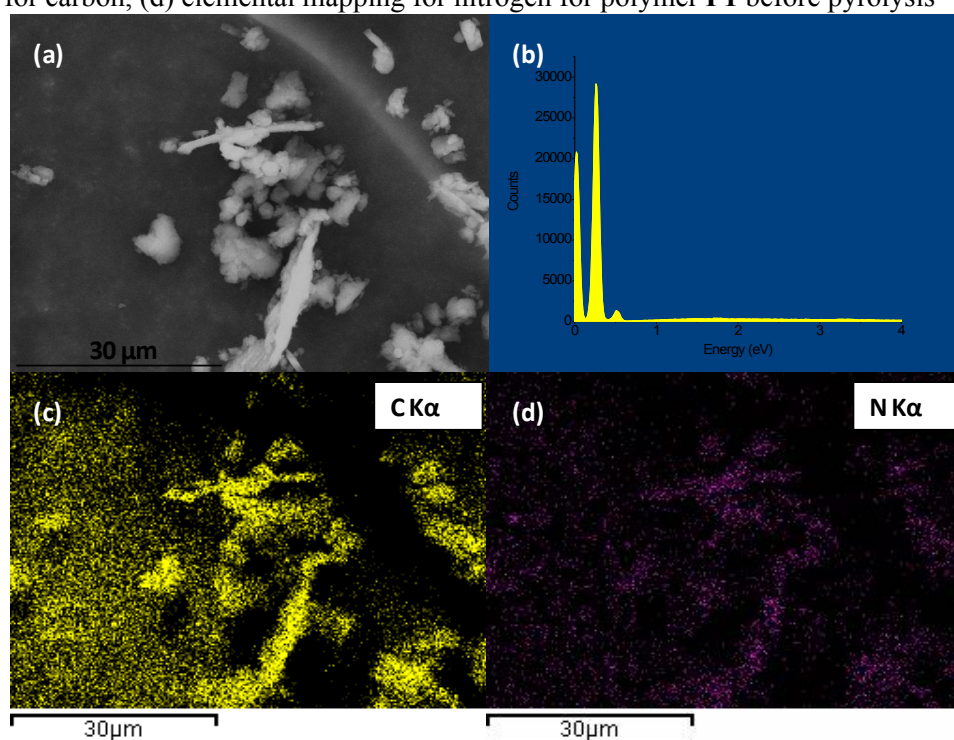


Figure S13: (a) SEM micrograph where EDS was performed, (b) EDS spectrum, (c) elemental mapping for carbon, (d) elemental mapping for nitrogen for polymer **P2** before pyrolysis

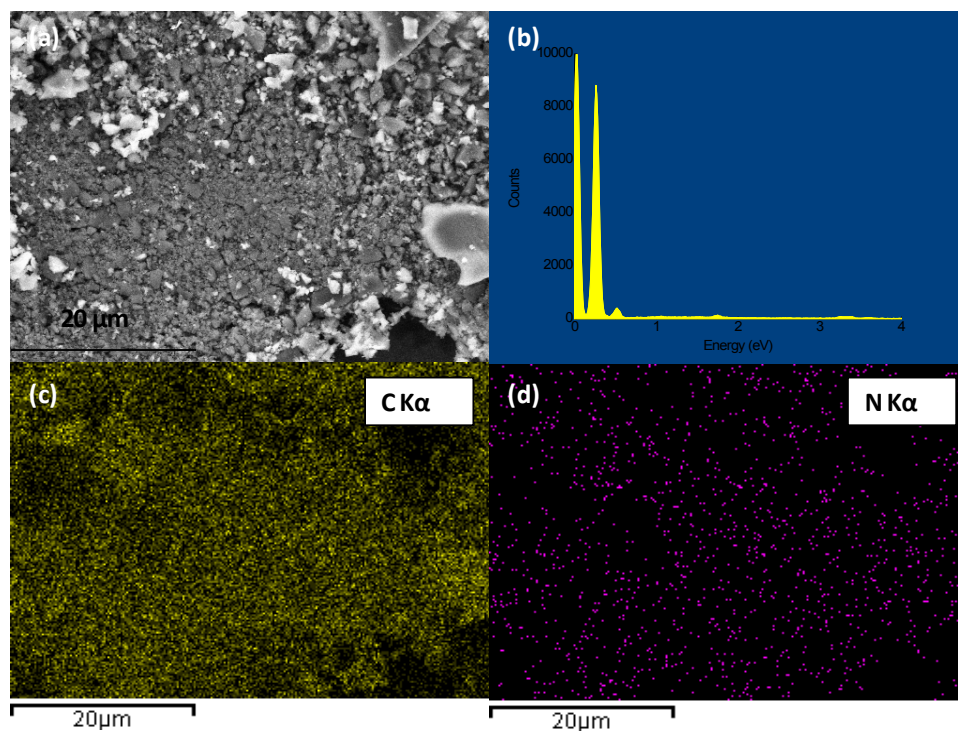


Figure S14: (a) SEM micrograph where EDS was performed, (b) EDS spectrum, (c) elemental mapping for carbon, (d) elemental mapping for nitrogen for polymer **P1** after pyrolysis (**G1**)

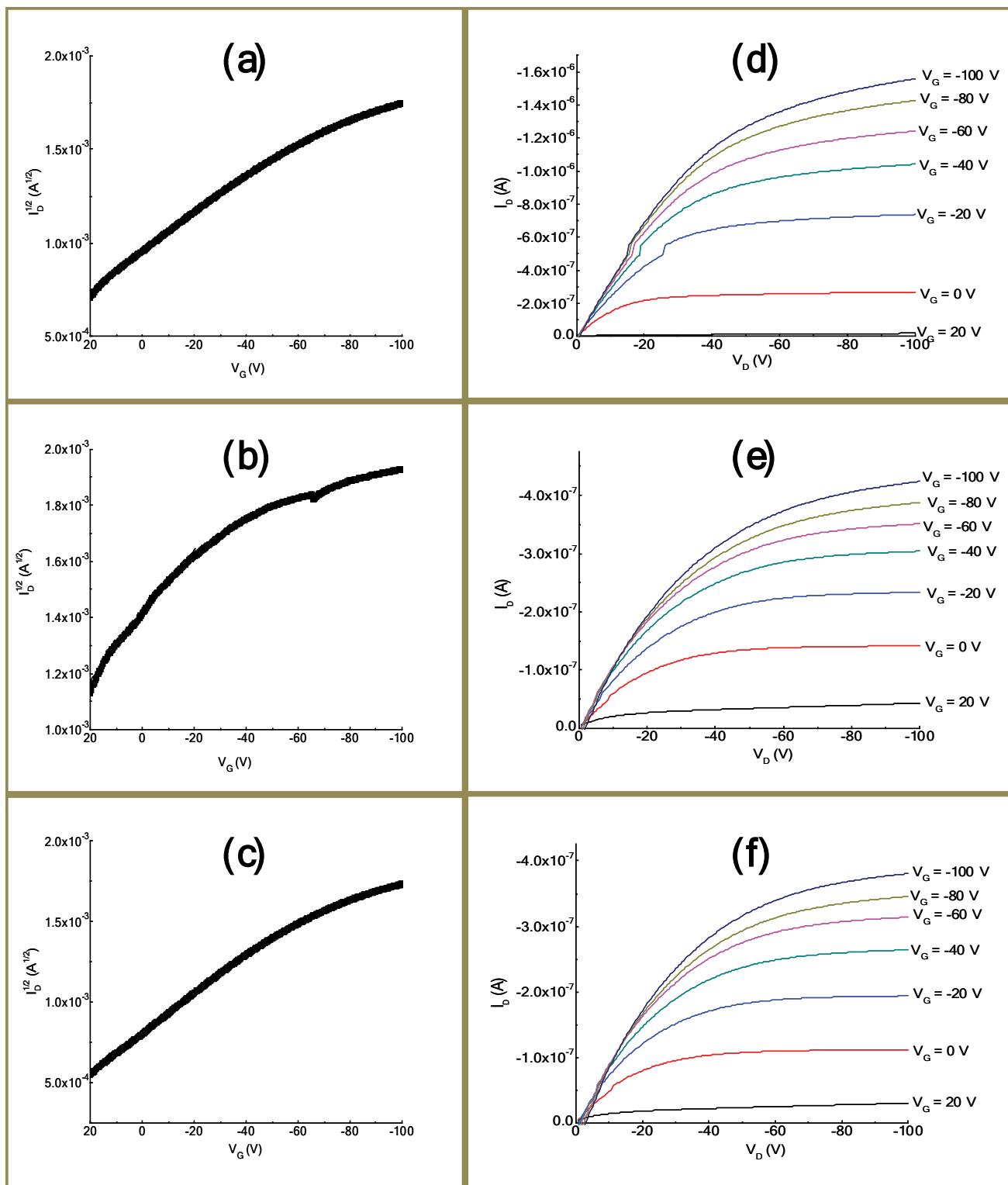


Figure S15: (Left) Transfer characteristics of FETs (a) P3HT, (b) P3HT/G1, (c) P3HT/G2, (right) output characteristics of FETs (d) P3HT, (e) P3HT/G1 and (f) P3HT/G2 for P3HT with $M_n = 13600 \text{ g mol}^{-1}$, PDI = 1.3

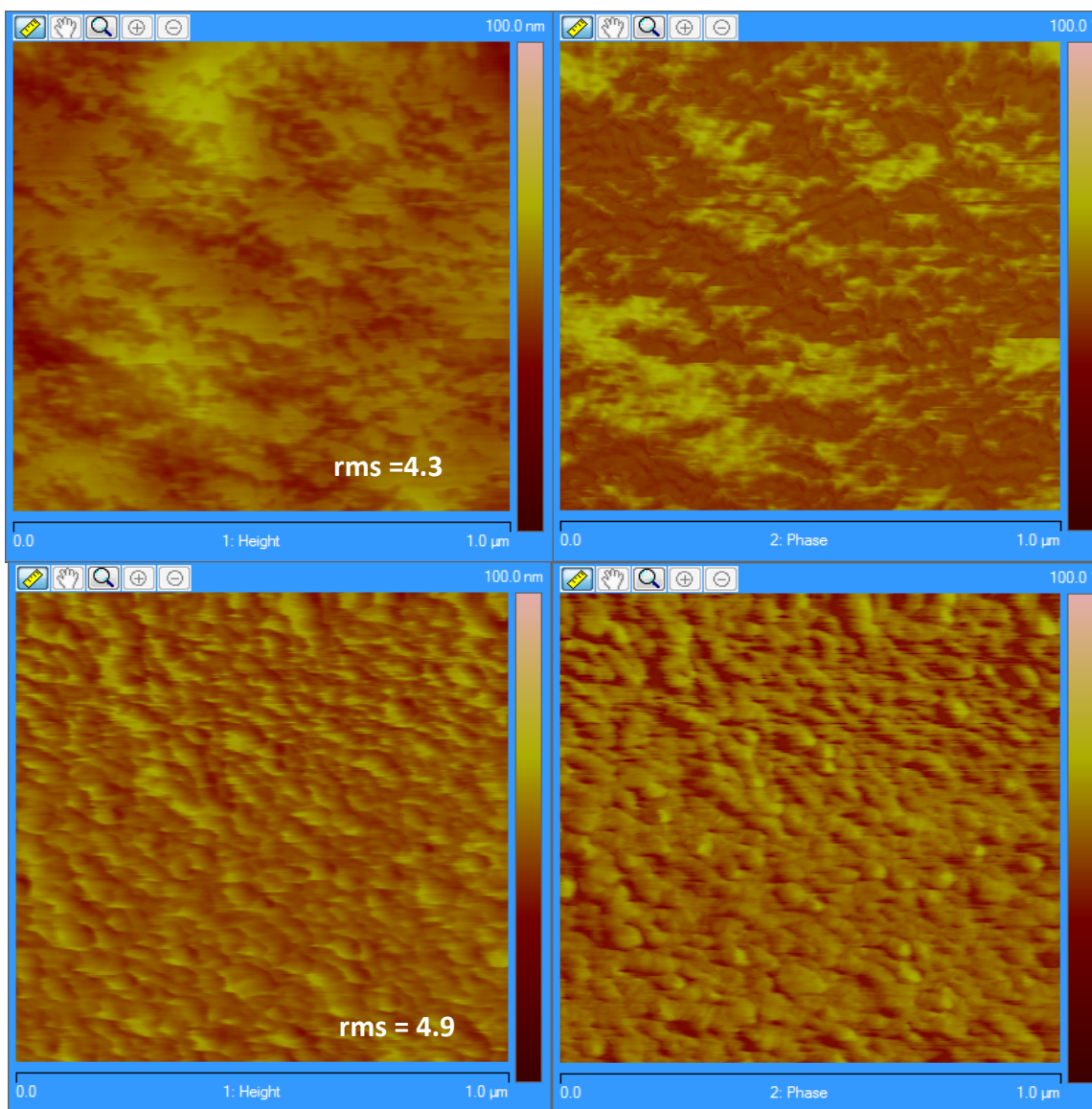


Figure S16: Height (left) and phase (right) TMAFM images in the channel region of FET devices with P3HT of molecular weight 51840 g mol⁻¹, PDI = 2.1, (top) P3HT/G1 composite, (bottom) P3HT/G2 composite.

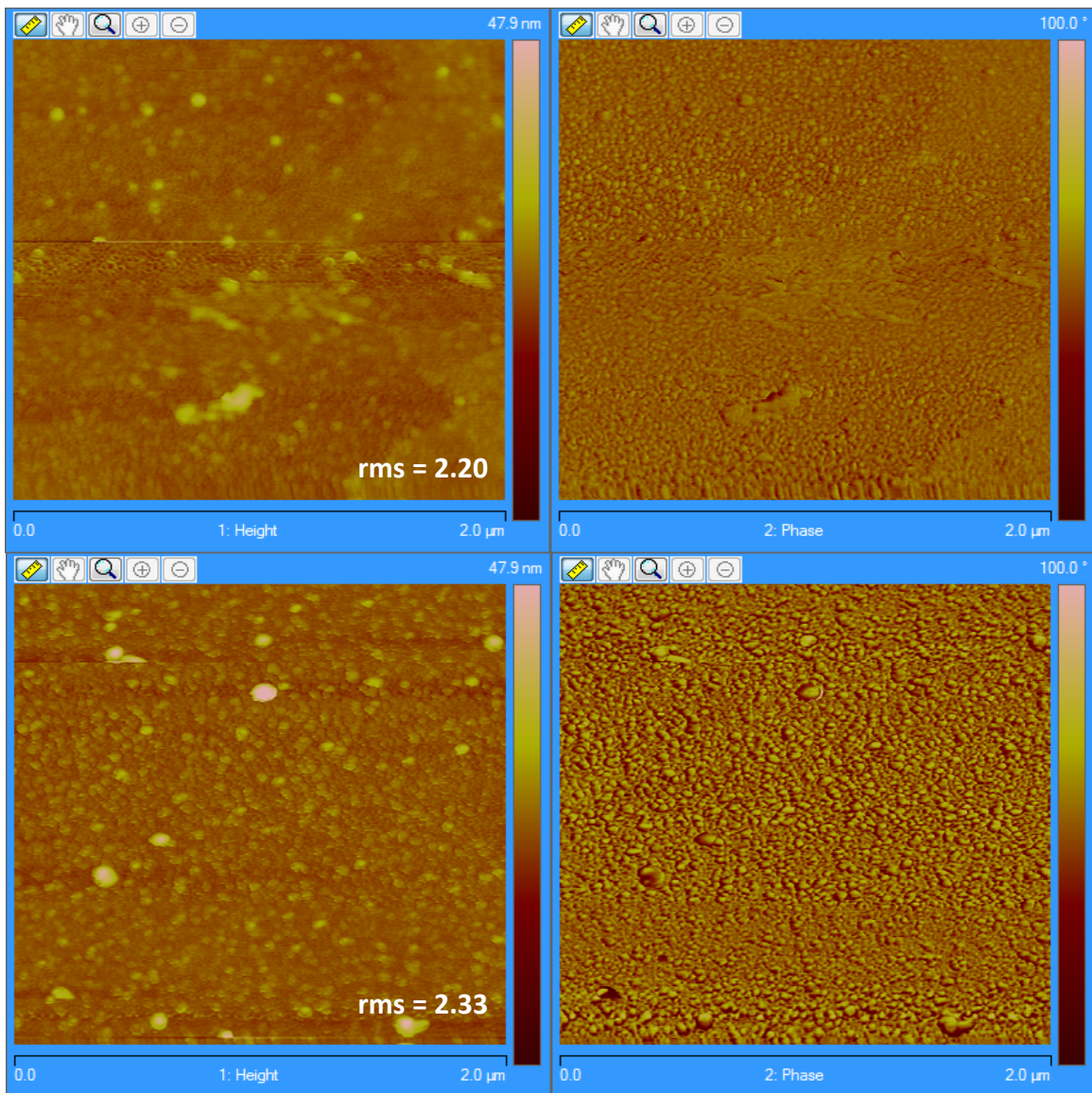


Figure S17: Height (left) and phase (right) TMAFM images in the channel region of FET devices with P3HT of molecular weight, 13600 g mol⁻¹, PDI = 1.3, (top) P3HT/G1 composite, (bottom) P3HT/G2 composite.

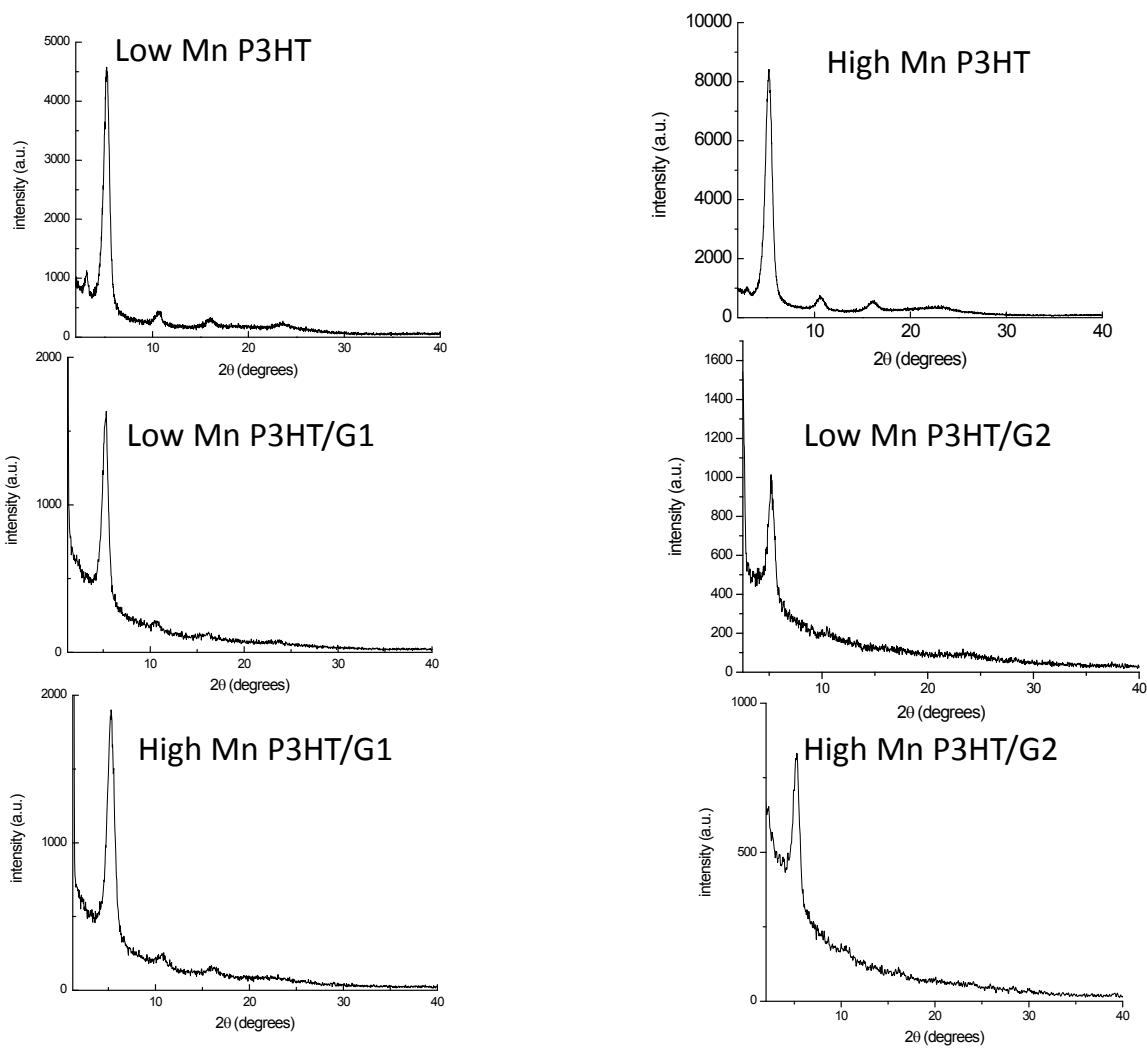


Figure S18: XRD patterns of the polymers and Polymer/G1 (or G2) composites

Table S1: d-spacing values of polymers and polymer/G1 (or G2) composites

	High Mn		Low Mn	
	2 θ	d-spacing	2 θ	d-spacing
P3HT	5.25	16.819	5.25	16.819
	10.64	8.308	10.66	8.292
	16.06	5.514	16.03	5.525
	23.21	3.829	23.57	3.772
P3HT/G1	5.25	16.819	5.31	16.629
	10.73	8.238	10.56	8.371
	16.28	5.44	16.21	5.464
			23.67	3.756
P3HT/G2	5.25	16.819	5.25	16.819
	10.52	8.395	10.34	8.548
	16.23	5.457	16.06	5.514

References:

1. S. S. Gunathilake, H. D. Magurudeniya, P. Huang, H. Nguyen, E. Rainbolt, M. C. Stefan, M. C. Biewer, *Polym. Chem.*, 2013, **4**, 5216.