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NEW POLYTHIOPHENES WITH OLIGO(OXYETHYLENE) SIDE CHAINS

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ABSTRACT. Four new phenyl-substituted polythiophenes containing oligo(oxyethylene) side chains were synthesised. The absorption and photoluminescence characteristics of the polymers were studied. All polymers turned out to be reasonably stable to light and air. These polymers may find applications in light emitting electrochemical cells since the oxygenated side chains may be capable of solvating ions and thus serve to transport ions.

INTRODUCTION

Polythiophenes have been synthesized by electrochemical and chemical oxidation reactions as well as by processes involving chemical coupling reactions [1,2]. Considerable effort has been directed towards the preparation of polythiophenes with improved processability and physical characteristics. For example, the solubility and processability of polythiophenes have been achieved by the introduction of flexible side chains at the 3- and/or 4-position.

Since the first report in 1990 of polymer light-emitting diodes using PPV as the light-emitting material [3], considerable effort has been directed towards the preparation of materials with improved properties such as wide tunability of emission wavelength and high photoluminescence and electroluminescence efficiency. Recently, Pei *et al.* invented solid state light-emitting electrochemical cells (LECs) which combine the electrochemical properties of conjugated polymers with the ionic conductivity of polymer electrolytes [4,5]. Such LECs provide an alternative opportunity for light emission from thin polymer films.

As part of our continued effort to prepare polythiophenes with a variety of applications, we have now synthesized four new polythiophenes containing oligo(oxyethylene) side chains. These polymers may find applications in light-emitting electrochemical cells (LECs). The conjugated polythiophene backbone is capable of transporting electrons while the 1,4,7-trioxaoctyl side chains are capable of solvating ions and thus serve to transport ions. Recently Pei and Yang have prepared a polyfluorene (BDOH-PF) containing oxygenated side groups and demonstrated its use in an LEC [6].

RESULTS AND DISCUSSION

Figure 1 shows the structures of the new polymers and Table 1 gives the molecular weights of these polymers. The synthetic pathways towards these polymers are depicted in Schemes 1 and 2. Monomer **7** was prepared starting from hydroquinone. Treatment of hydroquinone with 1-chloro-2-(2-methoxyethoxy)ethane gave compound **5** which was readily monobrominated by treatment with NBS in DMF [7] to afford compound **6**. Palladium(0) catalyzed coupling [8] of **6** with 3-thiopheneboronic acid gave monomer **7**. Compound **7** was characterized based on its HRMS, ^{1}H and ^{13}C NMR spectra.

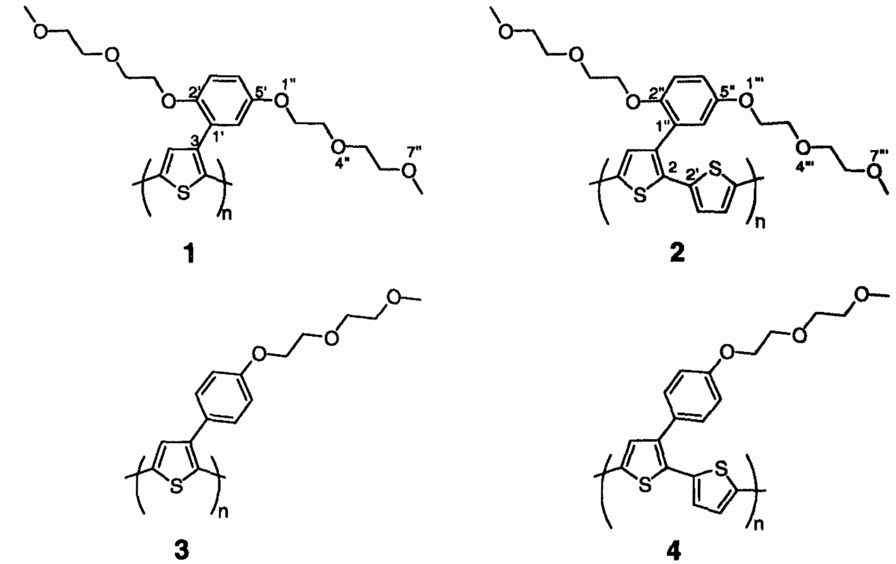
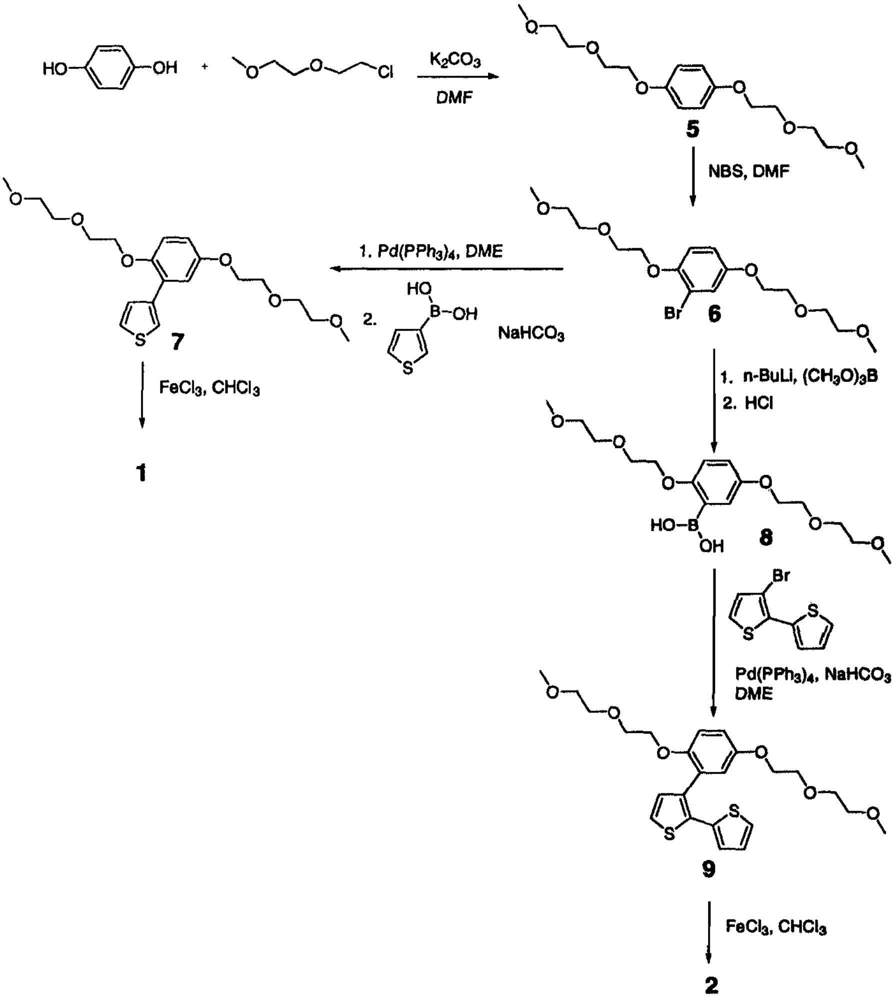


Figure 1. Structures of polymers **1-4**.

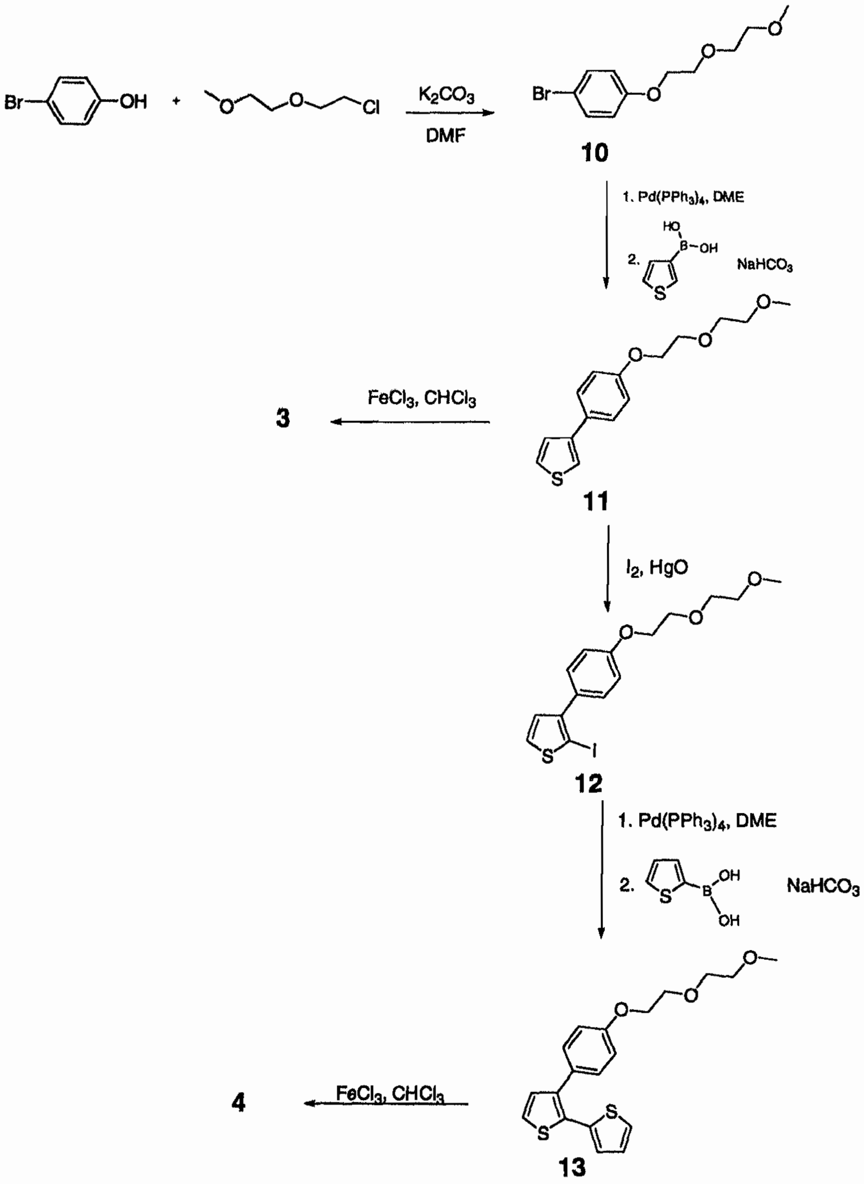
The polymerization of **7** was achieved by slow addition of a slurry of $FeCl_3$ in $CHCl_3$ [9] into a solution of the monomer in $CHCl_3$ at room temperature. Polymer **1** (poly[3-(2',5'-bis(1''4''7''-trioxaoctyl)phenyl)thiophene]) was obtained as a deep-red solid. A dilute solution of the polymer exhibited an orange fluorescence upon exposure to long-wavelength UV radiation. The UV-Vis spectrum (Table 2) of a thin film of polymer **1** on glass displayed an absorption maximum at 521 nm. The ^{1}H NMR spectrum showed aromatic proton resonances at δ 6.66, 6.72 and 6.87 with a relative ratio of 1:1:2, respectively. The methoxy and methylene proton resonances appeared at δ 3.22-4.06 and were well-resolved. Conclusions about the high regioregularity, with a high degree of head-to-tail (HT) coupling, could be drawn from the aromatic and aliphatic proton resonances in the ^{1}H NMR spectrum.

Monomer **9** was prepared through the Pd(0) catalyzed coupling of the boronic acid **8** with 3-bromo-2,2'-bithiophene. The ^{1}H NMR spectrum of compound **9** revealed doublets at δ 7.19 and 7.02 attributable to H-5 and H-4, respectively. The proton resonances at δ 7.10 (*dd*), and 6.96 (*dd*) are assignable to H-5' and H-3', respectively. The remaining aromatic proton resonances appeared at δ 6.81 (*dd*, H-6'') and 6.87-6.90 (H-4', H-3'' and H-4''). The aliphatic proton resonances appeared at δ 3.33-4.04 and integrate for a total of 22 protons. The ^{13}C NMR spectrum revealed 24 carbon resonances of which 14 appeared above 100 ppm in agreement with the structure of compound **9**. The polymerization of compound **9** was effected with $FeCl_3$ in $CHCl_3$ to afford poly[3-(2'',5''-bis(1''',4''',7'''trioxaoctyl)phenyl)-2,2'-bithiophene] (**2**) as a deep-red gummy polymer. Polymer **2** exhibited a molecular weight (M_w) of 41,900 as determined by GPC against polystyrene standard. The number average molecular weight (M_n) was 13,600 and the polydispersity was 3.07. The UV-Vis spectrum of a $CHCl_3$ solution of polymer **2** showed an absorption maximum at 495 nm while a thin film of the polymer on glass showed a maximum at 512 nm. The ^1H NMR spectrum displayed signals for aromatic protons at δ 6.7 -7.1 and aliphatic proton signals appeared at δ 3.2 - 4.1.



Scheme 1. Synthesis of polymers **1** and **2**.

Poly[3-(4'-(1'',4'',7''-trioxaoctyl)phenyl)thiophene] (**3**) was obtained in high yield from the oxidative polymerization of monomer **11** with $FeCl_3$ as shown in Scheme 2. Compound **11** was prepared starting from *p*-bromophenol. Thus treatment of *p*-bromophenol with 1-chloro-2-(2-methoxyethoxy)ethane afforded compound **10** which on Pd(0) catalyzed coupling with 3-thiopheneboronic acid gave **11** as a white crystalline



Scheme 2. Synthesis of polymers **3** and **4**.

solid. Polymer **3** was obtained as a dark colored solid after precipitation from methanol. Lower molecular weight and irregular compounds were removed by Soxhlet extraction with methanol and diethyl ether and polymer **3** was finally extracted with chloroform. The ^{1}H NMR spectrum of the chloroform soluble material displayed a singlet at δ 6.80 which is attributable to the thiophene ring proton. The doublets at δ 6.89 and 7.26 are assigned to the benzene ring protons. The side-chain methylene and methyl proton resonances appeared at δ 3.38, 3.57, 3.71, 3.86 and 4.16. The signals due to the C-2'' methylene protons were used to estimate the head-to-tail density of polymer **3** to be >85%. The $CHCl_3$ solution of the polymer had a deep-red color while the color became darker upon evaporating the solvent. The UV-Vis spectrum of a spin cast film of the polymer on glass showed an absorption maximum at 476 nm. Exposing this film to vapors of $CHCl_3$ resulted in a change of the color as well as a red shift of the absorption maximum (Table 2). The shift may be due to solvent-induced ordering giving rise to a more planar conformation [9]. Similar shifts were observed upon heat treatment of the film.

Monomer **13** was synthesized starting from **11** through a sequence of reactions involving iodination with I_2 and HgO followed by a Pd(0) catalyzed coupling reaction of the iodide **12** with 2-thiopheneboronic acid. Compound **13** was characterized based on its HRMS, ^1H and ^{13}C NMR data. Oxidative polymerization of **13** using anhydrous $FeCl_3$ afforded poly[3-(4''-(1''',4''',7'''-trioxaoctyl)phenyl)-2,2'-bithiophene] (**4**) as a dark red powder. A dilute solution of this material had an orange fluorescence when exposed to a long wavelength UV radiation. The UV-Vis spectrum of a thin film of the polymer on glass exhibited an absorption maximum at 496 nm. The ^1H NMR spectrum showed aromatic proton resonances at δ 6.80-7.34. The aliphatic proton resonances appeared at δ 3.39, 3.59, 3.73, 3.89 and 4.12.

Table 1. Molecular weight and melting point data on polymers **1-4**.

Polymer	M_W	M_N	Melting point
1	134000	20600	135°
2	41900	13600	74°
3	55800	20100	>300°
4	16500	2700	140°

M_W = weight average molecular weight; M_N = number average molecular weight.

Table 2. Absorption (λl) and photoluminescence (PL) data on polymers **1-4**.

Polymer	λ_{max} (nm)		PL_{max} (nm)		η_{PL} (%)	
	Film	Solution	Film	Solution	Film	Solution
1	521	486	612, 667	587	10	27
2	512	495	603, 652	583	10	36
3	476	461	616	584	8	20
3*	552	-	718, 786	-	-	-
4	499	469	626, 678	579	5	26

η_{PL} = photoluminescence efficiency; * = annealed films.

Stability to light and air. Spin-cast films of polymers **1-3** on glass were exposed to ordinary light and air and the UV-Vis spectra were recorded at intervals of time. It was noted that as the films got degraded the intensities of the absorption maxima decreased and at the same time showed blue shifts of the main absorption bands. Polymer **2** turned out to be the most stable of the three polymers. The film showed significant absorption after continuous exposure for more than 70 days. On the other hand films of polymers **1** and **3** got completely degraded after 49 days. It was also noted that annealing of polymer

3 with chloroform vapour or through heat treatment significantly improved the stability of the polymer towards light and air.

EXPERIMENTAL

Reagents. $Pd(PPh_3)_4$ was purchased from Aldrich and Acros. n-BuLi (1.6 M in hexanes) and trimethyl borate were purchased from Aldrich. $FeCl_3$ was heated at 100° for 30 min under vacuum and kept under vacuum for *ca* 6 h prior to use.

General. Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-5000 400 MHz NMR spectrometer. Mass spectra were recorded on a VG ZABSPEC instrument. UV-VIS spectra were obtained from a Cary 210 instrument. Molecular weights of the polymers were determined by size exclusion chromatography (relative to polystyrene standards) using a Waters 150-CV instrument and SDVB columns at 25 °C with THF or chloroform as eluent. Photoluminescence efficiency (η_{PL}) of the polymers was measured in an integrating sphere.

1,4-Bis(1'4'7'-trioxaoctyl)benzene (5). To a mixture of hydroquinone (12.7 g, 0.11 mol) and anhydrous K_2CO_3 in dry DMF (125 mL) was added drop-wise 1-chloro-2-(2-methoxyethoxy)ethane (32 g, 0.23 mol) drop-wise at 100°. The mixture was stirred for 20 h cooled and filtered. The filtrate was poured onto ice-cold water and acidified with 3 M HCl. It was then extracted with ether. The ether extract was washed with 5% NaOH solution and water, dried over anhydrous Na_2SO_4, filtered and the solvent was removed to afford a yellowish oil (19.6 g, 54%). The oil was purified by vacuum distillation and the material that boiled at 170-172° (0.6 mbar) was collected. HRMS: Calcd for $C_{16}H_{26}O_6$ 314.1729, found 314.1699. EIMS *m/z* (rel. int.): 314 (28), 226 (20), 103 (47), 59 (100). ^1H NMR ($CDCl_3$, 400 MHz): δ 6.80 (*s*, 4H), 4.05 (*dd*, 4H), 3.80 (*t*, 4H), 3.68 (*m*, 4H), 3.54 (*m*, 4H), 3.36 (*s*, 6H).

2-Bromo-1,4-bis(1'4'7'-trioxaoctyl)benzene (6). Compound **5** (10.1 g, 0.03 mol) was dissolved in 50 mL of dry DMF and the mixture was cooled in an ice-water bath. To this was added drop-wise a solution of NBS (5.72 g, 0.03 mol) in 75 mL of dry DMF. The mixture was stirred under N_2 atmosphere and the temperature was allowed to gradually rise to rt. After 29 h the mixture was poured onto water, acidified with 3 M HCl and extracted with ether. The combined ether extract was washed with water, dried over anhydrous Na_2SO_4 and the solvent was removed to afford a yellow oil. The oil was distilled under vacuum and the material that boiled at 182-184° (0.6 mbar) was collected. Yield 10.67 g, 84%. HRMS: Calcd for $C_{16}H_{25}O_6Br$ 392.0834, found 392.0807. EIMS *m/z* (rel. int.): 392 (42), 314 (26), 187 (8), 103 (100), 59 (54), 32 (61). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.11 (*d*, J = 2.8 Hz. 1H), 6.84 (*d*, J = 8.8 Hz, 1H), 6.79 (*dd*, J = 8.8, 2.8 Hz, 1H), 4.10 (*m*, 2H), 4.04 (*m*, 2H), 3.85 (*m*, 2H), 3.79 (*m*, 2H), 3.67 (*m*, 2H), 3.54 (*m*, 4H), 3.36 (*s*, 3H), 3.34 (*s*, 3H).

3-[2',5'-Bis(1",4",7"-trioxaoctyl)phenyl]thiophene (7). A mixture of compound **6** (5 g, 12.75 mmol) and $Pd(PPh_3)_4$ (0.75 g, 0.65 mmol) in DME (80 mL) was stirred at rt for 10 min and to it was added 3-thiopheneboronic acid (3.38 g, 26.4 mmol) followed by 1 M $NaHCO_3$ (62 mL). The mixture was heated under reflux for 5 h, cooled to rt and filtered.

The DME was removed by rotary evaporation and to the residue was added water (100 mL) and was extracted with ether. The combined ether extract was washed with water, dried over anhydrous Na_2SO_4 and the solvent was removed to afford a dark brown oil which was chromatographed over silica gel using diethyl ether:pentane 9:1 and diethyl ether. Compound **7** was obtained as a yellow oil (2.87 g, 57%). HRMS: Calcd for $C_{20}H_{28}O_6S$ 396.1607, found 396.1601. EIMS *m/z* (rel. int.): 396 (45), 314 (25), 192 (13), 103 (63), 59 (100). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75 (*dd*, *J* = 1.2, 2.8 Hz, 1H, H-2), 7.46 (*dd*, *J* = 2.8, 4.8 Hz, 1H, H-5), 7.29 (*dd*, *J* = 2.8, 4.8 Hz, 1H, H-4), 7.10 (*d*, *J* = 2.8 Hz, H-6'), 6.87 (*d*, *J* = 8.8 Hz, H-3'), 6.78 (*dd*, *J* = 2.8, 8.8 Hz, H-4') 4.10 (*m*, 4H), 3.82 (*m*, 4H), 3.70 (*m*, 2H), 3.64 (*m*, 2H), 3.55 (*m*, 4H), 3.37 (*s*, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.2 (C-2'), 150.2 (C-5'), 137.9 (C-3) 128.5 (C-2), 126.4 (C-1'), 124.3 (C-5), 123.8 (C-4), 116.4 (C-6'), 114.4 (C-4'), 113.5 (C-3'), 72.03, 72.0, 70.8, 70.7, 69.9, 69.8, 68.7, 68.0, 59.1 (C-8" and C-8"').

Polymer 1. To a solution of compound **7** (0.57 g 1.44 mmol) in $CHCl_3$ (20 mL) was added a slurry of $FeCl_3$ (2.9 g 17.8 mmol) in $CHCl_3$ (40 mL) over 2:30 h. The mixture was stirred for one more hour and poured onto MeOH. The red precipitate was collected by filtration and was redissolved in $CHCl_3$. The red solution was filtered through a sintered glass funnel and was then washed with conc. ammonia (6 times), 0.05 M EDTA (twice) and water (twice). The $CHCl_3$ was removed and the residue was dissolved in a small volume of $CHCl_3$ and the polymer was precipitated by adding into MeOH. Polymer **1** was obtained as a dark-red solid (250 mg).

Compound 8. Compound **6** (2.7 g, 6.87 mmol) was dissolved in 20 mL dry ether and cooled to -60°. To it was added a 1.6 M solution of n-BuLi (4.3 mL, 6.87 mmol) in hexane at once. After stirring for 5 min, trimethyl borate (0.71 g, 6.89 mmol) was added at once. The mixture was stirred for 3 h at -60°. The cooling was then removed and stirring continued for 1 h. The reaction was quenched with 1 M HCl and the ether layer was separated. The aqueous layer was extracted twice with ether. The combined ether extract was extracted with 1 M NaOH three times. The combined NaOH extract was acidified with 1 M HCl and was exhaustively extracted with ether. The combined ether extract was dried over anhydrous Na_2SO_4 and the solvent was removed to afford a yellowish oil (1.5 g, 61%) which was immediately subjected to a coupling reaction as discussed below.

3-[2",5"-Bis(1"',4"',7"'-trioxaoctyl)phenyl]-2,2'-bithiophene (9). To a solution of 3-bromo-2,2'-bithiophene (0.93 g, 3.4 mmol) in 20 mL DME was added $Pd(PPh_3)_4$ (0.2 g, 0.17 mmol) and the mixture was stirred for 10 min. A solution of the boronic acid **8** (1.5 g) in DME (10 mL) was added followed by the addition of 1 M $NaHCO_3$ (15 mL). The mixture was heated under reflux overnight, cooled to rt and filtered. DME was removed by rotary evaporation. Water was added to the residue and it was extracted with ether. The ether extract was washed with water, dried over anhydrous Na_2SO_4 and the solvent was removed to afford a yellow oil. Compound **9** (0.8 g, 44%) was obtained in pure form after column chromatography on silica gel using ether as eluent. HRMS: Calcd for $C_{24}H_{30}O_6S_2$ 478.1484, found 478.1528. EIMS *m/z* (rel. int): 478 (53), 390 (11), 314 (90), 274 (10), 212 (9), 136 (12), 103 (100). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.19 (*d*, *J* = 5.2 Hz, H-5), 7.10 (*dd*, *J* = 1.2, 5.2 Hz, H-5'), 7.02 (*d*, *J* = 5.2 Hz, H-4), 6.96 (*dd*, *J* = 1.2, 3.6 Hz, H-3'), 6.87 - 6.90 (unresolved, 3H, H-4', H-3", H-4"), 6.81 (*dd*, *J* = 1.2, 2.0 Hz, H-6”), 4.04 (*dd*, J = 4, 5.6 Hz, 2H), 3.92 (*t*, J = 5.6 Hz, 2H), 3.79 (*dd*, J = 3.6, 5.6 Hz, 2H), 3.69 (*m*, 2H), 3.56 (*m*, 4H), 3.48 (*m*, 2H), 3.40 (*m*, 2H), 3.38 (*s*, 3H), 3.33 (*s*, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.1 (C-2”), 151.0 (C-5”), 136.7 (C-3), 134.7 (C-2’), 133.1 (C-2), 131.5 (C-5), 127.1 (C-5’), 126.8 (C-1”), 125.4 (C-4), 125.2 (C-4’), 122.9 (C-3’), 117.9 (C-6”), 115.4 (C-3”), 114.6 (C-4”), 72.1, 72.0, 70.9, 70.8, 70.0, 69.7, 69.4, 68.1, 59.3, 59.2.

Polymer **2**. Compound **9** (710 g, 1.62 mmol) was dissolved in $CHCl_3$ (15 mL) and to it was added a slurry of $FeCl_3$ (1.68 g, 10.2 mmol) in $CHCl_3$ (17 mL) over 2:30 h. The mixture was stirred for 30 min and was poured onto MeOH. The red ppt. was collected by filtration and was dissolved in $CHCl_3$ and was washed with conc. ammonia (5 times), 0.05 M EDTA (twice) and filtered through a sintered glass funnel. The solution was then concentrated and poured onto MeOH. Polymer **2** was obtained as a dark-red gummy solid (400 mg).

1-Bromo-4-(1’,4’,7’-trioxaoctyl)benzene (10). To a mixture of *p*-bromophenol (15 g, 0.087 mol), anhydrous K_2CO_3 (48 g) and DMF (150 mL) heated to 100°, 1-chloro-2-(2-methoxyethoxy)ethane (12.0 g, 0.087 mol) was added drop-wise. The mixture was heated overnight, cooled to rt and filtered. The filtrate was acidified with 2 M HCl and extracted with ether. The ether extract was washed with 1 M NaOH and water, dried over anhydrous Na_2SO_4 and the solvent was removed to afford a yellowish oil (23 g, 97%). The oil was distilled under reduced pressure and the colorless oil distilling at 102-116° (1 mbar) was collected. HRMS: Calcd for $C_{11}H_{15}O_3Br$ 274.0204, found 274.0122. EIMS *m/z* (rel. int): 274 (19), 200 (6), 169 (10), 150 (7), 103 (55), 59 (100). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36 (*d*, J = 8.4 Hz, 2H, H-2, H-6), 6.80 (*d*, J = 8.4 Hz, 2H, H-3, H-5), 4.11 (*t*, 2H), 3.85 (*t*, 2H), 3.71 (*m*, 2H), 3.58 (*m*, 2H), 3.39 (*s*, 3H).

3-[4’-(1”,4”,7”-Trioxaoctyl)phenyl]thiophene (11). Compound **10** (8 g, 29.2 mmol) was dissolved in 150 mL DME and $Pd(PPh_3)_4$ (0.6 g, 0.52 mmol) was added. After stirring the mixture for 10 min, 3-thiopheneboronic acid (4.8 g, 37.5 mmol) was added followed by 100 mL of 1 M $NaHCO_3$. The mixture was then heated under reflux overnight, cooled to rt in which case a dark colored solid precipitated. More of the compound was obtained by extracting the filtrate with $CHCl_3$. The dark colored solid was dissolved in CH_2Cl_2 and passed through a short column of silica gel using CH_2Cl_2 as eluent. The solid obtained after removal of the solvent was recrystallized from MeOH to afford compound **11** (6.65 g, 82%) as white crystals. Mp. 76.1-76.9°. HRMS: Calcd for $C_{15}H_{18}O_3S$ 278.0977, found 278.0970. EIMS *m/z* (rel. int): 278 (60), 176 (71), 147 (14), 103 (32), 59 (100). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51 (*d*, J = 8.4 Hz, H-2’, H-6’), 7.31 - 7.33 (unresolved, 3H, H-2, H-4, H-5), 6.94 (*d*, J = 8.4 Hz, H-3’, H-5’), 4.17 (*t*, 2H), 3.88 (*t*, 2H), 3.73 (*m*, 2H), 3.59 (*m*, 2H), 3.40 (*s*, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.1 (C-4’), 142.0 (C-3), 128.9 (C-1’), 127.6 (C-2’, C-6’), 126.3 (C-5), 126.1 (C-2), 119.0 (C-4), 115.0 (C-3’, C-5’), 72.1, 70.9, 69.9, 67.6 59.2.

Polymer **3**. Compound **11** (500 mg, 1.798 mmol) was dissolved in $CHCl_3$ (18 mL) and to it was added a slurry of $FeCl_3$ (1.75 g, 10.77 mmol) in $CHCl_3$ (18 mL) over 2 h. The mixture was stirred for an additional 2:30 h and was poured onto MeOH. The dark colored solid was dissolved in $CHCl_3$ and was washed with conc. ammonia (6 times), 0.05 M EDTA (3 times) and water (twice). The $CHCl_3$ solution was filtered through a sintered glass funnel, concentrated to a small volume and the polymer was precipitated by adding onto MeOH. Lower molecular weight material was removed by Soxhlet extraction with MeOH and diethyl ether. Polymer **3** was obtained as dark-colored solid (350 mg) after reprecipitation from MeOH.

2-Iodo-3-[4'-(1",4",7"-trioxaoctyl)phenyl]thiophene (12). To an ice-cold solution of compound **11** (2.08 g, 7.48 mmol) in toluene (65 mL) was added a mixture of iodine (1.91 g, 7.5 mmol) and HgO (1.62 g, 7.5 mmol). The mixture was stirred for 3 h, filtered and the filtrate was washed with 5% $Na_2S_2O_3$ and water, dried over anhydrous Na_2SO_4 and the solvent was removed to afford compound **12** (3.0 g, 99%) as a yellowish oil. HRMS: Calcd for $C_{15}H_{17}O_3SI$ 403.9943, found 403.9882. EIMS *m/z* (rel. int): 404 (18), 292 (100), 165 (34), 121 (80), 59 (36). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47 (*d*, *J* = 5.2, 1H, H-5), 7.42 (*d*, *J* = 8.4, 2H, H-2', H-6'), 6.98 (*d*, *J* = 8.4, 2H, H-3', H-5'), 6.93 (*d*, *J* = 5.2, 1H, H-4), 4.19 (*t*, 2H), 3.89 (*t*, 2H), 3.74 (*m*, 2H), 3.59 (*m*, 2H), 3.41 (*s*, 3H).

3-[4"-(1"';4"',7"'-Trioxaoctyl)phenyl]-2,2'-bithiophene (13). Compound **12** (2.8 g, 6.93 mmol) and $Pd(PPh_3)_4$ (0.3 g, 0.26 mmol) were dissolved in DME (80 mL). After 10 min, 2-thiopheneboronic acid (1.2 g, 9.37 mmol) was added followed by 1 M $NaHCO_3$ (50 mL). The mixture was heated under reflux for 4 h, cooled and filtered. Water was added to the filtrate and extracted with ether. The ether extract was washed with water, dried over Na_2SO_4 and the solvent was removed. The resulting oil was chromatographed over silica gel using CH_2Cl_2 and CH_2Cl_2:MeOH (100:1) to afford compound **13** (2.3 g, 92%) as a yellowish oil. HRMS: Calcd for $C_{19}H_{20}O_3S_2$ 360.0854, found 360.0873. EIMS *m/z* (rel. int): 360 (100), 258 (45), 227 (13), 208 (7), 184 (11), 103 (29). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.26 (*d*, *J* = 8.8 Hz, 2H, H-2", H-6"), 7.24 (*d*, *J* = 5.2 Hz, 1H, H-5), 7.17 (*dd*, *J* = 1.2, 5.2 Hz, 1H, H-5'), 7.04 (*d*, *J* = 5.2 Hz, 1H, H-4), 6.98 (*dd*, *J* = 1.2, 3.6 Hz, 1H, H-3'), 6.93 (*dd*, *J* = 3.6, 5.2 Hz, 1H, H-4'), 6.89 (*d*, *J* = 8.8 Hz, 2H, H-3", H-5"), 4.16 (*t*, 2H). 3.88 (*t*, 2H), 3.73 (*m*, 2H), 3.59 (*m*, 2H), 3.40 (*s*, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.2 (C-4"), 138.7 (C-2'), 136.2 (C--2), 131.0 (C-3), 130.6 (C-5), 130.4 (C-2", C-6"), 128.8 (C-1"), 127.2 (C-5'), 126.5 (C-4), 125.7 (C-3'), 124.0 (C-4'), 114.5 (C-3", C-5"), 72.0, 70.8, 69.8, 67.4, 59.2.

Polymer 4. Compound **13** (538 mg, 1.49 mmol) was dissolved in $CHCl_3$ (15 mL) and to it was added a slurry of $FeCl_3$ (1.0 g, 6.15 mmol) in $CHCl_3$ (15 mL) over 2 h. The mixture was stirred for an additional 2:30 h and was poured onto MeOH. The ppt was collected by filtration and was dissolved in $CHCl_3$ and washed with conc ammonia (6 times), 0.05 M EDTA (twice) and water (twice). The $CHCl_3$ solution was passed through a sintered glass funnel, concentrated to a small volume and the polymer was precipitated from MeOH. Polymer **4** was obtained as a dark red powder (426 mg).

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