

Supporting Information

Self-assembly behaviour of conjugated terthiophene surfactants in water

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Experimental Section

General information

Starting materials were commercially available and were used without further purification. Synthesis of compounds **1'-OH**, **2-OH** was described in ref. 19, synthesis of **10** and **17** was performed according to literature procedures (ref. 20). Aldrich silica gel Merck grade 9385 (230-400 mesh) was used for column chromatography, in combination with the Teledyne Isco CombiFlash Companion with UV-detection. All solvent used for dry reactions were purified with the use of MBRAUN Solvent purification system MB SPS-800, MilliQ-water was used in case of measurements. ¹H NMR-spectra were recorded on a Bruker Avance-400 spectrometer (at 400MHz) or a Varian Inova-300 spectrometer (at 300MHz), at 25°C. The splitting patterns are noted as follows: s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), qt (quintet), m (multiplet) and bs (broad singlet). ¹³C NMR spectra were recorded on a Bruker Avance-400 spectrometer (at 100 MHz) or a Varian Inova-300 spectrometer (at 75 MHz). Multiplicity was determined by Attached Proton Test (APT) and chemical shifts are given in δ (ppm) referenced to the residual protic solvent peaks. Coupling constants *J*, are given in Hz. LC-MS was performed on a SHIMADZU Liquid Chromatograph Mass Spectrometer, LCMS-2010, LC-8A pump with a diode-array detector SPD-M20. The column used here was the Xbridge Shield RP 18.5 μ m (4.6x150mm) with a 95/5 v/v MeOH-H₂O mixture as eluent. For UV/Vis measurements an AnalytikJena Specord 250 spectrometer was used equipped with a deuterium-lamp and a halogen-lamp. Quartz cuvetts were used with path-lengths varying from 10mm-0.1mm. Fluorescence spectroscopy was done on a Jasco J-815 CD-spectrometer equipped with a fluorescence monochromator and detector, and an L-38 low wavelength filter (cut-off 380nm) placed between the sample and the detector. The cuvet used here was quartz with dimensions 3x3mm. Dynamic Light Scattering was performed on a ZetaSizer Nano series Nano-ZS by Malvern Instruments. For cryo-TEM, a few microliter of suspension was deposited on a bare 700 mesh copper grid. After blotting away the excess of liquid the grids were plunged quickly in liquid ethane. Frozen-hydrated specimens were mounted in a cryo-holder (Gatan, model 626) and observed in a Philips CM 120 electron microscope, operating at 120 kV. Micrographs were recorded under low-dose conditions on a slow-scan CCD camera (Gatan, model 794).

Experimentals

Description for synthesis of compounds 1-, 2- 3-OMe and 4-6.

2-bromo-3-hexadecylthiophene (11): 3-hexadecylthiophene (**10**) (2.5 g, 8.1 mmol) was dissolved in 10 ml of chloroform. To this *N*-bromosuccinimide NBS (2.9 g, 16 mmol) was added at room temperature. It was allowed to react overnight. The reaction was quenched with 50 ml saturated sodium bicarbonate solution. Then 40 ml of chloroform was added. Organic and water phases were separated. Organic phase was washed with water and brine and dried over MgSO₄. Solvent was removed under vacuum. The title compound was obtained as a light yellow solid after precipitation in cold methanol which was isolated after filtration and drying in vacuum in 90% yield (2.8 g, 7.3 mmol) and was not subdued to further purification. ¹H NMR (400 MHz, CDCl₃) δ_H: 0.88 (t, J₃ = 6.8 Hz, 3H), 1.20-1.38 (m, 26 H), 1.50-1.66 (m, 4H), 2.55 (t, J₃ = 7.8 Hz, 2H), 6.79 (d, J₃ = 5.6 Hz, 1H), 7.18 (d, J₃ = 5.6 Hz, 1H).

(3-hexadecylthiophen-2-yl)trimethylsilane (12)*: 2-bromo-3-hexadecylthiophene (**11**) (10.0 g, 25.8 mmol) was dissolved in 250 ml of dry THF and cooled to -78°C. Then *n*-butyllithium (21.0 ml, 33.6 mmol, 1.6M in hexane) was added drop wise. The mixture was allowed to react at -78°C for 2h. Then TMSCl (6.6 ml, 51.6 mmol) was slowly added. The mixture was allowed to react at -78°C for additional 2h and then left overnight to slowly reach room temperature and was then quenched with water. The mixture was extracted with THF and diethyl ether. The combined organic layers were then washed with brine. The organic layer was dried over MgSO₄ and filtered; the solvent was removed under vacuum. The resulting slightly yellowish liquid was identified as the title compound obtained as a colourless oil which solidified when cooled at 4°C to a soft off-white solid in 89% yield (9.4 g, 23.0 mmol) and was used without further purification. ¹H NMR (400MHz, CDCl₃) δ_H: 0.35 (s, 9H), 0.88 (t, J₃ = 6.7 Hz, 3H), 1.26-1.32 (m, 26H), 1.55-1.65 (m, 2H), 2.67 (t, J = 7.8 Hz, 2H), 7.05 (d, J₃ = 4.7 Hz, 1H), 7.45 (d, J₃ = 4.7 Hz 1H).

(3-hexadecylthiophen-2-yl)trimethylstannane (12): A solution of 2.0 g (5.2 mmol) of 2-bromo-3-hexadecylthiophene (**11**) in 15 ml of dry THF was cooled to -50°C. To this 1.05 equivalent of *n*-butyllithium (3.4 ml, 1.6 M in hexane) was slowly added and the reaction mixture was stirred for 4 hours. Then 6.3 ml of a 1M solution of trimethyltinchloride in THF was added slowly to the mixture. After addition the mixture was stirred for 2 hours at -50°C and was then allowed to slowly warm to room temperature overnight. The reaction was quenched with water. The organic and aqueous phases were separated and the organic phase was subsequently washed with water two times, then once with brine and dried over MgSO₄. After filtration, the solvent was removed in vacuum. The title compound was obtained as a colourless oil which solidifies when cooled at 4°C to a soft off-white solid in 82% yield (2.5 g, 4.3 mmol) and was not subdued to further purification. ¹H NMR (400MHz, CDCl₃) δ_H: 0.37 (s, 9H), 0.85-1.00 (s, 3H), 1.20-1.40 (m, 26H), 1.50-1.70 (m, 2H), 2.62 (t, J₃ = 7.8 Hz, 2H), 7.09 (d, J₃ = 4.6 Hz, 1H), 7.53 (d, J₃ = 4.7 Hz, 1H).

2,5-dibromo-3-hexadecylthiophene (13) : 3-hexadecylthiophene (**10**) (1.50 g, 4.9 mmol) was dissolved in chloroform. To this Br₂ (1.55 g, 9.7 mmol) (2 equivalent) was added at 0 °C. It was allowed to react overnight. The reaction was quenched with a saturated bicarbonate solution. Then chloroform was added. Organic and aqueous phases were separated. The organic phase was washed with water and brine, dried over MgSO₄. Solvent was removed and the title compound was obtained after precipitation in cold methanol which was isolated after filtration and drying under vacuum in 94% yield (2.0 g, 4.6 mmol). This was used without any further purification. ¹H NMR (400 MHz, CDCl₃) δ_H: 0.87 (t, J₃ = 6.8 Hz, 3H), 1.22-1.33 (m, 25H), 1.42-1.52 (m, 2H), 2.49 (t, J₃ = 7.7 Hz, 2H), 6.77 (s, 1H).

(3-hexadecylthiophen-2-yl-trimethylsilyl-5-yl)trimethylstannane (15): To 100ml of THF diisopropylamine (4.2 ml, 29.7 mmol) was added. The mixture was cooled to -78°C. Then *n*-butyllithium (16.9 ml, 27.0 mmol, 1.6M in hexane) was added drop wise. The mixture was allowed to react at -78°C for 2h. Then 3-hexadecylthiophen-2-yl)trimethylsilane (**12***) (9.4 g,

23.0 mmol) was added and the mixture was stirred for 4h. After this trimethyltinchloride (5.9 g, 29.7 mmol, 1M in THF) was slowly added. The mixture was allowed to react at -78°C for additional 2h and then left overnight to slowly reach room temperature and was then quenched with water. The mixture was extracted with THF and diethyl ether. The combined organic layers were then washed with brine. The organic layer was dried over MgSO₄ and filtered; the solvents were removed under vacuum. The resulting slightly yellowish liquid was identified as the title compound and was obtained as a colourless oil which solidified when cooled at 4°C to a soft off-white solid in 89% yield (12.4 g, 22.7mmol) and was used without further purification. ¹H NMR (400 MHz, CDCl₃) δ_H: 0.27 (s, 9H), 0.33 (s, 9H), 0.88 (t, J₃ = 6.7 Hz, 3H), 1.26-1.32 (m, 26H), 1.54-1.63 (m, 2H), 2.62 (t, J₃ = 7.8 Hz 2H), 7.03 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ_C: -8.12 (3*CH₃), 0.41 (3*CH₃), 22.54 (2*CH₂), 29.35(CH₂), 29.39 (CH₂), 29.49 (CH₂), 29.57 (CH₂), 29.60(CH₂), 29.65 (CH₂), 29.71 (CH₂), 30.29 (CH₂), 30.58 (CH₂), 31.25 (CH₂), 31.84 (CH₂), 31.94 (2*CH₂), 130.01 (CH), 135.25 (C), 142.7 (C).

1-(2,5-dibromothiophen-3-yl)-2,5,8,11,14-pentaoxapenta-decane (18): To a solution of *1-(2-bromothiophen-3-yl)-2,5,8,11,14-pentaoxapentadecane (17)* (0.5 g, 1.3 mmol) in 7 ml of DCM, *N*-bromosuccinimide (NBS) (0.23 g, 1.3 mmol) was added. After addition the mixture was stirred for overnight at room temperature and was then quenched with water. The mixture was extracted with DCM. The combined organic layers were then washed with a 1 M NaOH solution followed by water and brine. The organic layer was dried over MgSO₄ and filtered; the solvent was removed under vacuum. The resulting slightly yellowish liquid was identified as the title compound and obtained in 91% yield (0.55 g, 1.2 mmol). ¹H NMR (400 MHz, CDCl₃) δ_H: 3.37 (s, 3H), 3.56-3.52 (m, 2H), 3.70-3.60 (m, 14H), 4.43 (s, 2H), 6.99 (s, 1H).

2-[2-(2-methoxyethoxy)ethoxy]ethyl 2-[[2-(trimethylstannyl)-3-thienyl]methoxy]ethyl ether (19): A solution of 2.0 g (5.2 mmol) of *1-(2-bromothiophen-3-yl)-2,5,8,11,14-pentaoxapentadecane (17)* in dry THF was cooled to -78°C. To this 1.05 equivalent of *n*-butyllithium (3.44 ml, 1.6 M in hexane) was added slowly and the reaction mixture was stirred for 4 hours at -78°C, during this time the colour changed to black. Then 6.37 ml of a 1 M solution of trimethyltinchloride in THF was added slowly to the mixture. After addition the mixture was stirred for 2 hours at -78°C and was then allowed to slowly warm to room temperature overnight. The reaction was quenched with water. The organic and aqueous phases were separated and the organic phase was subsequently washed with water two times, then once with brine and dried over MgSO₄. After filtration and removal of solvent in vacuum, the title compound was obtained as a viscous yellow liquid in a 74% yield (1.8 g, 3.9 mmol). ¹H NMR (400 MHz, CDCl₃) δ_H: 0.36 (s, 9H), 3.37 (s, 3H), 3.65 (m, 16H), 4.55 (s, 2H), 7.17 (d, J₃ = 4.6 Hz, 1H), 7.54 (d, J₃ = 4.7 Hz, 1H).

2-[2-(2-methoxyethoxy)ethoxy]ethyl 2-[[2-(trimethylsilyl)-3-thienyl]methoxy]ethyl ether (20): A solution of *1-(2-bromothiophen-3-yl)-2,5,8,11,14-pentaoxapentadecane (17)* (13.0 g, 34 mmol) in 120 ml of dry THF under nitrogen atmosphere was cooled to -78°C. To this 1.05 equivalent of *n*-butyllithium (20 ml, 1.6 M in hexane) was added slowly and the reaction mixture was stirred for 3 hours. Then the reaction was quenched with trimethylsilylchloride (4.0 ml, 35.3 mmol) and stirred for an additional 3 hours at -78°C. After this the mixture was allowed to warm to room temperature slowly overnight and then quenched with water. The mixture was washed twice with water and once with brine and dried over MgSO₄. After filtration and removal of solvent under vacuum, the title compound was obtained as a yellowish oil in 86% yield (11.0 g, 29.3 mmol). The crude compound was used without further purification. ¹H-NMR (400 MHz, CDCl₃) δ_H: 0.34 (s, 9H), 3.37 (s, 3H), 3.52-3.56 (m, 2H), 3.60-3.69 (m, 14H), 4.59 (s, 2H), 7.20 (d, 1H, J₃ = 4.9 Hz), 7.48 (d, 1H, J₃ = 4.8Hz).

2-[2-(2-methoxyethoxy)ethoxy]ethyl2-[[2-(trimethylsilyl)-5-(trimethylstannyl)-3 thienyl]methoxy]ethyl ether (21): A solution of 4.0 ml diisopropylamine in 120 ml of dry THF was cooled to -78°C. To this 18.5 ml (29.6 mmol) of *n*-butyllithium was added. The mixture was then allowed to reach 0°C and was stirred at this temperature for 10 minutes. Then it was again cooled to -78°C and 11.0 g (29.3 mmol) of **20** was added dissolved in 30 ml of dry THF and the mixture was stirred for 4 hours. Then 6 ml of trimethyltinchloride solution (5 M in THF) was added and the mixture was continues to be stirred at -78°C. After 3 hours the reaction mixture was allowed to slowly warm to room temperature overnight. The reaction was

quenched with water with water and the layers were separated. The aqueous layer was extracted with diethyl ether. The combined organic layers were washed with water and then with brine. The organic phase was dried over MgSO_4 . After filtration and removal of solvent under vacuum, the crude compound was obtained in a 98% yield (15.2 g, 28.9 mmol). This compound was used without further purification. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ_{H} : 0.34 (s, 9H), 0.35 (t, 9H, $J_{\text{Sn}} = 29.7$ Hz), 3.37 (s, 3H), 3.52-3.56 (m, 2H), 3.62-3.69 (m, 14H), 4.62 (s, 2H), 7.28 (s, 1H).

(4-hexadecyl-3'-2,5,8,11,14-pentaoxapentadecyl-2,2'-bithiophen-5-yl)trimethylsilane (**22**): 1-(2-bromothiophen-3-yl)-2,5,8,11,14-pentaoxapentadecane (7.0 g, 18.4 mmol) was dissolved in 50 ml of dry DMF. Then palladium(tetrakis)triphenylphosphine (2.20 g, 1.9 mmol) was added to the solution. The mixture was stirred for 20 min at room temperature. Then a solution of **15** (10.0 g, 18.4 mmol) solution in 50 ml of toluene was added. The temperature was raised until 110°C and left overnight. Then the solvents were removed under vacuum. The crude was purified by column chromatography (silica gel, eluent petroleum ether/EtOAc (gradient 0-100% EtOAc) with 5% TEA) and gave the pure title compound as a yellow oil in 80% yield (8.0 g, 14.7 mmol). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ_{H} : 0.37 (s, 9H), 0.88 (t, $J_3 = 6.7$ Hz, 3H), 1.22-1.38 (m, 26H), 1.58-1.68 (m, 2H), 2.65 (t, $J_3 = 7.8$ Hz, 2H), 3.38 (s, 3H), 3.52-3.58 (m, 2H), 3.72-3.62 (m, 14H), 4.64 (s, 2H), 7.09 (s, 1H), 7.11 (d, $J_3 = 5.2$ Hz 1H), 7.17 (d, $J_3 = 5.2$ Hz 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ_{C} : 0.01 (3* CH_3), 14.00 (CH_3), 22.52 (2* CH_2), 29.34(CH_2), 29.37 (CH_2), 29.50 (CH_2), 29.55 (CH_2), 29.58(CH_2), 29.64 (CH_2), 29.70 (CH_2), 30.27 (CH_2), 30.56 (CH_2), 58.58 (CH_3), 66.58 (CH_2), 69.20 (CH_2), 70.31(CH_2), 70.48 (4* CH_2), 70.49 (CH_2), 71.30 (CH_2), 123.50 (CH), 129.51 (CH), 129.52 (CH), 133.52 (C), 134.25 (C), 134.51 (C), 138.58 (C), 150.58 (C).

4-hexadecyl-3'-2,5,8,11,14-pentaoxapentadecyl-5'-(trimethylstannyl)-2,2'-bithiophen-5-yl)trimethylsilane (**23**): To 100ml of THF diisopropylamine (1.9 ml, 13.5 mmol) was added. The mixture was cooled to -78°C . Then *n*-butyllithium (8.5 ml, 13.5 mmol, 1.6M in hexane) was added drop wise and the reaction was allowed to warm to room temperature. The mixture was then cooled to -78°C and **22** (7.3 g, 13.5 mmol) dissolved in THF was added dropwise. The mixture was allowed to react at -78°C for 2h. Then trimethyltinchloride (2.7 g, 13.5 mmol, 1M in THF) was slowly added. The mixture was allowed to react at -78°C for additional 2h and then left overnight to slowly reach room temperature and was then quenched with water. The mixture was extracted with THF and diethyl ether. The combined organic layers were then washed with brine. The organic layer was dried over MgSO_4 and filtered; the solvents were removed under vacuum. The resulting slightly yellowish liquid was determined as the title compound obtained in 78% yield (7.0 g, 10.5 mmol) and was used without further purification. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ_{H} : 0.36 (s, 9H), 0.38 (s, 9H), 0.88 (t, $J_3 = 6.7$ Hz, 3H), 1.22-1.38 (m, 26H), 1.58-1.68 (m, 2H), 2.65 (t, $J_3 = 7.8$ Hz, 2H), 3.38 (s, 3H), 3.52-3.58 (m, 2H), 3.72-3.62 (m, 14H), 4.65 (s, 2H), 7.09 (s, 1H), 7.19 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ_{C} : -8.12 (3* CH_3), 0.41 (3* CH_3), 14.10 (CH_3), 22.52 (2* CH_2), 29.42 (CH_2), 29.50 (2* CH_2), 29.51(4* CH_2), 29.53 (5* CH_2), 29.54 (CH_2), 58.88 (CH_3), 66.88 (CH_2), 69.30 (CH_2), 70.41(CH_2), 70.58 (4* CH_2), 70.60 (CH_2), 71.98 (CH_2), 129.38 (CH), 133.56 (C), 135.61 (C), 136.52 (C), 138.15 (CH), 139.24 (C), 142.21 (C), 151.00 (C).

1-(4'-hexadecyl-2,2'-bithiophen-3-yl)-2,5,8,11,14-pentaoxapentadecane (**24**): A solution of 7.3 g (19.1 mmol) of 1-(2-bromothiophen-3-yl)-2,5,8,11,14-pentaoxapentadecane, 2.0 g palladium(tetrakis)triphenylphosphine in 300 ml DMF was prepared under a nitrogen atmosphere and stirred for 20 minutes. To this, 9.0 g (19.1 mmol) of **14** in 100 ml toluene was added and heated at 110°C overnight. The reaction mixture was allowed to cool to room temperature solvent was removed under vacuum. The crude was purified by column chromatography (silica gel, eluent pentane/EtOAc (1:1), Rf: 0.45) and gave the pure title compound as a yellow oil in 71% yield (8.3 g, 13.6 mmol). $^1\text{H-NMR}$ (300 MHz): 0.87 (t, 3H, $J_3 = 6.9\text{Hz}$), 1.20-1.42 (m, 26H), 1.63-1.70 (m, 2H), 2.59 (t, 2H, $J_3 = 7.7\text{Hz}$), 3.37 (s, 3H), 3.51-3.57 (m, H), 3.61-3.69 (m, 14H), 4.61 (s, 2H), 6.90 (s, 1H), 6.99 (d, 1H, $J_4 = 1.3\text{Hz}$), 7.11 (d, 1H, $J_3 = 5.2\text{Hz}$), 7.17 (d, 1H, $J_3 = 5.0$ Hz).

1-(5'-bromo-4'-hexadecyl-2,2'-bithiophen-3-yl)-2,5,8,11,14-pentaoxapentadecane (**25**): To a solution of 8.3 g (13.6 mmol) of **24** in 75 ml DCM, 1.0 equivalent of *N*-bromosuccinimide was added. The mixture was stirred overnight. After completion the solvent was removed under vacuum. The crude was solubilised in cold heptane and filtered over celite. After evaporation

of the solvent, purification was done by column chromatography (silica gel, pentane/EtOAc (1:1)) and gave the pure title compound as a yellow oil in 95% yield (8.9 g, 12.9 mmol). ¹H-NMR (300 MHz): 0.87 (t, 3H, J₃= 6.9 Hz), 1.20-1.42 (m, 26H), 1.63-1.70 (m, 2H), 2.55 (t, 2H, J₃=7.5 Hz), 3.37 (s, 3H), 3.51-3.57 (m, H), 3.61-3.69 (m, 14H), 4.56 (s, 2H), 6.86 (s, 1H), 7.10 (d, 1H, J₃=5.4 Hz), 7.19 (d, 1H, J₃= 5.1 Hz).

(1-OMe): A solution of 0.9 g (1.9 mmol) of **13**, 0.1 g palladium(tetrakis)triphenylphosphine in 5 ml DMF was prepared and stirred for 20 minutes. To this, 1.8 g (4.3 mmol) of **19** was added and heated at 110°C overnight. The reaction mixture was allowed to cool to room temperature and filtrated to remove any solids. To the filtrate an excess of water was added and this was then extracted with di-ethyl ether. The obtained organic phase was washed with brine and then dried over Na₂SO₄. After filtration and removal of solvent in vacuum the crude was purified by column chromatography (silica gel, eluent pentane/EtOAc (gradient 0-100% EtOAc)) and gave the pure title compound as a yellow oil in a 38% yield (0.66 g, 0.72 mmol). ¹H NMR (400 MHz, CDCl₃) δ_H: 0.873 (t, J₃= 6,7 Hz, 3H), 1.30-1.180 (m, 28 H), 2.48 (t, J₃= 7.7 Hz, 2H), 3.36 (s, 6H), 3.70-3.60 (m, 32H), 4.47 (s, 2H), 4.63 (s, 2H), 7.03 (s, 1H), 7.13 (d, J₃= 5.2 Hz, 1H) 7.18 (d, J₃= 3.7, 1H), 7.19 (d, J₃= 3.7 Hz, 1H), 7.34 (d, J₃= 5.3 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ_C: 14.15 (CH₃), 22.62 (2*CH₂), 28.99 (CH₂), 29.43 (CH₂), 29.49 (2*CH₂), 29.69(7*CH₂), 30.69 (CH₂), 31.89 (CH₂), 58.98 (2*CH₃), 66.28 (2*CH₂), 69.35 (2*CH₂), 70.50 (2*CH₂), 70.55 (2*CH₂), 70.59 (8*CH₂), 71.89 (2*CH₂), 123.91 (CH), 126.05 (CH), 128.02 (CH), 128.17 (C), 128.59 (CH), 130.51 (CH), 131.11 (C), 135.12 (C), 135.21 (C), 138.25 (2*C), 143.26 (C). (ESI-MS) M/z-calc: 912.5; M/z-found: 935.5 (M+Na⁺).

(2-OMe-TMS): A solution of 5.1 g (7.4 mmol) of **25**, 0.32 g palladium(tetrakis)triphenylphosphine in 80 ml DMF/toluene (50/50) was prepared under a nitrogen atmosphere and stirred for 20 minutes. To this, 12.2 g (17.8 mmol) of **21** in 20 ml DMF/toluene (50/50) was added and heated at 110°C overnight. The solvents were removed under vacuum and the crude was purified by column chromatography (silica gel, eluent heptane/EtOAc gradient 0-100% EtOAc). This gave the pure title compound in 80% yield (5.9 g, 5.9 mmol). ¹H-NMR (400 MHz, CDCl₃) δ_H: 0.37 (s, 9H), 0.88 (t, 3H, J₃=7.4 Hz), 1.20-1.44 (m, 26H), 1.60-1.70 (m, 2H), 2.74 (t, 2H, J₃=7.8 Hz), 3.37 (s, 6H), 3.54-3.63 (m, 4H), 3.66-3.76 (m, 28H), 4.56 (s, 2H), 4.62 (s, 2H), 6.99 (s, 1H), 7.12 (d, 1H, J₃=5.2 Hz), 7.18 (d, 1H, J₃=5.6 Hz), 7.21 (s, 1H).

(2-OMe): 2-OMe-TMS (2.4 g, 2.3 mmol) was stirred overnight in a TBAF solution in THF. After removal of the solvent the yellow oil was dissolved in water and 100 g of a cationic ion-exchange resin (DOWEX MAC-3) was added and the suspension was stirred until the water became colourless and the resin yellow. This was then filtrated and washed several times with water to remove the TBAF. After extensive rinsing, the product was released from the resin by washing with methanol to obtain the pure title compound in quantitative yield as a yellow oil (2.6 g, 2.3 mmol). ¹H-NMR (400 MHz, CDCl₃) δ_H: 0.87 (t, 3H, J₃= 7.4Hz), 1.15-1.40 (m, 26H), 1.60-1.68 (m, 2H), 2.73 (t, 2H, J₃= 7.8 Hz), 3.37 (s, 6H), 3.54-3.63 (m, 4H), 3.66-3.76 (m, 28H), 4.55 (s, 2H), 4.64 (s, 2H), 6.99 (s, 1H), 7.08 (d, 1H, J₄=1.3 Hz), 7.12 (d, 1H, J₃= 5.2Hz), 7.19 (d, 1H, J₃=5.6Hz), 7.20 (d, 1H, J₄= 1.3Hz); ¹³C-NMR (100 MHz, CDCl₃) δ_C: 13.99 (CH₃), 22.50 (CH₂), 29.10 (CH₂), 29.17 (CH₂), 30.45 (CH₂), 31.53 (CH₂), 61.56 (CH₂), 66.77 (CH₂), 68.42 (CH₂), 69.30 (CH₂), 69.33 (CH₂), 70.18 (CH₂), 70.44 (CH₂), 70.47 (CH₂), 70.50 (CH₂), 72.45 (CH₂), 122.84 (CH), 123.85 (CH), 126.04 (CH), 129.20 (CH), 130.03 (CH), 132.98 (C), 134.99 (C), 136.13 (C), 139.64 (C), 140.06 (C). (ESI-MS) M/z-calc: 912.5; M/z-found: 935.5 (M+Na⁺).

(3-OMe). A solution of 1.1 g (2.5 mmol) of **13** and palladium(tetrakis)triphenylphosphine in 5ml DMF was prepared and stirred for 20 minutes. To this, 2.6 g (5.0 mmol) of **21** was added and heated at 110°C overnight. The solvent was removed under vacuum and redissolved in 10% HCl methanol solution and stirred for 4h. After removal of all volatile compounds under vacuum, crude was purified by column chromatography (silica gel, eluent PET 40-60/EtOAc in a gradient 0-100% EtOAc) and gave the pure title compound as a yellow oil in a 40% yield (900 mg, 1.0 mmol). ¹H NMR (400 MHz, CDCl₃) δ_H: 0.88 (t, J₃= 6.7 Hz, 3H), 1.22-1.38 (m, 26H), 1.58-1.68 (m, 2H), 2.70 (t, J₃= 8.0 Hz, 2H), 3.37 (s, 6H), 3.51-3.56 (m, 4H), 3.62-3.70 (m, 28H), 4.52 (s, 2H), 4.55 (s, 2H), 6.98 (s, 1H), 7.07 (s, 1H), 7.09 (s, 1H), 7.11 (s, 1H), 7.18 (s, 1H). ¹³C NMR

(100 MHz, CDCl₃) δ_C : 14.09 (CH₃), 22.65 (CH₂), 29.29(CH₂), 29.32 (CH₂), 29.44 (CH₂), 29.53 (CH₂), 29.57 (CH₂), 29.66 (CH₂), 30.52 (CH₂), 31.88 (CH₂), 68.48 (CH₂), 68.53 (CH₂), 69.40 (CH₂), 70.47 (CH₂), 70.57 (CH₂), 70.61 (CH₂), 71.89 (CH₂), 121.70 (CH), 122.74 (CH), 123.72 (CH), 125.98 (CH), 126.45 (CH), 129.59 (C), 135.01 (C), 136.37 (C), 137.67 (C), 139.75 (C), 140.22 (C), 140.27 (C). (ESI-MS) M/z-calc: 912.5; M/z-found: 930.7 (M+NH₄⁺).

(4): A solution of 0.6 g (1.3 mmol) of **18**, 0.1 g (0.1 mmol) palladium(tetrakis)triphenylphosphine in 5 ml DMF was prepared and stirred for 20 minutes. To this, 1.2 g (2.6 mmol) of **12** was added and heated at 110°C overnight. The reaction mixture was allowed to cool to room temperature and filtrated to remove any solids. To the residue an excess of water was added and this was then extracted with di-ethyl ether. The obtained organic phase was washed with brine and then dried over Na₂SO₄. After filtration and removal of solvent in vacuum the crude was purified by column chromatography (silica gel, eluent PET 40-60/EtOAc in a gradient 0-100% EtOAc) and gave the pure title compound as a yellow oil in a 40% yield (0.85 g, 0.9 mmol). ¹H NMR (400 MHz, CDCl₃) δ_H : 0.82-0.94 (m, 6H), 1.16-1.40 (m, 52H), 1.50-1.70 (m, 4H), 2.55 (t, J₃= 7.8 Hz, 2H), 2.77 (t, J₃= 7.75 Hz, 2H), 3.37 (s, 3H), 3.5-3.6 (m, 2H), 3.6-3.74 (m, 14H), 4.42 (s, 2H), 6.92 (d, J₃= 5.20 Hz, 1H), 6.97 (d, J₃= 5.2 Hz, 1H), 7.16 (d, J₃= 5.2 Hz, 1H), 7.17 (s, 1H), 7.31 (d, J₃= 5.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ_C : 14.11 (2*CH₃), 22.52 (2*CH₂), 29.33(CH₂), 29.35 (CH₂), 29.50 (CH₂), 29.49 (CH₂), 29.69(11*CH₂), 29.71 (10*CH₂), 30.71 (CH₂), 30.83 (CH₂), 31.92 (CH₂), 59.03 (CH₃), 66.75 (CH₂), 69.40 (CH₂), 70.50 (CH₂), 70.55 (CH₂), 70.61 (4*CH₂), 71.62 (CH₂), 123.70 (CH), 125.81 (CH), 126.99 (CH), 128.85 (CH), 130.01 (CH), 131.12 (C), 132.15 (C), 133.52 (C), 134.41 (C), 138.02 (C), 139.72 (C), 144.01 (C). (ESI-MS) M/z-calc: 916.6; M/z-found: 939.6 (M+Na⁺).

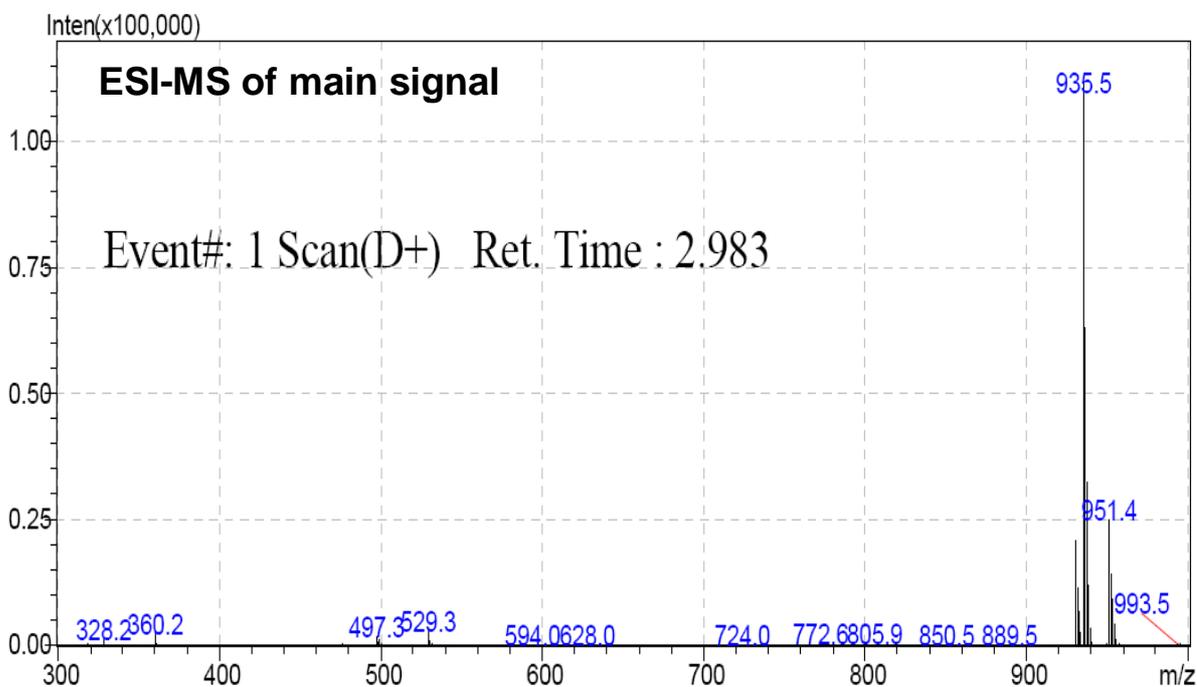
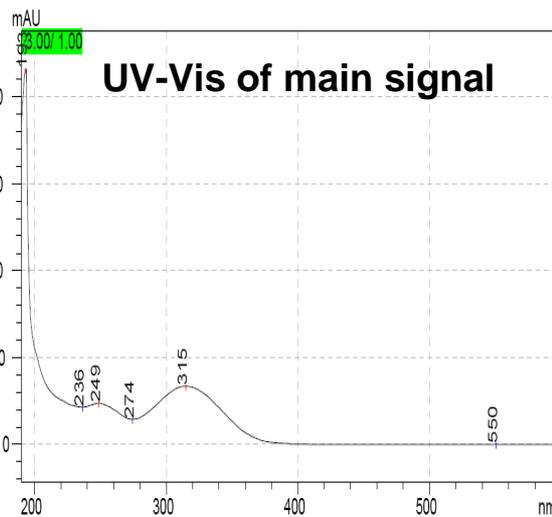
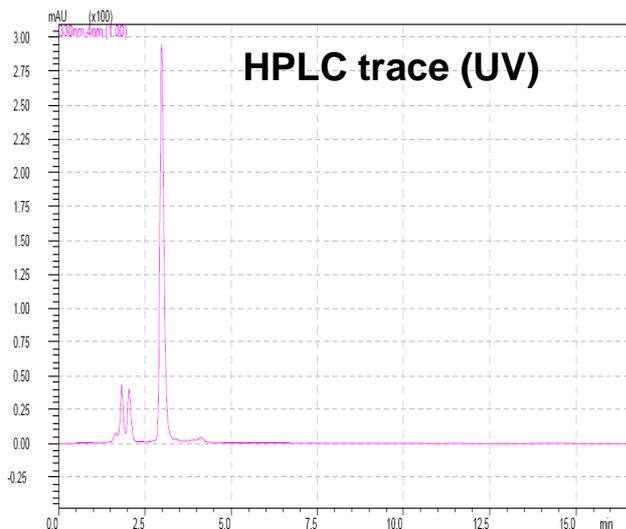
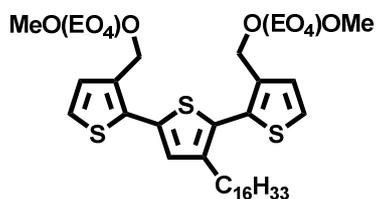
(5-TMS) 2-Bromo-3-hexadecylthiophene (**11**) (3.85 g, 9.9 mmol) was dissolved in 20 ml of toluene. Then palladium(tetrakis)triphenylphosphine (2.20 g, 1.9 mmol) was added to the solution. The mixture was stirred for 20 min at room temperature. Then **23** (7.0 g, 8.3 mmol) solution in 20 ml of toluene was added. The temperature was raised to 110°C and left overnight. Then the solvents were removed under vacuum. The crude was purified by column chromatography (silica gel, eluent petroleum ether 40-60/EtOAc (gradient0-100% EtOAc)) with 5% TEA and gave the pure title compound as a yellow oil in a 50% yield (4.0 g, 5.0 mmol). ¹H NMR (400 MHz, CDCl₃) δ_H : 0.36 (s, 9H), 0.88 (t, J₃= 6.7 Hz, 6H), 1.34-1.22 (m, 52H), 1.69-1.62 (m, 4H), 2.64 (t, J₃= 7.8 Hz, 2H), 2.77 (t, J₃= 7.8 Hz, 2H), 3.36 (s, 3H), 3.54-3.52 (m, 2H), 3.68-3.61 (m, 14H), 4.63 (s, 2H), 6.92 (d, J₃= 5.2 Hz, 1H), 7.10 (s, 1H), 7.12 (s, 1H), 7.15 (d, J₃= 5.2Hz, 1H).

(5): To 20 ml of 10% HCl solution in methanol **5-TMS** (300 mg, 0.3 mmol) was added. The mixture was allowed to react overnight at room temperature. Then solvent and HCl were removed under vacuum. The crude was purified by column chromatography (silica gel, petroleum ether 40-60/EtOAc (gradient0-100% EtOAc)) and gave the pure title compound in an 85% yield (250 mg, 0.26 mmol). ¹H NMR (400 MHz, CDCl₃) δ_H : 0.88 (t, J₃= 6.7 Hz, 6H), 1.34-1.22 (m, 52H), 1.69-1.62 (m, 4H), 2.60 (t, J₃= 7.6 Hz, 2H), 2.77 (t, J₃= 7.6 Hz, 2H), 3.37 (s, 3H), 3.54-3.52 (m, 2H), 3.69-3.61 (m, 14H), 4.61 (s, 2H), 6.92 (s, 1H), 6.92 (d, J₃= 5.2 Hz, 1H), 7.02 (d, J₄= 1.0 Hz, 1H), 7.12 (s, 1H), 7.16 (d, J₃= 5.2 Hz, 1H). ¹³C NMR (100MHz, CDCl₃) δ_C : 14.21 (2*CH₃), 22.75 (2*CH₂), 29.13(CH₂), 29.17 (CH₂), 29.45 (CH₂), 29.47 (CH₂), 29.68(11*CH₂), 29.70 (10*CH₂), 30.49 (CH₂), 30.71 (CH₂), 31.98 (CH₂), 59.00 (CH₃), 66.80 (CH₂), 69.40 (CH₂), 70.50 (CH₂), 70.55 (CH₂), 70.61 (4*CH₂), 71.91 (CH₂), 120.71 (CH), 127.81 (CH), 127.91 (CH), 128.51 (CH), 130.01 (CH), 134.09 (2*C), 134.49 (C), 134.99 (2*C), 139.71 (C), 143.95 (C). (ESI-MS) M/z-calc: 916.6; M/z-found: 939.5 (M+Na⁺).

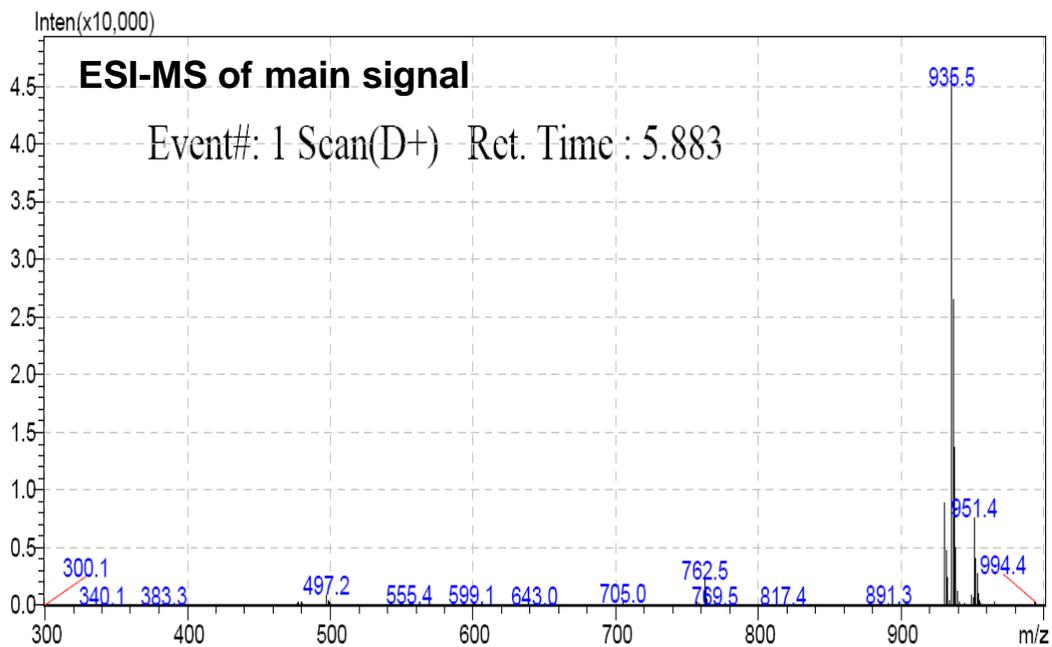
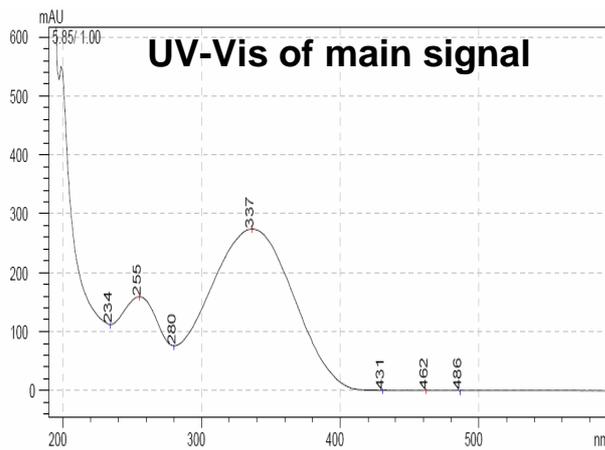
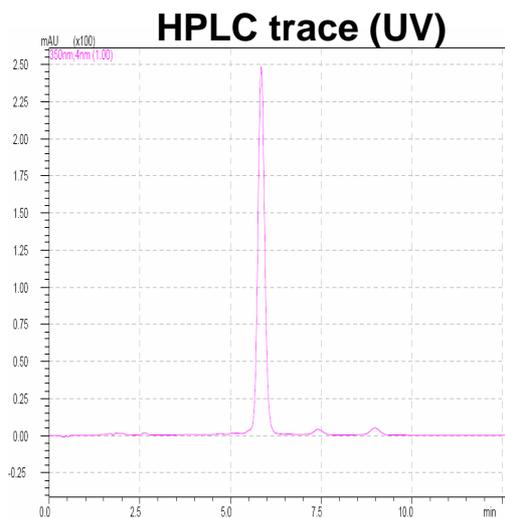
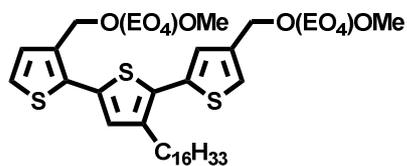
(6): A solution of **18** (432 mg, 0.93 mmol), palladium(tetrakis)triphenylphosphine (50 mg, 0.04 mmol) and CuO (77 mg, 0.97 mmol) in 5 ml of dry DMF was prepared. To this **14** (964 mg, 1.90 mmol) was added. The mixture was stirred overnight at 110°C. After this, the reaction was cooled to room temperature. Formed solids were filtered off and water was added to the reaction mixture. The mixture was extracted with diethylether. The combined organic layers were then washed with brine. The organic layer was dried over MgSO₄ and filtered; the solvent was removed under vacuum. The crude was subsequently purified by column chromatography (silica gel, petroleum ether 40-60/EtOAc (gradient 0-100% EtOAc)) and gave the pure title compound in a 45% yield (368 mg, 0.42 mmol). ¹H NMR (400 MHz, CDCl₃) δ_H : 0.88 (t, J₃ = 6.7 Hz, 6H), 1.22-1.38 (m,

52H), 1.58-1.68 (m, 4H), 2.64-2.54 (m, 4H), 3.36 (s, 3H), 3.55-3.51 (m, 2H), 3.72-3.61 (m, 14H), 4.59 (s, 2H), 6.79 (s, 1H), 6.9 (s, 1H), 6.99 (s, 1H), 7.00 (s, 1H), 7.15 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ_{C} : 14.11 (2* CH_3), 22.52 (2* CH_2), 29.23(CH_2), 29.25 (CH_2), 29.50 (CH_2), 29.51 (CH_2), 29.69(11* CH_2), 29.71 (10* CH_2), 30.49 (CH_2), 30.71 (CH_2), 31.92 (CH_2), 66.89 (CH_2), 69.41 (CH_2), 70.50 (CH_2), 70.55 (CH_2), 70.61 (4* CH_2), 71.91 (CH_2), 120.71 (CH), 123.71 (CH), 127.81 (CH), 128.51 (CH), 130.01 (CH), 134.29 (2*C), 134.49 (2*C), 134.59 (C), 139.71 (C), 143.95 (C). (ESI-MS) M/z -calc: 916.6; M/z -found: 939.5 ($\text{M}+\text{Na}^+$).

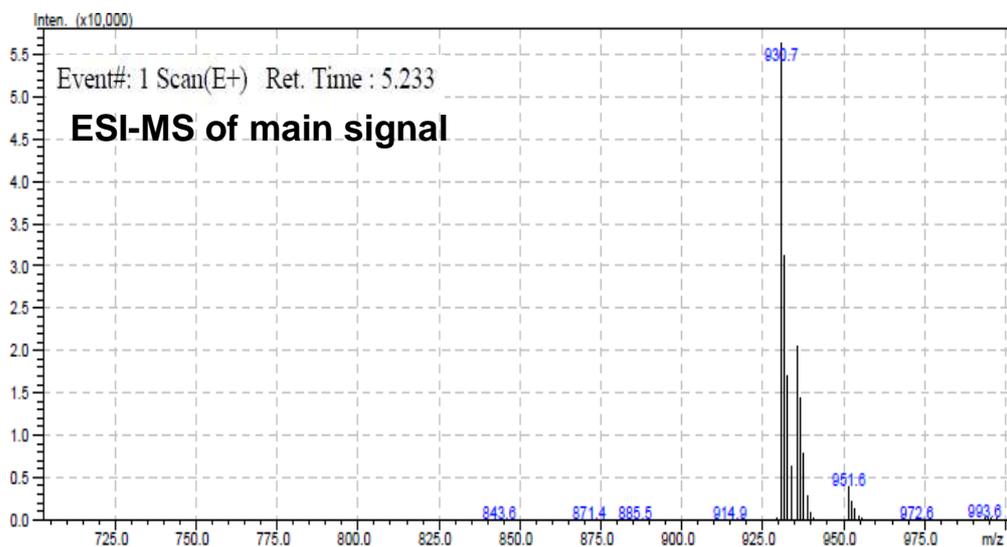
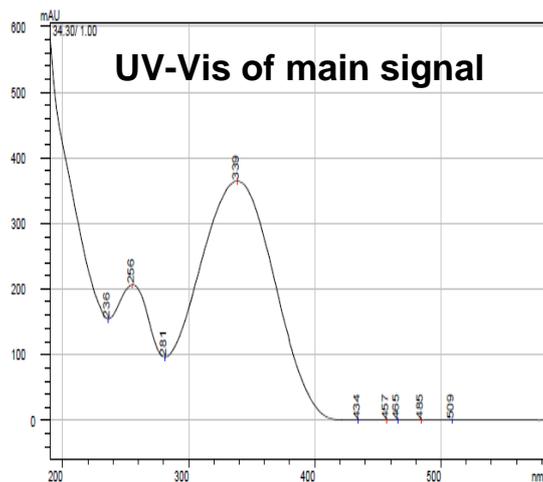
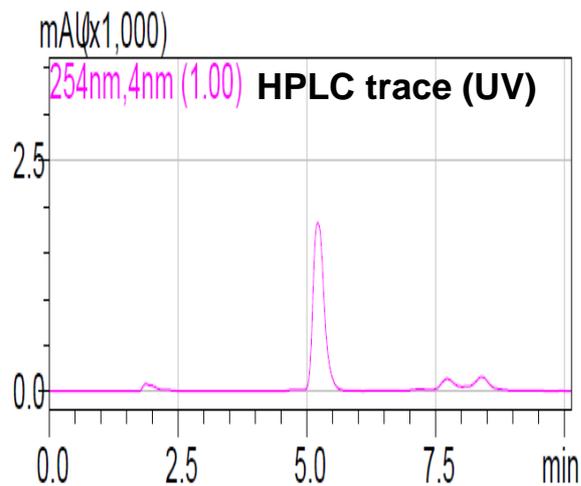
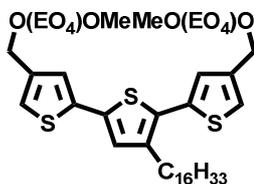
ESI-1^a: Isomer 1-OMe



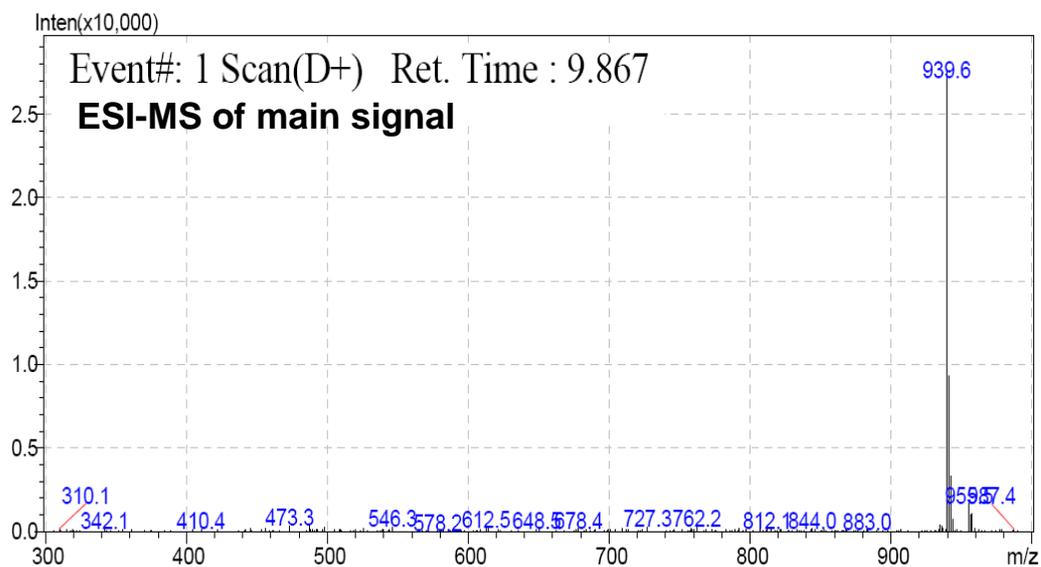
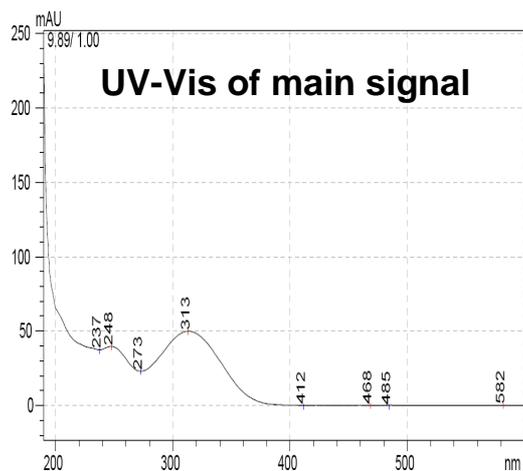
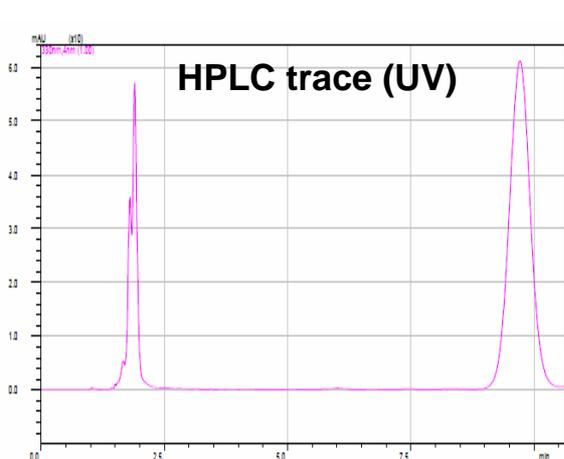
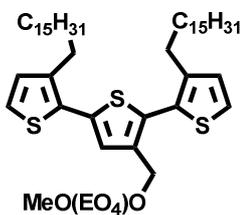
ESI-1^b: Isomer 2-OMe



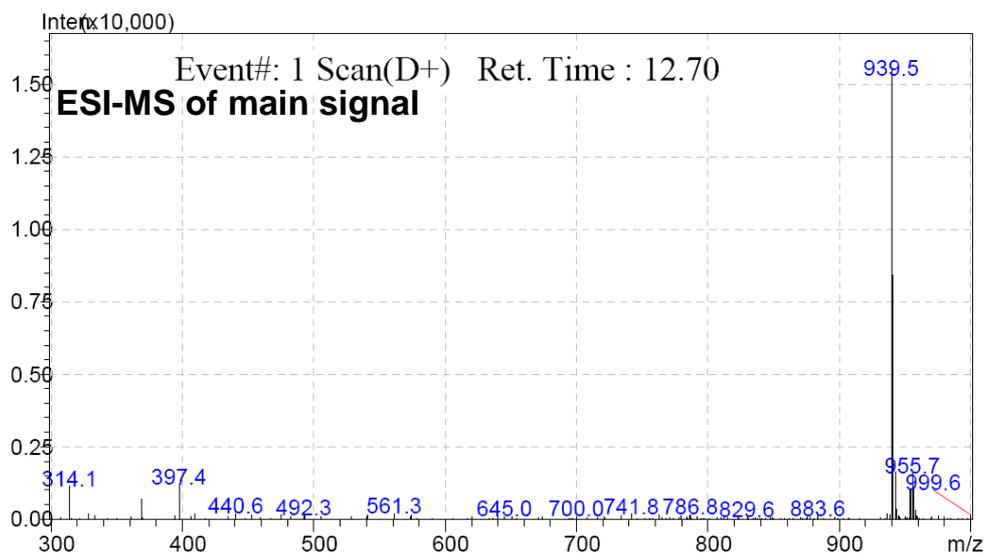
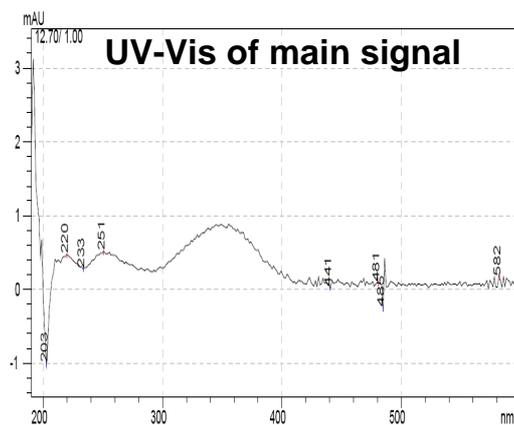
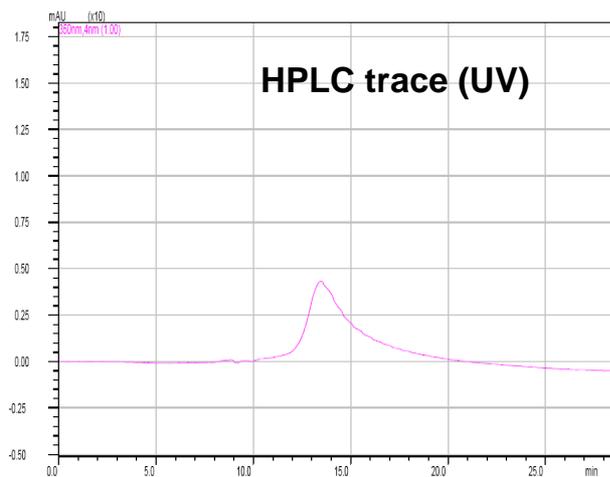
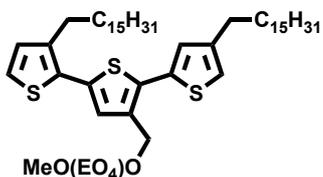
ESI-1^c: Isomer 3-OMe



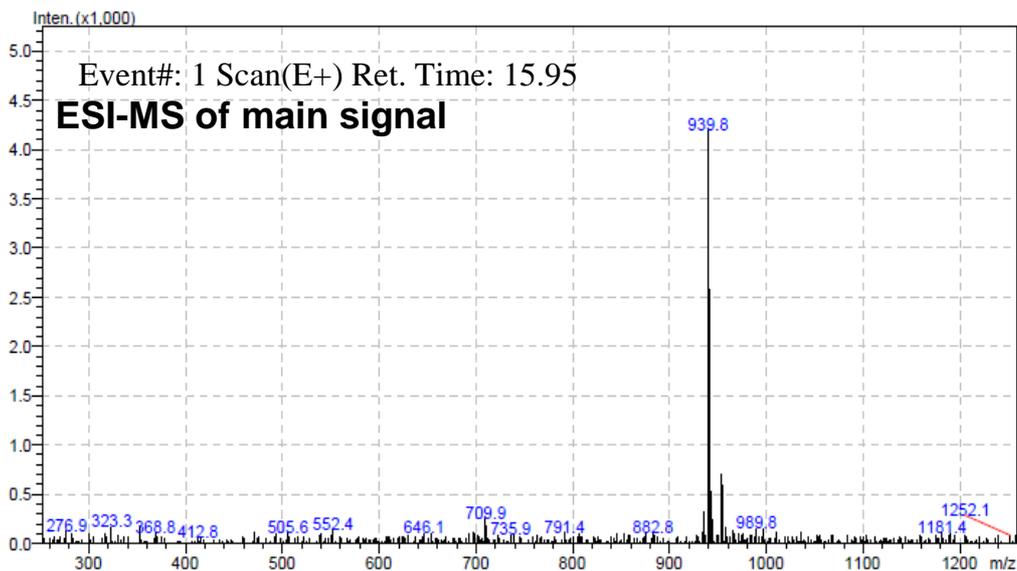
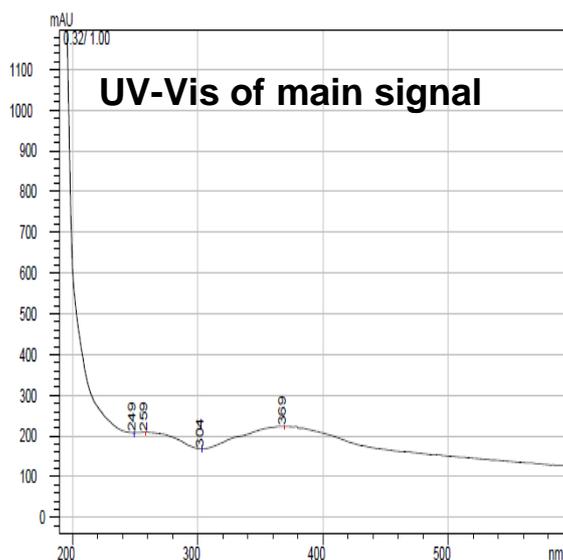
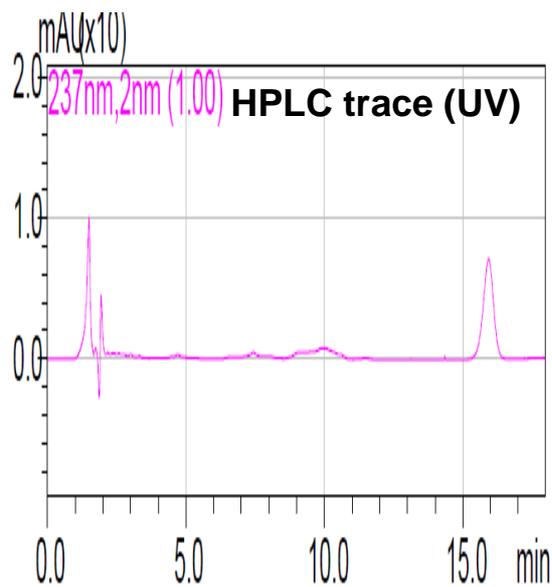
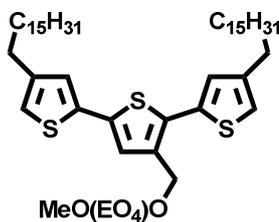
ESI-1^d: Isomer 4



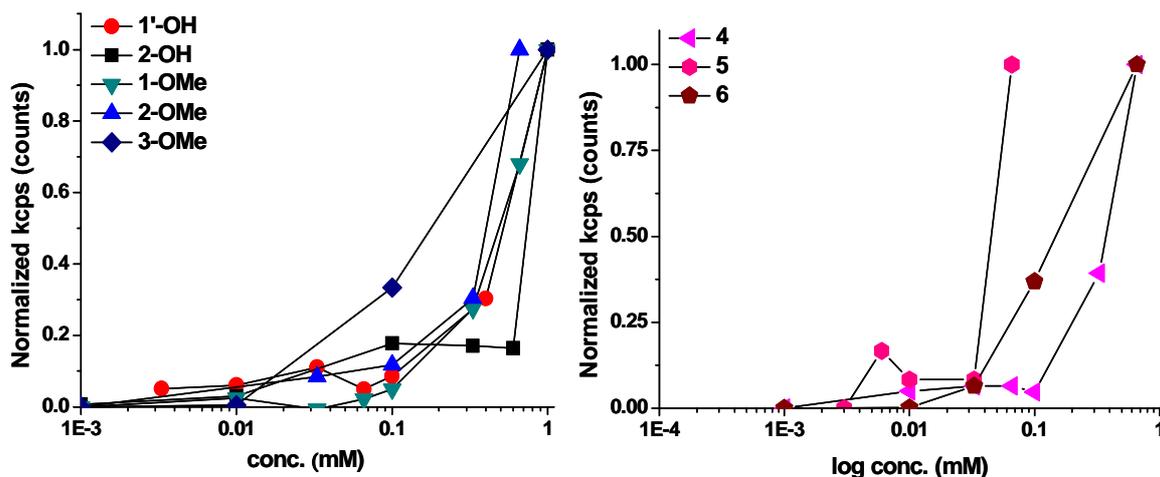
ESI-1^e: Isomer 5



ESI-1^f: Isomer 6

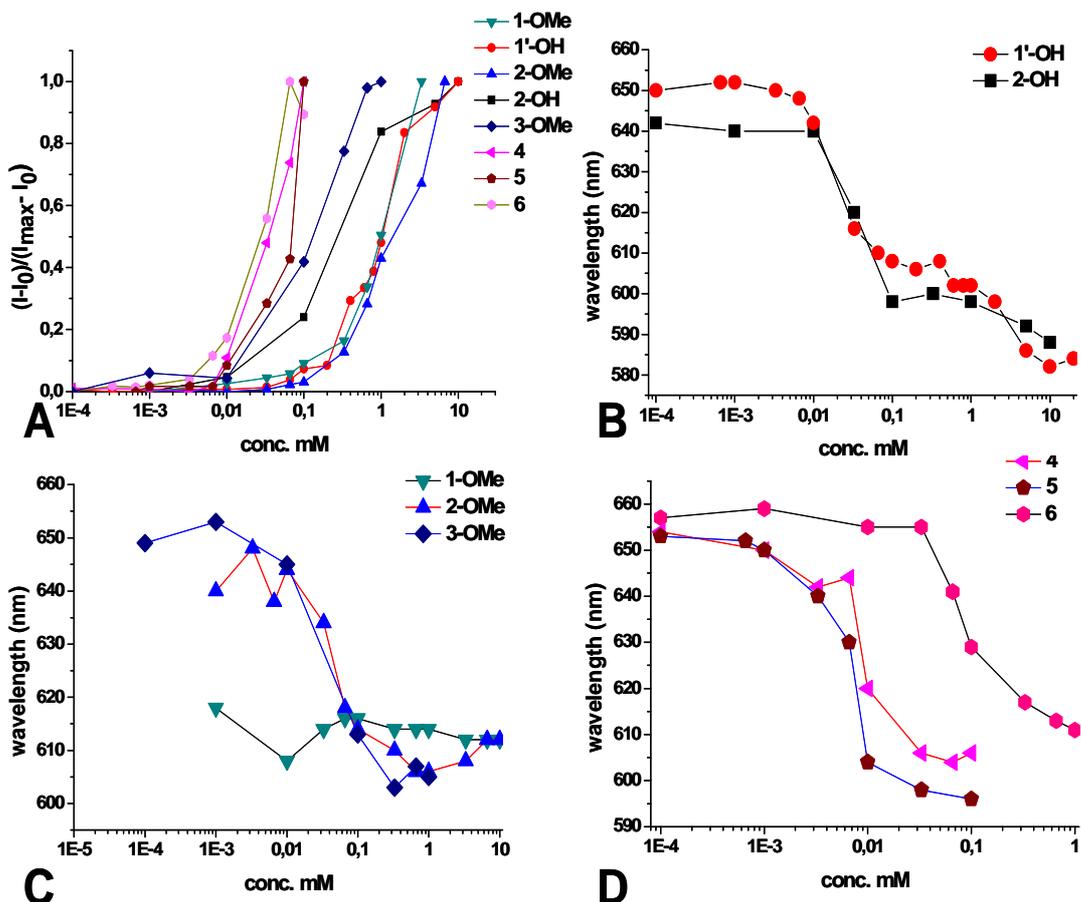


ESI 2



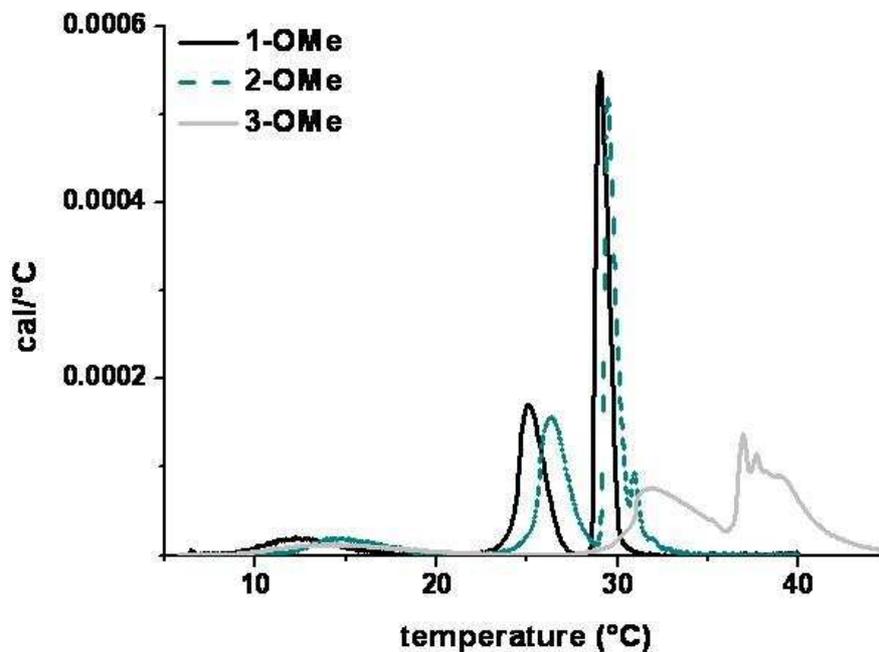
Concentration dependent scattering measurements of the different terthiophene amphiphiles in water at 20°C.

ESI 3



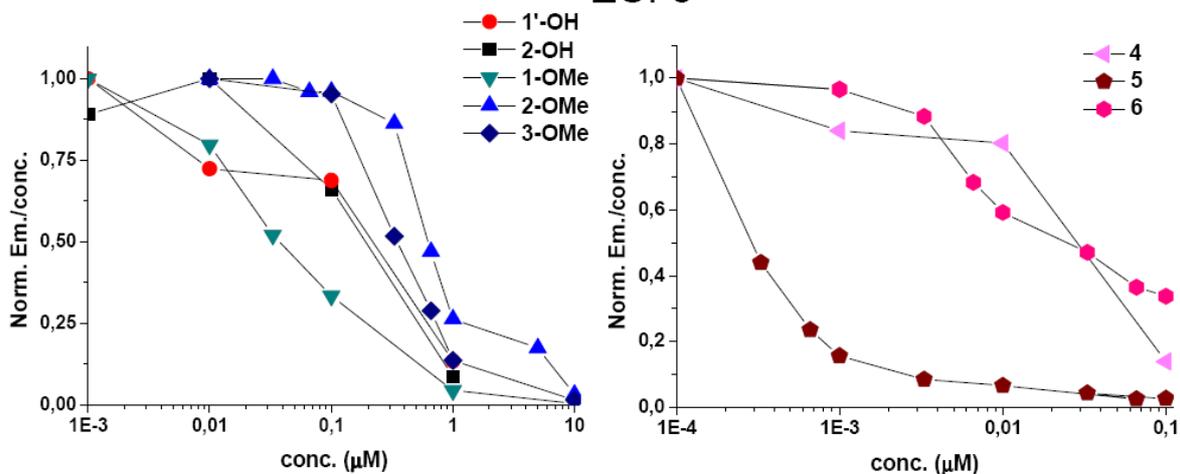
A) Emission intensity of Nile Red in combination with different concentrations of thiophene amphiphiles to determine the cmc of isomers **1-6** at 20°C and **B-D**) the shift in emission wavelength, displaying also a transition at lower concentrations which are attributed to premicellar aggregates.

ESI 4



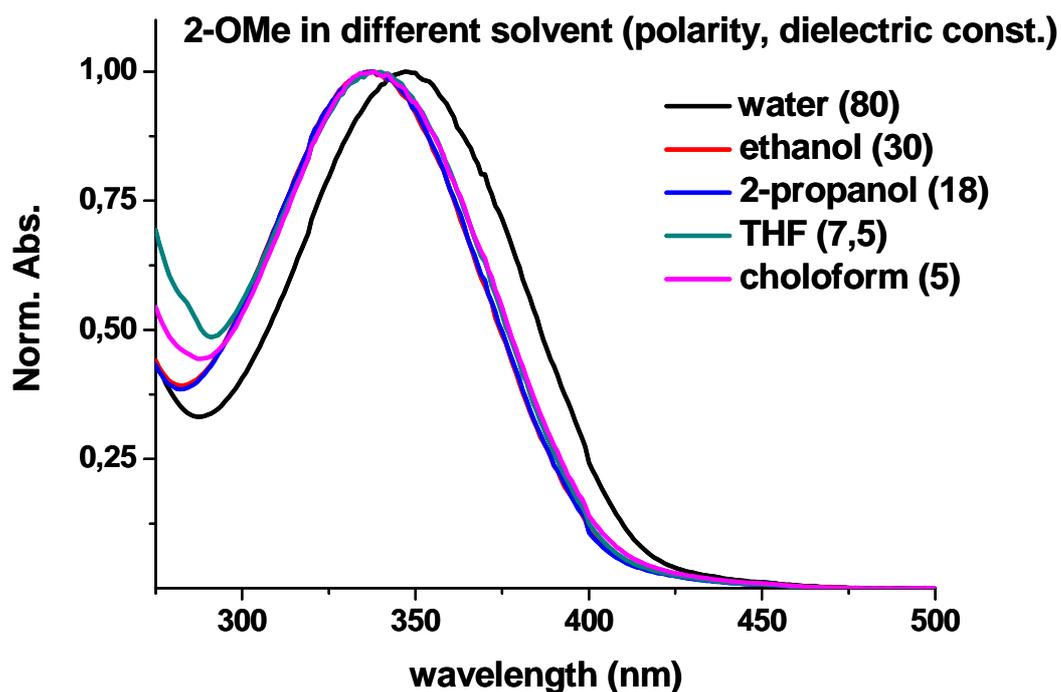
DSC of the different thiophene surfactants that display a temperature effect. Concentrations used were 1.0 mM for compounds 1-OMe and 2-OMe, for 3-OMe 10 mM was used and corrected for this to 1.0mM.

ESI 5



Normalized plot for the self-quenching of the concentration corrected emission with increasing concentration. The declining concentration corrected emission with increasing concentration depicts aggregation due to the electronic coupling between chromophores.

ESI 6



Normalized absorption-spectra of **2-OMe** in different solvents with different polarity in order to illustrate that the absorption maxima did not change with solvent polarity upon going from moderately polar (ethanol) to an apolar solvent (chloroform). Therefore, the different absorption maxima of the oligothiophenes in chloroform and water are most likely due to aggregation in the later.