Electronic Supplementary Information

Synthesis and Characterization of Novel Semiconducting Polymers Containing Pyrimidine for Organic Electronics

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Table of Contents

Experimental 2
Materials and Structural Analysis 2
Synthesis of 2-decyloxy-4,6-dimethylpyrimidine 3
Synthesis of 3,3’-dihexyl-2,2’-bithiophene-5,5’-dicarbaldehyde 4
Synthesis of 3-hexyl-3’-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-2,2’-bithiophene-5,5’-dicarbaldehyde 9
Synthesis of 3,3’-bis(2-ethylhexyl)-2,2’-bithiophene-5,5’-dicarbaldehyde 16
Synthesis of 2,5-dioctyloxyterephthalaldehyde 19
Synthesis of poly[2-(decyloxy)-4-vinyl-6-(4-vinylstyryl)pyrimidine] (P₁) 20
Synthesis of poly[2-(decyloxy)-4-vinyl-6-(2-(5-vinylthiophen-2-yl)vinyl)pyrimidine] (P₂) 23
Synthesis of poly[2-(decyloxy)-4-(2-(3,3’-dihexyl-5’-vinyl-2,2’-bithiophen-5-yl)vinyl)-6-vinylpyrimidine] (P₃) 24
Synthesis of poly[2-(decyloxy)-4-(2-(3’-hexyl-3-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5’-vinyl-2,2’-bithiophen-5-yl)vinyl)-6-vinylpyrimidine] (P₄) 27
Synthesis of poly[4-(2-(3,3’-bis(2-ethylhexyl)-5’-vinyl-2,2’-bithiophen-5-yl)vinyl)-2-(decyloxy)-6-vinylpyrimidine] (P₅) 30
Synthesis of poly[4-(2,5-bis(octyloxy)-4-vinylstyryl)-2-(decyloxy)-6-vinylpyrimidine] (P₆) 33
References 36
**Experimental**

*Materials and Structural Analysis*

2-Chloro-4,6-dimethylpyrimidine was purchased from AK Scientific, Inc. and all the other 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/benzophenoneketyl and freshly distilled prior to use. Thiophene-2,5-dicarbaldehyde, 1,4-dioctyloxybenzene and 1,4-dioctyloxy-2,5-diiodobenzene were prepared according to literature.\(^1\,^2\)

\(^1\)H and \(^13\)C NMR spectra were recorded at room temperature using either a 270 MHz JEOL or a 500 MHz Bruker spectrometer, as indicated, and were referenced to residual protio solvent (CHCl\(_3\): δ 7.26 ppm). The data are reported as follows: Chemical shifts are reported in ppm on δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet)

GC-MS was obtained on an Agilent 6890-5973 GC/MS work-station. The GC column was a Hewlett-packard fused silica capillary column cross-linked with 5% phenylmethylsiloxane. Helium was the carrier gas (1 mL/min).

Molecular weights of the synthesized polymers were measured by size exclusion chromatography (SEC) analysis on a Viscotec VE 3580 system equipped with ViscoGEL columns (GMHHR-M), connected to a refractive index (RI) detector. A GPC solvent/sample module (GPC\(_{\text{max}}\)) was used with HPLC grade THF as the eluent, and calibration was based on polystyrene standards.

The UV-Visible spectra of polymer solutions in chloroform solvents were carried out in 1 cm cuvettes using an Agilent 8453 UV-vis spectrometer. Thin films of polymer were obtained by evaporating of chloroform from polymer solutions on glass microscope slides.

The fluorescence spectra of polymer solutions in chloroform solvent were carried out in 1 cm cuvettes using Perkin Elmer Luminescence Spectrometer LS 508.

Cyclic voltagramograms were obtained with aBAS CV-50W voltammetric analyzer (Bioanalytical Systems, Inc.). Electrochemical grade tetrabutylammonium perchlorate (TBAP) was used without further purification. Acetonitrile was distilled over calcium hydride and collected over molecular sieves. The electrochemical cell was comprised of a platinum electrode, a platinum wire auxiliary electrode, and Ag/AgCl reference electrode. Acetonitrile solutions containing 0.1M TBAP were placed in a cell and purged with argon. A drop of polymer solution was evaporated in ambient air. The film was immersed into electrochemical cell containing the electrolyte, and the oxidation and reduction potentials were recorded. All electrochemical shifts were standardized to the ferrocene redox couple at 0.474 V.

X-ray diffraction patterns were obtained on a RIGAKU Ultima III diffractometer with Cu-K\(\alpha\) radiation (\(\lambda \sim 1.5406 \, \text{Å}\) source, scanning from 1 to 40 degrees (2\(\theta\)) at 0.04 degree intervals at a rate of 2 degrees/min. The polymers were dropcast from chloroform solution onto microscope cover glass substrate.
Monomer Synthesis

1) Synthesis of 2-decyloxy-4,6-dimethylpyrimidine

Scheme S1. Synthesis of 2-decyloxy-4,6-dimethylpyrimidine

To a warm (93 °C) suspension of 95% NaH (1.086 g, 0.043 mol) in 100 mL of toluene and 100 mL of DMF, decyl alcohol (8.10 mL, 6.68 g, 0.042 mol) was added drop-wise while stirring. The resulting mixture was heated at 115 °C for 2 hours. After 2 hours, 2-chloro-4,6-dimethylpyrimidine (4.000 g, 0.028 mol) dissolved in 25 mL of toluene was added slowly under stirring. The reaction mixture was heated at reflux overnight. The reaction mixture was cooled to room temperature and poured over ice. The product was extracted with 100 mL of diethyl ether, washed with water (3×100 mL), dried with anhydrous MgSO₄, concentrated to yield a dark brown oil which was purified by flash column chromatography on silica gel with (3:1) hexane:ethyl acetate as the eluent followed by vacuum distillation to obtain a clear oil. (5.890 g, 80%) ¹H-NMR (CDCl₃, 270 MHz) δ: 6.64 (s, 1H), 4.31 (t, 2H), 5.56 (s, 6H), 1.44 (m, 16H), 0.87 (t, 3H), ¹³C NMR (CDCl₃, 270MHz) δ: 169.01, 165.19, 113.58, 67.24, 31.91, 29.59, 29.42, 29.34, 29.01, 26.05, 23.81, 22.68, 14.01.

Figure S1. ¹H NMR spectrum of 2-decyloxy-4,6-dimethylpyrimidine
Figure S2. $^{13}$C NMR spectrum of 2-decyloxy-4,6-dimethylpyrimidine

2) Synthesis of 3,3’-dihexyl-2,2’-bithiophene-5,5’-dicarbaldehyde

Scheme S2. Synthesis of 3,3’-dihexyl-2,2’-bithiophene-5,5’-dicarbaldehyde

Synthesis of 3-hexylthiophene

3-Bromothiophene (50.000 g, 0.307 mol), Ni(dppp)Cl$_2$ (0.300 g, 0.554 mmol) and hexylmagnesium bromide(2M) (169.00 mL, 0.338 mol) were reacted in 100 mL of dry diethyl ether. The mixture was heated at reflux overnight, quenched in ~200 mL of water, extracted with 100 mL of diethyl ether, washed with water (3×100 mL), dried over anhydrous MgSO$_4$, and concentrated to yield a yellow oil, which was purified by column chromatography on silica gel using hexane as the eluent to obtain a clear oil. (41.38 g, 80%) $^1$H-NMR (CDCl$_3$, 270 MHz) δ: 7.57 (d, 1H), 7.28 (s, 1H), 7.24 (d, 1H) 2.96 (t, 2H), 1.65 (m, 8H), 1.23 (t, 3H) $^{13}$C NMR (CDCl$_3$, 270MHz) δ: 143.31, 128.39, 125.14, 119.84, 31.85, 30.70, 30.35, 29.10, 22.76, 14.23.
Synthesis of 2-bromo-3-hexylthiophene

3-Hexylthiophene (5.000 g, 0.030 mol) was diluted with THF:hexane (9:1) solvent mixture (60 mL) and N-bromosuccinimide (5.230 g, 0.029 mol) was added slowly while stirring at -5°C over a period of one hour. The mixture was stirred at room temperature for two hours, quenched in water, extracted with diethyl ether (100 mL), washed with water (3×100 mL), dried with anhydrous MgSO₄ and concentrated to obtain an oil which was purified by column chromatography on silica gel using hexane as the eluent to obtain a clear oil (5.00 g, 68%).

1H-NMR (CDCl₃, 270 MHz) δ: 7.20 (d, 1H), 6.82 (d, 1H), 2.58 (t, 2H), 1.32 (m, 8H), 0.91 (t, 3H).

13C-NMR (CDCl₃, 270 MHz) δ: 160, 140, 120, 100, 80, 60, 40, 20, 0.
NMR (CDCl$_3$, 270MHz) $\delta$: 142.05, 128.32, 125.21, 108.91, 31.75 29.83, 29.51, 29.02, 22.73, 14.21.

**Figure S5.** $^1$H NMR spectrum of 2-bromo-3-hexylthiophene

**Figure S6.** $^{13}$C NMR spectrum of 2-bromo-3-hexylthiophene

**Synthesis of 3,3’-dihexyl-2,2’-bithiophene**

(3-Hexylthiophen-2-yl)magnesium bromide was prepared by reacting magnesium (0.295 g, 0.0121mol) and 2-bromo-3-hexylthiophene (2.000 g, 8.097mmol) in the presence of 1 drop of 1,2-dibromoethane in 60 mL of anhydrous diethyl ether. The mixture was stirred under a nitrogen atmosphere for two hours. Catalyst (Ni(dppp)Cl$_2$) (0.219 g, 0.4048mmol) was added under nitrogen in a three neck round bottom flask to which the 2-bromo-3-hexylthiophene (2.000 g, 8.097 mmol) and 30 mL of anhydrous ether were added. The reaction mixture was stirred for 5
minutes. The Grignard reagent was cannulated to the flask containing 2-bromo-3-hexylthiophene and the catalyst and the mixture was heated at reflux overnight. The reaction mixture was quenched in water and the product was extracted with 200 mL diethyl ether, washed with water (3×100 mL), dried over anhydrous MgSO$_4$, and concentrated to yield a yellowish oil which was purified by column chromatography on silica gel with hexane as the eluent to obtain a clear oil (1.88 g, 70%) $^1$H-NMR (CDCl$_3$, 270 MHz) δ: 7.29 (d, 2H), 6.97 (d, 2H), 2.50 (t, 4H), 1.54 (m, 16H), 0.86 (t, 6H). $^{13}$C NMR (CDCl$_3$, 270MHz) δ: 142.42, 128.81, 128.61, 125.31, 31.75, 30.81, 29.21, 28.89, 22.68, 14.18.

**Figure S7.$^1$H NMR spectrum of 3,3’-dihexyl-2,2’-bithiophene**

**Figure S8.$^{13}$C NMR spectrum of 3,3’-dihexyl-2,2’-bithiophene**
**Synthesis of 3,3''-dihexyl-2,2''-bithiophene-5,5''-dicarbaldehyde**

3,3'-Dihexyl-2,2'-bithiophene (0.500 g, 1.496 mmol) was diluted with ~30 mL of dry THF under nitrogen. n-BuLi (2.5 M in hexane) (1.30 mL, 3.250 mmol) was added slowly at 0°C while stirring. The mixture was stirred at 0°C for 15 minutes before adding dry dimethyl formamide (0.46 mL, 5.984 mmol) at 0°C and stirred for an additional 10 minutes at 0°C. The mixture was warmed to room temperature followed by refluxing for two hours. The mixture was cooled down to room temperature and quenched in 50 mL of 1% cold hydrochloric acid. The desired product was extracted with 100 mL of diethyl ether, washed with water (3×100 mL) dried with anhydrous MgSO₄, concentrated to yield a brown oil, which was purified by column chromatography on silica gel with hexane eluent to obtain a clear oil (0.550 g, 94%).

**1H-NMR** (CDCl₃, 270 MHz) δ: 9.87 (s, 2H), 7.66 (s, 2H), 2.56 (t, 4H), 1.24 (m, 16), 0.85 (t, 6H)

**13C NMR** (CDCl₃, 270MHz) δ: 182.87, 144.54, 143.50, 137.52, 31.56, 30.55, 29.00, 28.94, 22.56, 14.08.

**Figure S9.** ¹H NMR spectrum of 3,3’-dihexyl-2,2’-bithiophene-5,5’-dicarbaldehyde
Figure S10. $^{13}$C NMR spectrum of 3,3’-dihexyl-2,2’-bithiophene-5,5’-dicarbaldehyde

3) Synthesis of 3-hexyl-3’-(2-(2-(methoxyethoxy)ethoxy)ethoxy)-2,2’-bithiophene-5,5’-dicarbaldehyde

Scheme S3. Synthesis of 3-hexyl-3’-(2-(2-(methoxyethoxy)ethoxy)ethoxy)-2,2’-bithiophene-5,5’-dicarbaldehyde

Synthesis of 3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)thiophene
In a dry 250 mL three-neck round bottom flask, equipped with a water condenser, 95% NaH (3.790 g, 0.158 mol) was mixed with anhydrous DMF (100 mL) under a nitrogen atmosphere. Triethylene glycol monomethyl ether (77.60 mL, 0.480 mol) was added drop-wise over a period of 30 minutes at 0°C. The solution was allowed to stir for additional 1 hour to assure complete consumption of NaH, while the temperature was maintained at 0 °C. To this reaction mixture,
bromothiophene (16.300 g, 0.099 mol) and CuBr (1.434 g, 9.998 mmol) were added. The ice bath was replaced with an oil bath and the solution was heated up to 110 °C. After 30 minutes at the elevated temperature, an aliquot was taken out, quenched with 1M aqueous solution of NH₄Cl, extracted with diethyl ether and subjected to GC-MS analysis. Note, if a relative abundance of the starting material was detected, an equimolar amount of CuBr was added and the reaction was allowed to proceed for an additional 30 minutes at the elevated temperature. The mixture was then poured into a 1M aqueous solution of NH₄Cl (100 mL) and stirred for 10 minutes. The organic phase was extracted with hexanes, dried over anhydrous MgSO₄. The product was purified by vacuum distillation to obtain a clear oil (14.938 g, 60%). $^1$H-NMR (CDCl₃, 270 MHz) δ: 7.14 (d,1H), 6.74 (d,1H), 6.23 (d,1H), 4.09 (t, 2H), 3.67 (t, 2H), 3.61 (m, 6H, 3.54 (m, 3H), 3.35 (s,3H). $^{13}$C NMR (CDCl₃, 270MHz) δ: 157.65, 124.69, 119.64, 97.55, 71.99, 70.83, 70.70, 70.62, 69.74, 69.63, 59.08.

**Figure S11.** $^1$H NMR spectrum of 3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)thiophene
Figure S12. $^{13}$C NMR spectrum of 3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)thiophene

Synthesis of 2-bromo-3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)thiophene

3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)ethoxy)thiophene (10.086 g, 0.0405 mol) was diluted with 200 mL of THF:Hexane (9:1) solvent mixture. The reaction mixture was cooled to -5 °C and N-bromosuccinimide (7.209 g, 0.0405 mol) was added slowly while stirring over a period of one hour. The mixture was stirred for two hours at 0°C and the product was extracted with hexane (300 mL). The organic phase was dried with anhydrous MgSO$_4$, and concentrated to yield a brown oil. The product was purified by column chromatography on silica gel by using hexane:ethylacetate (6:4) as the eluent to obtain a light red color oil (11.035 g, 83%). $^1$H-NMR (CDCl$_3$, 270 MHz) δ: 7.16 (d, 1H), 6.78 (d, 1H), 4.16 (t, 2H), 3.78 (t, 2H), 3.62 (m, 8H), 3.34 (s, 3H). $^{13}$C NMR (CDCl$_3$, 270MHz) δ: 154.44, 124.29, 118.03, 92.29, 71.99, 71.72, 71.00, 70.72, 70.60, 69.89, 59.08.
Figure S13. $^1$H NMR spectrum of 2-bromo-3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)thiophene

Figure S14. $^{13}$C NMR spectrum of 2-bromo-3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)thiophene

**Synthesis of 3-hexyl-3'-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)bithiophene**

(3-Hexylthiophen-2-yl)magnesium bromide was prepared by reacting 2-bromo-3-hexylthiophene (2.168 g, 8.744 mmol) with magnesium turnings (0.315 g, 0.0131 mol) in 50 mL of THF. The mixture was stirred at 60 °C for two hours. 2-Bromo-3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)thiophene (2.868 g, 8.744 mmol) and Ni(dppp)Cl$_2$ (0.454 g, 0.8385 mmol) were added to 50 mL of THF in a separate flask under nitrogen. The Grignard reagent was cannulated to the flask containing 2-bromo-3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)thiophene and the catalyst. The reaction mixture was heated at reflux under stirring for 3 days. The mixture was quenched in 100 mL of water, extracted with
200 mL of hexane, dried with anhydrous MgSO₄, and concentrated to yield a brown oil which was purified by column chromatography on silica gel by using hexane:ethylacetate(7:3) as the eluent to obtain a red color oil (2.52 g, 30 %). ¹H-NMR (CDCl₃, 270 MHz) δ: 7.18 (d,1H), 7.16 (d,1H), 6.91 (d,1H), 6.88 (d,1H), 4.14 (t,2H), 3.65 (t,2H), 3.62 (m,8H), 3.36 (s, 3H), 2.66 (t, 2H), 1.31 (m,8H), 0.86(t,3H). ¹³C NMR (CDCl₃, 270MHz) δ: 153.30, 140.90, 128.91, 127.56, 124.62, 123.34, 118.21, 114.53, 70.90, 70.72, 70.60, 59.10, 31.76, 29.41, 29.32, 22.69, 14.18.

Figure S15. ¹H NMR spectrum of 3-hexyl-3’-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)bithiophene

Figure S16. ¹³C NMR spectrum of 3-hexyl-3’-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)bithiophene
Synthesis of 3-hexyl-3’-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-2,2’-bithiophene-5-carbaldehyde

Dry dimethylformamide (0.74 mL, 9.615 mmol) was added to a three neck round bottom flask equipped with a reflux condenser and it was diluted with 5 mL of dichloroethane. The solution was kept in an ice bath and POCl₃ (0.90 mL, 9.615 mmol) was added drop-wise under stirring. The ice bath was removed and the mixture was stirred at room temperature for 30 minutes. The ice bath was replaced and 3-hexyl-3’-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-2,2’-bithiophene (1.000 g, 2.404 mmol) in 20 mL of dichloroethane was added slowly over a period of 15 minutes. After complete addition the mixture was refluxed for 2 hours. The mixture was cooled to room temperature, followed by the addition of sodium acetate (1.970 g, 24.038 mmol) dissolved in 10 mL of water and refluxed for 15 minutes. The mixture was cooled to room temperature and transferred to an extraction funnel. The dichloroethane layer was separated, and aqueous layer was extracted with diethyl ether (3×50 mL). The dichloroethane and diethyl ether layers were combined, washed with saturated aqueous sodium carbonate (3×100 mL), dried with anhydrous MgSO₄, concentrated to yield a dark brown oil. The product was purified by column chromatography on silica gel using hexane: ethyl acetate (3:2) to obtain a light red color oil (0.420 g, 39%).

1H-NMR (CDCl₃, 500 MHz) δ: 9.82 (s, 1H), 7.55 (s, 1H), 7.28 (d, 1H), 6.94 (d, 1H), 4.25 (t, 2H), 3.69 (t, 2H), 3.61 (m, 8H), 3.34 (s, 3H), 2.77 (t, 2H), 1.30 (m, 8H), 0.87 (t, 3H).

Figure S17. 1H NMR spectrum of 3-hexyl-3’-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-2,2’-bithiophene-5-carbaldehyde

Synthesis of 3-hexyl-3’-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-2,2’-bithiophene-5,5’-dicarbaldehyde

Dry dimethylformamide (1.40 mL, 0.0173 mol) was taken in to a three neck round bottom flask equipped with a reflux condenser and it was diluted with 5 mL of dichloroethane. The solution was kept in an ice bath and POCl₃ (1.62 mL, 0.0173 mol) was added drop-wise under stirring. The ice bath was removed and the mixture was stirred at room temperature for 30 minutes. The ice bath was replaced and 3-hexyl-3’-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-2,2’-bithiophene-
5-carbaldehyde (0.770 g, 1.734 mmol) in 20 mL of dichloroethane was added slowly over a period of 15 minutes. After complete addition the mixture was refluxed overnight. The mixture was cooled down to room temperature, sodium acetate (1.419 g, 0.0173 mmol) dissolved in 20 mL of water was added and refluxed for 15 minutes. The mixture was cooled down to room temperature, transferred to a extraction funnel, dichloroethane layer was separated, and aqueous layer was extracted with diethyl ether (3×50 mL). Dichloroethane and diethyl ether layers were combined, washed with saturated aqueous sodium carbonate (3×100 mL), dried with anhydrous MgSO₄, concentrated to yield a dark brown oil. The product was purified by column chromatography on silica gel using hexane: ethyl acetate (3:2) to obtain a red oil (0.294g, 36%).

1H-NMR (CDCl₃, 500 MHz) δ: 9.89 (s, 1H), 9.85 (s, 1H), 7.61 (s, 2H), 4.18 (t, 2H), 3.75 (t, 2H), 3.72 (m, 8H), 3.63 (s, 3H), 2.85 (t, 2H), 1.32 (m, 8H), 0.89 (t, 3H)

13C-NMR (CDCl₃, 500 MHz) δ: 183.19, 182.34, 155.12, 142.66, 141.91, 139.29, 138.03, 123.98, 123.66, 71.42, 70.76, 42.88, 31.68, 30.28, 30.05, 29.24, 22.63, 14.13.

Figure S18. 1H NMR spectrum of 3-hexyl-3’-(2-(2-methoxyethoxy)ethoxy)ethoxy)-2,2’-bithiophene-5,5’-dicarbaldehyde
Figure S19. $^{13}$C NMR spectrum of 3-hexyl-3’-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-2,2’-bithiophene-5,5’-dicarbaldehyde

4) Synthesis of 3,3’-bis(2-ethylhexyl)-2,2’-bithiophene-5,5’-dicarbaldehyde

Scheme S3. 3,3’-bis(2-ethylhexyl)-2,2’-bithiophene-5,5’-dicarbaldehyde

Synthesis of 2-bromo-3-(2-ethylhexyl)thiophene

(2-Ethylhexyl)magnesium bromide was prepared by reacting 2-ethylhexylbromide (10.000 g, 0.05178 mol) with magnesium turnings (1.887 g, 0.07767 mol) in anhydrous diethyl ether (50 mL) under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2 hours and cannulated to a flask containing 3-bromothiophene (8.442 g, 0.05178 mol) and Ni(dppp)Cl$_2$ (0.140 g, 0.2589 mmol) in anhydrous diethyl ether (50 mL) under nitrogen. The mixture was heated at reflux overnight. The mixture was quenched in (100 mL) of water and the product was extracted with 150 mL of hexane. The organic phase was washed with water (3×100 mL), dried over anhydrous MgSO$_4$, concentrated to yield a yellowish oil, which was purified by column chromatography on silica gel with hexane eluent to yield a colorless oil (4.840 g, 48%).

3-(2-Ethylhexyl)thiophene (4.706 g, 0.02401 mol) was diluted with 200 mL of THF:hexane (9:1) and N-bromosuccinimide (4.231g, 0.02377 mol) was added slowly at -5 °C over a period of 1 hour. The mixture was stirred at the same temperature for 3 hours. The mixture was quenched in water and extracted with 200 mL of hexane. The organic phase was washed with water (3×100 mL), dried with anhydrous MgSO$_4$, concentrated to yield a yellowish oil. The product was
purified by column chromatography on silica gel with hexane eluent to yield a colorless oil (3.40 g, 52%). $^1$H-NMR (CDCl$_3$, 270 MHz) $\delta$: 7.19 (d, 1H), 6.78 (d, 1H), 2.49 (d, 2H), 1.30 (m, 9H), 0.91 (t, 6H). $^{13}$C NMR (CDCl$_3$, 270MHz) $\delta$: 141.24, 128.87, 125.02, 109.51, 40.06, 33.69,32.56, 31.69, 28.87, 25.75, 23.12, 22.76, 14.21, 10.90.

**Figure S20.** $^1$H NMR spectrum of 2-bromo-3-(2-ethylhexyl)thiophene

**Figure S21.** $^{13}$C NMR spectrum of 2-bromo-3-(2-ethylhexyl)thiophene

**Synthesis of 3,3’-bis(2-ethylhexyl)2,2’-bithiophene**

(3-(2-Ethylhexyl)thiophen-2-yl)magnesium bromide was prepared in a three neck round bottom flask fitted with a reflux condenser by reacting 2-bromo-3-(2-ethylhexyl)thiophene (1.400 g, 5.0725 mmol) with magnesium turnings (0.1826 g, 7.6086 mmol) in 50 mL of dry THF under a nitrogen atmosphere. The reaction mixture was heated at 60 °C for two hours under stirring. In a
separate three neck round bottom flask fitted with a reflux condenser, 2-bromo-3-(2-ethylhexyl)thiophene (1.400 g, 5.0725 mmol) and Ni(dppp)Cl₂ (0.138 g, 0.254 mmol) were added under nitrogen in 50 mL of dry THF. The Grignard reagent was cannulated into the other flask and the mixture was heated at reflux for 2 days. The progress of the reaction was monitored by taking aliquots which were quenched in water, extracted into diethyl ether and subjected to GC-MS analysis. Note, if a relative abundance of starting materials were detected, an equimolar amount of Ni(dppp)Cl₂ was added and refluxed for another day. After 3 days, THF was evaporated and the product was extracted with 200 mL of hexane, washed with water (3x100mL), dried with anhydrous MgSO₄, concentrated to yield a brown oil, which was purified by column chromatography on silica gel with hexane as the eluent, followed by fractional distillation under vacuum. Even after vacuum distillation product was contaminated with 2-bromo-3-(2-ethylhexyl)thiophene, and the mixture was used in the next step.

**Synthesis of 3,3’-di-3-(2-ethylhexyl)-2,2’-bithiophene-5,5’-dicarbaldehyde**

3,3’-bis(2-ethylhexyl)2,2’-bithiophene (3.102 g, 7.955 mmol) was diluted with 100 mL of dry THF under nitrogen. n-BuLi (2.5M in hexane) (9.60 mL, 0.0239 mol) was added at 0 °C and the mixture was stirred at 0°C for 2 hours. Dry DMF (3.10 mL, 0.0398 mol) was added to the mixture at 0°C and stirred for another 15 minutes. Ice bath was replaced with an oil bath and the mixture was heated at reflux overnight. The mixture was cooled down to room temperature and quenched in 1% HCl (200 mL), extracted with hexane (150 mL), washed with water (3x100 mL), dried over anhydrous MgSO₄ and concentrated to yield a dark brown oil. The desired product was purified by column chromatography on silica gel using hexane:ethyl acetate (9:1) as the eluent to obtain a reddish orange oil (1.49 g, 60%) ¹H-NMR (CDCl₃, 500 MHz) δ: 9.85 (s, 2H), 7.60 (s, 2H), 2.42 (d, 4H), 1.41 (m, 2H), 1.11 (m, 16H), 0.71 (t, 12H) ¹³C-NMR (CDCl₃, 500 MHz) δ: 182.84, 143.76, 143.44, 138.17, 137.87, 40.44, 33.15, 32.58, 31.63, 28.78, 25.72, 22.95, 22.70, 14.11, 10.73.

**Figure S22.** ¹H NMR spectrum of 3,3’-bis(2-ethylhexyl)-2,2’-bithiophene-5,5’-dicarbaldehyde
Figure S23. $^{13}$C NMR spectrum of 3,3'-bis(2-ethylhexyl)-2,2'-bithiophene-5,5'-dicarbaldehyde

5) Synthesis of 2,5-dioctyloxyterephthalaldehyde

[Diagram of the reaction]

Scheme S4. 2,5-dioctyloxy terephthalaldehyde

1,4-Dioctyloxybenzene and 1,4-dioctyloxy-2,5-diiodobenzene were prepared according to previously published methods. Grignard reagent of 1,4-dioctyloxy-2,5-diiodobenzene was prepared by reacting 1,4-dioctyloxy-2,5-diiodobenzene (3.500 g, 5.969 mmol) and magnesium turnings (0.580 g, 0.024 mol) in 60 mL of THF. The mixture was stirred at 60 °C for 2 hours. Dry dimethylformamide (9.30 mL, 0.119 mol) was added and the mixture was stirred at the same temperature for 5 hours. The mixture was cooled to room temperature, quenched in 1% HCl (200 mL), extracted with diethyl ether, washed with water (3×100 mL), dried over anhydrous MgSO$_4$, and concentrated to yield a dark yellow oily solid. The product was purified by column chromatography on silica gel using hexane: ethyl acetate (9.5:0.5) to obtain a bright yellow solid. (0.698 g, 30%) $^1$H-NMR (CDCl$_3$, 500 MHz) δ: 10.52 (s, 2H), 7.42 (s, 2H), 4.08 (t, 4H), 1.30 (m, 24H), 0.88 (t, 6H) $^{13}$C-NMR (CDCl$_3$, 500 MHz) δ: 189.54, 155.31, 129.35, 111.68, 69.32, 31.85, 29.34, 29.27, 29.12, 26.09, 22.72, 14, 16.
Figure S24. $^1$H NMR spectrum of 2,5-dioctyloxyterephthalaldehyde

Figure S25. $^{13}$C NMR spectrum of 2,5-dioctyloxyterephthalaldehyde

Polymer Synthesis

1) Synthesis of poly[2-(decyloxy)-4-vinyl-6-(4-vinylstyryl)pyrimidine] (P1)

2-Decyloxy-4,6-dimethylpyrimidine (0.500 g, 1.894 mmol) was added to a three neck round bottom flask equipped with a reflux condenser and degassed with nitrogen for 15 minutes. THF (5mL) was added before adding $K^+(CH_3)CO^-$ (0.531 g, 4.735 mmol) and 18-crown-6 (1.250 g, 4.735 mmol) dissolved in dry THF (15 mL) drop-wise and stirred at room temperature for 30 minutes. Terephthaldicarbaldehyde(0.254 g, 1.894 mmol) dissolved in dry THF (15 mL) was added and the mixture was stirred at reflux temperature under nitrogen for 2 hours and the
polymer was precipitated in methanol. The polymer was filtered and was purified by Soxhlet extractions with methanol, hexane and chloroform. The polymer was obtained by evaporating chloroform as a dark red solid (0.246, 20%; $M_n = 7500$ g/mol, PDI = 1.6).

**Figure S26.** $^1$H-NMR spectrum of poly[2-(decoxy)-4-vinyl-6-(4-vinylstyrlyl)pyrimidine](P1)

**Figure S27.** UV-Vis absorption (blue) and photoluminescence (red) spectra of polymer poly[2-(decoxy)-4-vinyl-6-(4-vinylstyrlyl)pyrimidine](P1) in chloroform solution
Figure S28. Change in fluorescence intensity upon changing concentration of poly[2-(decyloxy)-4-vinyl-6-(4-vinylstyryl)pyrimidine](P1) in chloroform solution. (All the other polymers show the same trend and only the plot for P1 is shown)

Figure S29. Cyclic voltammogram of poly[2-(decyloxy)-4-vinyl-6-(4-vinylstyryl)pyrimidine](P1)
**Synthesis of poly[2-(decoxy)-4-vinyl-6-(2-(5-vinylthiophen-2-yl)vinyl)pyrimidine] (P2)**

2-Decyloxy-4,6-dimethylpyrimidine (0.289 g, 1.096 mmol) was added to a three neck round bottom flask equipped with a reflux condenser and degassed with nitrogen for 15 minutes. THF (5 mL) was added before adding K⁺(CH₃)₃CO⁻ (0.307 g, 1.096 mmol) and 18-crown-6 (0.722 g, 2,734 mmol) dissolved in dry THF (10 mL) drop-wise and stirred at room temperature for 30 minutes. 3,3’-dihexyl-2,2’-bithiophene-5,5’-dicarbaldehyde (0.530 g, 3.788 mmol) dissolved in dry THF (10 mL) was added and the mixture was stirred at reflux temperature under nitrogen for 24 hours and the polymer was precipitated in methanol. The polymer was filtered and was purified by Soxhlet extractions with methanol, hexane and chloroform. The polymer was obtained by evaporating the chloroform layer to obtain the polymer as a dark red solid (0.156 g, 30%, Mₙ = 8300 g/mol, PDI = 4.4).

![Figure S30.1H-NMR spectrum of poly[2-(decoxy)-4-vinyl-6-(2-(5-vinylthiophen-2-yl)vinyl)pyrimidine](P2)](image)

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**Figure S31.** UV-Vis absorption (blue) and photoluminescence (red) spectra of poly[2-(decyloxy)-4-vinyl-6-(2-(5-vinylthiophen-2-yl)vinyl)pyrimidine](P2) in chloroform

**Figure S32.** Cyclic voltammogram of poly[2-(decyloxy)-4-vinyl-6-(2-(5-vinylthiophen-2-yl)vinyl)pyrimidine](P2)

**Synthesis of poly[2-(decyloxy)-4-(2-(3,3'-dihexyl-5'-vinyl-2,2'-bithiophen-5-yl)vinyl)-6-vinylpyrimidine] (P3)**
2-Decyloxy-4,6-dimethylpyrimidine (0.289 g, 1.096 mmol) was added to a three neck round bottom flask equipped with a reflux condenser and degassed with nitrogen for 15 minutes. THF (5 mL) was added before adding K^+(CH_3)_3CO^- (0.307 g, 1.096 mmol) and 18-crown-6 (0.722 g,
2,734 mmol) dissolved in dry THF (10 mL) drop-wise and stirred at room temperature for 30 minutes. 3,3’-dihexyl-2,2’-bithiophene-5,5’-dicarbaldehyde (0.530 g, 3.788 mmol) dissolved in dry THF (10 mL) was added and the mixture was stirred at reflux temperature under nitrogen for 24 hours and the polymer was precipitated in hexane. The polymer was filtered and was purified by Soxhlet extractions with hexane, methanol and chloroform. The polymer was obtained by evaporating the chloroform layer to obtain the polymer as a dark red solid (0.396 g, 37%, $M_n = 9800$ g/mol, PDI = 3.8).

**Figure S3.** $^1$H-NMR spectrum of poly[2-(decyloxy)-4-(2-(3,3’-dihexyl-5’-vinyl-2,2’-bithiophen-5-yl)vinyl)-6-vinylpyrimidine] (P3)

**Figure S34.** UV-vis absorption spectra of poly[2-(decyloxy)-4-(2-(3,3’-dihexyl-5’-vinyl-2,2’-bithiophen-5-yl)vinyl)-6-vinylpyrimidine] (P3) in chloroform (blue line) and in thin-film (red line)
**Figure S35.** UV-Vis absorption (blue) and photoluminescence (red) spectra of poly[2-(decyloxy)-4-(2-(3,3'-dihexyl-5'-vinyl-2,2'-bithiophen-5-yl)vinyl)-6-vinylpyrimidine](P3) in chloroform.

**Figure S36.** Cyclic voltammogram of poly[2-(decyloxy)-4-(2-(3,3'-dihexyl-5'-vinyl-2,2'-bithiophen-5-yl)vinyl)-6-vinylpyrimidine](P3)
Figure S37. XRD of poly[2-(decyloxy)-4-(2-(3,3'-dihexyl-5'-vinyl-2,2'-bithiophen-5-yl)vinyl)-6-vinylpyrimidine](P3) in thin film on glass substrate

Synthesis of poly[2-(decyloxy)-4-(2-(3'-hexyl-3-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5'-vinyl-2,2'-bithiophen-5-yl)vinyl)-6-vinylpyrimidine](P4)

2-Decyloxy-4,6-dimethylpyrimidine (0.164 g, 0.623 mmol) was added to a three neck round bottom flask equipped with a reflux condenser and degassed with nitrogen for 15 minutes. THF (2 mL) and toluene (2 mL) was added before adding K+(CH3)3CO− (0.174 g, 1.557 mmol) and 18-crown-6 (0.411 g, 1.557 mmol) dissolved in dry THF (8 mL) and toluene (8 mL) drop-wise and stirred at room temperature for 30 minutes. 3-Hexyl-3’-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-2,2’-bithiophene-5,5’-dicarbaldhyde (0.294 g, 0.623 mmol) dissolved in dry THF (5 mL) and toluene (5 mL) were added and the mixture was stirred at reflux under nitrogen for 24 hours. The polymer was precipitated in hexane. The polymer was filtered and was purified by Soxhlet extractions with hexane and chloroform. The chloroform layer was washed with water (3×100 mL) and dried with anhydrous MgSO4. The polymer was obtained from the chloroform fraction on evaporation of the solvent. The polymer was obtained as a dark red solid (0.353 g, 50%, Mn = 11565 g/mol, PDI = 1.7).
Figure S38. $^1$H-NMR spectrum of poly[2-(decyloxy)-4-(2-(3'-hexyl-3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5'-vinyl-2,2'-bithiophen-5-yl)vinyl)-6-vinylpyrimidine](P4)

Figure S39. UV-Vis absorption spectra of poly[2-(decyloxy)-4-(2-(3'-hexyl-3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5'-vinyl-2,2'-bithiophen-5-yl)vinyl)-6-vinylpyrimidine] (P4) in chloroform (blue line) and in thin-film (red line)
Figure S40. UV-Vis absorption (blue) and photoluminescence (red) spectra of poly[2-(decyloxy)-4-(2-(3’-hexyl-3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5’-vinyl-2,2’-bithiophen-5-yl)vinyl)-6-vinylpyrimidine](P4) in chloroform.

Figure S41: Cyclic voltogram of poly[2-(decyloxy)-4-(2-(3’-hexyl-3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)ethoxy)-5’-vinyl-2,2’-bithiophen-5-yl)vinyl)-6-vinylpyrimidine](P4)
Figure S42: XRD of poly[2-(decyloxy)-4-(2-(3'-hexyl-3-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5'-vinyl-2,2'-bithiophen-5-yl)vinyl]-6-vinylpyrimidin] (P4) in thin film on glass substrate

Synthesis of poly[4-(2-(3,3'-bis(2-ethylhexyl)-5'-vinyl-2,2'-bithiophen-5-yl)vinyl]-2-(decyloxy)-6-vinylpyrimidine] (P5)

2-Decyloxy-4,6-dimethylpyrimidine (0.526 g, 1.991 mmol) was added to a three neck round bottom flask equipped with a reflux condenser and degassed with nitrogen for 15 minutes. THF (5 mL) and toluene (5 mL) were added before adding K(CH₃)₃CO⁻ (0.558 g, 4.976 mmol) and 18-crown-6 (1.314 g, 4.976 mmol) dissolved in dry THF (15 mL) and toluene (15 mL) drop-wise and stirred at room temperature for 30 minutes. 3,3'-Bis(2-ethylhexyl)-2,2'-bithiophene-5,5'-dicarbaldehyde (0.888 g, 1.991 mmol) dissolved in dry THF (10 mL) and toluene (10 mL) were added and the mixture was stirred at reflux under nitrogen for 24 hours. The polymer was precipitated in methanol. The polymer was filtered and was purified by Soxhlet extractions with methanol, hexane and chloroform. The polymer was obtained from the chloroform fraction on evaporation of the solvent. The polymer was obtained as a dark red solid (0.903 g, 42%, Mₙ = 5039 g/mol, PDI = 1.8).
**Figure S42:** $^1$H-NMR spectrum of poly[4-(2-(3,3′-bis(2-ethylhexyl)-5′-vinyl-2,2′-bithiophen-5-yl)vinyl)-2-(decyloxy)-6-vinylpyrimidine](P5)

**Figure S44.** UV-Vis absorption spectra of poly[4-(2-(3,3′-bis(2-ethylhexyl)-5′-vinyl-2,2′bithiophen-5-yl)vinyl)-2-(decyloxy)-6-vinylpyrimidine] (P5) in chloroform (blue line) and in thin-film (red line)
Figure S45. UV-vis absorption (blue) and photoluminescence (red) spectra of poly[4-(2-(3,3'-bis(2-ethylhexyl)-5'-vinyl-2,2'-bithiophen-5-yl)vinyl)-2-(decyloxy)-6-vinylpyrimidine](P5) in chloroform

Figure S46. Cyclic voltammogram of poly[4-(2-(3,3'-bis(2-ethylhexyl)-5'-vinyl-2,2'-bithiophen-5-yl)vinyl)-2-(decyloxy)-6-vinylpyrimidine](P5)
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Figure S47. XRD of poly[4-(2-(3,3′-bis(2-ethylhexyl)-5′-vinyl-2,2′-bithiopen-5-yl)vinyl)-2- (decyloxy)-6-vinylpyrimidine](P5) in thin film on glass substrate

Synthesis of poly[4-(2,5-bis(octyloxy)-4-vinylstyryl)-2-(decyloxy)-6-vinylpyrimidine] (P6)
2-decyloxy-4,6-dimethylpyrimidine (0.406 g, 1.538 mmol) was added to a three neck round bottom flask equipped with a reflux condenser and degassed with nitrogen for 15 minutes. THF (4 mL) and toluene (4 mL) were added before adding K⁺(CH₃)₂CO⁻ (0.431 g, 3.845 mmol) and 18-crown-6 (1.015 g, 3.84 mmol) dissolved in dry THF (10 mL) and toluene (10 mL) drop-wise and stirred at room temperature for 30 minutes. 2,5-bis(octyloxy)terephthalaldehyde (0.600 g, 1.538 mmol) dissolved in dry THF (6 mL) and toluene (6 mL) was added and the mixture was stirred at reflux temperature under nitrogen for 24 hours and the polymer was precipitated in methanol. The polymer was filtered and was purified by Soxhlet extractions with methanol, hexane and chloroform. The polymer was obtained from the chloroform fraction on evaporation of the solvent. The polymer was obtained as a dark red solid (0.534 g, 53%, Mₙ = 10420, PDI = 3.8).
Figure S48. $^1$H-NMR spectrum of poly[4-(2,5-bis(decyloxy)-4-vinylstyrlyl)-2-(decyloxy)-6-vinylpyrimidine] (P6)

Figure 49. UV-vis absorption spectra of poly[4-(2,5-bis(octyloxy)-4-vinylstyrlyl)-2-(decyloxy)-6-vinylpyrimidine] (P6) in chloroform (blue line) and in thin-film (red line)
**Figure S50.** UV-Vis absorption (blue) and photoluminescence (red) spectra of poly[4-(2,5-bis(decyloxy)-4-vinylstyryl)-2-(decyloxy)-6-vinylpyrimidine] (P6) in chloroform

**Figure S51.** Cyclic voltammogram of poly[4-(2,5-bis(decyloxy)-4-vinylstyryl)-2-(decyloxy)-6-vinylpyrimidine] (P6)
Figure S52. XRD of poly[4-(2,5-bis(decyloxy)-4-vinylstyril)-2-(decyloxy)-6-vinylpyrimidine] (P6) in thin film on glass substrate

Figure S53. The plot of integrated fluorescence intensity vs absorbance for Rhodamine B standard and for the six polymers

References: