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Synthesis and characterization of novel semiconducting polymers containing pyrimidine

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Synthesis and characterization of novel semiconducting polymers containing pyrimidine†

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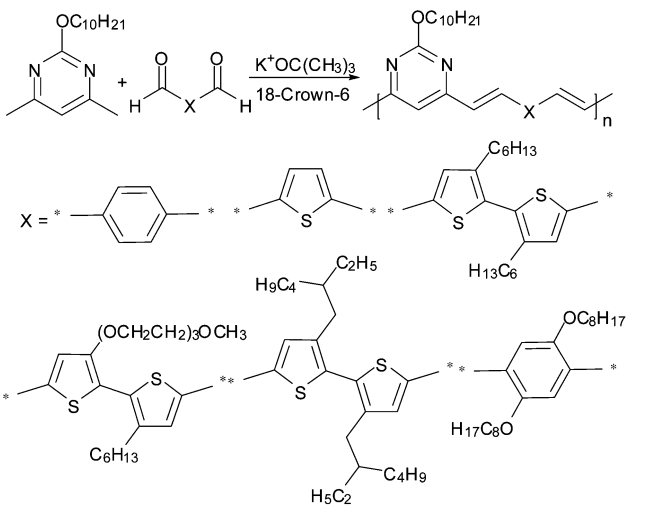
The acidic methyl protons of 4,6-dimethylpyrimidines can be easily deprotonated with a base to generate a resonance stabilized carbanion which can be used as a substrate for aldol condensation reactions. A series of novel conjugated polymers were synthesized by the aldol condensation reaction of 2-decyloxy-4,6-dimethylpyrimidine with various aromatic dialdehydes.

The syntheses of new conjugated polymers containing pyrimidine have been reported during the last decade. These polymers have been used as liquid crystalline materials,[1] n-type semiconductors,[2] components of electroluminescent diodes,[3,4] fluorescent molecules[5,6] and as two photon absorption chromophores.[7,8] The aromatic pyrimidine building block has electron withdrawing character, can participate in dipolar interactions and displays pH sensitivity. Moreover, the nitrogen atoms in pyrimidine can participate in hydrogen bonding and also can coordinate various metal ions. These desirable properties make pyrimidine an attractive building block for the synthesis of conjugated polymers for which one can envision the formation of various supramolecular assemblies that can be used in sensing applications.[9] For example, halogen, amino, and methyl derivatives of pyrimidine are commercially available and can be used as the building blocks for the synthesis of conjugated polymers. Due to its electron deficient character, halogenated pyrimidine can participate in oxidative addition of palladium to halogen–carbon bonds in positions 2, 4 and 6.[7,8] Various cross-coupling reactions with halogenated pyrimidine have been reported. For example, Suzuki,[10–12] Stille,[13] Negishi,[12,14] Sonogashira[15,16] and Corriu–Kumada[17] cross-coupling reactions have been employed for the synthesis of conjugated systems.[18,19] The synthesis of various vinyl pyrimidines through aldol reactions of methyl-substituted pyrimidines has been reported and the compounds have been employed as liquid crystals and non-linear optical materials.[20,21]

One report described the synthesis of pyrimidine polymers through aldol condensation reactions but the polymers had limited solubility due to the lack of solubilizing alkyl substituents.[20]

We are reporting here for the first time the synthesis and characterization of novel pyrimidine conjugated polymers by the aldol condensation reaction of 2-decyloxy-4,6-dimethylpyrimidine and various aromatic dialdehydes. The synthesis of pyrimidine conjugated polymers by the aldol condensation polymerization is shown in Scheme 1.

Six different dialdehyde monomers were employed in this study. The terephthal-dicarboxaldehyde was purchased from Aldrich. Thiophene-2,5-dicarbaldehyde, 3,3′-dihexyl-2,2′-bithiophene-5,5′-dicarbaldehyde and 3,3′-bis(2-ethylhexyl)-2,2′-bithiophene-5,5′-dicarbaldehyde monomers were synthesized by reacting the corresponding thiophene and bithiophenes with



Scheme 1 Synthesis of pyrimidine conjugated polymers by aldol condensation.

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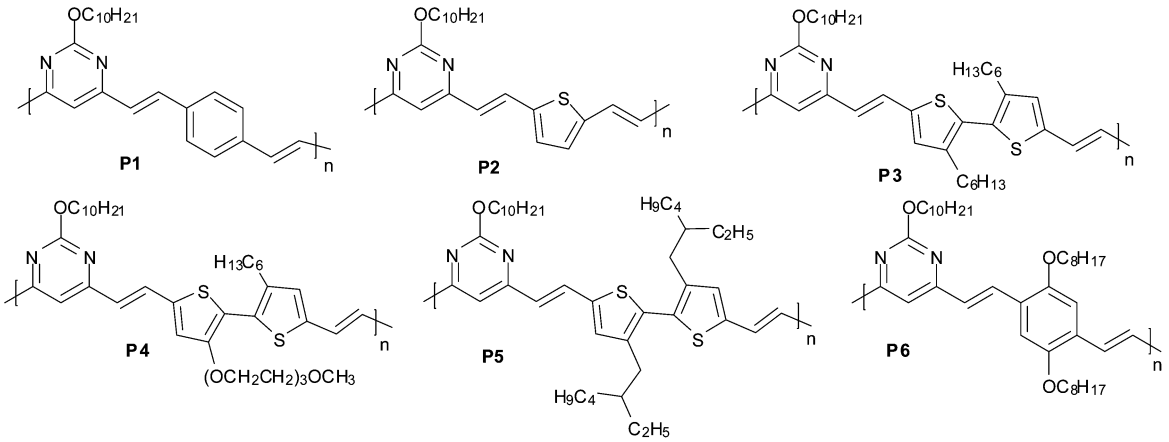
† Electronic supplementary information (ESI) available: Experimental section, UV-vis spectra, fluorescence spectra and CV. See DOI: 10.1039/c3py00137g



Scheme 2 Structures of the synthesised polymers: poly[2-(decyloxy)-4-vinyl-6-(4-vinylstyryl)pyrimidine] (**P1**), poly[2-(decyloxy)-4-vinyl-6-(2-(5-vinylthiophen-2-yl)vinyl)-pyrimidine] (**P2**), poly[2-(decyloxy)-4-(2-(3,3′-dihexyl-5′-vinyl-2,2′-bithiophen-5-yl)vinyl)-6-vinylpyrimidine] (**P3**), poly[2-(decyloxy)-4-(2-(3′-hexyl-3-(2-(2-(2-methoxy-ethoxy)ethoxy)ethoxy)-5′-vinyl-2,2′-bithiophen-5-yl)-6-vinylpyrimidine] (**P4**), poly[4-(2-(3,3′-bis(2-ethylhexyl)-5′-vinyl-2,2′-bithiophen-5-yl)vinyl)-2-(decyloxy)-6-vinyl-pyrimidine] (**P5**), and poly[4-(2,5-bis(octyloxy)-4-vinylstyryl)-2-(decyloxy)-6-vinylpyrimidine] (**P6**).

n-BuLi and DMF, followed by acidic work up. Monomer 3-hexyl-3′-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-2,2′-bithiophene-5,5′-dicarbaldehyde was obtained by two successive Vilsmeier reactions of 3-hexyl-3′-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-2,2′-bithiophene. Monomer 2,5-bis(octyloxy)terephthaldehyde was obtained by reacting 1,4-diiodo-2,5-bis(octyloxy)benzene with magnesium and DMF followed by acidic work up. The experimental procedures for the synthesis of pyrimidine monomer, dialdehyde monomers, and polymers are shown in the ESI.† The structures of the synthesized pyrimidine polymers are shown in Scheme 2.

Several bases such as sodium hydroxide, lithium-*tert*-butoxide, potassium-*tert*-butoxide, and 1,8-diazabicyclo[5.4.0]undec-7-ene were tested and of those potassium-*tert*-butoxide gave the best polymerization yields and the highest molecular weights. 18-Crown-6 was used as an additive to improve the solubility of potassium-*tert*-butoxide in the THF polymerization solvent. Polymers **P1** and **P2** had limited solubility due to the lack of alkyl or alkoxy substituents on the aromatic dialdehyde used to form the polymers. Although better solubility was expected for polymer **P3**, it turned out to have limited solubility in common organic solvents such as THF, chloroform and chlorobenzene. By contrast, polymers **P4**, **P5** and **P6** had good solubility in common organic solvents. The number-average molecular weights (M_n) and the polydispersity indices (PDI) of the synthesized polymers are shown in Table 1. The UV-vis spectra of the synthesized polymers were also recorded. For polymers **P1** and **P2** only the UV-vis spectra in chloroform solution were recorded (Table 1). Due to their very limited solubility the formation of good films from polymers **P1** and **P2** was difficult. For polymers **P3–6**, the UV-vis spectra were recorded both in chloroform solution and in a thin film (Table 1 and ESI†). All polymers displayed one absorption maximum due to π–π* transition along the backbone of the polymer. A small red shift was observed in the absorption spectra of the thin films indicating the ordering of the polymer chains in the solid state. Polymers **P1–3** had absorption maxima in the range of 365 nm to 385 nm, while polymers **P4** and **P6** had red-shifted absorption maxima of 443 and 423 nm, respectively. The blue-shifted absorption maximum of polymer **P5** is most likely due to its low molecular weight as compared to the other polymers. (All UV-vis spectra are included in the ESI†)

Photoluminescence spectra of polymers were recorded in chloroform solution (ESI†). It has been reported that

Table 1 Molecular weights and optoelectronic properties of the polymers

Polymer	M_n[a] (g mol^{-1})	PDI	λ_{max} ($CHCl_3$)[b] (nm)	λ_{max} (film)[c] (nm)	HOMO[d] (eV)	LUMO[e] (eV)	Electrochemical band gap (eV)	Optical band gap[f] (eV)
P1	7500	1.6	385	N/A	−5.81	−3.46	2.35	N/A
P2	8300	4.4	365	N/A	N/A	−3.59	N/A	N/A
P3	9800	3.8	381	395	−5.49	−3.48	2.00	1.99
P4	11 565	1.7	443	458	−5.08	−3.44	1.64	1.53
P5	5040	1.8	376	378	−5.51	−3.43	2.08	1.92
P6	10 420	3.8	423	424	−5.00	−3.03	1.97	1.96

[a] Estimated from SEC analysis against polystyrene calibration (THF eluent). [b] UV-vis absorption maximum of polymer solution in chloroform. [c] UV-vis absorption maximum of the polymer film drop cast from chloroform solution. [d] Estimated from the onset oxidation peak from a cyclic voltammogram. [e] Estimated from the onset reduction peak from a cyclic voltammogram. [f] Estimated from the onset of a UV-visible absorption peak in the solid state.

Table 2 UV-vis absorption maxima, photoluminescence emission maxima, and quantum yields of polymers **P1–6**

Polymer	λ_{max} (nm) ($CHCl_3$)[a]	λ_{max} (nm) ($CHCl_3$)[b]	Fluorescence quantum yield[c]
P1	385	434	83%
P2	365	417	26%
P3	381	534	12%
P4	443	548	11%
P5	376	521	5%
P6	423	509	68%

[a] UV-vis absorption maximum of polymer solution in chloroform solvent. [b] Photoluminescence emission maximum of polymer solution in chloroform solvent. [c] Fluorescence quantum yields of polymer in chloroform solution compared to rhodamine B dye.

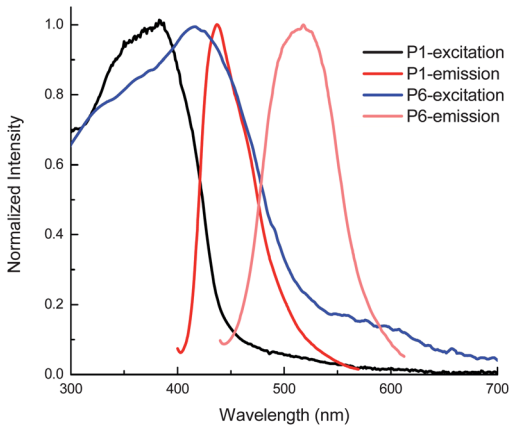


Fig. 1 Excitation and emission spectra of polymers **P1** and **P6** in chloroform.

significant reduction of the HOMO–LUMO energy band gap and improvement of the fluorescence quantum yield can be observed upon the incorporation of pyrimidine into the conjugated backbone.[20,21] The fluorescence quantum yields of the polymers in chloroform solution were compared to rhodamine B dye according to the method described by Williams *et al.*[22] The measured fluorescence quantum yields are given in Table 2. The fluorescence intensity increased upon increasing the concentration of polymer in chloroform solvent (ESI†). According to the calculated quantum yield values we expect polymer **P6** to be a good light emitting material for polymer light emitting diodes (PLEDs). The excitation and emission spectra of polymers with highest quantum yields, **P1** and **P6**, are shown in Fig. 1.

The favourable HOMO and LUMO energy levels for efficient hole and electron injection indicated that the polymers are appropriate for organic electronics applications. For example, polymer **P4** has a HOMO level of −5.08 eV and a reduced band gap; it is a good candidate to be employed as a donor material in bulk heterojunction solar cells (BHJSCs). Because of the proper energy level match between HOMO of **P4** and C_{60} acceptor, we expect higher open circuit voltage in BHJSCs.[23]

Thin film X-ray diffraction measurements were conducted for polymers **P3–6**. The broad peaks at $2\theta = 20.10°$ for **P3**; 20.29° for **P4**; 19.97° for **P5** and 20.24° for **P6** correspond to *d*-spacings of 4.41 Å, 4.37 Å, 4.44 Å, and 4.38 Å respectively. These halo-like broad peaks indicate that the polymers are amorphous.[24,25]

In summary, six novel semiconducting polymers containing pyrimidine in the backbone were synthesized by aldol condensation reaction between dimethyl pyrimidine and various aromatic dialdehydes. These polymers show favorable HOMO and LUMO energy levels and good fluorescence quantum yields. The applications of these semiconducting polymers in various electronic devices are currently under investigation.

Financial support for this project from NSF (Career DMR-0956116) and Welch Foundation (AT-1740) is gratefully acknowledged. We gratefully acknowledge the NSF-MRI grant (CHE-1126177) used to purchase the Bruker Advance III 500 NMR instrument.

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Electronic Supplementary Information

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

Samodha S. Gunathilake, Harsha D. Magurudeniya, Peishen Huang, Hien Q. Nguyen, Elizabeth A. Rainbolt, Mihaela C. Stefan, and Michael C. Biewer

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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, mulpilicity (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_{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.

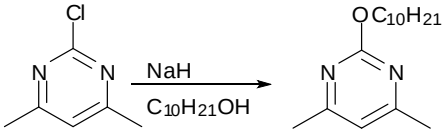
The fluorescence spectra of polymer solutions in chloroform solvent were carried out in 1 cm cuvettes using Perkin Elmer Luminescence Spectrometer LS 508.

Cyclic voltagrams 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-Kα radiation (λ ~ 1.5406 Å) source, scanning from 1 to 40 degrees (2θ) 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 $MgSO_4$, 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%) ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 6.64 (s, 1H), 4.31 (t, 2H), 5.56 (s, 6H), 1.44 (m, 16H), 0.87 (t, 3H), ^{13}C NMR ($CDCl_3$, 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.

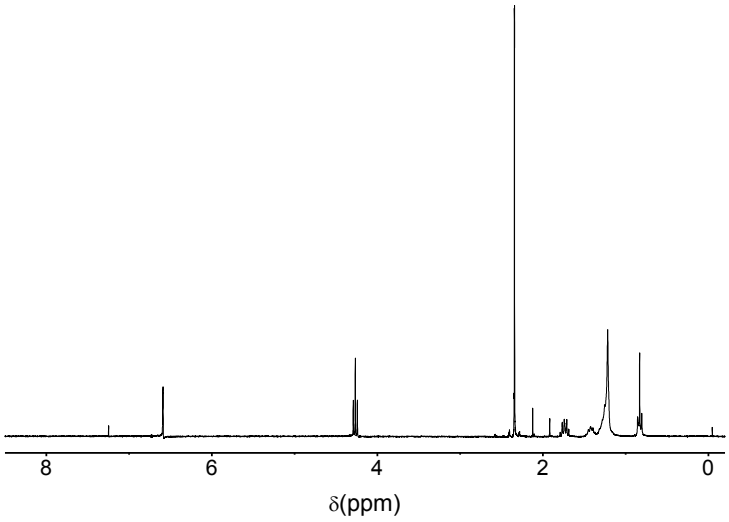


Figure S1. ^{1}H NMR spectrum of 2-decyloxy-4,6-dimethylpyrimidine

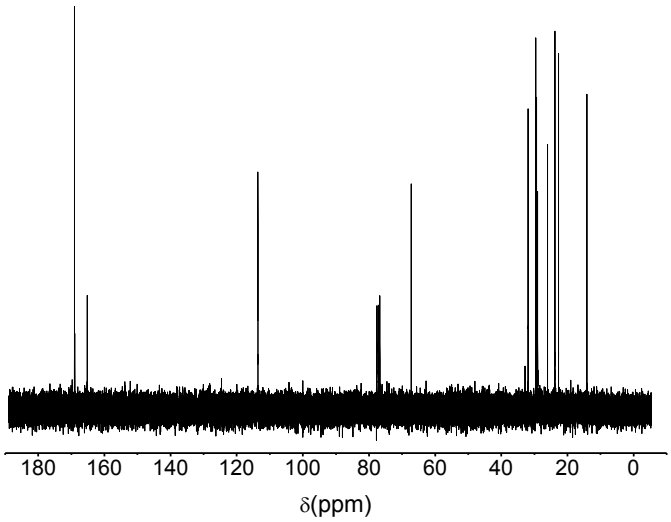
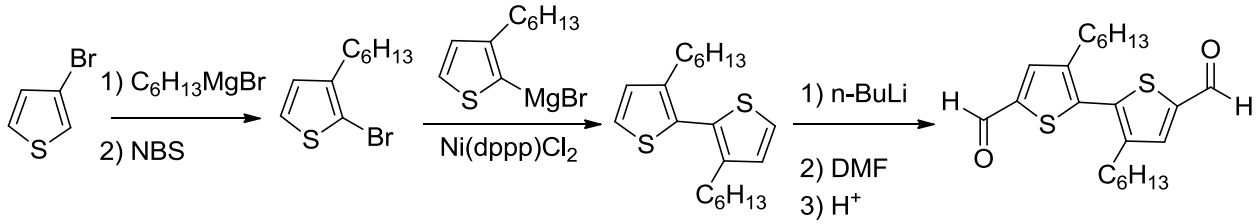


Figure S2. ^{13}C NMR spectrum of 2-decyloxy-4,6-dimethylpyrimidine

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.

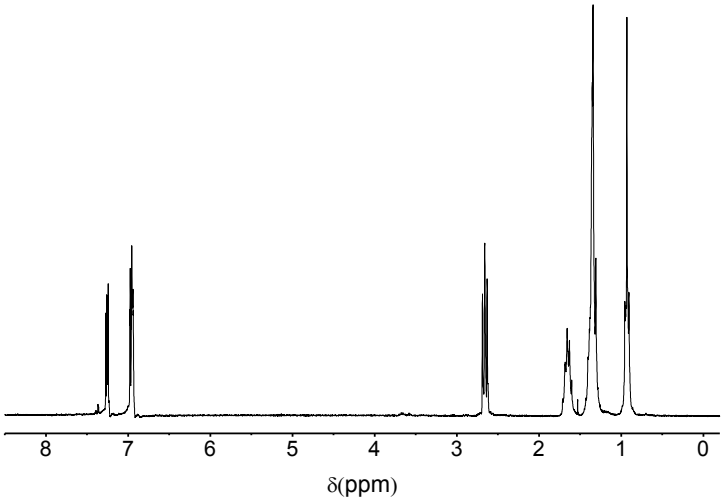


Figure S3. ^{1}H NMR spectrum of 3-hexylthiophene

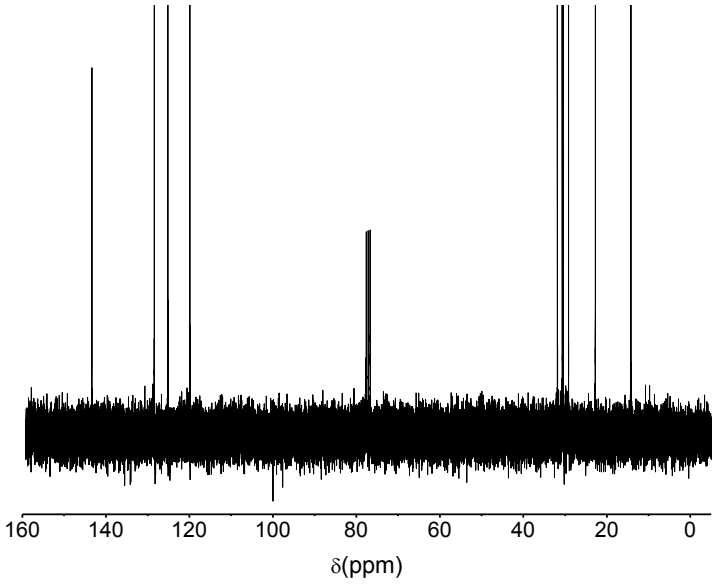


Figure S4. ^{13}C NMR spectrum of 3-hexylthiophene

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 $MgSO_4$ 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%).^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 7.20 (d,1H), 6.82 (d,1H), 2.58 (t, 2H), 1.32 (m, 8H), 0.91 (t, 3H) ^{13}C

NMR ($CDCl_3$, 270MHz) δ: 142.05, 128.32, 125.21, 108.91, 31.75 29.83, 29.51, 29.02, 22.73, 14.21.

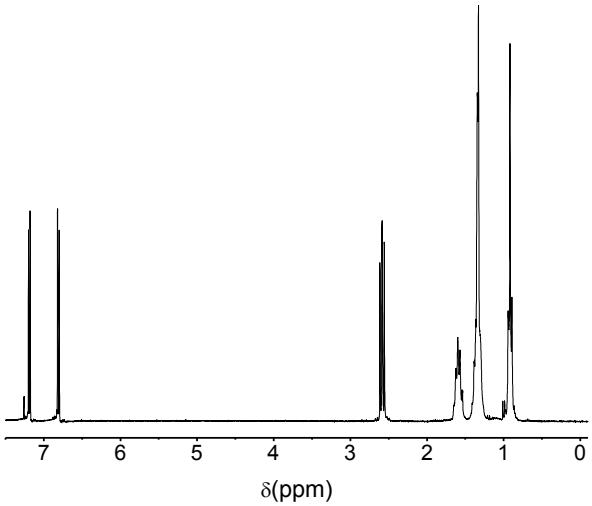


Figure S5. ^{1}H NMR spectrum of 2-bromo-3-hexylthiophene

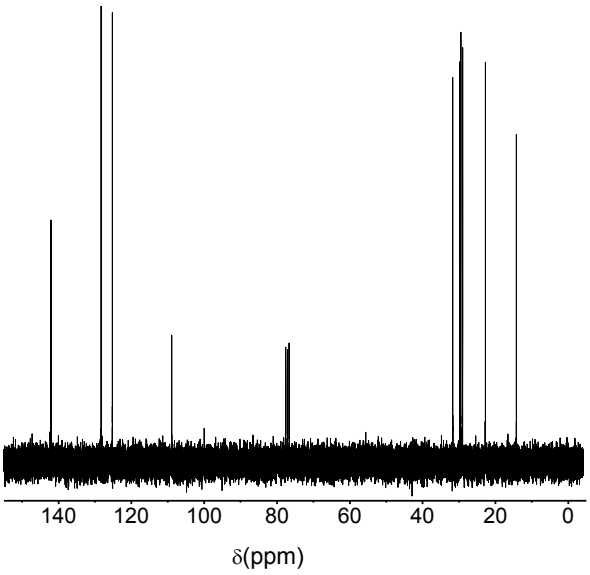


Figure S6. ^{13}C NMR spectrum of 2-bromo-3-hexylthiophene

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 cannulatedto 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.

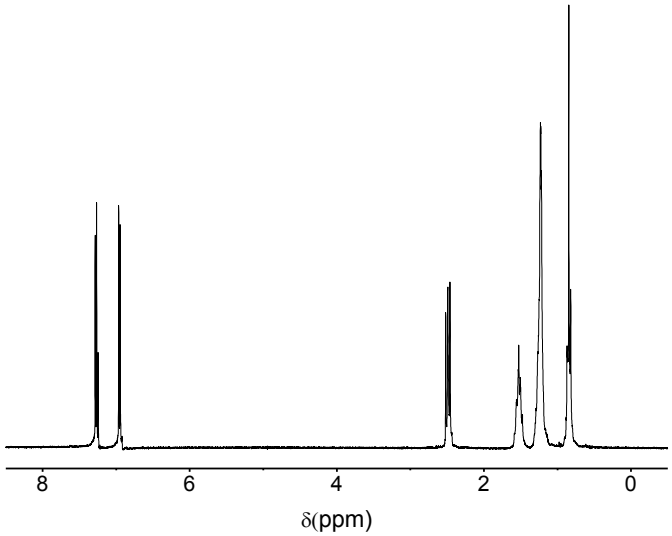


Figure S7. ^{1}H NMR spectrum of 3,3'-dihexyl-2,2'-bithiophene

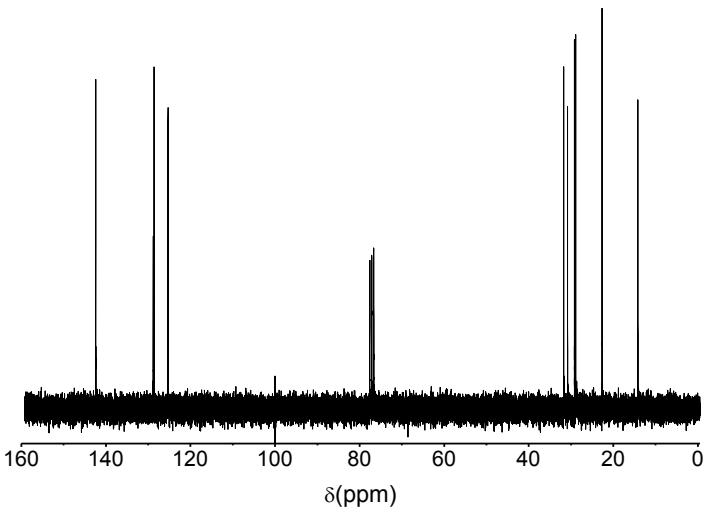


Figure S8. ^{13}C NMR spectrum of 3,3'-dihexyl-2,2'-bithiophene

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 $MgSO_4$, 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%). ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 9.87 (s, 2H), 7.66 (s, 2H), 2.56 (t, 4H), 1.24 (m, 16), 0.85 (t, 6H) ^{13}C NMR ($CDCl_3$, 270MHz) δ: 182.87, 144.54, 143.50, 137.52, 31.56, 30.55 29.00, 28.94, 22.56, 14.08.

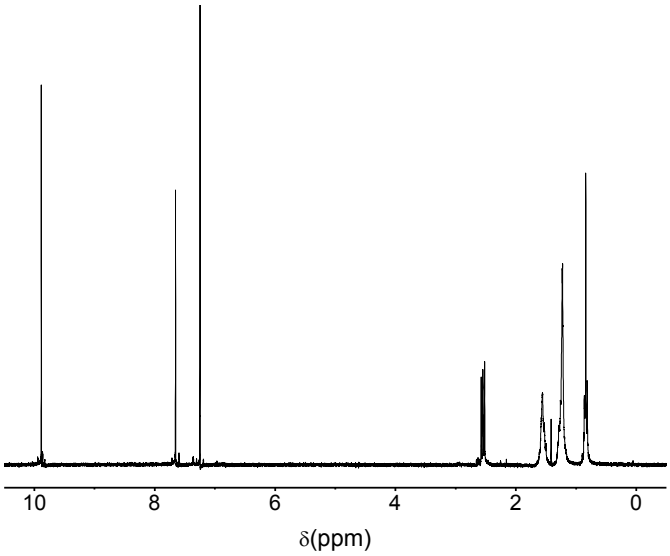


Figure S9. ^{1}H NMR spectrum of 3,3'-dihexyl-2,2'-bithiophene-5,5'-dicarbaldehyde

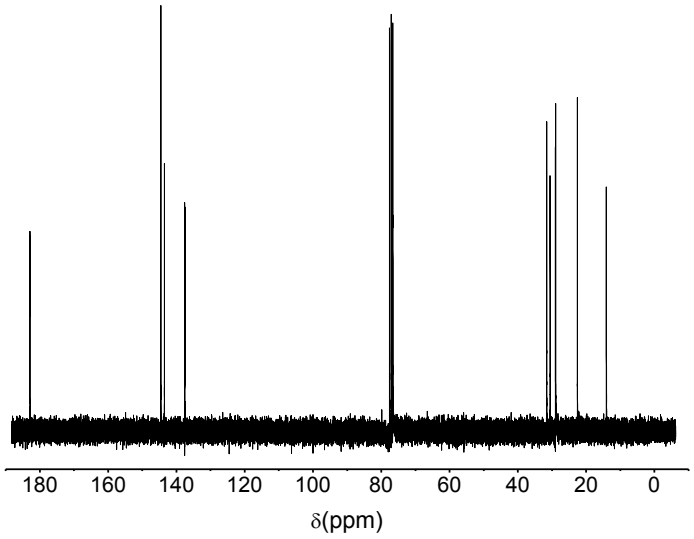
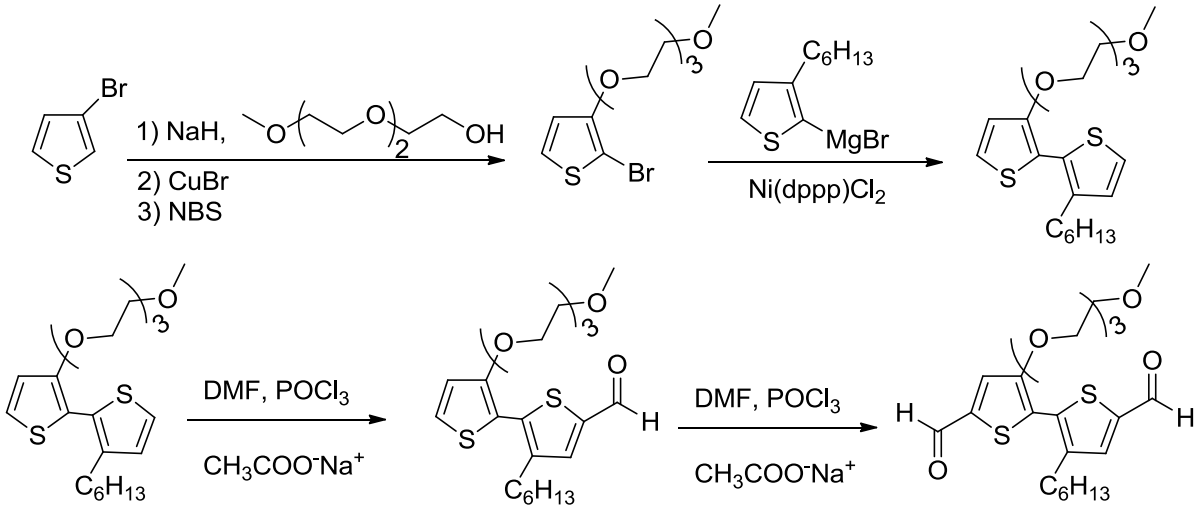


Figure S10. ^{13}C NMR spectrum of 3,3'-dihexyl-2,2'-bithiophene-5,5'-dicarbaldehyde

3) Synthesis of 3-hexyl-3'-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-2,2'-bithiophene-5,5'-dicarbaldhyde



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

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, 3-

bromothiophene (16.300 g, 0.099mol) 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 NH_4Cl, 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 NH_4Cl (100 mL) and stirred for 10 minutes. The organic phase was extracted with hexanes, dried over anhydrous $MgSO_4$. The product was purified by vacuum distillation to obtain a clear oil (14.938 g, 60%).^{1}H-NMR ($CDCl_3$, 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 ($CDCl_3$, 270MHz) δ: 157.65, 124.69, 119.64, 97.55, 71.99, 70.83, 70.70, 70.62, 69.74, 69.63, 59.08.

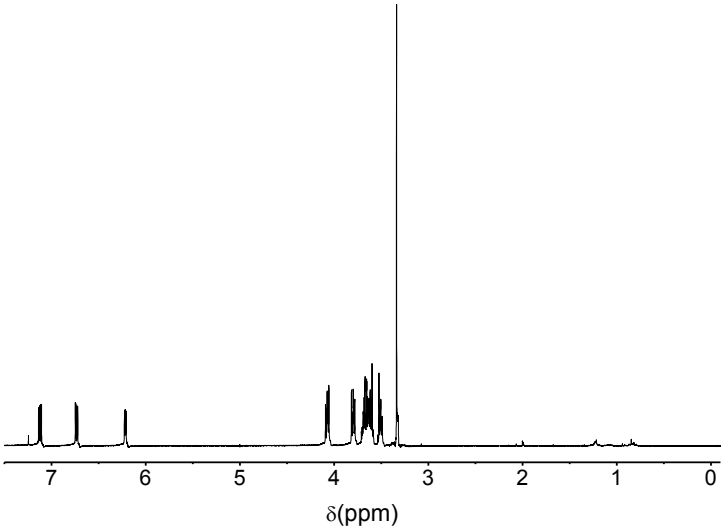


Figure S11.^{1}H NMR spectrum of 3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)thiophene

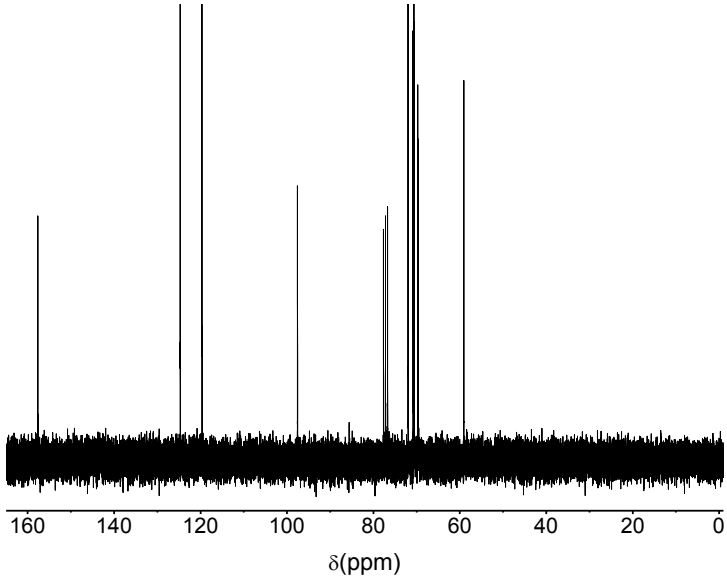


Figure S12. ^{13}C NMR spectrum of 3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)thiophene

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

3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)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 (11.035g, 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.

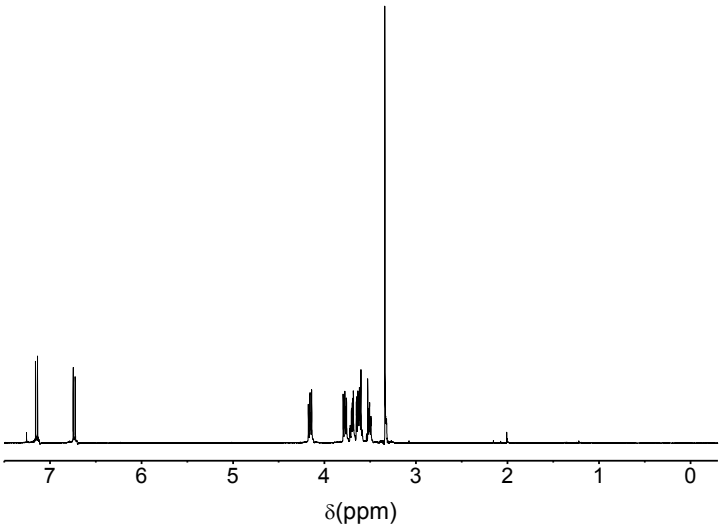


Figure S13. ^{1}H NMR spectrum of 2-bromo-3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)thiophene

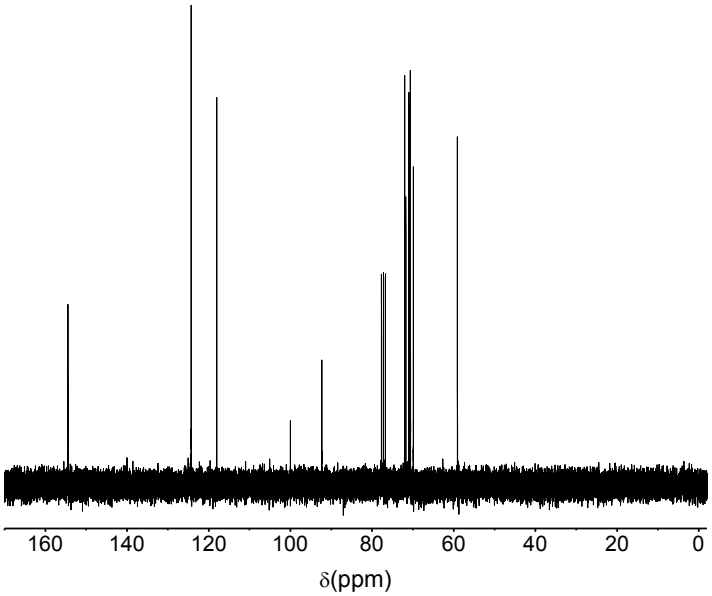


Figure S14. ^{13}C NMR spectrum of 2-bromo-3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)thiophene

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 $MgSO_4$, 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 %).^{1}H-NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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.

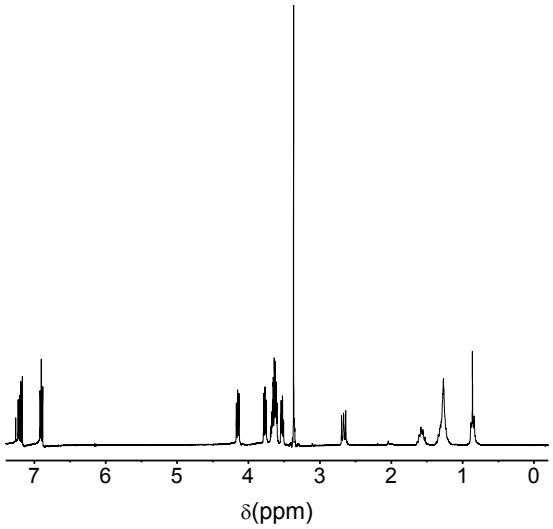


Figure S15. ^{1}H NMR spectrum of 3-hexyl-3'-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)bithiophene

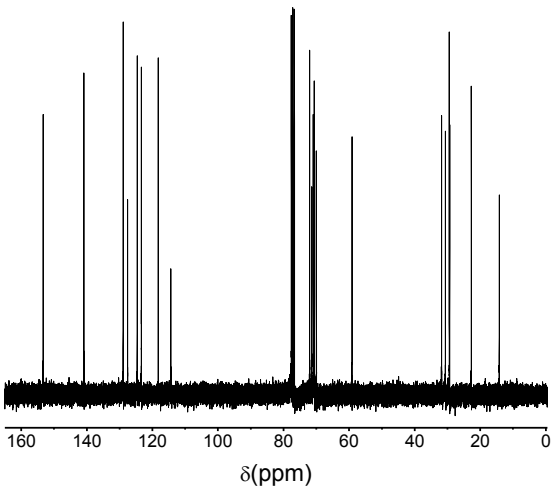


Figure S16. ^{13}C NMR spectrum of 3-hexyl-3'-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)bithiophene

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 $POCl_3$(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 a 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 $MgSO_4$, 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%).^{1}H-NMR ($CDCl_3$, 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).

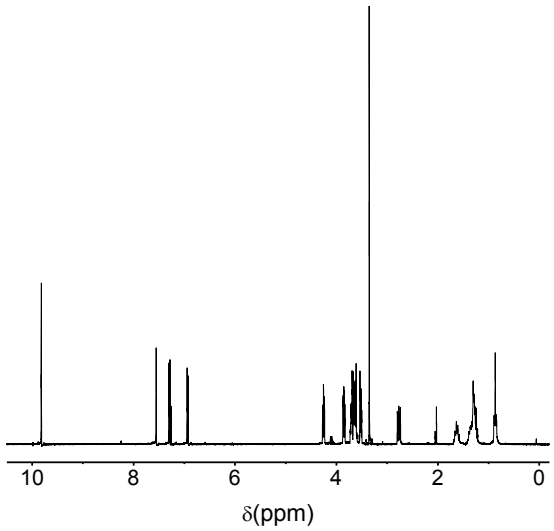


Figure S17.^{1}H NMR spectrum of 3-hexyl-3'-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-2,2'-bithiophene-5-carbaldehyde

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 $POCl_3$ (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 $MgSO_4$, 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%). ^{1}H-NMR ($CDCl_3$, 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) ^{13}C-NMR ($CDCl_3$, 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.

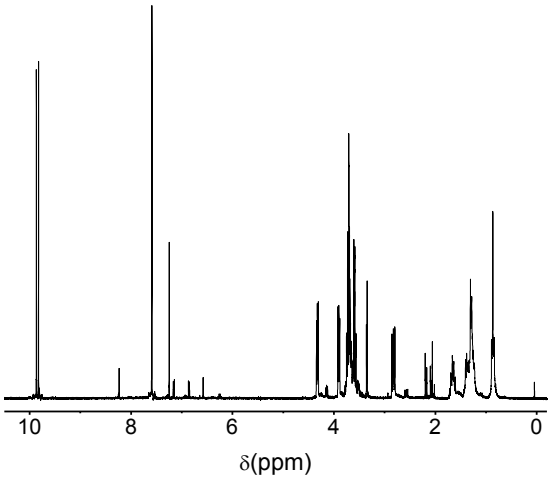


Figure S18. ^{1}H NMR spectrum of3-hexyl-3'-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-2,2'-bithiophene-5,5'-dicarbaldehyde

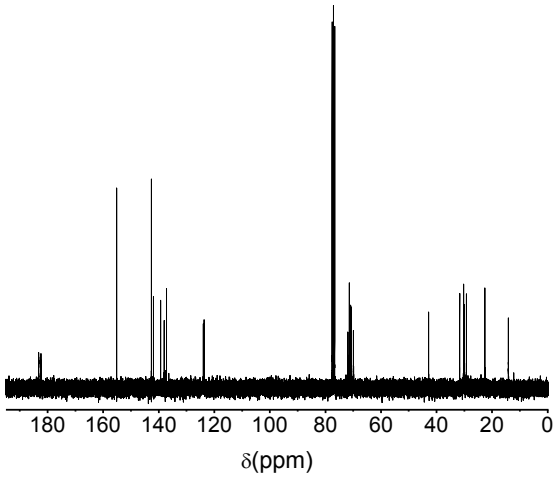
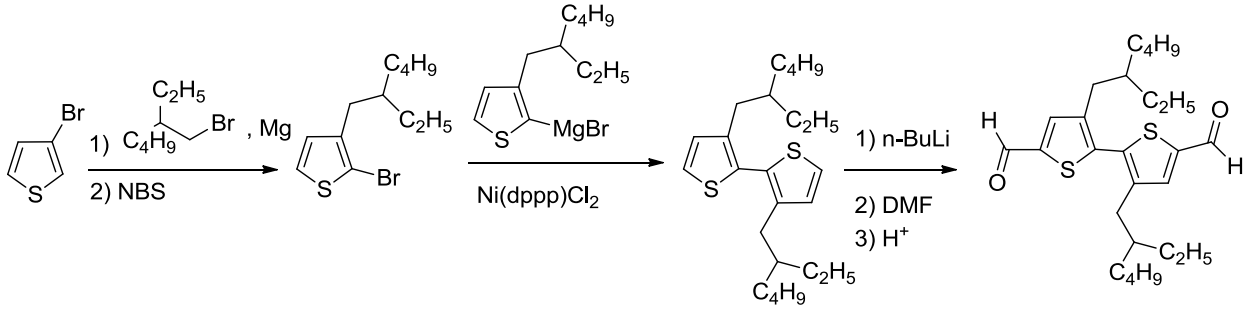


Figure S19. ^{13}C NMR spectrum of 3-hexyl-3'-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-2,2'-bithiophene-5,5'-dicarbaldehyde

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 bromidewas 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) δ: 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) δ: 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.

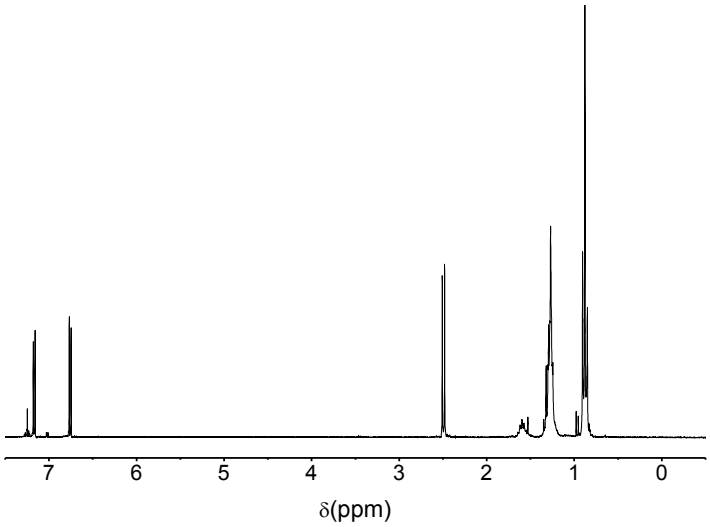


Figure S20.^{1}H NMR spectrum of 2-bromo-3-(2-ethylhexyl)thiophene

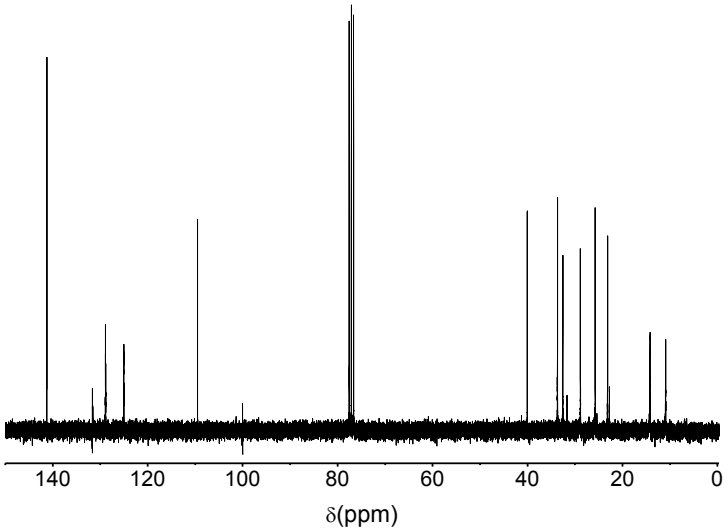


Figure S21.^{13}C NMR spectrum of 2-bromo-3-(2-ethylhexyl)thiophene

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)Cl_2(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)Cl_2 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 (3×100mL), dried with anhydrous $MgSO_4$, 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°Cand 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 (3×100 mL), dried over anhydrous $MgSO_4$ 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%) ^{1}H-NMR ($CDCl_3$, 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) ^{13}C-NMR ($CDCl_3$, 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.

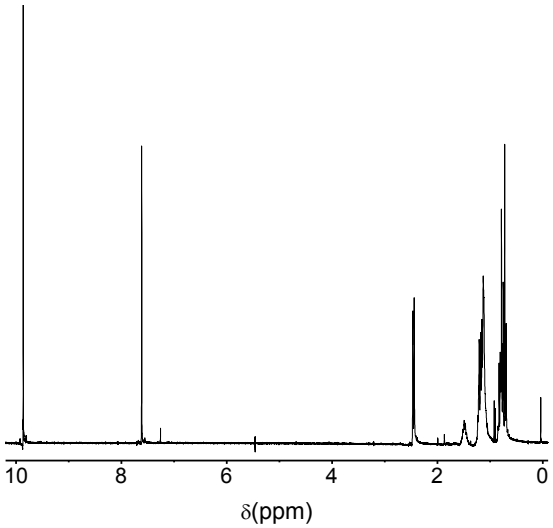


Figure S22. ^{1}H NMR spectrum of 3,3'-bis(2-ethylhexyl)-2,2'-bithiophene-5,5'-dicarbaldehyde

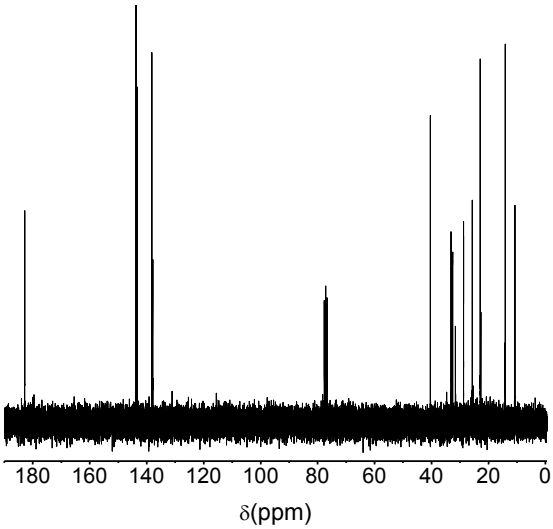
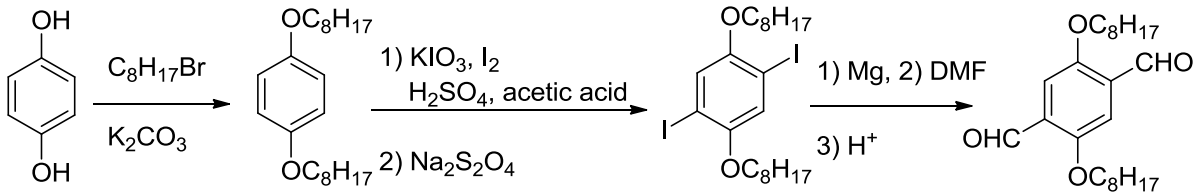


Figure S23. ^{13}C NMR spectrum of 3,3'-bis(2-ethylhexyl)-2,2'-bithiophene-5,5'-dicarbaldehyde

5) Synthesis of 2,5-dioctyloxyterephthalaldehyde



Scheme S4.2,5-dioctyloxy terephthalaldehyde

1,4-Dioctyloxybenzene and 1,4-dioctyloxy-2,5-diiodobenzene were prepared according to previously published methods.[2]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.

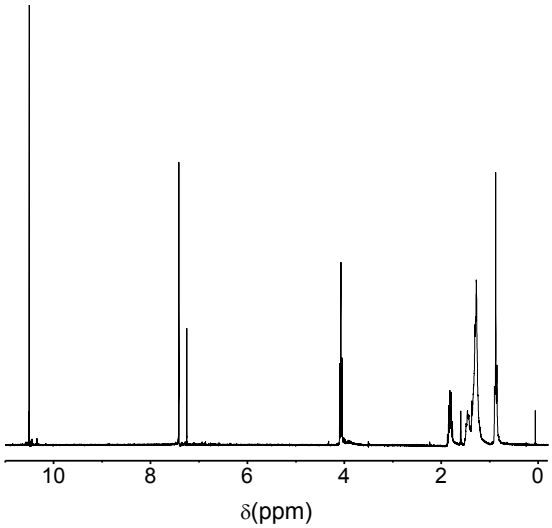


Figure S24. ^{1}H NMR spectrum of 2,5-dioctyloxyterephthalaldehyde

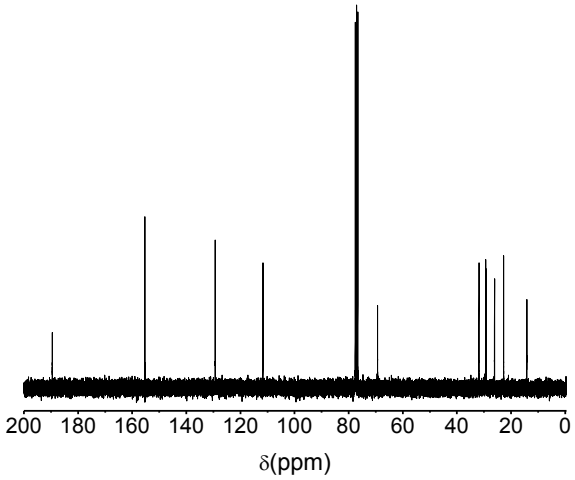


Figure S25. ^{13}C NMR spectrum of 2,5-dioctyloxyterephthalaldehyde

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 $K^{+}(CH_3)_3CO^{-}$ (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).

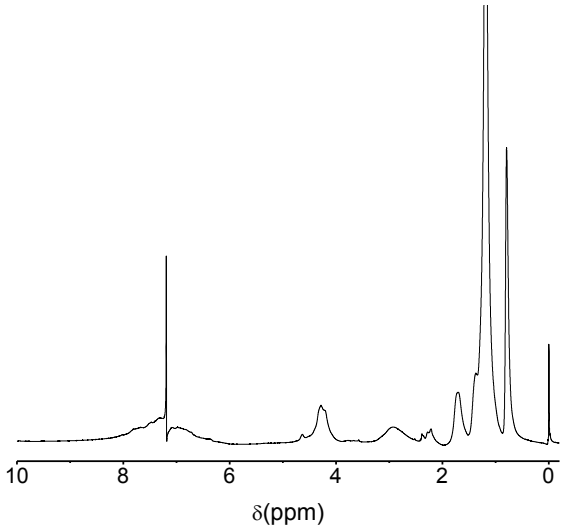


Figure S26. ^{1}H-NMR spectrum of poly[2-(decyloxy)-4-vinyl-6-(4-vinylstyryl)pyrimidine](**P1**)

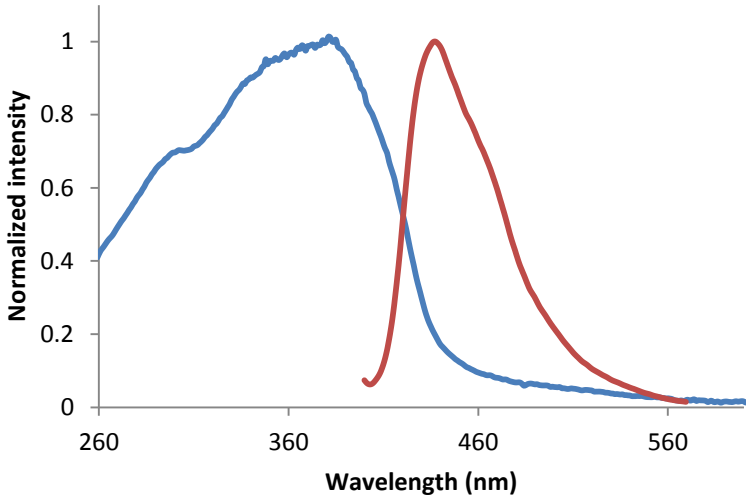


Figure S27. UV-Vis absorption (blue) and photoluminescence (red) spectra of polymer poly[2-(decyloxy)-4-vinyl-6-(4-vinylstyryl)pyrimidine](**P1**) in chloroform solution

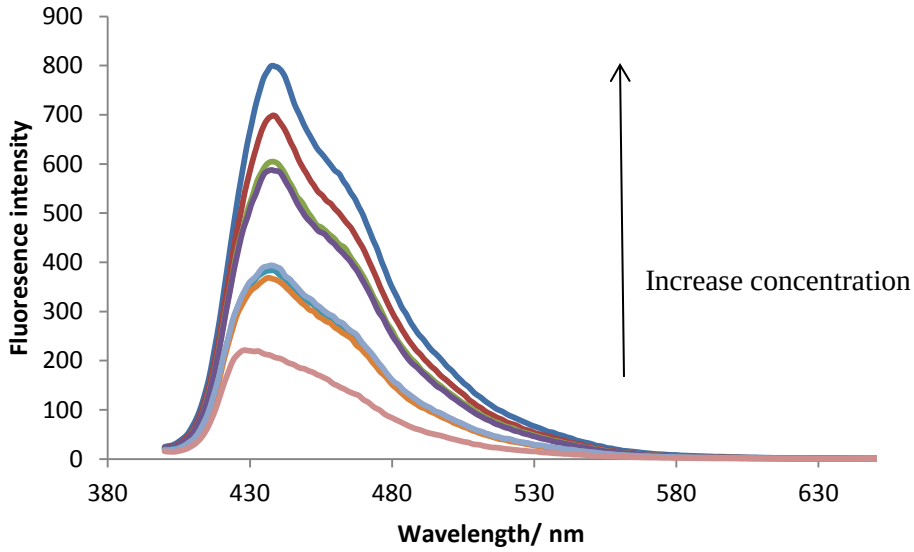


Figure S28. Change in fluorescence intensity upon changing concentration of poly[2-(decyloxy)-4-vinyl-6-(4-vinylstyryl)pyrimidine](**P1**) in chloroform solution. (All the other polymers show the same trend and only the plot for **P1** is shown)

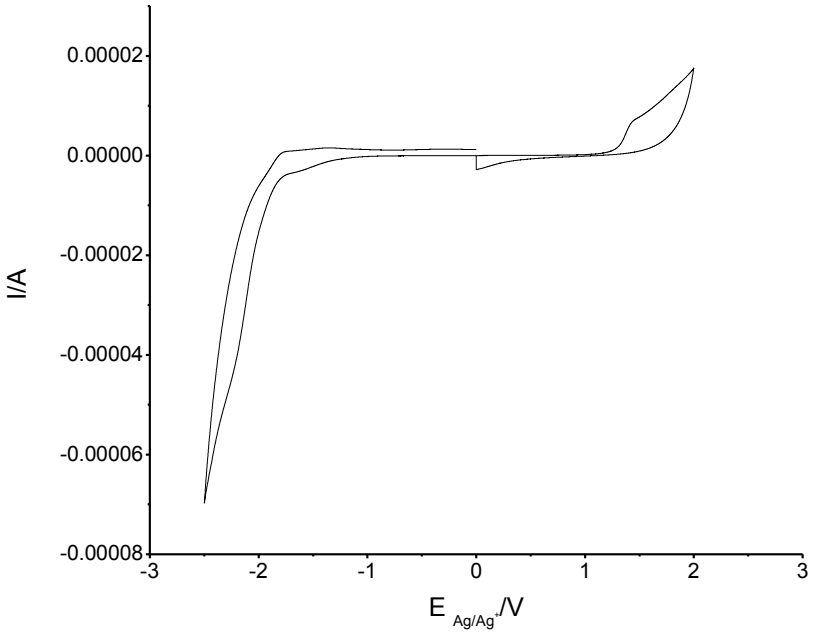


Figure S29. Cyclic voltammogram of poly[2-(decyloxy)-4-vinyl-6-(4-vinylstyryl)pyrimidine](**P1**)

Synthesis of poly[2-(decyloxy)-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 $K^+(CH_3)_3CO^-$ (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 an dthe 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 (0.156g, 30%, M_n = 8300 g/mol, PDI = 4.4).

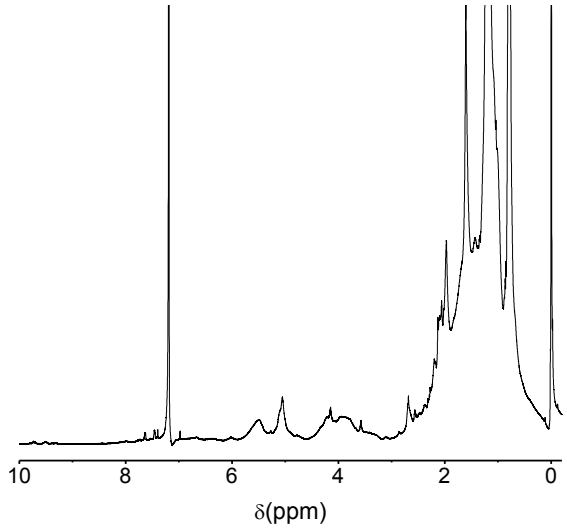


Figure S30. ^{1}H-NMR spectrum of poly[2-(decyloxy)-4-vinyl-6-(2-(5-vinylthiophen-2-yl)vinyl)pyrimidine](**P2**)

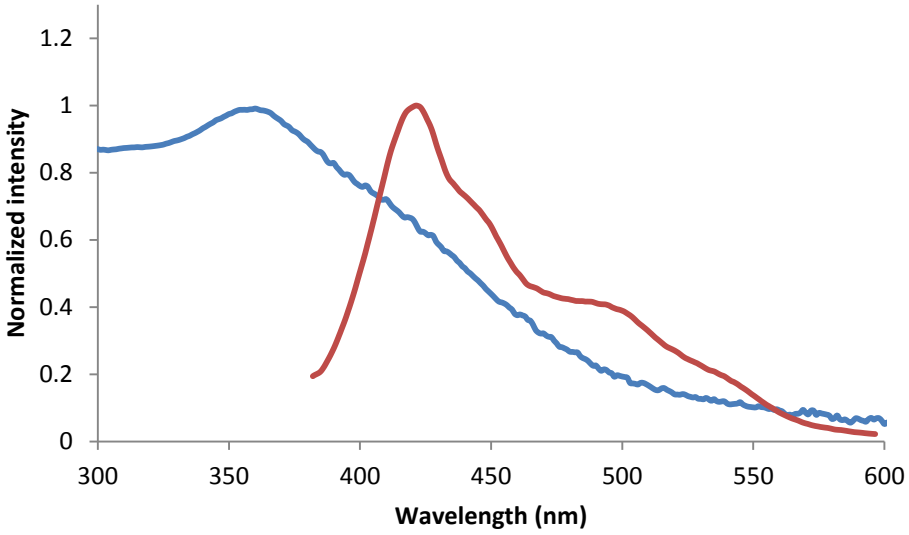


Figure S31. UV-Vis absorption (blue) and photoluminescence (red) spectra of poly[2-(decyloxy)-4-vinyl-6-(2-(5-vinylthiophen-2-yl)vinyl)pyrimidine](**P2**) in chloroform

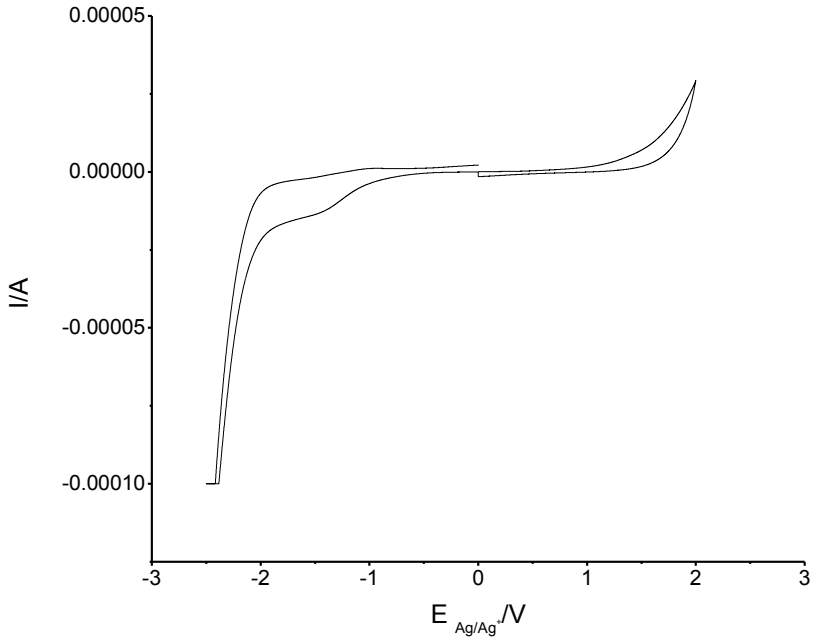


Figure S32. Cyclic voltammogram of poly[2-(decyloxy)-4-vinyl-6-(2-(5-vinylthiophen-2-yl)vinyl)pyrimidine](**P2**)

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, 1.096mmol) 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, mathanol and chloroform. The polymer was obtained by evaporating the chloroform layer to obtain the polymer as a dark red solid (0.396g, 37%, M_n = 9800 g/mol, PDI = 3.8).

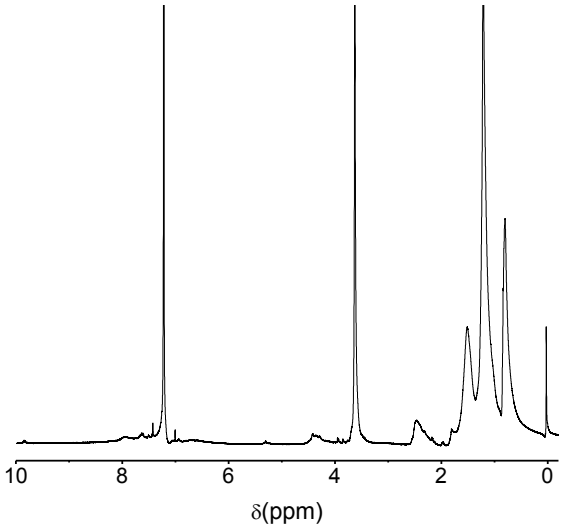


Figure S33. ^{1}H-NMR spectrum of poly[2-(decyloxy)-4-(2-(3,3'-dihexyl-5'-vinyl-2,2'-bithiophen-5-yl)vinyl)-6-vinylpyrimidine](**P3**)

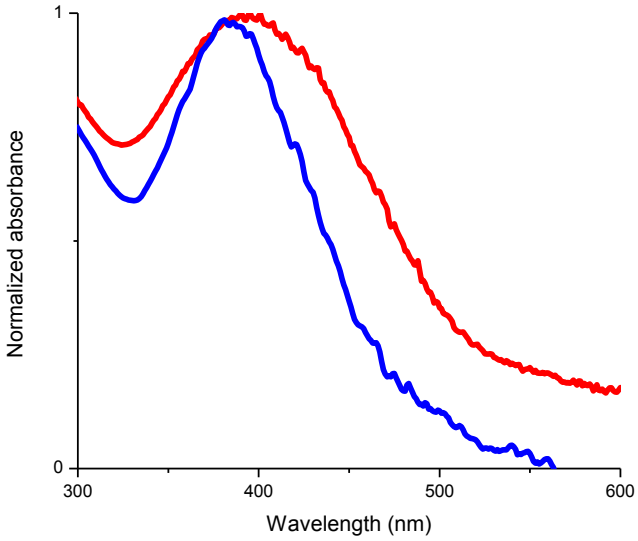


Figure S34. UV-vis absorption spectra of poly[2-(decyloxy)-4-(2-(3,3'-dihexyl-5'-vinyl-2,2'-bithiophen-5-yl)vinyl)-6-vinylpyrimidine] (**P3**) in chloroform (blue line) and in thin-film (red line)

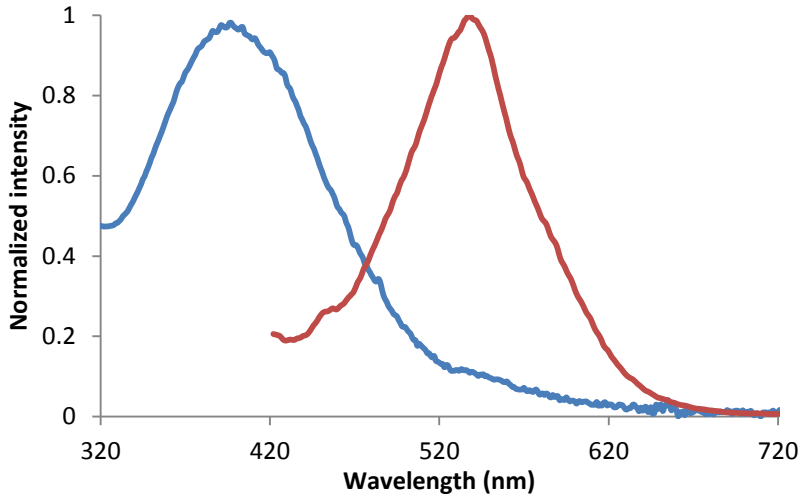


Figure S35. UV-Vis absorption (blue) and photoluminescence (red) spectra ofpoly[2-(decyloxy)-4-(2-(3,3'-dihexyl-5'-vinyl-2,2'-bithiophen-5-yl)vinyl)-6-vinylpyrimidine](**P3**)in chloroform

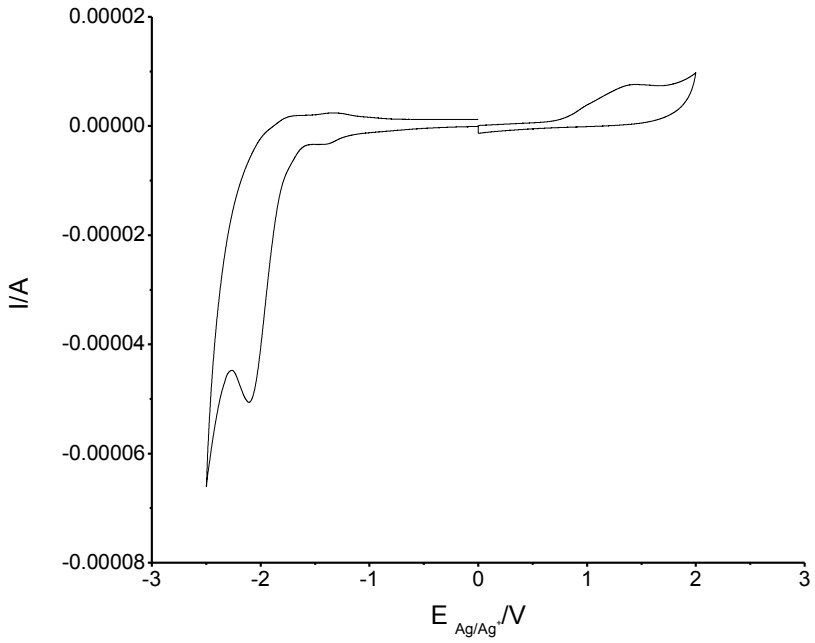


Figure S36. Cyclic voltammogram of poly[2-(decyloxy)-4-(2-(3,3'-dihexyl-5'-vinyl-2,2'-bithiophen-5-yl)vinyl)-6-vinylpyrimidine](**P3**)

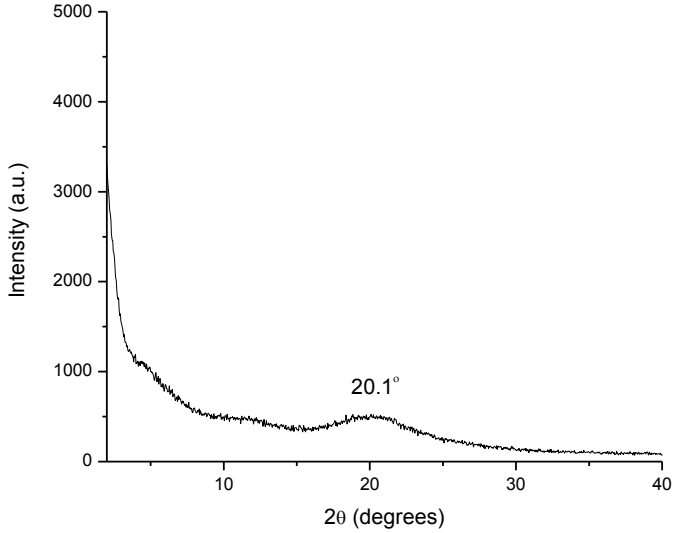


Figure S37. XRD of poly[2-(decyloxy)-4-(2-(3,3'-dihexyl-5'-vinyl-2,2'-bithiophen-5-yl)vinyl)-6-vinylpyrimidine](**P3**) in thin film on glass substrate

Synthesis of poly[2-(decyloxy)-4-(2-(3'-hexyl-3-(2-(2-(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 $K^{+}(CH_3)_3CO^{-}$ (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 (5mL) 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 $MgSO_4$. The polymer was obtained from the chloroform fraction on evaporation of the solvent. The polymer was obtained as a dark red solid (0.353g, 50%,M_n = 11565 g/mol, PDI = 1.7).

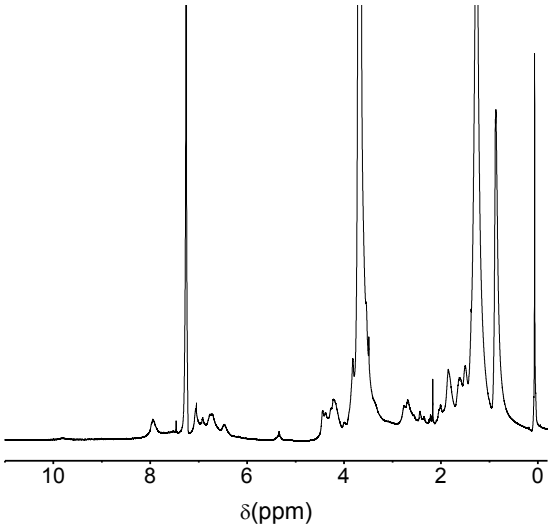


Figure S38. ^{1}H-NMR spectrum of poly[2-(decyloxy)-4-(2-(3'-hexyl-3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5'-vinyl-2,2'-bithiophen-5-yl)vinyl)-6-vinylpyrimidine](**P4**)

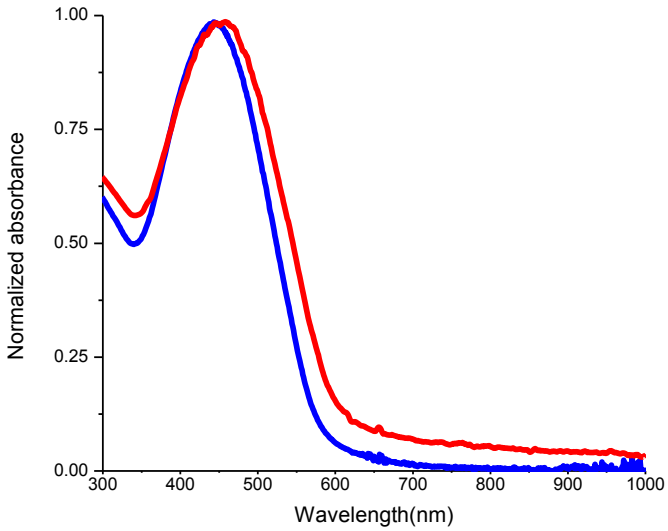


Figure S39. UV-Vis absorption spectra of poly[2-(decyloxy)-4-(2-(3'-hexyl-3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5'-vinyl-2,2'-bithiophen-5-yl)-6-vinylpyrimidine] (**P4**) in chloroform (blue line) and in thin-film (red line)

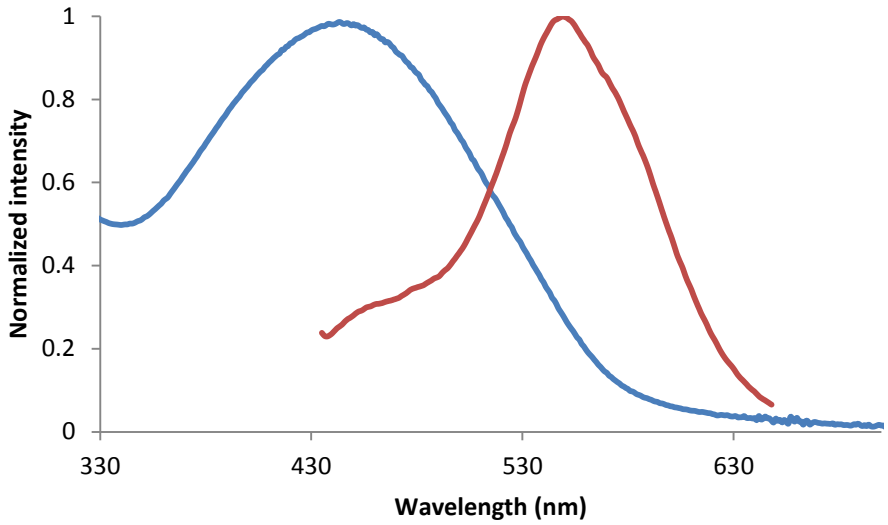


Figure S40. UV-Vis absorption (blue) and photoluminescence (red) spectra of poly[2-(decyloxy)-4-(2-(3'-hexyl-3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5'-vinyl-2,2'-bithiophen-5-yl)vinyl)-6-vinylpyrimidine](**P4**)in chloroform

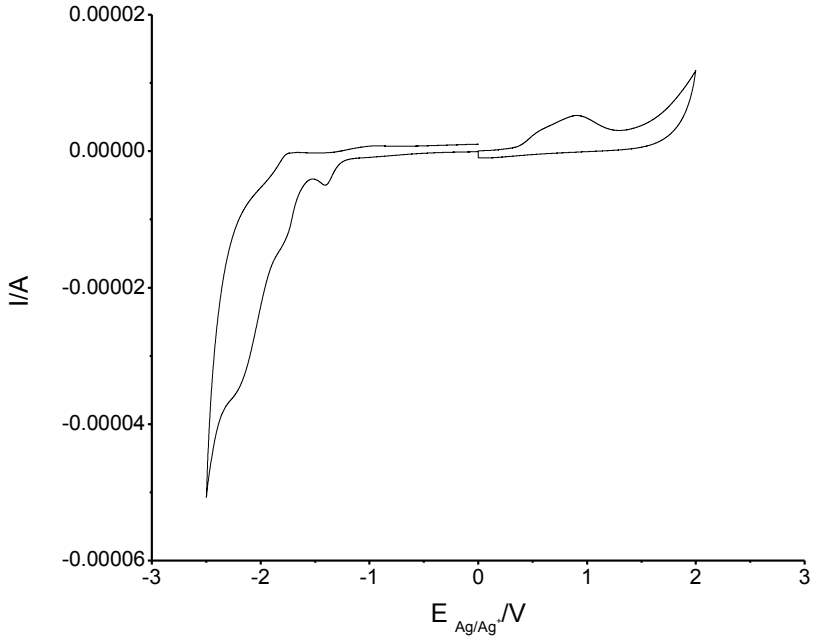


Figure S41: Cyclicvoltagram of poly[2-(decyloxy)-4-(2-(3'-hexyl-3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5'-vinyl-2,2'-bithiophen-5-yl)vinyl)-6-vinylpyrimidine](**P4**)

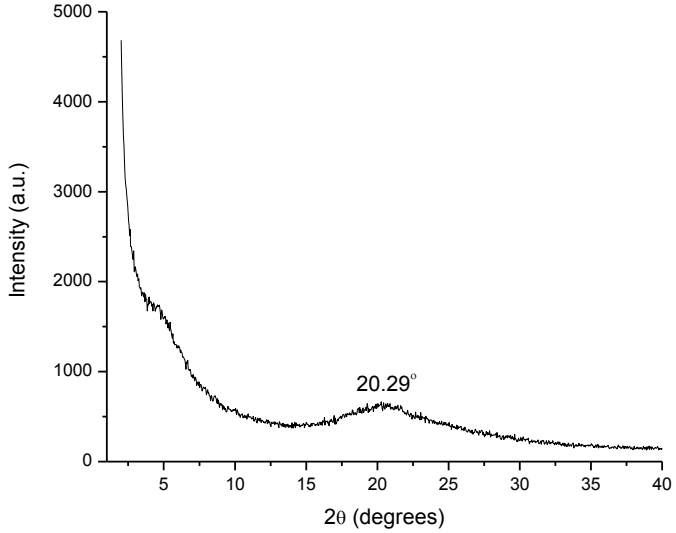


Figure S42: XRD of poly[2-(decyloxy)-4-(2-(3'-hexyl-3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5'-vinyl-2,2'-bithiophen-5-yl)vinyl)-6-vinylpyrimidine](**P4**) in thin film on glass substrate

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 $K^+(CH_3)_3CO^-$ (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 (10mL) 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 (0.903g, 42%, M_n = 5039 g/mol, PDI = 1.8).

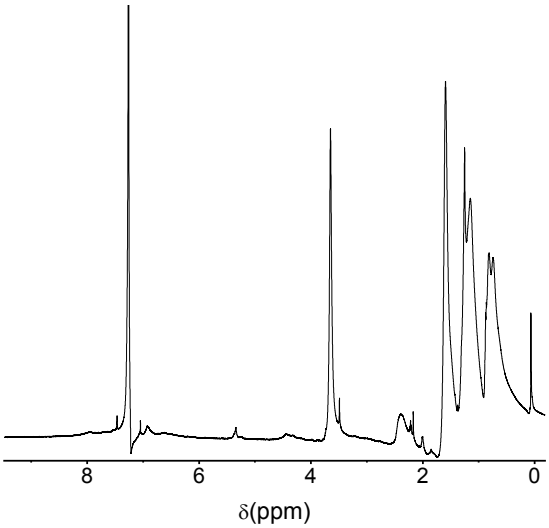


Figure S42: ^{1}H-NMR spectrum of poly[4-(2-(3,3'-bis(2-ethylhexyl)-5'-vinyl-2,2'-bithiophen-5-yl)vinyl)-2-(decyloxy)-6-vinylpyrimidine](P5)

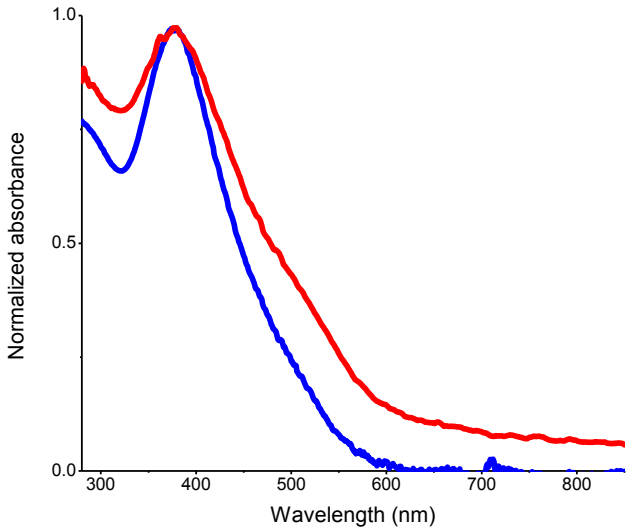


Figure S44.UV-Vis absorption spectra of poly[4-(2-(3,3'-bis(2-ethylhexyl)-5'-vinyl-2,2'bithiophen-5-yl)vinyl)-2-(decyloxy)-6-vinylpyrimidine] (**P5**) in chloroform (blue line) and in thin-film (red line)

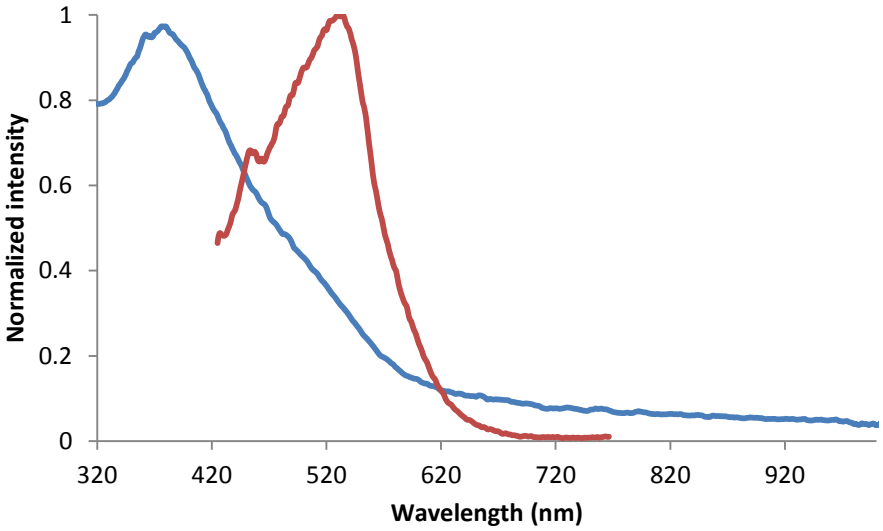


Figure S45. UV-vis absorption (blue) and photoluminescence (red) spectra of poly[4-(2-(3,3'-bis(2-ethylhexyl)-5'-vinyl-2,2'-bithiophen-5-yl)vinyl)-2-(decyloxy)-6-vinylpyrimidine](**P5**)in chloroform

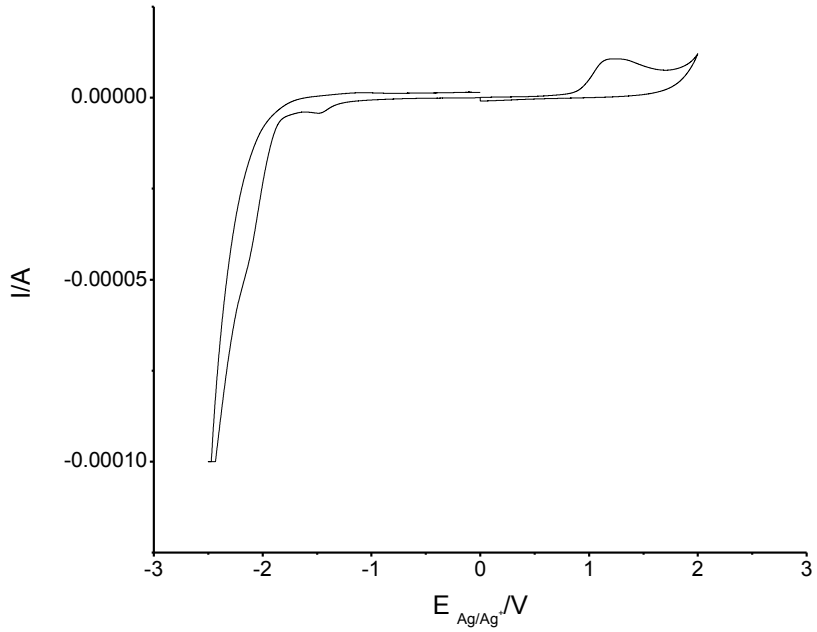


Figure S46. Cyclic voltammogram of poly[4-(2-(3,3'-bis(2-ethylhexyl)-5'-vinyl-2,2'-bithiophen-5-yl)vinyl)-2-(decyloxy)-6-vinylpyrimidine](**P5**)

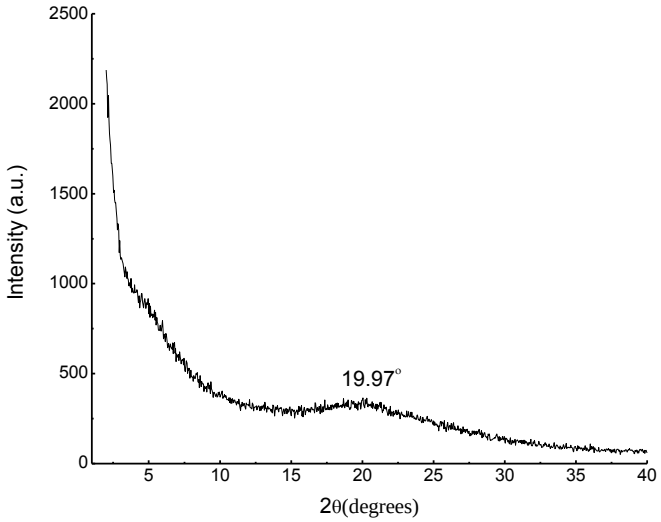


Figure S47. XRD of poly[4-(2-(3,3'-bis(2-ethylhexyl)-5'-vinyl-2,2'-bithiophen-5-yl)vinyl)-2-(decyloxy)-6-vinylpyrimidine](**P5**) in thin film on glass substrate

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 $K^+(CH_3)_3CO^-$ (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 (6mL) 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%, M_n = 10420, PDI = 3.8).

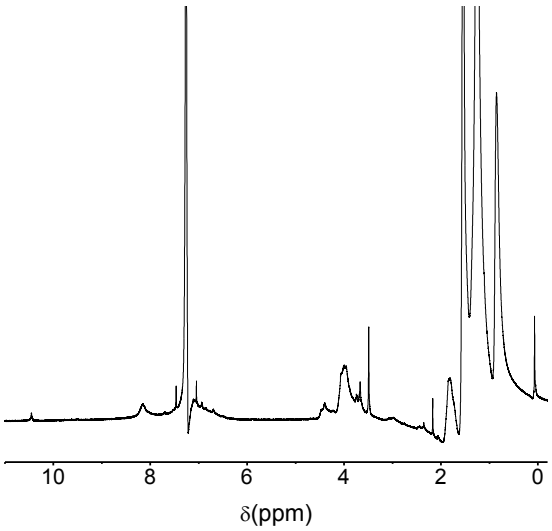


Figure S48. ^{1}H-NMR spectrum of poly[4-(2,5-bis(decyloxy)-4-vinylstyryl)-2-(decyloxy)-6-vinylpyrimidine] (**P6**)

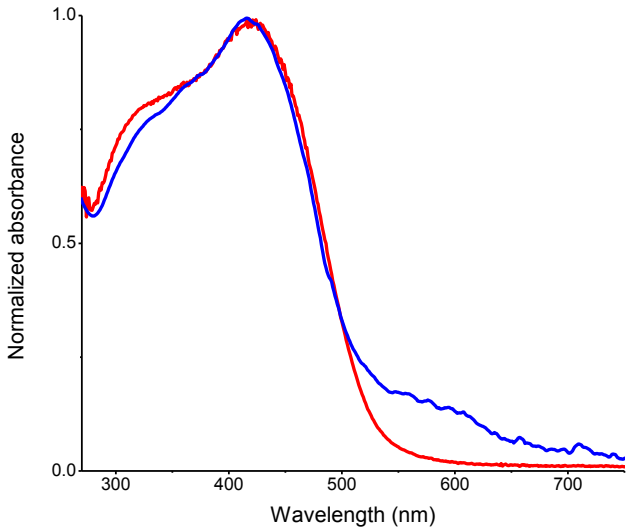


Figure 49. UV-vis absorption spectra of poly[4-(2,5-bis(octyloxy)-4-vinylstyryl)-2-(decyloxy)-6-vinylpyrimidine] (**P6**) in chloroform (blue line) and in thin-film (red line)

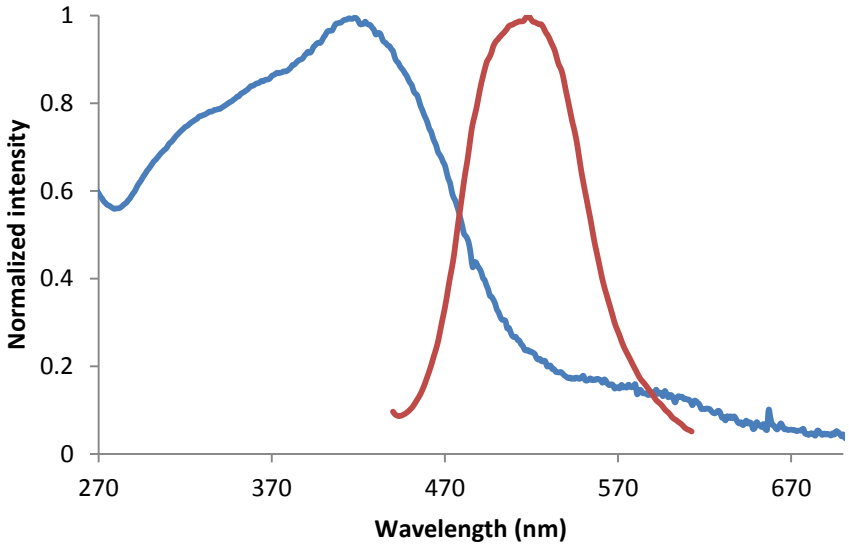


Figure S50. UV-Vis absorption (blue) and photoluminescence (red) spectra of poly[4-(2,5-bis(decyloxy)-4-vinylstyryl)-2-(decyloxy)-6-vinylpyrimidine] (**P6**)in chloroform

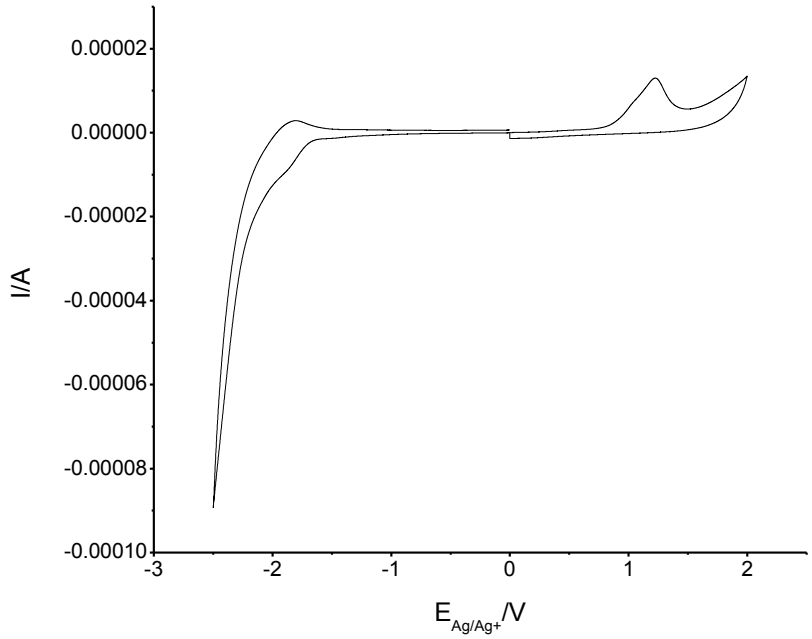


Figure S51. Cyclic voltammogram of poly[4-(2,5-bis(decyloxy)-4-vinylstyryl)-2-(decyloxy)-6-vinylpyrimidine] (**P6**)

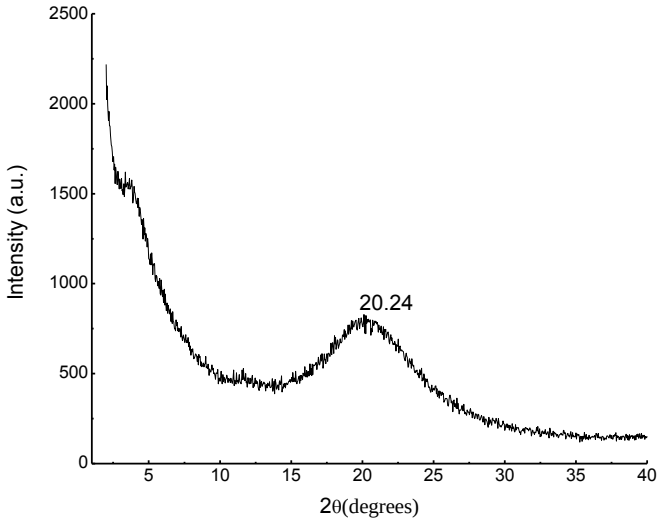


Figure S52. XRD of poly[4-(2,5-bis(decyloxy)-4-vinylstyryl)-2-(decyloxy)-6-vinylpyrimidine] (**P6**) in thin film on glass substrate

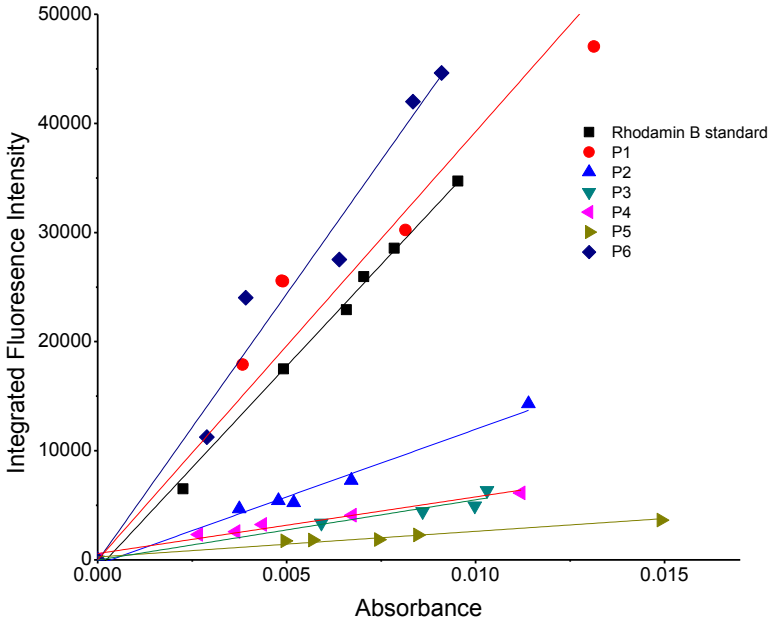


Figure S53. The plot of integrated fluorescence intensity vs absorbance for Rhodamine B standard and for the six polymers

References:

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2) Swager, T. M.; Gil, C.J.; Wrighton, M. S., *J. Phys. Chem*., 1995,**99**, 4886.