Fluorene functionalised sexithiophenes – utilising intramolecular charge transfer to extend the photocurrent spectrum in organic solar cells

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Experimental

General

Melting points were taken using a Stuart Scientific SMP1 Melting Point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity Innova instrument at 300 and 75 MHz in $CDCl_3$; chemical shifts are given in ppm; all *J* values are in Hz. Mass spectra (EI) and high resolution mass spectra were recorded on Micromass Trio 2000 and Kratos Concept spectrometers, respectively. Elemental analyses were obtained on a Carlo Erba Instruments EA1108 elemental analyser. Electron absorption spectra were measured on a Unicam UV 300 spectrophotometer.

Cyclic Voltammetry

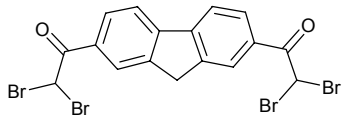
Electrochemistry experiments were carried out with a BAS-CV50W electrochemical workstation with positive feedback compensation. Cyclic voltammetry was performed in a three-electrode cell equipped with a platinum disk (∅ 1.6 or 1.0 mm) as working electrode, platinum wire as a counter electrode and a non-aqueous Ag/Ag^{+} reference electrode (0.01 M $AgNO_3$ in dry MeCN). CV measurements were performed under argon atmosphere in dry benzonitrile as a solvent and 0.1 M tetrabutylammonium hexafluorophospate (Bu_4NPF_6) as supporting electrolyte. The potential of the reference electrode was checked against the ferrocene/ferrocenium couple (Fc/Fc^{+}) before and after the experiments, which showed the average potentials against the reference electrode of +0.187 V

Spectroelectrochemistry

Spectroelectrochemical measurements in dry benzonitrile under argon were performed in a 1 mm quartz cell using a Pt grid as the working electrode, Pt wire as the counter electrode and Ag wire as the reference electrode, with 0.1 M Bu_4NF_6 supporting electrolyte. BAS-CV50W electrochemical workstation was used as a potentiostat in SEC experiments. After applying the potential (in 10–50

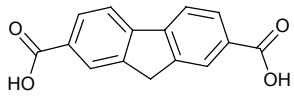
mV steps), the system kept until equilibrium for 2-4 min and electron absorption spectra have been recorded. UV-Vis-NIR absorption spectra were recorded on a Genesys 10 spectrophotometer (300–100 nm) (Fig. 2) or Perkin Elmer Lambda 900 spectrophotometer (300–1600 nm)

2,7-Bis(dibromoacetyl)fluorene 5



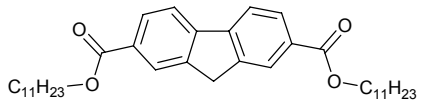
2,7-Diacetylfluorene[1] **4** (10.55 g, 42.2 mmol) was dissolved in acetic acid (400 ml) at 85 °C, and to this solution 9.5 ml of bromine (186 mmol) was added on vigorous stirring in one portion. The mixture was stirred at 95–100 °C for 3 min, cooled to ca. 50 °C and diluted with an equal volume of water, yielding 23.1 g (97%) of essentially pure product, m.p. 198–201 °C, (Found: C, 35.97, H, 1.55, Br, 56.0; $C_{17}H_{10}Br_4O_2$ requires C, 36.08, H, 1.78, Br, 56.48 %); ^{1}H NMR: δ_H 8.38 (2H, s), 8.24 (2H, d, *J* 7.9), 8.02 (2H, d, *J* 7.9), 6.81 (2H, s) and 4.16 (2H, s); ^{13}C NMR: δ_C 185.66, 145.75,144.82, 130.40, 129.20, 126.56, 121.25, 39.67 and 36.97; MS (APCI): *m/z* 564 (M^-) $C_{17}H_{10}Br_4O_2$ requires 564.

Fluorene-2,7-dicarboxylic acid 6



In a 3-neck flask, equipped with mechanical stirrer, bis(dibromoacetyl)fluorene **5** (23.1 g, 41.0 mmol) was dissolved in 420 ml of 1,4-dioxane at 70 °C and to this solution on vigorous stirring was added warm (50 °C) solution of 40.0 g (378 mmol) sodium carbonate in 200 ml of water immediately followed by 6.3 ml (122 mmol) of bromine. In 30 sec, 300 ml of water (50 °C) was added, followed in 1 min intervals by portions of 300, 300 and 600 ml of warm water. The mixture was boiled to remove bromoform and then refluxed for 3 h to allow coagulation of product that was isolated by filtration (10.4 g, 100 %) and used in subsequent steps without further purification.

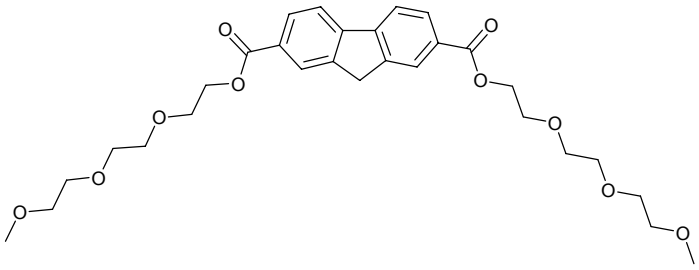
Fluorene-2,7-dicarboxylic acid diundecyl ester 7a



Fluorene-2,7-dicarboxylic acid **6** (2.0 g, 7.87 mmol) was refluxed in a mixture of thionyl chloride (10 ml) and 3 drops of DMF for 1 h, 15 ml of dry toluene was added and the volume of the mixture was reduced to ca 15 ml at ambient pressure. After cooling to 50 °C, 10 ml of petrol ether was added and the resulting dichloroanhydride was filtered off. This product was placed back in the reaction flask, dried *in vacuo* under dry nitrogen, 4.9 ml 23 mmol) of undecanol-1 was added and the mixture was stirred *in vacuo* (20-30 mm Hg) for 15 min at 120-130 °C. The excess of undecanol was then removed at 0.1 mm Hg, and the residue taken up in 20 ml of dichloromethane (DCM). The solution was filtered through a layer of silica (∅35×30 mm) which was subsequently washed with 50 ml of DCM, the volume reduced to ca. 10ml, 30 ml of acetone added and the remaining DCM was evaporated at ambient pressure. After cooling in a fridge, the product was filtered off and reprecipitated with acetone from DCM in the same way, yielding 3.0 g (68%) of slightly contaminated product that was used in subsequent steps without further purification. Alternatively, pure product (60%) could be obtained by column chromatography (silica, DCM:petrol ether=1:1) of the residue after removal the excess of undecanol. M.p. 69–72 °C (Found: C, 78.90, H, 9.92; $C_{37}H_{54}O_4$ requires C, 78.96, H, 9.67 %); ^{1}H NMR: δ_H 8.16 (2H, s), 8.03 (2H, d, *J* 7.9), 7.78 (2H, d, *J* 7.9), 4.26 (4H, t, *J* 6.6), 3.91 (2H, s), 1.72 (4H, m), 1.1–1.4 (32 H, m),

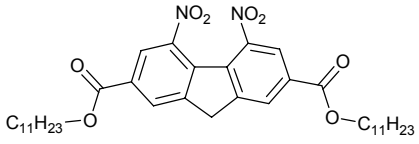
and 0.80 (6H, t, *J* 6.5); ^{13}C NMR: δ_C 166.60, 144.77,143.99, 129.62, 128.67, 126.22, 120.27, 36.68, 31.85, 29.55, 29.49, 29.29, 29.26, 28.70, 26.01, 22.62, and 14.05[i]; HRMS (CI): *m/z* 563.4099 ($[M+H]^+$), $C_{37}H_{55}O_4$ requires 563.4100.

Fluorene-2,7-dicarboxylic acid di(triethylene glycol monomethyl ether) ester 7b



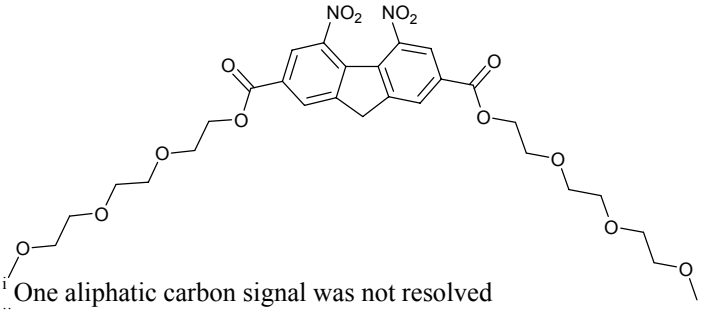
Crude product, obtained as described above from 1.57 g (6.18 mmol) of fluorene-2,7-dicarboxylic acid **6**, was purified by column chromatography (silica, ethyl acetate) to give 1.95 g (58 %) of pure product, m.p. 49–50 ^{o}C (from diethyl ether), (Found: C, 63.85, H, 6.90; $C_{29}H_{38}O_{10}$ requires C, 63.72, H, 7.01 %); ^{1}H NMR: δ_H 8.31 (2H, s), 8.14 (2H, d, *J* 7.9), 7.92 (2H, d, *J* 7.9), 4.56 (4H, t, *J* 4.8), 4.05 (2H, s), 3.91 (4H, m3.78 (4H, m), 3.72 (8H, m), 3.58 (4H, m), and 3.41 (6H, s); ^{13}C NMR: δ_C 166.51, 144.92, 144.04, 129.24, 128.86, 126.42, 120.36, 71.57, 70.61, 70.57, 70.52, 69.19, 64.13, 58.94, and 36.68; HRMS (CI): *m/z* 547.2541 ($[M+H]^+$), $C_{27}H_{39}O_{10}$ requires 547.2543.

4,5-Dinitrofluorene-2,7-dicarboxylic acid diundecyl ester 8a



1.50 g (2.67 mmol) of powdered fluorene-2,7-dicarboxylic acid diundecyl ester **7a** was quickly dissolved in 25 ml of conc. sulphuric acid, and this solution was added on vigorous stirring over 20-30 sec at room temperature to a mixture of concentrated sulphuric acid (25 ml) and fuming nitric acid (5 ml). In 30 sec the reaction mixture was poured in a mixture of ice and 50 ml of DCM, the aqueous phase extracted with 50 ml of DCM, combined organic phases washed with water, brine, dried over magnesium sulphate, evaporated to dryness, and the residue was recrystallised three times from ethyl acetate-dioxane mixture (30 ml per gram of compound) three times to give 780 mg (45%) of product, m.p. 178–181 ^{o}C; ^{1}H NMR: δ_H 8.67 (2H, d, *J* 1.4), 8.55 (2H, d, *J* 1.4), 4.45 (4H, t, *J* 6.7), 4.32 (2H, s), 1.86 (4H, m), 1.28-1.54 (32 H, m), and 0.92 (6H, t, *J* 6.6); ^{13}C NMR: δ_C 164.109, 147.61, 146.62, 133.83, 131.72, 129.82, 124.69, 66.31, 37.69, 31.82,29.52, 29.43, 29.24, 29.19, 28.55, 25.89, 22.60, and 14.03[ii]; MS (ES–): *m/z* 651 ($[M–H]^–$),[iii] $C_{37}H_{52}N_2O_{10}$ requires 652.3.

4,5-Dinitrofluorene-2,7-dicarboxylic acid di(triethylene glycol monomethyl ether) ester 8b

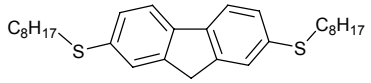


Finely powdered fluorene-2,7-dicarboxylic acid di(triethylene glycol monomethyl ether) ester **7b** (220 mg, 0.402 mmol) was quickly dissolved in ice-cold concentrated sulphuric acid, and to this solution on vigorous stirring was added chilled mixture

[i] One aliphatic carbon signal was not resolved
[ii] One aliphatic carbon signal was not resolved
[iii] Losing a proton in employed conditions was found to be a common feature of studied nitrated fluorene derivatives, due to their known high CH-acidity.

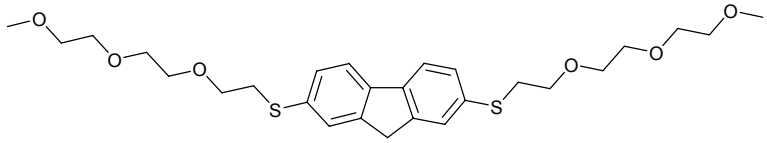
of 5 ml H_2SO_4 and 5 ml of fuming nitric acid. The reaction mixture was immediately poured in a mixture of ice and 20 ml DCM, the aqueous phase extracted with DCM, the combined organic phases washed with water and brine, dried over magnesium sulphate, evaporated to dryness in vacuo, and the residue was twice reprecipitated from 1 ml of acetone by addition of 5 ml of diethyl ether to give 146 mg (55%) of product, m.p. 76–78 °C (Found: C, 55.06, H, 5.50, N, 4.40; $C_{29}H_{36}N_2O_{14}$ requires C, 54.71, H, 5.70, N, 4.40%); ^{1}H NMR: δ_H 8.59 (2H, d, *J* 1.1), 8.47 (2H, d, *J* 1.1), 4.51 (4H, t, *J* 4.8), 4.21 (2H, s), 3.81 (4H, m), 3.66 (4H, m), 3.62 (8H, m), 3.48 (4H, m), and 3.30 (6H, s); ^{13}C NMR: δ_C 164.03, 147.65, 146.61, 133.39, 131.36, 129.99, 124.85, 71.82, 70.60, 70.56, 70.53, 68.87, 65.07, 58.95, and 37.69; MS (ES–): *m/z* 635 ($[M–H]^-$),[iii] $C_{29}H_{36}N_2O_{14}$ requires 636.2.

2,7-di(octylthio)fluorene 10a



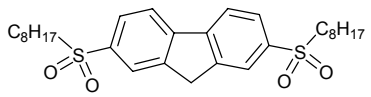
Fluorene-2,7-disulphochloride[2] **9** (1.00g, 2.75 mmol) was dissolved in warm dry THF (15 ml), and this solution was added under dry nitrogen to vigorously stirred mixture of 15 ml of dry THF and 11 ml of 1 M solution of lithium aluminium hydride in THF (11 mmol). The mixture was refluxed for 1 h, a solution of 0.5 g of sodium hydroxide in 20 ml of methanol was added carefully from a syringe followed by 1.9 ml (11 mmol) of n-octylbromide. The reaction mixture was refluxed overnight, poured in 300 ml water, and filtered. The precipitate was treated with 100 ml of diluted hydrochloric acid, filtered, dried, and subjected to column chromatography (silica, DCM) to give 0.84 g (67%) of product, m.p. 106–108 °C (Found: C, 76.56, H, 9.57, S, 14.51; $C_{29}H_{42}S_2$ requires C, 76.59, H, 9.31, S, 14.10%); ^{1}H NMR: δ_H 7.68 (2H, d, *J* 8.0), 7.54 (2H, s), 7.38 (2H, d, *J* 8.0), 3.89 (2H, s), 3.00 (4H, t, *J* 7.3), 1.70 (4H, m), 1.47 (4H, m), 1.32 (16H, br), and 0.91 (6H, t, *J* 6.9); ^{13}C NMR: δ_C 143.66, 139.31, 135.04, 127.99, 125.88, 129.86, 36.53, 34.22 31.74, 29.15, 29.12, 29.08, 28.79, 22.59, and 14.04; HRMS (CI): *m/z* 454.2723 (M^+), $C_{29}H_{42}S_2$ requires 454.27278.

2,7-di(2-[2-(2-methoxyethoxy)ethoxy]ethylsulfanyl)-9*H*-fluorene 10b



Reduction of disulphochloride **9** (1.00 g, 2.75 mmol) was carried out as described above after which a solution of 1 g of sodium iodide and 0.5 g of sodium hydroxide in 20 ml of methanol was added, followed by 2 ml (12 mmol) of 1-chloro-2-[2-(2-methoxyethoxy)ethoxy]ethane.[3] After refluxing for 20 h, the reaction mixture was poured in a mixture of water (200 ml) and DCM (100 ml), filtered, the organic layer was washed with diluted hydrochloric acid, brine, dried over magnesium sulphate, and the solvent was removed. The excess of alkyl halide was distilled off *in vacuo* (0.1 mm Hg), and the residue was subjected to column chromatography (silica, DCM with gradual change to DCM:diethyl ether=1:1) to give product (0.98 g, 68%) as a pale yellow oil, (Found: C, 61.76, H, 7.72; $C_{27}H_{38}S_2$ requires C, 62.04, H, 7.33%); ^{1}H NMR: δ_H 7.66 (2H, d, *J* 8.0), 7.57 (2H, s), 7.41 (2H, d, *J* 8.0), 3.94 (2H, s), 3.7 (16H, m), 3.58 (4H, m), 3.40 (6H, s), and 3.19 (4H, t, *J* 7.1); ^{13}C NMR: δ_C 143.78, 139.61, 134.07, 128.55, 126.38, 120.02, 71.41, 70.52, 70.49, 70.31, 69.95, 58.96, 36.50, and 33.56; HRMS (CI): *m/z* 523.2198 ($[M+H]^+$), $C_{27}H_{39}S_2$ requires 523.21878.

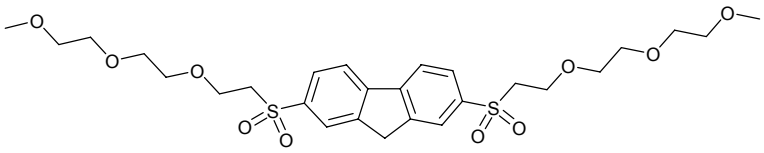
2,7-di(octylsulfonyl)fluorene 11a



2,7-di(octylthio)fluorene **10a** (835 mg, 1.84 mmol) was refluxed with a mixture of acetic acid (20 ml) and 30% aqueous hydrogen

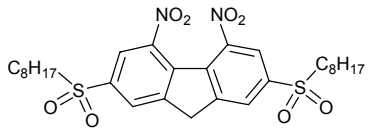
peroxide (5 ml) for 5 min, 5 ml of water was added, the mixture cooled to room temperature and filtered to give 870 mg (91 %) of product, m.p. 160–162 °C (Found: C, 67.00, H, 8.51, S, 12.87; $C_{29}H_{42}O_4S_2$ requires C, 67.14, H, 8.16, S, 12.36 %); ^{1}H NMR: δ_H 8.08 (2H, s), 7.98 (2H, d, *J* 8.1), 7.93 (d2H, dd, *J* 8.1 and 1.5), 4.05 (2H, s), 3.07 (4H, m), 1.65 (4H, m), 1.28 (4H, m), 1.16 (16H, br), and 0.78 (6H, t, *J* 7.0); ^{13}C NMR: δ_C 144.79, 144.74, 138.78, 127.46, 125.00, 121.48, 56.44, 37.00, 31.56, 28.87, 28.80, 28.19, 22.66, 22.46, and 13.94; HRMS (CI): *m/z* 519.2596 ($[M+H]^+$), $C_{29}H_{43}O_4S_2$ requires 518.25244.

2,7-di(2-[2-(2-methoxyethoxy)ethoxy]ethylsulfonyl)-9*H*-fluorene 11b



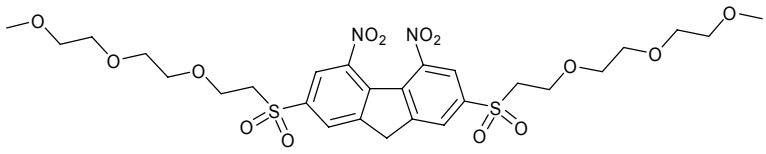
2,7-di(2-[2-(2-methoxyethoxy)-ethoxy]ethylsulfanyl)-9*H*-fluorene **10b** (935 mg, 1.79 mmol) was oxidized as above, the mixture was poured in water, neutralized with sodium bicarbonate, extracted with 3 × 30 ml of ethyl acetate, the combined extracts washed with brine, dried and the solvant was removed *in vacuo* to give 1.03 g (98 %) of product as pale yellow tar, (Found: C, 54.77, H, 6.91; $C_{27}H_{38}O_{10}S_2$ requires C, 55.27, H, 6.53%); ^{1}H NMR: δ_H 8.20 (2H, s), 8.06 (4H, d[i],), 4.14 (2H, s), 3.92 (4H, t, *J* 6.5), 3.54 (20H, m), and 3.36 (6H, s); ^{13}C NMR: δ_C 144.75, 144.70, 139.44, 127.54, 125.07, 121.34, 71.72, 70.44, 70.39, 70.20, 64.47, 58.90, 56.34, and 36.96; HRMS (CI): *m/z* 604.2249 ($[M+NH_4]^+$), $C_{27}H_{42}NO_4S_2$ requires 604.22499.

4,5-Dinitro-2,7-di(octylsulfonyl)fluorene 12a



2,7-Di(octylsulfonyl)fluorene **11a** (300 mg, 0.579 mmol) was mixed up with 2 ml of acetic acid, 6 ml of fuming nitric acid was added dropwise on stirring and the solution was stirred for 30 min at 50 °C. The reaction mixture was poured on ice, the precipitate filtered, dried and subjected to column chromatography (silica, DCM:diethyl ether = 15:1). After removal of the solvent, the product was recrystallised from ethyl acetate to give 210 mg (60%) of product, m.p. 208–210 °C (Found: C, 57.16, H, 6.53, N, 4.78, S, 10.59 %; $C_{29}H_{40}N_2O_8S_2$ requires C, 57.22, H, 6.62, N, 4.60, S, 10.53 %); ^{1}H NMR: δ_H 8.57 (2H, d, *J* 1.2), 8.48 (2H, d, *J* 1.2), 4.45 (2H, s), 3.26 (4H, m), 1.84 (4H, m), 1.46 (4H, m), 1.30 (16H, br), and 0.90 (6H, t, *J* 7.0); ^{13}C NMR: δ_C 148.42, 146.84, 141.33, 134.17, 128.56, 123.66, 56.30, 38.05, 31.55, 28.84, 28.80, 28.17, 22.46[ii], and 13.94; MS (ES–): *m/z* 607 ($[M–H]^-$), $C_{29}H_{40}N_2O_8S_2$ requires 608.2.

4,5-Dinitro-2,7-di(2-[2-(2-methoxyethoxy)ethoxy]ethylsulfonyl)-9*H*-fluorene 12b

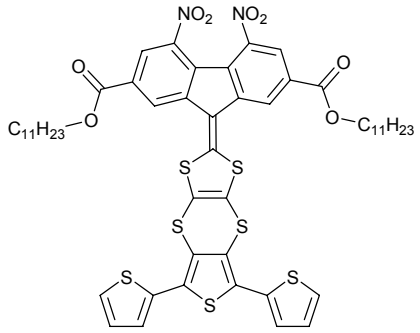


2,7-Di(2-[2-(2-methoxyethoxy)ethoxy]ethylsulfonyl)-9*H*-fluorene **11b** (954 mg, 1.62 mmol) was dissolved in 10 ml of acetic acid, 30 ml of fuming nitric acid was added dropwise and the solution was stirred for 2.5 h at 30 °C. The reaction mixture was poured on ice, extracted with 3x30 ml of

[i] Almost coincident two aromatic *ortho*-doublets with weak side bands
[ii] Very strong, probably two coincident signals (*cf.* the spectrum of non-nitrated compound)

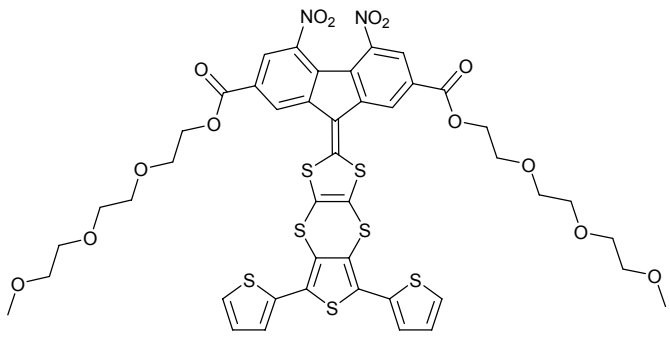
DCM, the combined extracts washed with water, brine, and dried. After removal of the solvent, the residue was subjected to column chromatography (silica, ethyl acetate:THF = 10:1 with gradual change to 5:1), to give 750 mg (68%) of product as a brown tar that gradually crystallized. M.p. 89–91 °C (Found: C, 48.49, H, 5.62, N, 3.99, S, 9.30; $C_{27}H_{34}N_2O_{14}S_2$ requires C, 47.92, H, 5.36, N, 4.14, S, 9.48%); ^{1}H NMR: δ_H 8.63 (2H, d, *J* 1.5), 8.51 (2H, d, *J* 1.5), 4.42 (2H, s), 4.00 (4H, t, *J* 5.4), 3.59 (8H, m), 3.50 (12H, m), and 3.35 (6H, s); ^{13}C NMR: δ_C 148.37, 146.40, 142.99, 133.99, 128.97, 124.08, 71.64, 70.56, 70. 26, 69.97, 64.66, 58.84, 56.83, and 38.03; MS (APCI): *m/z* 676 (M^-), $C_{27}H_{34}N_2O_{14}S_2$ requires 676.2.

1-9-[5,7-di(2-thienyl)[1,3]dithiolo[4,5-*b*]thieno[3,4-*e*][1,4]dithiin-2-yliden]-4,5-dinitro-9*H*-2-fluorenyl-2,7-dicarboxylic acid diundecyl ester 15a



A mixture of 633 mg (1.43 mmol) of 5,7-di(2-thienyl)[1,3]dithiolo[4,5-*b*]thieno[3,4-*e*][1,4]dithiine-2-thione **13**[4], 6 ml of dry chloroform, and 0.7 ml of methane trifluorosulphonate was stirred under nitrogen for 3 days at 20-25 °C. Then 15 ml of dry diethyl ether was added and the mother liquor was carefully removed from the precipitate with a syringe, and the precipitate was rinsed with 10 ml of dry diethyl ether. The salt **14** was dissolved in 2 ml of dry DMF, a solution of 778 mg (1.19 mmol) of **8a** in 10 ml of dry chloroform was added, followed by 0.5 ml of pyridine. In 15 min, 10 ml of methanol was added, the precipitate was filtered, washed with 30 ml portions of of methanol-chloroform (1:1) mixture, methanol, water, methanol and 50 ml of diethyl ether. The crude product was subjected to column chromatography (silica, DCM) to afford 556 mg (44%) of a dark purple solid, m.p. 147–150 °C (Found: C, 58.87, H, 5.57, N, 2.67, S, 21.37; $C_{52}H_{56}N_2O_8S_7$ requires C, 58.84, H, 5.32, N, 2.64, S, 21.15%); ^{1}H NMR: δ_H 8.65 (2H, d, *J* 1.3), 8.49 (2H, d, *J* 1.1), 7.44 (2H, dd, *J* 5.1 and 1.0), 7.24 (2H, dd, *J* 3.6 and 1.0), 7.10 (2H, d, *J* 5.1 and 3.6), 4.47 (4H, t, *J* 6.7), 1.88 (4H, m), 1.54-1.28 (32 H, m), and 0.92 (6H, t, *J* 6.9); ^{13}C NMR: δ_C 164.37, 152.27, 146.23, 139.67, 132.61, 130.77, 130.28, 127.83, 127.41, 127.31, 127.25, 126.95, 126.19, 126.14, 121.81, 116.07, 66.32, 31.85, 29.56, 29.49, 29.29, 29.24, 28.61, 25.96, 22.62, and 14.06[i]; MS (APCI): *m/z* 1060 (M^-), $C_{52}H_{56}N_2O_8S_7$ requires 1060.

1-(9-[5,7-di(2-thienyl)[1,3]dithiolo[4,5-*b*]thieno[3,4-*e*][1,4]dithiin-2-yliden]-7-[2-(4-methoxy-butoxy)-ethylperoxycarbonyl]-4,5-dinitro-9H-fluorene-2-carboxylic acid 2-[2-(2-methoxy-ethoxy)-ethoxy]-ethyl ester 15b

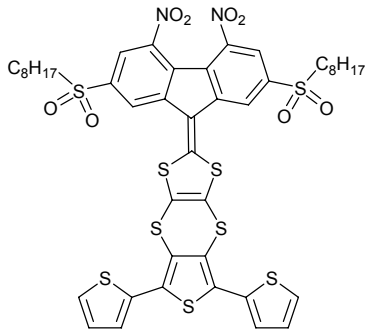


To the salt **14** prepared as above from 41 mg (0.092 mmol) of 5,7-di(2-thienyl)[1,3]dithiolo[4,5-*b*]thieno[3,4-*e*][1,4]dithiine-2-thione **13** and 0.2 ml of methane trifluorosulphonate in 1 ml of dry chloroform, was added the solution of 53 mg (0.083 mmol) of **8b** in 1 ml of dry DMF. After the precititate had dissolved, 0.1 ml of pyridine was added and in 15 min the product was precipitated by addition of 2 ml of methanol and 5 ml of water. The precipitate filtered, washed with methanol, diethyl ether and subjected to column chromatography (silica, DCM:THF=4:1). The volume of eluate was reduced to

[i] One aliphatic carbon signal unresolved

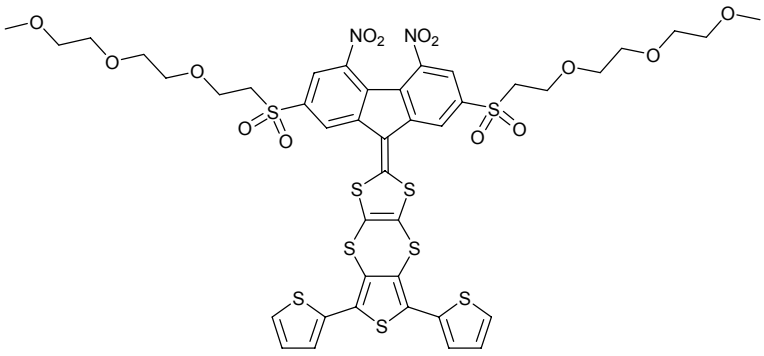
10 ml, diethyl ether (30 ml) was added, the precipitate was filtered, refluxed with 25 ml of ethyl acetate, cooled and filtered, to give 44 mg (46%) of the product as an almost black powder, m.p. 45 ^{o}C (dec.) (Found: C, 50.56, H, 3.59, N, 2.63, S, 21.26; $C_{44}H_{40}N_2O_{14}S_7$ requires C, 50.56, H, 3.86, N, 2.68, S, 21.47%); ^{1}H NMR: δ_H 8.65 (2H, d, *J* 1.1), 8.50 (2H, d, *J* 1.1), 7.45 (2H, dd, *J* 5.2 and 1.0), 7.20 (2H, dd, *J* 3.7 and 1.1), 7.10 (2H, d, *J*5.2 and 3.7), 4.63 (4H, t[i]), 3.95 (4H, m), 3.80 (4H, m), 3.72 (8H, m), 3.57 (4H, m), and 3.39 (6H, s); ^{13}C NMR: δ_C 164.32, 152.53, 146.22, 139.68, 132.55, 130.39, 130.26, 127.88, 127.44, 127.26, 127.05, 126.28, 126.09, 121.90, 115.97, 71.84, 70.61, 70.54, 68.87, 65.19, and 58.96[ii]; MS (APCI): *m/z* 1044 (M^-), $C_{44}H_{40}N_2O_{14}S_7$ requires 1044.

2-[2,7-di(octylsulfonyl)- 4,5-dinitro-9*H*-9-fluorenyliden]-5,7-di(2-thienyl)[1,3]dithiolo[4,5-*b*]thieno[3,4-*e*][1,4]dithiine 16a



To the salt **14** prepared as above from 85 mg (0.191 mmol) of **13**, a solution of 90 mg (0.174 mmol) of **12a** in 1.5 ml of dry DMF was added and the mixture was stirred for 10 min. After addition of 3 ml of methanol, the *precipitate* was filtered, washed with mixture DMF-methanol (1:1), methanol, water, methanol and finally diethyl ether. Column chromatography (silica, DCM) yielded 81 mg (46%) of a dark purple solid, m.p. >250 ^{o}C (Found: C, 51.90, H, 4.18, N, 2.76, S, 27.99; $C_{44}H_{44}N_2O_8S_9$ requires C, 51.94, H, 4.36, N, 2.75, S, 28.37%); ^{1}H NMR: δ_H 8.73 (2H, d, *J* 1.3), 8.46 (2H, d, *J* 1.3), 7.53 (2H, dd, *J* 5.1 and 1.1), 7.37 (2H, dd, *J* 3.6 and 1.1), 7.10 (2H, d, *J* 5.1 and 3.6), 3.28 (4H, m), 1.88 (4H, m), 1.46 (4H, m), 1.28 (16H, m), and 0.87 (6H, t, *J* 7.0); ^{13}C NMR: δ_C 156,73, 146.59, 140.10, 140.00, 132.37, 130.86, 128.01, 127.65, 127.62, 126.86, 125.83, 125.16, 120.09, 114.82, 56.52, 31.55, 28.88, 28.84, 28.21, 22.48, 22.45, 13.96[iii]; MS (APCI): *m/z* 1016 (M^-), $C_{44}H_{44}N_2O_8S_9$ requires 1016.

2-[2,7-di(2-[2-(2-methoxyethoxy)ethoxy]ethylsulfonyl)- 4,5-dinitro-9*H*-9-fluorenyliden]-5,7-di(2-thienyl)[1,3]dithiolo[4,5-*b*]thieno[3,4-*e*][1,4]dithiine 16b



To the salt **14** prepared as above from 1.02 g (2.30 mmol) of **13** and 1.2 ml methyl trifluorosulfonate in 12 ml of dry chloroform, a solution of **12b** in 18 ml of dry DMF was added. After stirring for 1 h, the reaction mixture was diluted with 10 ml of methanol and 15 ml of water, the precipitate was filtered and washed with methanol and ethyl acetate and subjected to flash chromatography on a short column (silica, DCM with gradual switch to DCM:THF=5:1). The volume of eluent was reduced to 40 ml, and the product was precipitated with 160 ml of ethyl acetate with subsequent cooling in fridge, to give 1.57 g (71%) of a dark purple solid, m.p. 185–189 ^{o}C (Found: C, 46.48, H, 3.51, N, 2.58, S, 26.06; $C_{42}H_{40}N_2O_{14}S_9$ requires C, 46.48, H, 3.71, N, 2.58, S, 26.59 %); ^{1}H NMR: δ_H 8.75 (2H, d, *J* 1.2), 8.51 (2H, d, *J* 1.2), 7.53 (2H, dd, *J* 5.2 and 1.2), 7.37 (2H, dd, *J* 3.7 and 1.2), 7.21 (2H, d, *J* 5.2 and 3.7), 4.02 (4H, t, *J* 5.5), 3.60 (8H, m), 3.46 (12 H, m), and 3.32 (6H, s); ^{13}C NMR: δ_C 156.12, 146.21, 141.12, 139.74, 132.38,

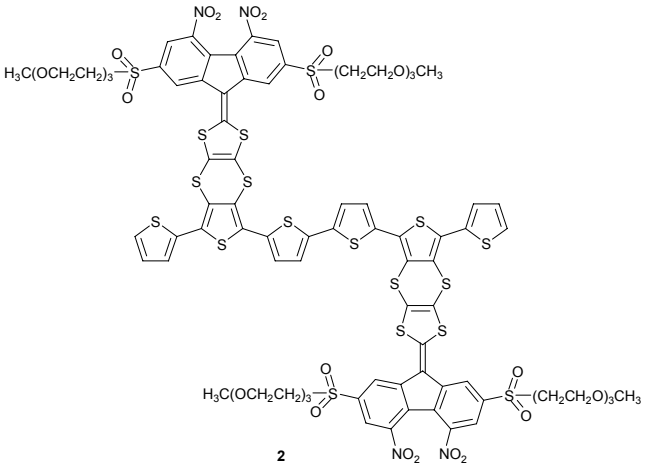
[i] Unsymmetrical - simplified multiplet.
[ii] One aromatic carbon signal unresolved
[iii] One aromatic carbon signal unresolved

130.72, 128.00, 127.63, 127.54, 127.38, 126.81, 125.80, 125.29, 120.82, 71.66, 70.66, 70.33, 70.07, 64.63, 58.84, and 56.93; MS (APCI): *m/z* 1083 (M^-), $C_{42}H_{40}N_2O_{14}S_9$ requires 1084.

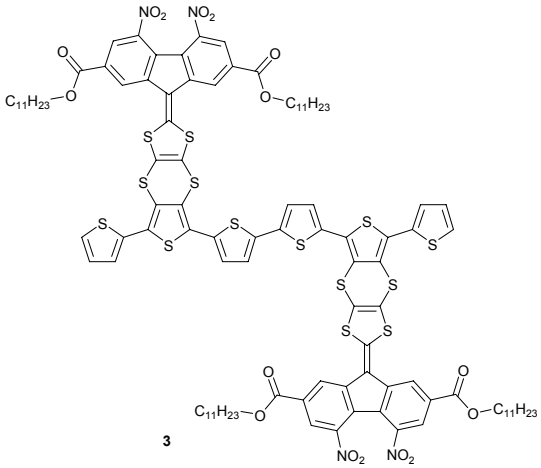
Solubility of terthiophenes **15** and **16** at rt:
in methanol, Et_2O – insoluble;
in acetone, ethyl acetate, toluene, THF – moderately or poorly soluble depending on structure;
from volatile solvents of low and medium polarity - all best soluble in CH_2Cl_2 and
in $CHCl_3$ [mg/ml]: compound **15a** >200 compound **15b** >200
compound **16a** ca. 30 compound **16b** ca. 100

TEG ester and sulphone (**15b** and **16b**) are well soluble in DMF, however, this solvent is not ideal for polymerisation (difficult to remove).

General procedures are given for the reactions of 15a with $FeCl_3$:



2



3

To a solution of **15a** (120 mg, 0.113 mM) in dry nitrobenzene (12 ml) was added $FeCl_3$ in nitrobenzene (1.8 ml, 0.5M (8 eq)). The reaction mixture was allowed to stir for 3 hour at room temperature before the addition of 200 ml of methanol and 10 ml of water. The resulting precipitate was filtered, washed with methanol, water, methanol and subjected to two successive columns on silica, eluting with DCM to afford 23 mg (19%) of compound **3**.

Dimerization in slight excess of $FeCl_3$:

To a solution of **15a** (107 mg, 0.101 mM) in dry nitrobenzene (10 ml) was added $FeCl_3$ in nitrobenzene (0.24 ml, 0.5M (1.2 eq)). The reaction mixture was allowed to stir for 24 hour at room temperature before the addition of 200 ml of methanol and 10 ml of water. The resulting precipitate was filtered and washed with methanol. After column chromatography on silica gel (eluting with CH_2Cl_2) 55 mg (51 %) of starting compound was recovered and 29 mg (27 %) of the dimer **3** was isolated as a dark purple solid. M.p. > 250 $^{\circ}$C (Found: C, 58.62; H, 5.08; N, 2.53; $C_{104}H_{110}N_4O_{16}S_{14}$ requires C, 58.90; H, 5.23; N, 2.64%); ^{1}H NMR: δ_H 8.24 (2H, s), 8.16 (2H, s), 8.08 (2H, s), 8.07 (2H, s), 7.18 (2H, d, *J* 4.87), 6.99 (2H, d, *J* 2.74), 6.89 (2H, d, *J* 2.41), 6.81 (2H, d, *J* 2.80), 6.77 (2H, t, *J* 4.02), 4.29 (8H, m), 1.81 (8H, m), 1.29 (64H, m), 0.89 (6H, t, *J* 6.63), 0.86 (6H, t, *J* 7.01). See Fig S1 for the ^{1}H NMR spectrum.

Procedures for the reactions of **16b** with $FeCl_3$:
To a solution of **16b** (121 mg, 0.111 mM) in dry nitrobenzene (12 ml) was added $FeCl_3$ in nitrobenzene (1.8 ml, 0.5M (8 eq)). The reaction mixture was allowed to stir for 3 hours at room temperature before the addition of 200 ml of methanol and 12 ml of water. The resulting precipitate was filtered, washed with methanol, water and methanol once again. The crude product was dissolved in DCM using an ultrasonic bath and chromatographed, eluting with DCM:MeOH 100:3 to afford 28 mg (23%) of compound **2**.

Dimerisation in slight excess of $FeCl_3$:

To a solution of **16b** (120 mg, 0.111 mM) in dry nitrobenzene (12 ml) was added $FeCl_3$ in nitrobenzene (0.27 ml, 0.5M (1.2 eq)). The reaction mixture was allowed to stir for 24 hour at room temperature before the addition of 200 ml of methanol and 12 ml of water. The resulting precipitate was filtered and washed with methanol. After loading onto a column of silica, the product was eluted with DCM:MeOH 100:3, enabling the starting compound to be recovered (74 mg, 62 %), and

the dimer **2** isolated as a dark purple solid (18 mg, 15 %). The product was sparingly soluble in dichloromethane and chloroform; in the case of $CHCl_3$, the dimer formed a gel after ultrasonic treatment. M.p. > 250 ºC (Found: C, 46.14; H, 3.54; N, 2.53; $C_{84}H_{78}N_4O_{28}S_{18}$ requires C, 46.52; H, 3.63; N, 2.58%).

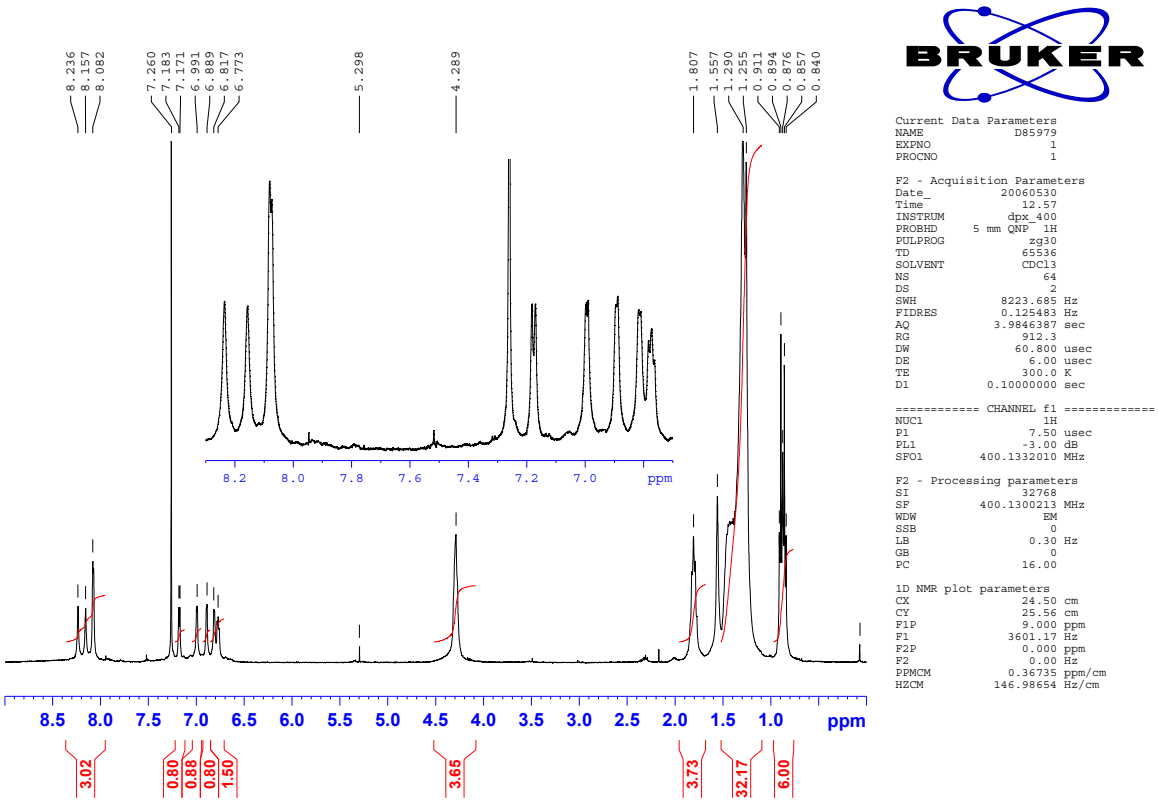


Figure S1 Proton NMR of **3** (integrals of aromatic protons and the first two methylene links in the undecyl chains are slightly reduced due to slow relaxation time).

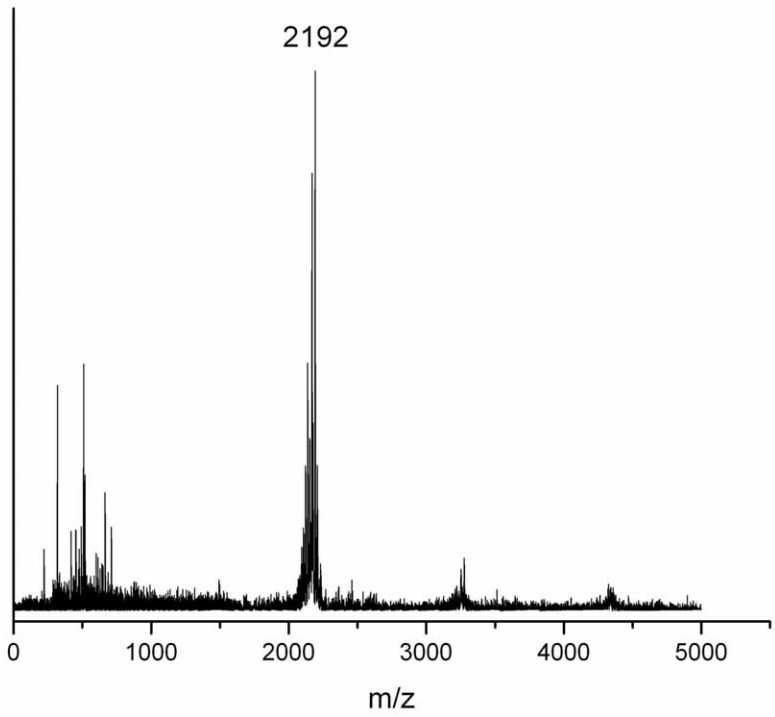
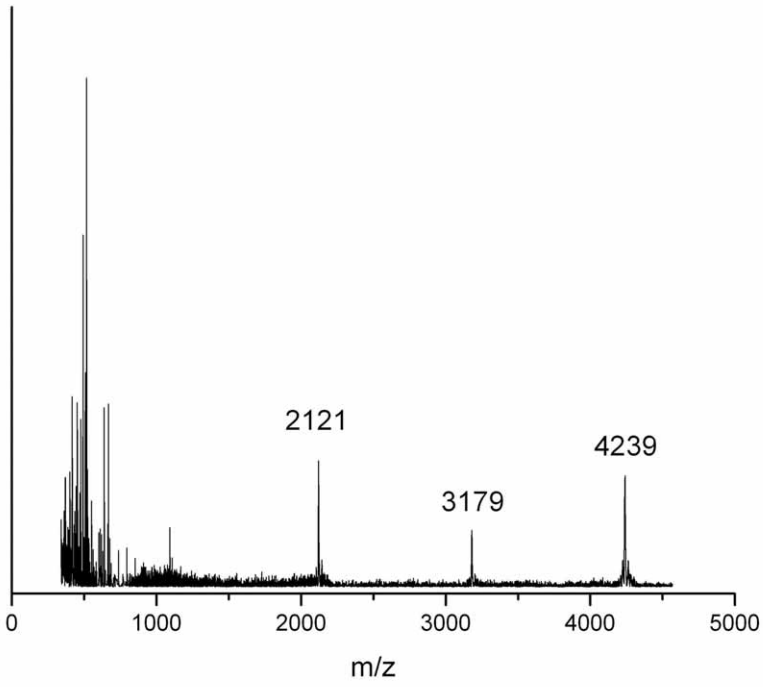


Figure S2 MALDI-TOF mass spectra of compound **2**. Molecular weight of $C_{84}H_{78}N_4O_{28}S_{18}$ = 2169 (peak gives $[M + Na]^+$).



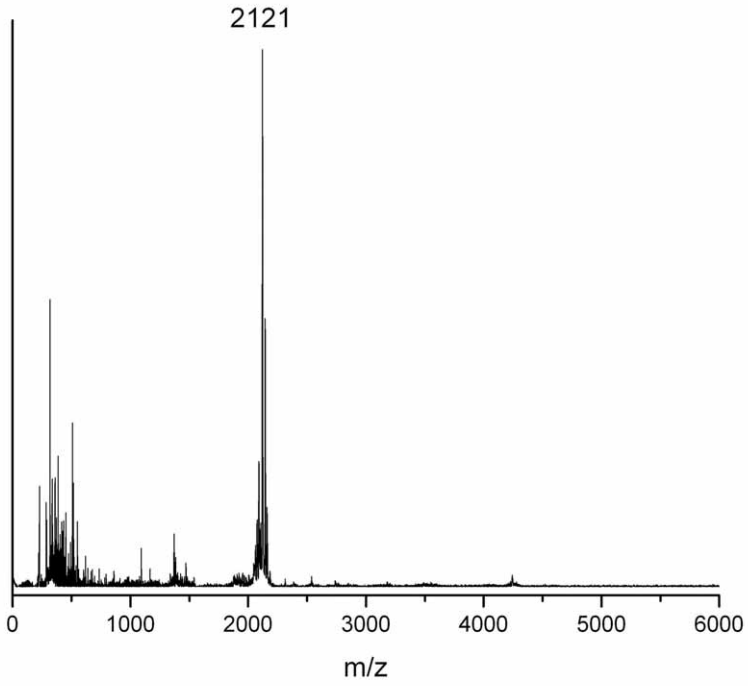


Figure S3 MALDI-TOF mass spectra of compound **3** with higher oligomers (top) and purified compound **3** (bottom). Molecular weight of $C_{104}H_{110}N_4O_{16}S_{14}$ = 2121.

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