2,5-Substituted PPV-Derivatives with Different Polarities:

The Effect of Side Chain Polarity on Solubility, Optical and Electronic Properties

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Electrical Characterization

The conjugated polymer samples for thin film electrical characterization were prepared and measured in a glove box system under an inert N\textsubscript{2} atmosphere with less than 1 ppm O\textsubscript{2} and H\textsubscript{2}O. The polymers were suspended in chlorobenzene, stirred and heated at 50 °C on a hotplate until completely dissolved. Films of different thickness were prepared by spin coating. In case of the sandwich structures used for impedance spectroscopy, an aluminum contact was evaporated. The relative permittivity was obtained from spectral impedance measurements of ITO/polymer/aluminum sandwich structures. The samples consisted of a glass substrate with two indium tin oxide (ITO) strips acting as electrodes, a spin coated polymer layer acting as dielectric and four evaporated aluminum contacts acting as counter-electrodes (Figure 1a).
The intersections of the metal electrodes and the ITO-strips defined capacitors of different sizes. The polymers were spin coated with varying film thickness to extend the number of different capacitor geometries. The complex impedance of the samples was measured with a HP4284 LCR-meter by applying a bias voltage of 0.8 V superposed by an oscillating voltage of 25 mV. Assuming the equivalent circuit in Figure 1b, with a capacitance $C$, a parallel resistance $R_p$ and a serial resistance $R_s$, the capacitance can be determined from the constant region of the susceptance. By plotting the capacitances $C$ against the geometric factor $A/d$, the relative permittivity $\varepsilon_r$ can be extracted from the slope of the graph, following the equation:

$$C = \varepsilon_0 \cdot \varepsilon_r \cdot \frac{A}{d}$$

where $A$ is the size of the capacitor defined by the intersection of an ITO-strip and an aluminum electrode, $d$ is the distance of the two electrodes determined by the thickness of the polymer film and $\varepsilon_0$ is the permittivity of free space.

To determine the field effect mobility $\mu$ and the conductivity $\sigma$, field effect transistors (FETs) were prepared. The FET substrates consisted of a doped silicon wafer with an insulating oxide on top of it, an evaporated aluminum gate electrode on the backside and evaporated source and drain contacts made of gold on the front side. In between the source and drain contacts
thin gold lips separated by a gap, represented channels of different geometries, i.e. width to
length ratio, and different layouts, i.e. simple channels and interdigitated ones. The channels
were filled with the polymer under investigation by spin coating thin films. Finally the FET
substrates were glued with carbon paste on ceramic substrates to contact the gate electrode.
To determine the mobility, the source-drain voltage as well as the gate voltage were swept
from 0 V to -70 V. The mobility was extracted from the saturation regime by fitting the
corresponding transfer characteristic in accordance with the parabolic approximation

$$I_{sd} = \frac{1}{2} \frac{W}{L} \mu C_{ox} \cdot (V_g - V_t)^2$$

In this equation, \(I_{sd}\) represents the source-drain current, \(W\) and \(L\) the channel width and
length, \(\mu\) the mobility, \(C_{ox}\) the specific capacitance of the insulating oxide (~17 nF/cm²), \(V_g\)
the gate voltage and \(V_t\) the threshold voltage. The mobility is obtained independently from the
threshold voltage from the coefficient of the quadratic \(V_g\) term.

For determining the conductivity the gate electrode was disconnected and the measured I-V-
characteristic was retrieved from the linear regime by using the equation:

$$\sigma = \frac{L}{t \cdot W} \frac{\partial I_{sd}}{\partial V_{sd}}$$

where \(t\) is the thickness of the polymer film measured by a micro-profiler and \(\frac{\partial I_{sd}}{\partial V_{sd}}\) is the
slope of the linear region determined from fitting a straight line through the measurement
points.
**Synthesis**

**Toluene-4-sulfonic acid 2-(2-(2-methoxy-ethoxy)-ethoxy)-ethyl ester 1.** A three-necked round bottom flask equipped with mechanical stirrer, thermometer and N\textsubscript{2} inlet, is charged with 2-(2-(2-methoxy ethoxy)ethoxy)ethylalcohol (60.0 g, 0.37 mol), \textit{p}-toluenesulfonyl chloride (71.5 g, 0.38 mol) and CH\textsubscript{2}Cl\textsubscript{2} (250 mL). The homogeneous mixture is cooled to 0 \degree C with a CO\textsubscript{2}(s)-acetone bath. Freshly powdered KOH (83.1 g, 1.47 mol) is added in small amounts under vigorous stirring while maintaining the reaction mixture below 5 \degree C (exothermic reaction). The mixture is stirred for 3 h at 0 \degree C after which CH\textsubscript{2}Cl\textsubscript{2} (250 mL) and ice-water (300 mL) are added. The organic phase is separated and the aqueous phase is extracted with CH\textsubscript{2}Cl\textsubscript{2} (2 x 150 mL). The combined organic layer is washed with water (150 mL), dried (MgSO\textsubscript{4}) and concentrated under reduced pressure. The pure product was obtained in 98\% yield as a colorless oil. \textsuperscript{1}H-NMR (CDCl\textsubscript{3}): \( \delta = 7.60 \) (d, 2H), 7.17 (d, 2H), 3.96 (t, 2H), 3.49 (t, 2H), 3.42-3.38 (m, 8H), 3.17 (s, 3H), 2.25 (s, 3H); MS (EI): \textit{m/z} = 318 [M\textsuperscript{+}], 273, 259, 243, 229, 199, 172, 155, 91, 59, 45.

**4-(\textit{n}-Nonyloxy)phenol 2.** A mixture of 4-methoxyphenol (25.0 g, 0.23 mol), NaOH (7.0 g, 0.17 mol) in EtOH (175 mL) was stirred for 2 h at ambient temperature under Ar atmosphere, after which a mixture of 1-bromononane (36.2 g, 175 mmol) and sodium iodide (0.6 g, 0.004 mol) in EtOH (75 mL) was added dropwise over a period of 1 h. The reaction mixture was stirred for 6 h at reflux temperature and overnight at 50 \degree C. After the total volume was reduced to 50 mL by evaporation and the solution was cooled down to ambient temperature, the product was extracted with CH\textsubscript{2}Cl\textsubscript{2} (3 x 75 mL). The organic extracts were dried over anhydrous MgSO\textsubscript{4} and the solvent was evaporated to give the crude product as brown crystals. The pure product was obtained by column chromatography (SiO\textsubscript{2}, eluent CH\textsubscript{2}Cl\textsubscript{2})
(22.7 g, 55 % yield). $^1$H-NMR (CDCl$_3$): $\delta = 6.75 + 6.74$ (d, 4H), 3.87 (t, 2H), 1.73 (m, 2H), 1.39 (m, 12H), 0.86 (t, 3H); MS (EI): $m/z = 236$ [M$^+$].

1-(n-Nonyloxy)-4-(2-(2-(2-methoxy-ethoxy)-ethoxy)-ethoxy)benzene 3a. To a stirred solution of 2 (20.0 g, 0.085 mol) and KOH (5.2 g, 0.093 mol) in EtOH (150 mL) was added 1 (26.9 g, 0.085 mol) under N$_2$ atmosphere. The reaction mixture was stirred at reflux temperature. As soon as the starting products are consumed (TLC monitoring), the total volume was reduced by evaporation and the solution was cooled down to ambient temperature. The product was extracted with CH$_2$Cl$_2$ (3 x 100 mL) and the organic extracts were dried over anhydrous MgSO$_4$. Removal of solvent gave the crude product. The pure product was obtained by column chromatography (SiO$_2$, eluent diethylether) to yield 3a as white crystals (20.5 g, 63 % yield). $^1$H-NMR (CDCl$_3$): $\delta = 6.81 + 6.80$ (d, 4H), 4.07 (t, 2H), 3.86 (t, 2H), 3.80 (m, 6H), 3.66 (m, 6H), 3.52 (2H), 3.36 (s, 3H), 1.72 (m, 2H), 1.25 (m, 12H), 0.86 (t, 3H); MS (EI): $m/z = 382$ [M$^+$].

Methoxy-4-(2-(2-(2-methoxy-ethoxy)-ethoxy)-ethoxy)-benzene 3b. Compound 3b was prepared following the procedure described for 3a using 4-hydroxy anisol (2.0 g, 0.016 mol) as the alcohol functionalized molecule in the reaction. A Kugelrohr distillation gave 3b as a light yellow liquid (4.3 g, 99% yield). $^1$H-NMR (CDCl$_3$): $\delta = 6.69 + 6.70$ (d, 4H), 3.92 (t, 2H), 3.69 (t, 2H), 3.60 (m, 5H), 3.51 (m, 4H), 3.43 (m, 4H), 3.24 (s, 3H); MS (EI): $m/z = 270$ [M$^+$], 151, 147, 136, 124, 109, 92, 77, 59.

1,4-Bis(2-(2-(2-methoxy-ethoxy)-ethoxy)-ethoxy)-benzene 3c. Compound 3c was prepared following the procedure described for 3a using hydroquinone (9.4 g, 0.08 mol) as the alcohol functionalized molecule and 2.2 equivalent 1. The pure product was obtained by Kugelrohr distillation as a light yellow liquid (32.05 g, 93 % yield). $^1$H-NMR (CDCl$_3$): $\delta = 6.70$ (s, 4H), 3.93 (t, 4H), 3.69 (t, 4H), 3.70- 3.51 (m, 12H), 3.41 (t, 4H), 3.24 (s, 6H); MS (EI): $m/z = 402$ [M$^+$], 175, 151, 147, 136, 110, 103.
1,4-Bis(chloromethyl)-2-(\(n\)-nonyloxy)-5-(2-(2-(2-methoxy-ethoxy)-ethoxy)-ethoxy)benzene 4a. To a stirred mixture of 3a (14.7 g, 0.044 mol) and \(p\)-formaldehyde (3.6 g, 0.12 mmol), concentrated HCl (21 mL) was added dropwise under N\(_2\) atmosphere. Subsequently, acetic anhydride (44 mL, 0.47 mol) was added at such a rate that the temperature did not exceed 70 °C. After addition was complete, the resulting solution was stirred at 70 °C for 3 h after which it was cooled down to room temperature and poured into water (100 mL). The reaction mixture was extracted with CH\(_2\)Cl\(_2\) (3 x 100 mL) and dried over anhydrous MgSO\(_4\). Evaporation of the solvent under reduced pressure gave a white solid (20.3 g, 96 % yield). \(^1\)H-NMR (CDCl\(_3\)): \(\delta = 6.93 + 6.88 \ (2s, \ 2H), 4.62 + 4.60 \ (2s, \ 4H), 4.14 \ (t, \ 2H), 3.95 \ (t, \ 2H), 3.84 \ (t, \ 2H), 3.72 \ (t, \ 2H), 3.64(m, \ 4H), 3.53 \ (t, \ 2H), 3.36 \ (s, \ 3H), 1.25 \ (m, \ 14H), 0.86 \ (t, \ 3H); MS (EI): \(m/z = 480 \ [M^+], 445, 410.\)

Bis-tetrahydrothiopheniumsalt of 1,4-Bis(chloromethyl)-2-(\(n\)-nonyloxy)-5-(2-(2-(2-methoxy-ethoxy)-ethoxy)-ethoxy)-ethoxy)benzene 5a. To a solution of 4a (25.0 g, 0.038 mol) in MeOH (150 mL), tetrahydrothiophene (17 mL, 0.190 mol) was added, after which the white solution turned bright yellow. The mixture was allowed to react for 4 h at 50 °C, after which
the total volume was reduced to 50 mL by evaporation. Subsequently the product was precipitated in cold diethylether (500 mL) after which the bissulfonium salt was filtered off, washed with diethylether (3 x 100 mL) and dried under vacuum. A white solid was obtained (15.7 g, 63% yield). $^1$H-NMR (D$_2$O): $\delta = 7.13+7.12$ (2s, 2H), 4.44 + 4.41 (2s, 4H), 4.16 (t, 2H), 4.01 (t, 2H), 3.83 (t, 2H), 3.65 (t, 2H), 3.58(m, 6H), 3.38 (m, 8H), 3.24 (s, 3H), 2.23 (m, 8H), 1.72 (t, 2H), 1.13 (m, 12H), 0.71 (t, 3H).

Bis-tetrahydrothiopheniumsalt of 1,4-Bis(chloromethyl)-2-methoxy-5-(2-(2-(2-methoxy-ethoxy)-ethoxy)-ethoxy)-benzene 5b. Following the procedure described for 5a using 4b (23.0 g, 0.063 mol) as reagent and 72 h reaction time at ambient temperature, 5b was obtained as a white solid (27.0 g, 77% yield). $^1$H-NMR (D$_2$O): $\delta = 7.10$ (s, 2H), 4.40-4.45 (2s, 4H), 4.18 (m, 2H), 3.83 (m, 2H), 3.80 (s, 3H), 3.45-3.64 (m, 8H), 3.36 (m, 8H), 3.24 (s, 3H), 2.21 (m, 8H).

Bis-tetrahydrothiopheniumsalt of 1,4-Bis(chloromethyl)-2-methoxy-5-(2-(2-(2-methoxy-ethoxy)-ethoxy)-ethoxy)-ethoxy)-benzene 5c. Following the procedure described for 5a using 4c (22.6 g, 0.045 mol) as reagent and 72 h reaction time at ambient temperature, 5c is obtained as a white solid (25.9 g, 82% yield). $^1$H-NMR (D$_2$O): $\delta = 7.13$ (s, 2H), 4.45 (s, 4H), 4.19 (m, 4H), 3.84 (m, 4H), 3.48-3.67 (m, 16H), 3.36 (m, 8H), 3.25 (s, 6H), 2.21 (m, 8H).

1-Chloromethyl-2-(n-nonyloxy)-4-octylsulfanylmethyl-5-(2-(2-(2-methoxy-ethoxy)-ethoxy)-ethoxy)-ethoxy)benzene and 1-Chloromethyl-2-(2-(2-(2-methoxy-ethoxy)-ethoxy)-ethoxy)-4-octylsulfanylmethyl-5-(n-nonyloxy)benzene 6a. A mixture of n-octane thiol (3.4 g, 0.023 mol) and NaOtBu (2.3 g, 0.023 mol) in MeOH (150 mL) was stirred for 30 min at room temperature after which a clear solution was obtained. This solution was added dropwise (during 1 h) to solution of 5a (15.4 g, 0.023 mol) in MeOH (500 mL). The reaction mixture was stirred for 2 h, after which it was concentrated under reduced pressure. Subsequently, n-octane (100 mL) was added and evaporated again to remove the
tetrahydrothiophene. This sequence was repeated three times. The residue was redissolved in CH₂Cl₂ (100 mL) and extracted with water (3 x 100 mL). The organic layers were dried over anhydrous MgSO₄ and concentrated under reduced pressure giving the crude product as a yellow viscous oil, which was used without further purification (13.2 g, 95% yield). ¹H-NMR (CDCl₃): δ = 6.88+6.86 (2s, 2H), 4.62+4.60 (2s, 2H), 4.12 (m, 2H), 3.93 (m, 2H), 3.82(m, 2H), 3.64 (m, 10H), 3.36 (s, 3H), 2.43 (t, 2H), 1.54 (m, 26H), 0.85 (t, 6H).

1-Chloromethyl-2-methoxy-4-octylsulfanylmethyl-5-(2-(2-(2-methoxy-ethoxy)-ethoxy)-ethoxy)benzene and 1-Chloromethyl-2-(2-(2-(2-methoxy-ethoxy)-ethoxy)-ethoxy)-4-octylsulfanylmethyl-5-methoxybenzene 6b. Using 5b (10.0 g, 0.018 mol) as reagent and the same procedure as for 6a, 6b was obtained as a yellowish oil and used without further purification (8.50 g, 100% yield). ¹H-NMR (CDCl₃): δ = 6.87 + 6.84 + 6.84 + 6.82 (4s, 2H), 4.62 + 4.58 (2s, 2H), 4.10 (m, 2H), 3.84-3.50 (m, 15H), 3.34 (s, 3H), 2.42 (t, 2H), 1.52 (m, 2H), 1.33-1.22 (m, 10H), 0.84 (t, 3H).

1-Chloromethyl-2,5-bis(2-(2-(2-methoxy-ethoxy)-ethoxy)-ethoxy)-4-octylsulfanylmethylbenzene 6c. Using 5c (3.6 g, 0.0053 mol) as reagent and the same procedure as for 6a, 6c was obtained as a yellowish oil after column chromatographic purification (SiO₂, eluent diethylether) (2.36 g, 75% yield). ¹H-NMR (CDCl₃): δ = 6.88+6.85 (2s, 2H), 4.62 (s, 2H), 4.12 (m, 4H), 3.83 (m, 4H), 3.75-3.52 (m, 18H), 3.36 (s, 6H), 2.43 (t, 2H), 1.59 (m, 2H), 1.29-1.20 (m, 10H), 0.86 (t, 3H).
UV-Vis Solution Characteristics

Figure 2  Solution UV-Vis absorption spectra of 9a in various solvents.

Figure 3  Solution UV-Vis absorption spectra of 9b in various solvents.
Figure 4   Solution UV-Vis absorption spectra of MDMO-PPV in various solvents.