

Polymers based on thieno[3,4-c]pyrrole-4,6-dione and pyromellitic diimide by CH-CH arylation reaction for high-performance thin-film transistors

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KEYWORDS: thieno[3,4-c]pyrrole-4,6-dione, CH-CH arylation, thin-film transistors

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1. Materials

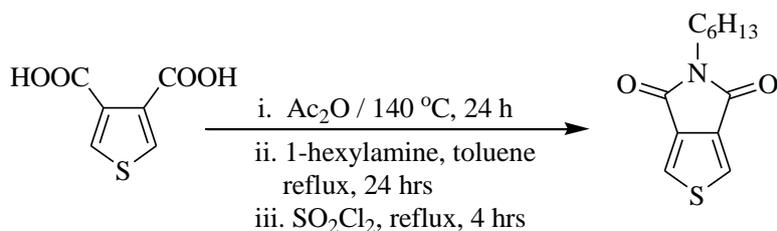
All manipulations and reactions involving air sensitive reagents were performed under a dry oxygen-free nitrogen atmosphere. All reagents and solvents were obtained from commercial sources and dried using standard procedures before use. Pyromillitic acid diimide, palladium acetate and potassium acetate were obtained from Sigma-Aldrich. Tetrabutylammonium bromide (TBAB) was obtained from TCI Company. Thiophene-3,4-dicarboxylic acid was obtained from Matrix Scientific. 5-hexyl-5H-thieno[3,4-c]pyrrole-4,6-dione (HTPD); 5-(ethylhexyl)-thieno[3,4-c]pyrrole-4,6-dione (ETPD),¹ and 5,7 bis(tributylstannyl)-2,3-dihydrothieno-[3,4-b][1,4]dioxin² were prepared according to literature procedures. All reactions were monitored by TLC to follow their completion.

2. Instruments and measurements

All ¹H- and ¹³C-NMR spectra were measured on a Varian spectrometer (400 MHz for ¹H-NMR and 100 MHz for ¹³C-NMR) in CDCl₃ or DMSO-D₆ at 25 °C with TMS as the internal standard. Chemical shifts were recorded in ppm units. The molecular weight was confirmed by LC/MS

1. Synthesis of precursory monomers and π- conjugated dimers

1.1. Synthesis of 5-hexyl-5H-thieno[3,4-c]pyrrole-4,6-dione (HTPD)¹



A solution of thiophene-3,4-dicarboxylic acid (3.0 g, 17.4 mmol) in acetic anhydride (150 ml) was heated and stirred under reflux at 140 °C for 24 h. The solvent was removed and the crude product was used for the next step after recrystallization using toluene to afford pale yellow crystals of thieno[3,4-c]furan-1,3-dione (2.41 g, yield = 90%). Thieno[3,4-c]furan-1,3-dione (2.41 g, 15.6 mmol) was then dissolved in toluene (300 ml) followed by adding 1.5 equiv. of 1-hexylamine (2.37 g, 23.4 mmol) and the reaction mixture was refluxed with stirring for 24 h followed by cooling to room temperature. The solvent was removed under reduced pressure and the solid thus obtained was dissolved in thienyl chloride (20 ml) and the mixture was refluxed for 4 h. The volatiles were removed under reduced pressure and the crude product thus remained in the flask was purified by silica gel column chromatography (CH₂Cl₂: hexane /2:1) affording the desired product **HTPD** as pale yellow crystals (2.96 g; yield = 80%). ¹H-NMR: δ = 8.29 (s, 2H), 3.48 (t, 2H), 1.5 (m, 2H), 1.3-1.2 (m, 6H), 0.99 (t, 3H). ¹³C-NMR: δ = 163.9, 136.7, 128.8, 30.6, 28.4, 23.2, 22.5, 14.1, 11.2.

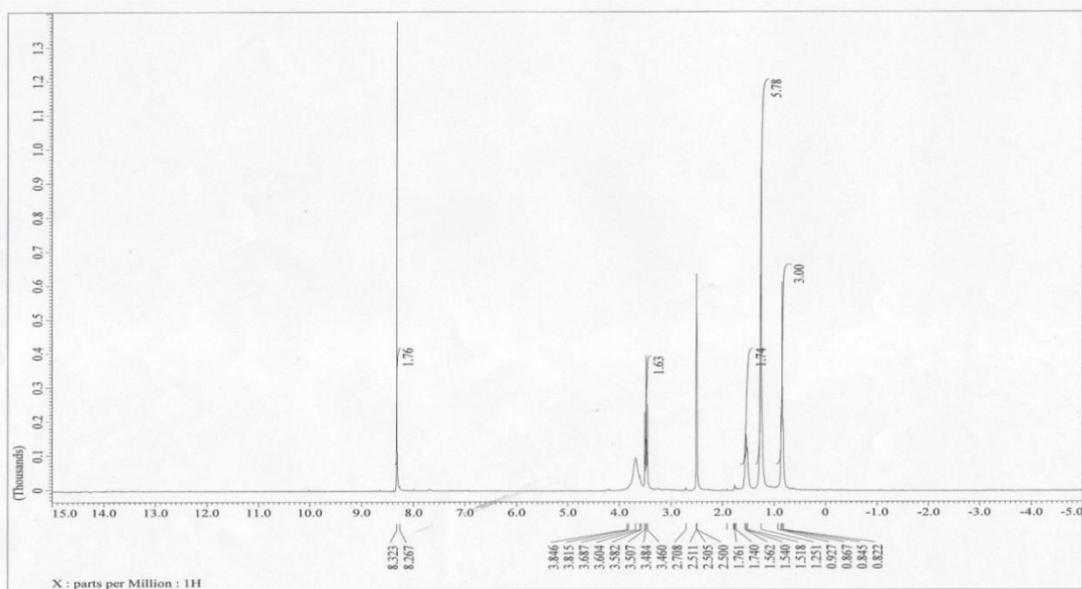


Figure S1. ¹H NMR (400 MHz) spectrum of compound HTPD in DMSO-D⁶

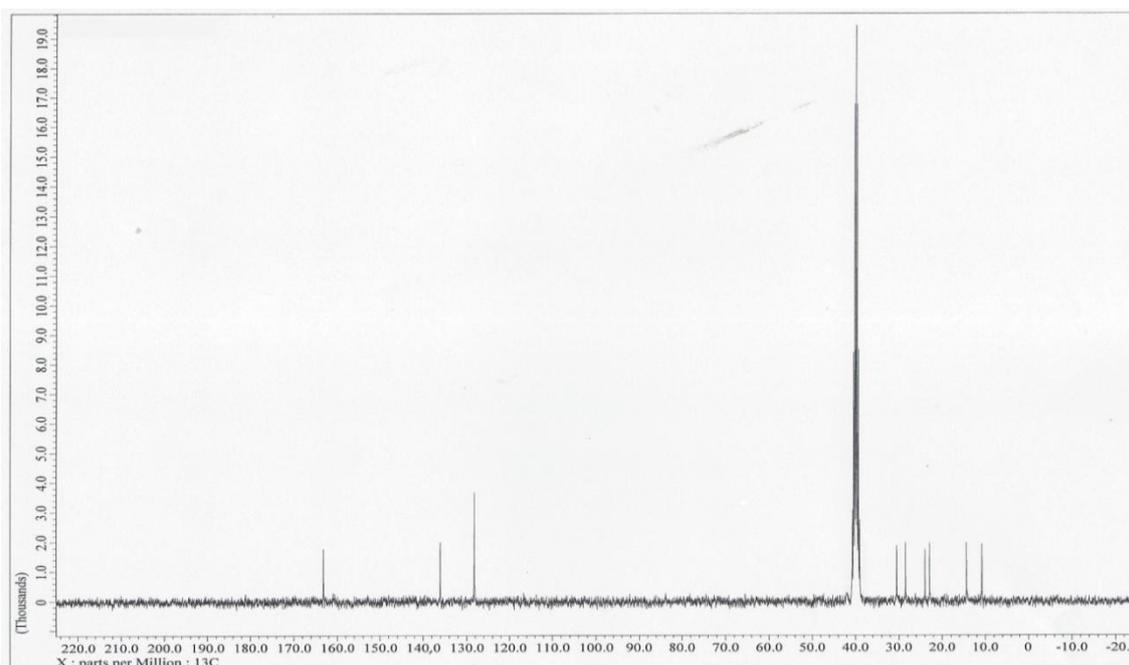
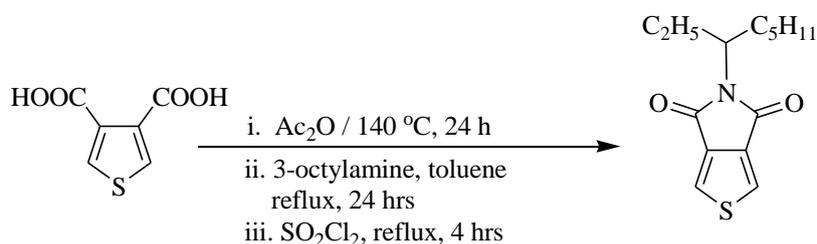


Figure S2. ^{13}C NMR (100 MHz) spectrum of compound HTPD in DMSO-D_6

1.2. Synthesis of 5-(2-ethylhexyl)-5*H*-thieno[3,4-*c*]pyrrole-4,6-dione (ETPD)¹



A solution of thiophene-3,4-dicarboxylic acid (3.0 g, 17.4 mmol) in acetic anhydride (150 ml) was heated and stirred under reflux at 140 °C for 24 h. The solvent was re-moved and the crude product thus obtained was recrystallized using toluene affording pale yellow crystals of thieno[3,4-*c*]furan-1,3-dione (2.41 g; yield = 90%). Thieno[3,4-*c*]furan-1,3-dione (2.41 g, 15.6 mmol) was dissolved in toluene (300 ml) followed by adding 1.5 equiv. of 3-octylamine (3.03 g, 23.4 mmol) and the mixture was refluxed with stirring for 24 h. The reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The crude solid thus obtained was dissolved in thienyl chloride (20 ml) and the mixture was refluxed again for 4 h. After the removal of the volatiles, the crude product was purified by silica gel column chromatography (CH_2Cl_2 : hexane /2:1) affording the desired product **ETPD** as a white solid (3.4 g; yield = 82%). $^1\text{H-NMR}$: δ =7.81 (s, 2H), 3.50

(m, 2H), 1.8 (m, 1H), 1.3-1.2 (m, 8H), 0.91 (t, 6H). $^{13}\text{C-NMR}$: δ = 160.7, 134.8, 113.0, 42.7, 38.2, 30.6, 28.6, 23.9, 23.0, 14.1, 10.4.

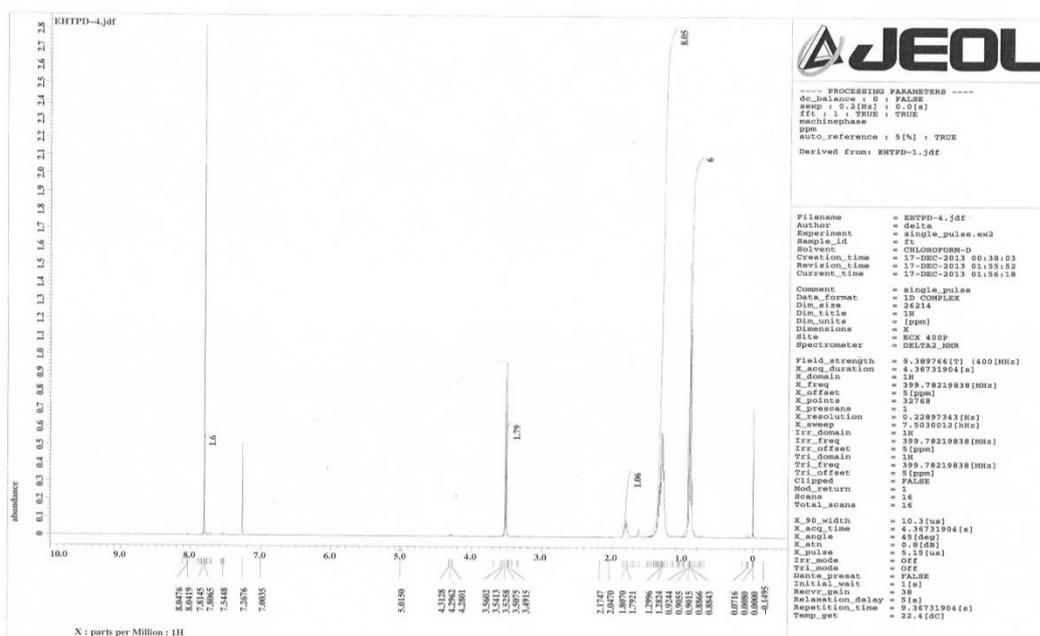


Figure S3. ^1H NMR (400 MHz) spectrum of compound **ETPD** in CDCl_3

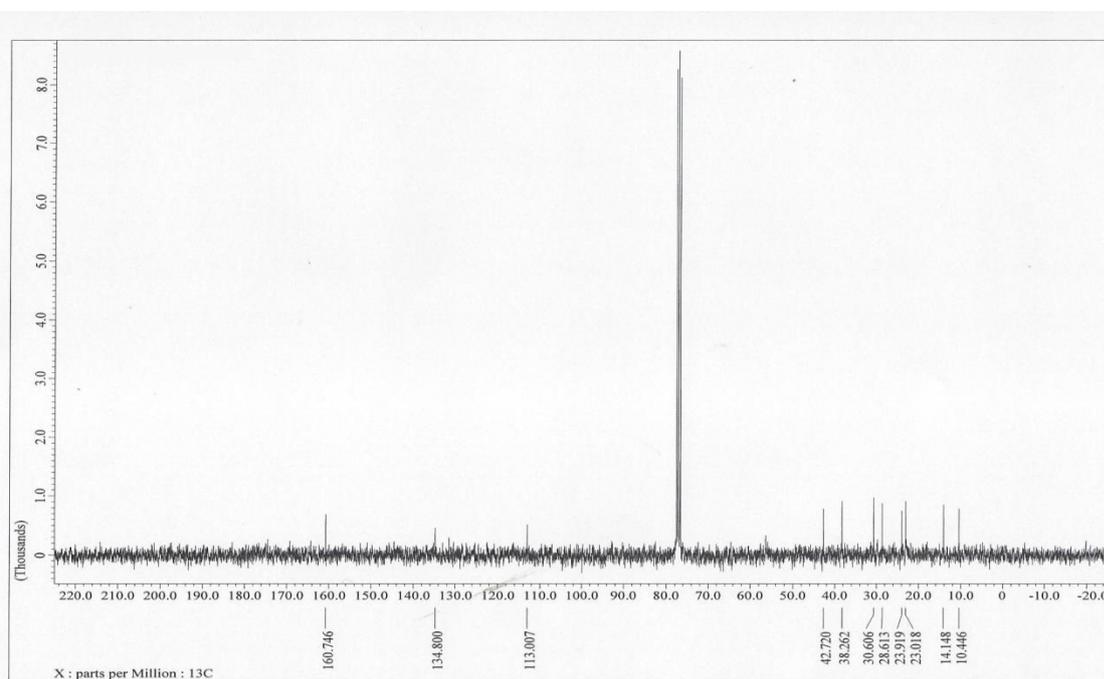
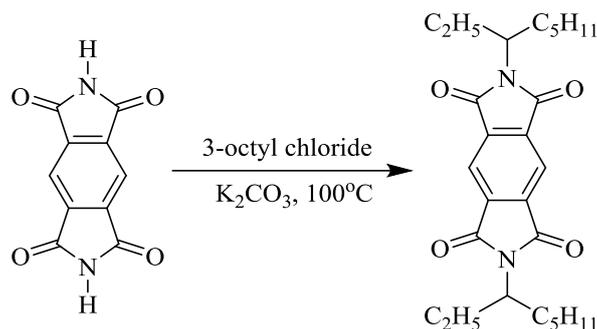


Figure S4. ^{13}C NMR (100 MHz) spectrum of compound **ETPD** in CDCl_3

1.3. Synthesis of 1,5-di(2-ethylhexyl)-pyromellitic-1,5-diimide (EPDI)



To a suspension of pyromellitic acid diimide (0.50 g, 2.31 mmol) and potassium carbonate (0.957 g, 6.94 mmol) in DMF (40 ml), 3-octyl chloride (1.02 g, 6.94 mmol) was injected through a septum under nitrogen. The reaction mixture was stirred for 24 h at $100^\circ C$ and then poured into water (200 ml). The reaction mixture was extracted with CH_2Cl_2 and the collected organic layers were washed with brine and dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure and the white solid thus obtained was purified by silica column chromatography (CH_2Cl_2 :hexane/1:2) affording the desired product **3** (0.76 g; yield = 75%). 1H -NMR: $\delta = 8.25$ (s, 2H), 3.65 (m, 4H), 1.85 (m, 2H), 1.33-1.29 (m, 16H), 0.87 (t, 12H). ^{13}C -NMR: $\delta = 167.0, 137.5, 118.4, 42.8, 38.5, 31.1, 28.5, 24.0, 23.0, 14.5, 10.5$.

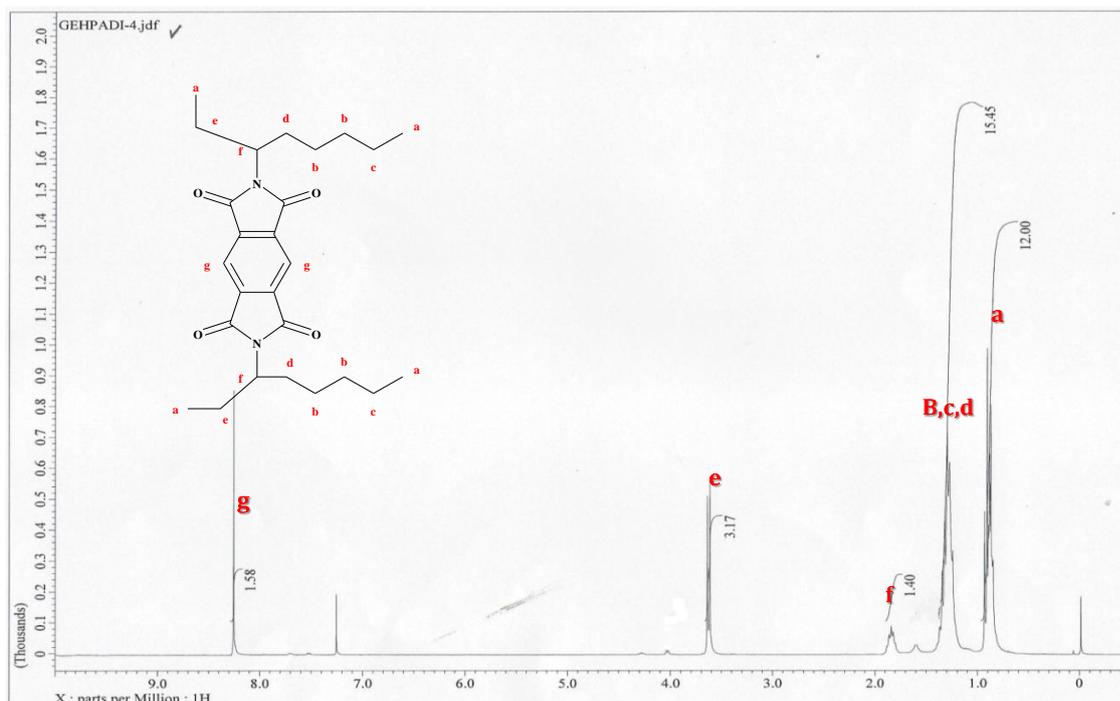


Figure S5. 1H -NMR (300 MHz) spectrum of compound **3** in $CDCl_3$

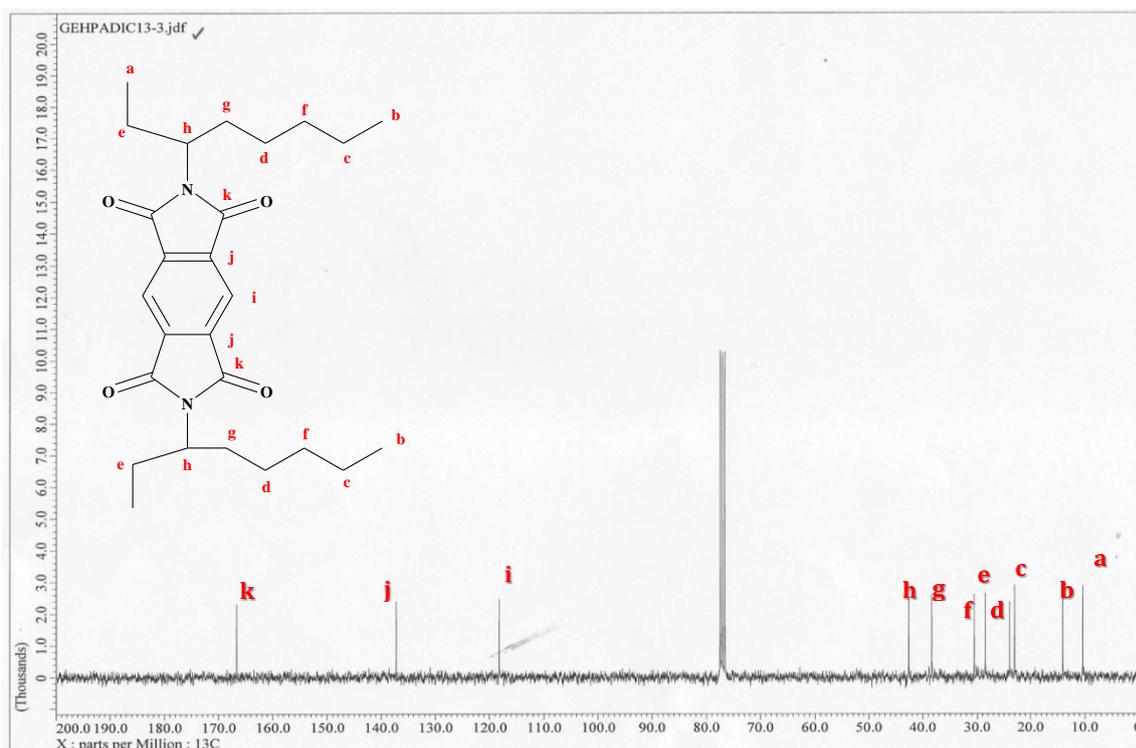
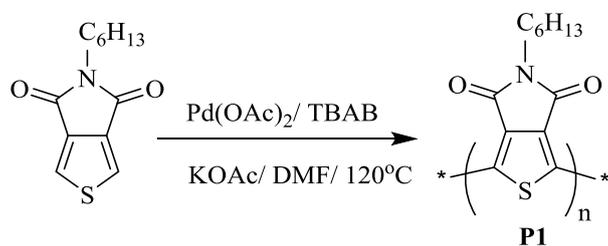


Figure S6. ^{13}C -NMR (100 MHz) spectrum of compound **3** in CDCl_3

2. Synthesis of π -conjugated homopolymers

2.1. Synthesis of poly[5-hexyl-5*H*-thieno[3,4-*c*]pyrrole-4,6-dione] (**P1**)



Potassium acetate bromide (0.280 g, 0.843 mmol), and palladium acetate (0.009 g, 0.08 mmol) was added to a stirred solution of **1** (0.10 g, 0.421 mmol) in anhydrous DMF (25 ml). The resulting reaction mixture was heated under reflux for 48 h at 120 °C, followed by cooling to room temperature and poured into methanol. The crude polymer thus precipitated was collected via filtration and washed successively with methanol. The solid crude polymer was loaded into an extraction thimble and washed repeatedly with methanol (48 h), followed by hexane (48 h) and finally dried under vacuum to give the desired polymer **P1**. ^1H -NMR: δ =3.48 (br, 2H), 2.1 (br, 2H), 1.5-0.99 (br, 11H).

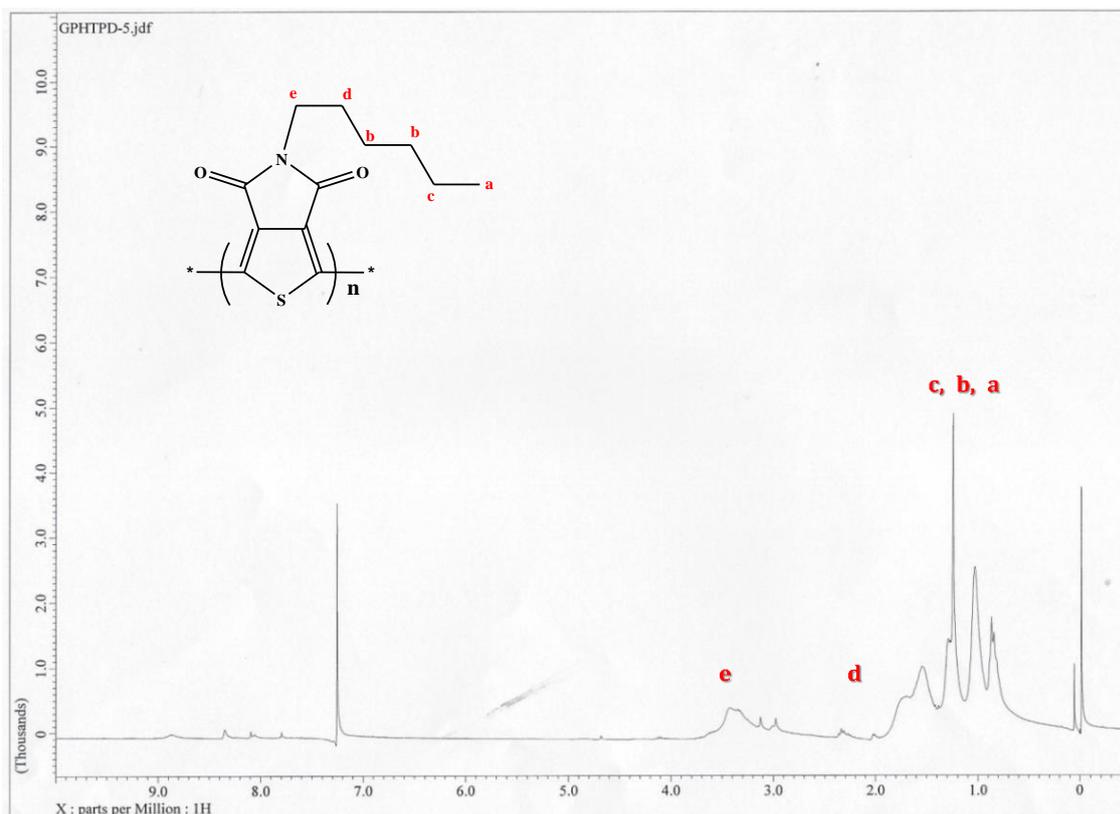
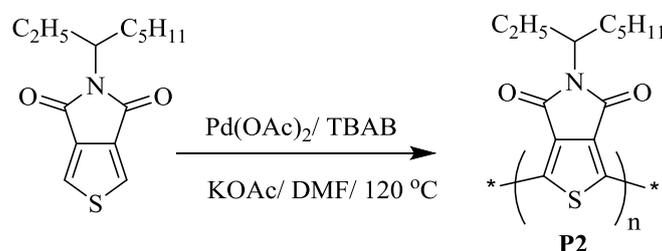


Figure S7. $^1\text{H-NMR}$ (300 MHz) spectrum of compound **P1** in CDCl_3

2.2. Synthesis of poly[5(2-ethylhexyl)-5*H*-thieno[3,4-*c*]pyrrolo-4,6-dione] (**P2**)



Potassium acetate (0.222 g, 2.26 mmol), tetrabutylammonium bromide (0.250 g, 0.754 mmol), and palladium acetate (0.008 g, 0.037 mmol) were added to a stirred solution of **2** (0.10 g, 0.377 mmol) in anhydrous DMF (25 ml). The resulting mixture was heated under reflux for 48 h at 120 °C. The reaction mixture was cooled to room temperature and then poured into methanol. The precipitated solid was collected via filtration and washed successively with methanol. The residual solid was loaded into an extraction thimble and washed repeatedly with methanol (48 h), followed by hexane (48 h) and finally dried under vacuum affording the desired polymer **P2**. $^1\text{H-NMR}$: $\delta=7.9$ (br, 2H), 3.50 (br, 2H), 2.90 (br, 1H), 1.8-0.91 (br, 14H).

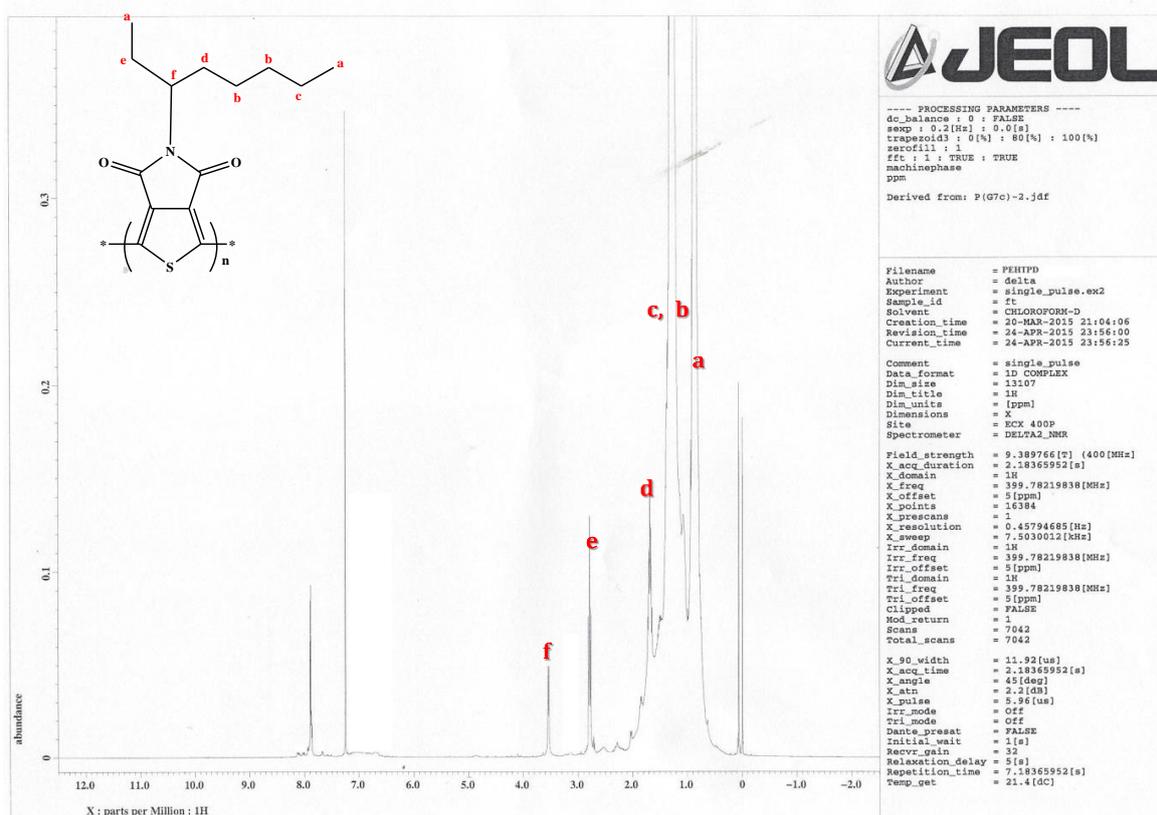
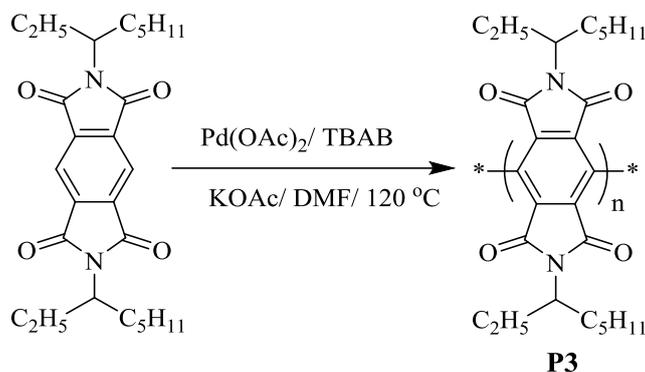


Figure S8. ¹H-NMR (300 MHz) spectrum of compound **P2** in CDCl₃

2.3. Synthesis of poly[1,5-di(2-ethylhexyl)-pyromellitic-1,5-diimide] (**P3**)



Potassium acetate (0.133 g, 1.36 mmol), tetrabutylammonium bromide (0.150 g, 0.454 mmol), and palladium acetate (0.005 g, 0.022 mmol) were added to a stirred solution of **3** (0.10 g, 0.227 mmol) in anhydrous DMF (25 ml). The resulting suspension was heated under reflux for 48 h at 120 °C, followed by cooling to room temperature. The reaction mixture was poured into methanol and the solid thus precipitated was collected via filtration and washed successively with methanol. The residual solid was loaded into an extraction thimble and washed repeatedly with methanol (48 h), followed by hexane

(48 h) and finally dried under vacuum to give the desired polymer **P3**. $^1\text{H-NMR}$ $\delta = 4.1$ (br, 2H), 3.6 (br, 4H), 1.8 (br, 4H), 0.90 (br, 24H).

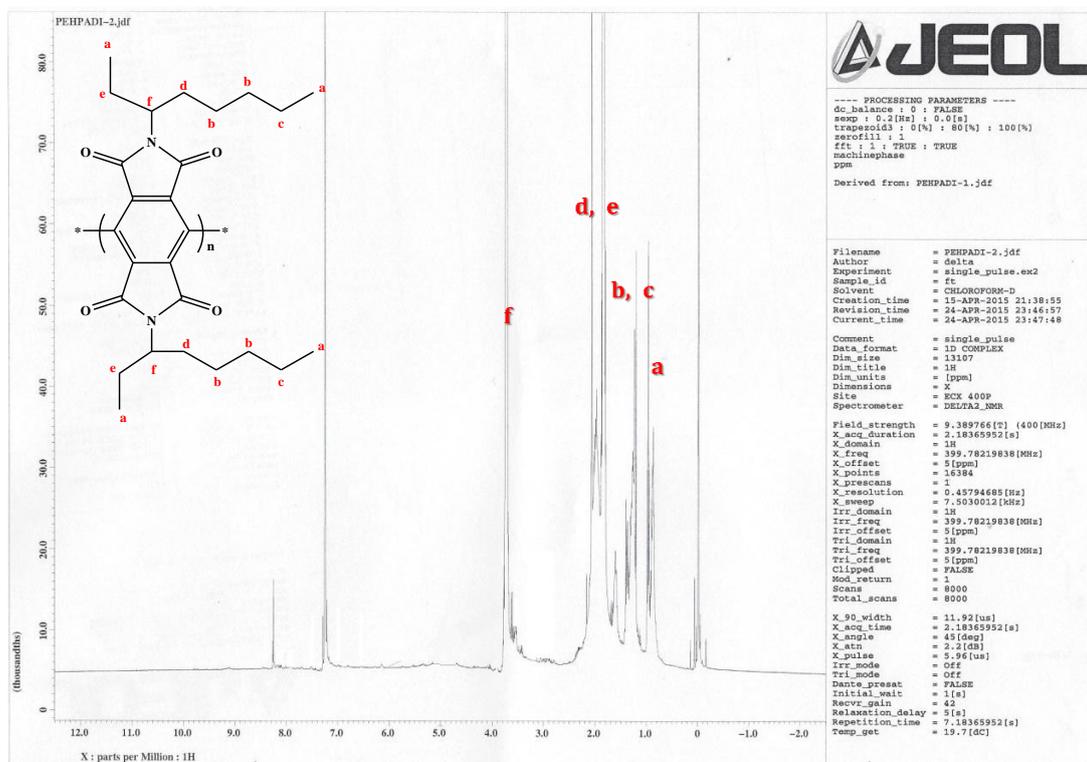


Figure S9. $^1\text{H-NMR}$ (300 MHz) spectrum of compound **P3** in CDCl_3

3. Optical and electrochemical properties of P1, P2 and P3

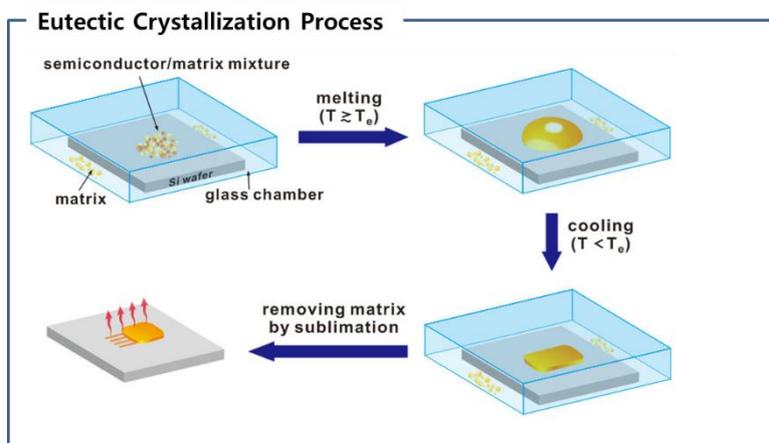
Table S1. Optical properties of **P1, P2 and P3**

| Polymer | UV-vis absorption | | | |
|---------|-------------------------------|-----------------------------|-------------------------------|------------------------|
| | Solution | | film | |
| | λ_{onset} (nm) | λ_{max} (nm) | λ_{onset} (nm) | E_g^{op} (eV) |
| P1 | 445 | 545 | 581 | 2.13 |
| P2 | 290 | 542 | 580 | 2.13 |
| P3 | 355 | 547 | 593 | 2.08 |

Table S2. Electrochemical properties of **P1, P2 and P3**

| Polymer | $E_g^{\text{elect.}}$ (eV) | HOMO (eV) | (LUMO eV) |
|-----------|-------------------------------|-----------|-----------|
| P1 | 1.90 | -5.64 | -3.74 |
| P2 | 1.89 | -5.61 | -3.72 |
| P3 | 1.75 | -5.64 | -3.89 |

4. FET device data



Scheme S1. The preparation method of organic semiconducting nanowires by eutectic melt crystallization.³

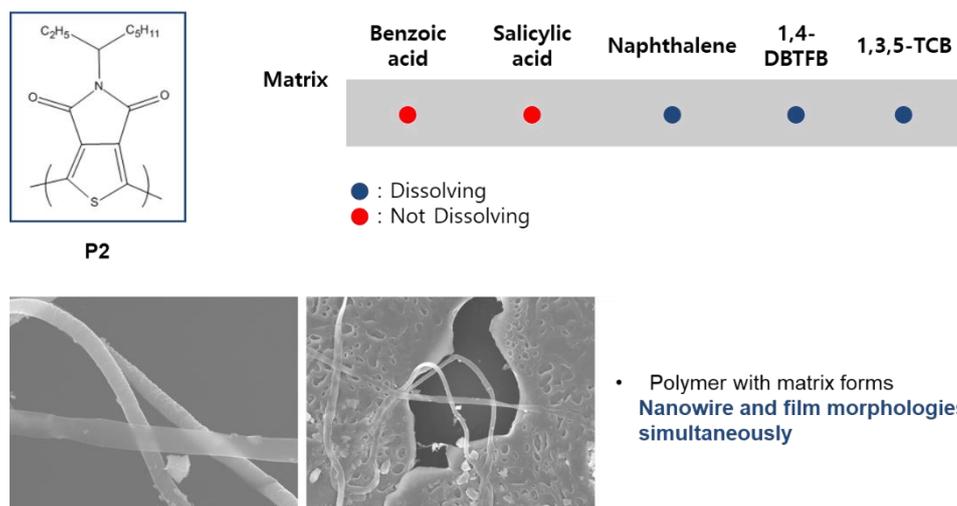


Figure S10. The formation of nanowires from **P2** and matrix by eutectic melt crystallization.

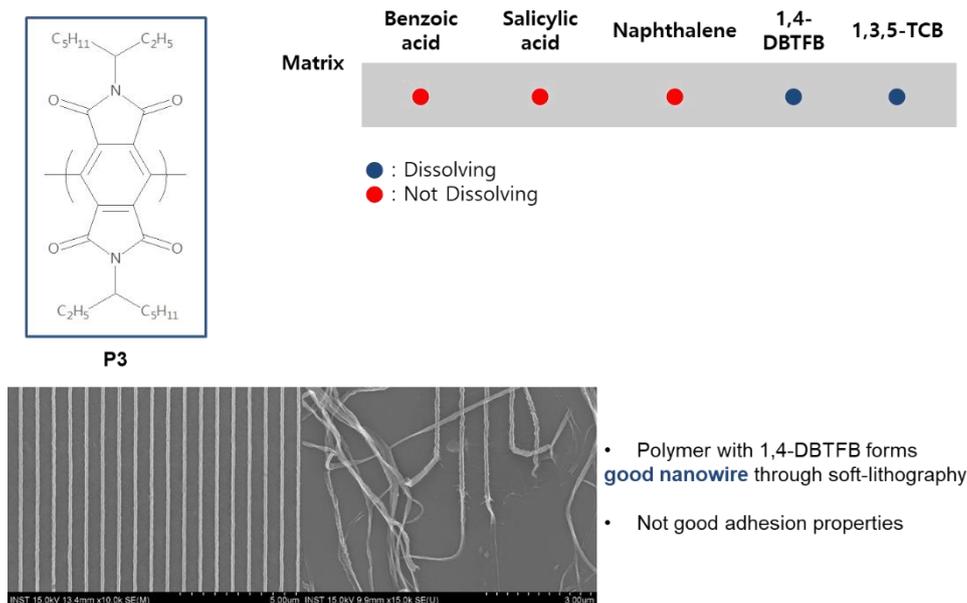


Figure S11. The formation of nanowires from P3 and matrix by eutectic melt crystallization.

5. References

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