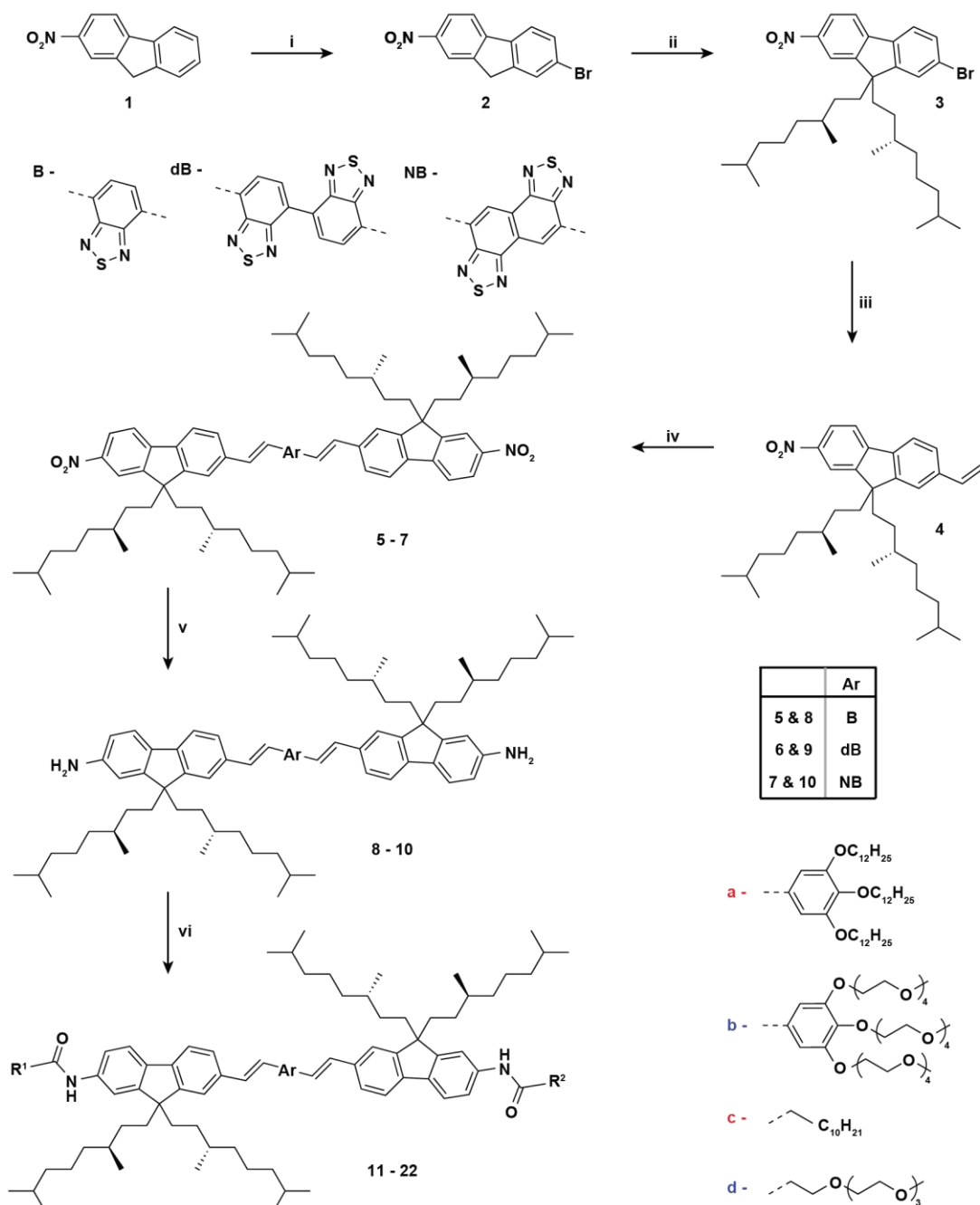


Supporting information

General remarks

All solvents employed were obtained from Biosolve BV and used without purification unless stated otherwise. The reagents were obtained from Sigma-Aldrich and used without purification. Analytical thin layer chromatography (TLC) was carried out using Merck pre-coated silica gel using ultraviolet light irradiation at 254 and 365 nm. Manual column chromatography was performed using Merck 60 Å pore size silica gel (particle size: 63 – 200 µm). All the NMR data were recorded on a Bruker Advance-III 400 MHz equipped with a BBFO probe from Bruker (400 MHz for ¹H-NMR and 100 MHz for ¹³C-NMR). Chemical shifts are reported in parts per million (ppm) referenced to an internal standard of residual chloroform-*d* (7.26 ppm for ¹H-NMR and 77 ppm for ¹³C-NMR, relative to tetramethylsilane (TMS) as internal standard). ¹H-NMR and ¹³C-NMR signals were assigned with the aid of two-dimensional ¹H, ¹³C -HSQC and ¹H, ¹³C -HMBC spectra. Matrix assisted laser desorption/ionisation time-of-flight mass spectra (MALDI-TOF-MS) were measured on a PerSeptive Biosystems Voyager-DE Pro spectrometer with a Biospectrometry workstation using 2-[(2E)-3-(4-t-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) and α-cyano-4-hydroxycinnamic acid (CHCA) as matrix material and methylene chloride as solvent. Dynamic light scattering experiments (DLS) were performed on a Malvern Instruments Limited Zetasizer µV (model: ZMV2000). The incident beam was produced by a HeNe laser operating at 632 nm. Visualization by TEM was performed by a Technai G2 Sphera by FEI operating at an acceleration voltage of 80 kV. Samples were prepared by drop-casting a 1.5 × 10⁻⁵ m aqueous PDI solution on a carbon film on a 400 square mesh copper grid and dried for 1 minute.

Synthetic procedure



	Ar	R ¹	R ²	%	Ar	R ¹	R ²	%	Ar	R ¹	R ²	%	Ar	R ¹	R ²	%			
11	B	a	a	18	14	dB	a	a	27	17	NB	a	a	28	20	B	c	c	22
12	B	a	b	34	15	dB	a	b	47	18	NB	a	b	45	21	B	c	d	47
13	B	b	b	23	16	dB	b	b	25	19	NB	b	b	25	22	B	d	d	19

Scheme S1: Synthetic route towards fluorene co-oligomers 11 – 22. i) Bromine, methylene chloride, RT, 3h, 79%; ii) (S)-1-bromo-3,7-dimethyloctane, KOH, KI, dimethylsulfoxide, RT, 16h, 32%; iii) tributyl(vinyl)stannane, 2,6-di-*tert*-butylphenol, PdCl₂(PPh₃)₂, toluene, 16h, 100 °C, 78%; iv) dibromo-benzothiadiazole (OF 5 & 7) or dibromo-naphthobisthiadiazole (OF 6), Pd(OAc)₂, Pd(PPh₃)₄, K₂CO₃, dimethylformamide, 16h, 100 °C, 56% (OF 5), 10% (OF 6), 34% (OF 7); v) stannous chloride, ethanol:ethyl acetate (1:1), 16h, reflux, quant.; vi) both gallic acyl-chloride derivatives, triethylamine, tetrahydrofuran, 1h, RT (OF 11 – 19) or methyl-PEG₄-NHS, lauric acid-NHS, triethylamine, methylene chloride, 16h, RT (OF 20 – 22).

2-bromo-7-nitro-fluorene (2) | Br₂ (2.7 μL, 52.1 mmol) was added to a stirred solution of 2-nitrofluorene (5 g, 23.7 mmol) in dry methylene chloride (24 mL). The HBr, which soon evolved from solution was guided through a trap to a scrubbing solution of 2N NaOH and the mixture was stirred for 3 h. A yellow precipitate appeared, which was filtered off, washed with 5% NaHSO₃ and water and dried with MgSO₄. The solvent was removed in vacuo, yielding a light yellow solid (5.4 g, 18.6 mmol, 79%). ¹H NMR (400 MHz, CDCl₃) δ 8.40 (s, 1H), 8.30 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.77 (s, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 1H), 4.01 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 147.04, 146.98, 146.59, 143.57, 138.45, 130.74, 128.74, 123.32, 123.11, 122.51, 120.56, 120.03, 36.79. GCMS (ESI) calc. for C₁₃H₈BrNO₂ [M] 290.12; observed [M]⁺ 290.25.

2-bromo-9,9-bis((S)-3,7-dimethyloctyl)-7-nitro-fluorene (3) | 2-bromo-7-nitro-fluorene (**2**, 5 g, 17.2 mmol) was added to a mixture of powdered KOH (3.9 g, 68.9 mmol) and potassium iodide (0.4 g, 2.6 mmol) in DMSO (17 mL), which gave a viscous, dark green reaction mixture. (S)-1-bromo-3,7-dimethyloctan (9.5 g, 43.1 mmol) was added and the mixture was stirred overnight at room temperature. Water was added and the aqueous phase was extracted with methylene chloride. After drying the combined organic layer over MgSO₄ and removal of the solvent, a black oil was obtained. Column chromatography (silica, heptane + 20% methylene chloride) gave an orange oil that slowly solidified into yellow crystal plates (3.1 g, 5.4 mmol, 32%). ¹H NMR (400 MHz, CDCl₃) δ 8.27 (dd, *J* = 8.4, 2.1 Hz, 1H), 8.19 (d, *J* = 2.2 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.56 – 7.51 (m, 2H), 2.12 – 1.93 (m, 4H), 1.50 – 1.36 (m, 2H), 1.18 – 1.11 (m, 2H), 1.10 – 0.95 (m, 8H), 0.90 – 0.85 (m, 4H), 0.83 – 0.75 (m, 12H), 0.69 (dd, *J* = 6.6, 2.4 Hz, 6H), 0.61 – 0.32 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 154.33, 151.57, 147.43, 146.51, 137.80, 130.75, 126.52, 123.71, 123.43, 122.46, 119.95, 118.21, 55.86, 39.12, 37.31, 37.24, 36.53, 36.50, 32.74, 30.42, 27.92, 27.90, 24.56, 24.50, 22.65, 22.62, 22.55, 19.43, 19.40. GCMS (ESI) calc. for C₃₃H₄₈BrNO₂ [M] 570.66; observed [M]⁺ 571.30.

9,9-bis((S)-3,7-dimethyloctyl)-2-nitro-7-vinyl-fluorene (4) | 2-bromo-9,9-bis((S)-3,7-dimethyloctyl)-7-nitro-fluorene (**3**, 3.0 g, 5.25 mmol) and 2,6-di-tert-butylphenol (16.2 mg, 78.9 μmol) were dried under vacuum for 30 min. Then, tributyl(vinyl)stannane (2.3 mL, 7.9 mmol) dissolved in toluene (30 mL) was added and the mixture was degassed by freeze pumping. After the addition of Pd(PPh₃)₂Cl₂ (55.3 mg, 78.9 μmol) the reaction mixture was stirred overnight at 100 °C. The solvent was removed in vacuo and the resulting dark oil was subjected to column chromatography (silica, cyclohexane + 5 - 30% methylene chloride) yielding a yellow oil (2.11 g, 4.07 mmol, 78%). ¹H NMR (400 MHz, CDCl₃) δ 8.26 (dd, *J* = 8.3, 2.1 Hz, 1H), 8.21 (d, *J* = 2.0 Hz, 1H), 7.75 (dd, *J* = 13.7, 8.1 Hz, 2H), 7.47 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.41 (d, *J* = 1.5 Hz, 1H), 6.82 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.86 (d, *J* = 17.5 Hz, 1H), 5.34 (d, *J* = 10.8 Hz, 1H), 2.05 (dddd, *J* = 20.8, 15.3, 10.2, 6.5 Hz, 4H), 1.42 – 1.33 (m, 2H), 1.24 – 0.86 (m, 12H), 0.79 (dd, *J* = 6.7, 1.5 Hz, 12H), 0.69 (dd, *J* = 6.6, 1.2 Hz, 6H), 0.64 – 0.37 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 152.84, 152.23, 147.49, 147.18, 138.89, 138.70, 137.05, 125.84, 123.45, 121.38, 120.89, 119.83, 118.25, 114.75, 55.59, 39.25, 37.50, 37.43, 36.68, 36.59, 32.96, 32.88, 30.54, 28.02, 28.00, 27.05, 24.69, 24.60, 22.75, 22.73, 22.66, 19.63, 19.59, 19.53, 17.40, 13.72. GCMS (ESI) calc. for C₃₅H₅₁NO₂ [M] 517.78; observed [M]⁺ 517.50.

General procedure for the Heck coupling which is used to synthesize 5 and 7 | 9,9-bis((S)-3,7-dimethyloctyl)-2-nitro-7-vinyl-fluorene (**4**, 2.1 eq.) and an aryl dibromide were dried under vacuum for 30 min. Then, K₂CO₃ (5 eq.) dissolved in DMF (1.5 ml) was added and the mixture was degassed by freeze pumping. After the addition of diacetoxypalladium (0.1 eq.) and Pd(PPh₃)₄ (0.02 eq.), the reaction mixture was stirred overnight at 90 °C. The solvent was removed in vacuo and the resulting dark oil was subjected to column chromatography (silica, cyclohexane + 5 - 30% ethyl acetate) yielding a red oil.

7,7'-(benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(9,9-bis((S)-3,7-dimethyloctyl)-2-nitro-7-vinyl-fluorene) (5) | 4,7-dibromobenzo[c][1,2,5]thiadiazole (135 mg, 0.460 mmol); *Y* = 56%; ¹H NMR (400 MHz, CDCl₃) δ 8.29 (dd, *J* = 8.3, 2.2 Hz, 2H), 8.24 (s, 2H), 8.17 (d, *J* = 16.2 Hz, 2H), 7.87 – 7.61 (m, 12H), 2.27 – 1.99 (m, 8H), 1.50 – 1.32 (m, 4H), 1.24 – 1.14 (m, 4H), 1.12 – 0.86 (m, 24H), 0.81 – 0.75 (m, 24H), 0.73 – 0.69 (m, 12H), 0.67 – 0.37 (m, 8H). ¹³C NMR (100 MHz, CDCl₃) δ 154.35, 154.07, 154.05, 153.13, 153.10, 152.35, 152.32, 147.40, 147.38, 147.26, 147.23, 139.23, 139.12, 138.83, 138.72, 134.27, 133.68, 131.57, 130.49, 129.52, 128.56, 127.59, 127.25, 126.56, 126.49, 125.37, 125.22, 123.54, 121.77, 121.69, 121.62, 119.99, 119.95, 118.29, 55.75, 55.71, 39.27, 39.26, 37.61, 37.54, 36.68, 36.65, 32.93, 30.64, 30.61, 28.02, 24.71, 24.65, 24.62, 22.77, 22.74, 22.67, 19.61. MALDI-ToF (*m/z*): calc. for C₇₆H₁₀₂N₄O₄S [M] 1166.76; observed [M]⁺ 1166.78.

7,7'-(bis(benzo[c][1,2,5]thiadiazole-4,7-diyl))bis(9,9-bis((S)-3,7-dimethyloctyl)-2-nitro-7-vinyl-fluorene) (6) was additionally extracted from the reaction mixture of **5** which was formed through palladium-catalyzed Ullmann homocoupling^[35] of the aryl bromides. Y = 10%; ¹H NMR (400 MHz, CDCl₃) δ 8.52 (d, J = 7.4 Hz, 2H), 8.38 – 8.14 (m, 6H), 7.95 (d, J = 7.5 Hz, 2H), 7.92 – 7.70 (m, 8H), 7.67 (s, 2H), 2.26 – 1.92 (m, 8H), 1.47 – 1.35 (m, 4H), 1.22 – 0.96 (m, 24H), 0.94 – 0.87 (m, 4H), 0.78 (d, J = 6.6 Hz, 24H), 0.71 (d, J = 6.5 Hz, 12H), 0.64 – 0.40 (m, 8H). ¹³C NMR (100 MHz, CDCl₃) δ 154z.40, 154.10, 153.16, 152.37, 147.41, 147.28, 139.27, 138.74, 134.32, 131.57, 130.55, 128.63, 127.27, 126.60, 125.25, 123.57, 121.77, 121.72, 120.02, 118.33, 55.77, 39.30, 39.28, 37.64, 37.58, 36.70, 32.96, 30.67, 28.04, 24.73, 24.67, 22.80, 22.77, 22.69, 19.62. MALDI-ToF (m/z): calc. for C₈₂H₁₀₄N₆O₄S₂ [M] 1300.76; observed [M]⁺ 1300.64.

7,7'-(naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole)-5,10-diyl)bis(9,9-bis((S)-3,7-dimethyloctyl)-2-nitro-7-vinyl-fluorene) (7) | 5,10-dibromonaphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole) (20 mg, 0.050 mmol); Y = 34%; ¹H NMR (400 MHz, CDCl₃) δ 8.94 (s, 2H), 8.33 (d, J = 16.2 Hz, 2H), 8.31 – 8.28 (m, 2H), 8.24 (d, J = 2.1 Hz, 2H), 7.91 – 7.74 (m, 8H), 7.71 (s, 2H), 2.14 (tq, J = 18.0, 6.6, 5.0 Hz, 8H), 1.47 – 1.36 (m, 4H), 1.26 – 1.16 (m, 4H), 1.12 – 0.87 (m, 24H), 0.81 – 0.75 (m, 24H), 0.73 – 0.69 (m, 12H), 0.68 – 0.40 (m, 8H). ¹³C NMR (100 MHz, CDCl₃) δ 153.82, 153.68, 153.19, 152.42, 147.35, 139.46, 138.56, 134.99, 129.98, 126.69, 125.40, 125.14, 124.61, 123.60, 121.89, 121.79, 120.07, 118.36, 55.80, 39.30, 39.28, 37.63, 36.75, 36.73, 33.00, 30.73, 28.05, 27.06, 24.74, 24.70, 22.80, 22.77, 22.68, 19.66, 19.63. MALDI-ToF (m/z): calc. for C₈₀H₁₀₂N₆O₄S₂, (m/z): [M] 1274.74; observed [M]⁺ 1274.74.

General procedure for the reduction used to synthesize 8, 9 and 10 | A mixture of dinitro-containing precursors **5**, **6** or **7** in ethanol:ethyl acetate (1:1) was purged with argon for 10 minutes. Then, dichloro-l2-stannane (8 eq.) was added and the mixture was stirred and refluxed for 16 h. The ethanol was removed in vacuo and the residue was poured in ethyl acetate and extracted with 1 N NaOH, which resulted in a clear phase separation after 2 hours. The organic fraction was collected and washed another two times with 1 N NaOH, once with H₂O and dried over MgSO₄. The organic fraction was concentrated in vacuo and a red/brown solid was obtained. In order to remove residual tin salts, short path column chromatography (silica, cyclohexane + 30% ethyl acetate and 0.1% triethylamine) was performed quantitatively yielding the dark red solids.

7,7'-(benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(9,9-bis((S)-3,7-dimethyloctyl)-2-amine-7-vinyl-fluorene) (8) | 7,7'-(benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(9,9-bis((S)-3,7-dimethyloctyl)-2-nitro-7-vinyl-fluorene) (**5**, 250 mg, 214 μmol), 5 mL solvent; ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 16.2 Hz, 2H), 7.80 – 7.44 (m, 12H), 6.67 (s, 4H), 3.78 (s, 4H), 2.08 – 1.87 (m, 8H), 1.52 – 1.35 (m, 4H), 1.23 – 0.90 (m, 28H, 4CH), 0.81 – 0.76 (m, 24H), 0.73 – 0.69 (m, 12H), 0.69 – 0.47 (m, 8H). ¹³C NMR (100 MHz, CDCl₃) δ 154.19, 153.24, 150.44, 146.36, 142.35, 134.98, 134.12, 132.35, 129.46, 126.72, 126.15, 122.92, 121.10, 120.80, 118.69, 114.17, 109.78, 54.78, 39.40, 38.17, 36.82, 33.15, 30.67, 28.07, 24.83, 22.84, 19.71. MALDI-ToF (m/z): calc. for C₇₆H₁₀₆N₄S [M] 1106.81; observed [M]⁺ 1106.83.

7,7'-(bis(benzo[c][1,2,5]thiadiazole-4,7-diyl))bis(9,9-bis((S)-3,7-dimethyloctyl)-2-amine-7-vinyl-fluorene) (9) | 7,7'-(bis(benzo[c][1,2,5]thiadiazole-4,7-diyl))bis(9,9-bis((S)-3,7-dimethyloctyl)-2-nitro-7-vinyl-fluorene) (**6**, 27.3 mg, 21.0 μmol), 1 mL solvent; ¹H NMR (400 MHz, CDCl₃) δ 8.48 (d, J = 7.5 Hz, 2H), 8.12 (d, J = 16.3 Hz, 2H), 7.91 (d, J = 7.6 Hz, 2H), 7.75 (d, J = 16.2 Hz, 2H), 7.65 – 7.49 (m, 12H), 2.11 – 1.85 (m, 8H), 1.30 – 1.22 (m, 4H), 1.16 – 0.96 (m, 24H), 0.91 – 0.86 (m, 4H), 0.84 – 0.74 (m, 24H), 0.74 – 0.68 (m, 12H), 0.65 – 0.44 (m, 8H). ¹³C NMR (100 MHz, CDCl₃) δ 154.44, 154.23, 153.30, 150.51, 146.44, 142.59, 135.12, 134.81, 132.32, 131.54, 131.10, 128.02, 126.30, 126.22, 122.65, 121.28, 120.87, 118.73, 114.20, 109.80, 54.83, 39.39, 38.16, 38.04, 36.84, 36.79, 33.14, 30.70, 28.08, 24.83, 24.74, 22.84, 22.75, 22.72, 19.68. MALDI-ToF (m/z): calc. for C₈₂H₁₀₈N₆S₂ [M] 1240.81; observed [M]⁺ 1240.79.

7,7'-(naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole)-5,10-diyl)bis(9,9-bis((S)-3,7-dimethyloctyl)-2-nitro-7-vinyl-fluorene) (10) | 7,7'-(naphtho[1,2-c:5,6-c']bis([1,2,5]thiadiazole)-5,10-diyl)bis(9,9-bis((S)-3,7-dimethyloctyl)-2-nitro-7-vinyl-fluorene) (**7**, 21.6 mg, 17.0 μmol), 1 mL solvent; ¹H NMR (400 MHz, CDCl₃) δ 8.27 (d, J = 16.2 Hz, 2H), 7.77 (d, J = 16.2 Hz, 2H), 7.73 – 7.63 (m, 2H), 7.63 – 7.56 (m, 6H), 7.56 – 7.48 (m, 2H), 6.76 – 6.61 (m, 4H), 2.09 – 1.93 (m, 8H), 1.43 – 1.43 (m, 4H), 1.22 – 1.16 (m, 4H), 1.15 – 0.97 (m, 24H), 0.82 – 0.75 (m, 24H), 0.74 (dd, J = 6.5, 1.9 Hz, 12H), 0.69 – 0.53 (m, 8H). ¹³C NMR (100 MHz, CDCl₃) δ 153.89, 153.36, 150.53, 146.49, 142.75, 135.69, 134.72, 132.31, 130.24, 126.41, 125.15, 123.58, 122.61, 121.39, 120.93, 118.81, 114.22, 109.80, 54.84, 39.41, 39.39, 38.18, 36.87, 36.82, 33.18, 30.74, 28.08, 27.07, 24.84, 24.78, 22.84, 22.75, 22.72, 19.74, 19.70. MALDI-ToF (m/z): calc. for C₈₀H₁₀₆N₆S₂ [M] 1214.79; observed [M]⁺ 1214.78.

General procedure for the synthesis of OF 11 – 19 | To a solution of tris(dodecyloxy)benzoic acid (1.5 eq.) and tris(PEG₄)benzoic acid (1.5 eq.) in dry DCM (0.3 mL) under inert conditions in separate flasks, Ghosez reagent (3 eq.) was added dropwise in order to convert to the acyl-chloride derivatives. After 1 hour of stirring, NMR confirmed full conversion of the benzoic acid to the acyl-chloride derivatives. The solution was concentrated in vacuo in the dark for 90 minutes. In a separate flask, **8** (29.9 mg, 27.0 μmol), **9** (14.3 mg, 11.5 μmol) or **10** (13.3 mg, 11.0 μmol) was dissolved in dry THF (0.3 mL) under inert conditions and triethylamine (1.2 eq.) was added. The acyl-chloride derivatives (1.5 eq. each) were both dissolved in dry THF (0.3 mL), mixed and added dropwise to the solution containing the starting material and stirred for 1h at room temperature. The solution was concentrated in vacuo and the resulting red residue was subjected to column chromatography (silica, heptane + 30 - 70% THF) to yield three derivatives in each one-pot reaction mixture as red solids.

OF **11** | Y = 18%; ¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, J = 16.2 Hz, 2H), 7.86 – 7.66 (m, 14H), 7.57 – 7.50 (m, 2H), 7.10 (s, 4H), 4.05 (dt, J = 12.4, 6.5 Hz, 12H), 2.10 – 1.99 (m, 8H), 1.91 – 1.70 (m, 12H), 1.51 – 1.25 (m, 112H), 1.16 – 0.97 (m, 28H), 0.88 (t, J = 6.6 Hz, 18H), 0.77 (d, J = 6.5 Hz, 24H), 0.71 (dd, J = 6.5, 2.0 Hz, 12H), 0.67 – 0.47 (m, 8H). ¹³C NMR (100 MHz, CDCl₃) δ 165.54, 154.18, 153.43, 152.53, 151.36, 141.75, 141.38, 140.64, 137.61, 137.49, 136.31, 130.23, 129.52, 127.04, 126.18, 123.78, 121.39, 120.33, 119.78, 118.90, 114.73, 106.07, 73.74, 69.72, 55.33, 39.36, 36.78, 33.12, 33.08, 32.09, 30.50, 29.92, 29.87, 29.81, 29.75, 29.56, 29.53, 28.08, 26.26, 24.81, 24.71, 22.85, 22.82, 22.73, 22.71, 19.72, 19.67, 14.28. MALDI-ToF (m/z): calc. for C₁₆₂H₂₅₈N₄O₈S [M] 2419.96; observed [M+H]⁺ 2420.98.

OF **12** | Y = 34%; ¹H NMR (400 MHz, CDCl₃) δ 8.41 (s, 1H), 8.11 (d, J = 16.2 Hz, 2H), 7.81 – 7.56 (m, 16H), 7.29 (s, 2H), 7.10 (s, 2H), 4.30 – 4.25 (m, 6H), 4.05 (dt, J = 12.8, 6.5 Hz, 6H), 3.84 – 3.83 (m, 6H), 3.73 – 3.67 (m, 30H), 3.57 – 3.52 (m, 6H), 3.39 (s, 9H), 2.04 (s, 8H), 1.86 – 1.76 (m, 6H), 1.37 – 1.27 (m, 58H), 1.11 – 0.99 (m, 28H), 0.85 – 0.82 (m, 9H), 0.76 (d, J = 6.6 Hz, 24H), 0.72 – 0.69 (m, 12H), 0.64 – 0.46 (m, 8H). ¹³C NMR (100 MHz, CDCl₃) δ 168.94, 154.17, 153.42, 152.73, 152.33, 151.35, 142.68, 141.73, 141.31, 138.40, 138.00, 137.61, 137.47, 130.58, 129.87, 126.53, 126.05, 123.71, 121.37, 121.21, 120.53, 119.82, 118.91, 114.74, 109.97, 106.08, 72.51, 72.09, 71.02, 70.96, 70.83, 70.78, 70.75, 70.73, 70.71, 70.66, 70.56, 69.92, 69.73, 69.45, 69.08, 59.17, 59.10, 45.46, 39.35, 36.79, 32.08, 31.07, 29.85, 29.80, 29.55, 29.52, 28.06, 26.25, 24.70, 22.84, 22.70, 19.65, 14.27. MALDI-ToF (m/z): calc. for C₁₅₃H₂₄₀N₄O₂₀S [M] 2485.76; observed [M+H]⁺ 2486.81.

OF **13** | Y = 23%; ¹H NMR (400 MHz, CDCl₃) δ 8.42 (s, 2H), 8.11 (d, J = 16.1 Hz, 2H), 7.87 – 7.48 (m, 16H), 7.29 (s, 4H), 4.26 (dt, J = 10.5, 4.9 Hz, 12H), 3.84 (dt, J = 22.7, 4.9 Hz, 12H), 3.73 – 3.61 (m, 60H), 3.56 – 3.51 (m, 12H), 3.36 (d, J = 17.6 Hz, 18H), 2.14 – 1.96 (m, 8H), 1.40 (dd, J = 12.9, 6.5 Hz, 5H), 1.19 – 0.95 (m, 28H), 0.76 (d, J = 6.7 Hz, 24H), 0.72 – 0.69 (m, 12H), 0.63 – 0.50 (m, 8H). ¹³C NMR (100 MHz, CDCl₃) δ 169.36, 160.35, 154.18, 153.59, 152.73, 151.41, 141.70, 140.35, 137.85, 137.11, 136.49, 134.48, 134.16, 130.33, 129.53, 127.18, 126.47, 123.88, 121.45, 121.15, 120.84, 120.24, 118.87, 117.55, 115.84, 108.06, 72.47, 72.10, 72.06, 70.84, 70.82, 70.77, 70.73, 70.65, 69.97, 69.45, 69.25, 59.17, 59.13, 39.36, 37.80, 36.80, 33.05, 30.81, 28.07, 24.89, 24.69, 22.71, 19.73. MALDI-ToF (m/z): calc. for C₁₄₄H₂₂₂N₄O₃₂S [M] 2551.56; observed [M+H]⁺ 2552.34.

OF **14** | Y = 27%; ¹H NMR (400 MHz, CDCl₃) δ 8.50 (d, J = 7.4 Hz, 2H), 8.17 (d, J = 16.3 Hz, 2H), 7.99 – 7.89 (m, 2H), 7.86 – 7.59 (m, 12H), 7.58 – 7.49 (m, 2H), 7.09 (s, 4H), 4.05 (dt, J = 12.7, 6.5 Hz, 12H), 2.20 – 1.93 (m, 8H), 1.82 (dp, J = 23.4, 7.6, 7.1 Hz, 12H), 1.52 – 1.26 (m, 112H), 1.21 – 0.95 (m, 28H), 0.88 (t, J = 6.6 Hz, 18H), 0.77 (d, J = 6.5 Hz, 24H), 0.72 (dd, J = 6.5, 2.1 Hz, 12H), 0.67 – 0.49 (m, 8H). ¹³C NMR (100 MHz, CDCl₃) δ 165.45, 153.452, 141.70, 135.93, 128.41, 125.67, 124.32, 123.49, 121.44, 119.92, 118.94, 114.55, 106.11, 105.97, 73.75, 69.73, 69.52, 39.36, 37.67, 36.80, 36.58, 34.39, 32.09, 30.48, 29.87, 29.82, 29.56, 29.53, 28.08, 26.26, 24.82, 22.86, 22.73, 21.34, 19.73, 14.28. MALDI-ToF (m/z): calc. for C₁₆₈H₂₆₀N₆O₈S₂ [M] 2553.96; observed [M+H]⁺ 2554.97.

OF **15** | Y = 47%; ¹H NMR (400 MHz, CDCl₃) δ 8.50 (d, J = 7.3 Hz, 2H), 8.17 (d, J = 16.2 Hz, 2H), 7.94 (d, J = 7.7 Hz, 2H), 7.89 – 7.64 (m, 14H), 7.54 (d, J = 15.1 Hz, 2H), 7.10 (s, 2H), 4.34 – 4.15 (m, 6H), 4.05 (dt, J = 13.0, 6.6 Hz, 6H), 3.96 – 3.46 (m, 42H), 3.38 (s, 9H), 2.20 – 1.96 (m, 8H), 1.80 (dp, J = 29.5, 6.8 Hz, 6H), 1.51 – 1.23 (m, 58H), 1.19 – 0.93 (m, 28H), 0.88 (t, J = 6.6 Hz, 9H), 0.77 (d, J = 6.5 Hz, 24H), 0.74 – 0.67 (m, 12H), 0.66 – 0.47 (m, 8H). ¹³C NMR (100 MHz, CDCl₃) δ 164.50, 151.64, 140.27, 135.90, 128.38, 126.50, 126.28, 125.65, 121.53, 121.48, 119.76, 118.92, 114.76, 106.10, 73.73, 72.06, 72.03, 70.79, 70.72, 70.61, 69.94, 59.15, 59.11, 39.35, 34.99, 34.36, 32.08, 30.47, 29.80, 29.61, 28.06, 26.25, 24.89, 24.08, 22.84, 22.72, 21.33, 19.72, 14.26. MALDI-ToF (m/z): calc. for C₁₅₉H₂₄₂N₆O₂₀S₂ [M] 2619.75; observed [M+H]⁺ 2620.76.

OF 16 | Y = 25%; ¹H NMR (400 MHz, CDCl₃) δ 8.50 (d, J = 7.4 Hz, 2H), 8.16 (d, J = 16.3 Hz, 2H), 7.94 (d, J = 8.8 Hz, 2H), 7.85 – 7.51 (m, 18H), 4.29 – 4.23 (m, 12H), 3.92 – 3.77 (m, 24H), 3.77 – 3.58 (m, 36H), 3.58 – 3.46 (m, 24H), 3.33 (s, 18H), 2.06 (s, 8H), 1.51 – 1.42 (m, 4H), 1.21 – 0.93 (m, 28H), 0.81 – 0.75 (m, 24H), 0.75 – 0.68 (m, 12H), 0.66 – 0.51 (m, 8H). ¹³C NMR (100 MHz, CDCl₃) δ 165.34, 157.07, 140.26, 135.90, 128.38, 126.07, 125.65, 121.82, 121.63, 119.97, 117.53, 114.27, 107.51, 72.56, 72.07, 70.79, 70.73, 70.64, 69.96, 69.55, 69.43, 59.17, 59.10, 38.19, 34.36, 31.37, 30.46, 29.61, 28.06, 26.48, 24.88, 22.83, 21.33, 19.44, 14.24. MALDI-ToF (m/z): calc. for C₁₅₀H₂₂₄N₆O₃₂S₂ [M] 2685.55; observed [M+H]⁺ 2686.57.

OF 17 | Y = 28%; ¹H NMR (400 MHz, CDCl₃) δ 8.34 (d, J = 16.2 Hz, 2H), 7.90 – 7.63 (m, 14H), 7.60 – 7.51 (m, 2H), 7.10 (s, 4H), 4.09 – 4.01 (m, 12H), 2.19 – 1.97 (m, 8H), 1.81 (dt, J = 30.1, 7.4 Hz, 12H), 1.50 – 1.27 (m, 112H), 1.21 – 0.96 (m, 28H), 0.89 (t, J = 6.6 Hz, 18H), 0.77 (dd, J = 6.6, 1.8 Hz, 24H), 0.74 – 0.71 (m, 12H), 0.69 – 0.51 (m, 8H). ¹³C NMR (100 MHz, CDCl₃) δ 167.86, 153.44, 153.01, 151.66, 144.92, 135.91, 128.39, 127.41, 125.66, 119.19, 118.75, 118.61, 114.75, 110.16, 106.10, 73.88, 69.52, 39.36, 36.83, 34.38, 32.09, 30.48, 29.90, 29.85, 29.81, 29.77, 29.67, 29.52, 29.35, 28.08, 26.26, 26.20, 26.14, 22.85, 22.73, 21.34, 19.74, 14.27. MALDI-ToF (m/z): calc. for C₁₆₆H₂₅₈N₆O₈S₂ [M] 2527.94; observed [M+H]⁺ 2528.97.

OF 18 | Y = 45%; ¹H NMR (400 MHz, CDCl₃) δ 8.34 (d, J = 16.8 Hz, 2H), 7.96 – 7.61 (m, 18H), 7.11 (s, 2H), 4.28 (s, 6H), 4.09 – 4.02 (m, 6H), 3.62 (d, J = 51.0 Hz, 42H), 3.37 (s, 9H), 2.26 – 1.96 (m, 8H), 1.86 – 1.75 (m, 6H), 1.53 – 1.27 (m, 58H), 1.22 – 0.94 (m, 28H), 0.89 (t, J = 6.6 Hz, 9H), 0.77 (dd, J = 6.6, 1.7 Hz, 24H), 0.74 – 0.70 (m, 12H), 0.68 – 0.47 (m, 8H). ¹³C NMR (100 MHz, CDCl₃) δ 166.91, 153.19, 140.15, 135.91, 127.16, 126.39, 125.66, 119.79, 118.88, 118.24, 117.98, 114.36, 110.08, 106.11, 72.06, 70.83, 70.75, 70.72, 70.64, 69.96, 69.72, 59.13, 58.72, 39.36, 36.89, 34.38, 32.09, 30.47, 29.90, 29.86, 29.81, 29.75, 29.62, 29.56, 29.53, 28.07, 26.26, 22.85, 22.73, 19.63, 14.28. MALDI-ToF (m/z): calc. for C₁₅₇H₂₄₀N₆O₂₀S₂ [M] 2593.74; observed [M+H]⁺ 2594.76.

OF 19 | Y = 25%; ¹H NMR (400 MHz, CDCl₃) δ 8.34 (d, J = 15.3 Hz, 2H), 7.97 – 7.54 (m, 20H), 4.43 – 4.14 (m, 12H), 3.82 – 3.54 (m, 84H), 3.36 (s, 18H), 2.28 – 1.93 (m, 8H), 1.45 – 1.40 (m, 4H), 1.17 – 0.97 (m, 28H), 0.84 – 0.76 (m, 24H), 0.74 – 0.71 (m, 12H), 0.69 – 0.51 (m, 8H). ¹³C NMR (100 MHz, CDCl₃) δ 167.96, 151.65, 140.17, 135.91, 128.39, 125.72, 125.66, 119.90, 118.48, 118.05, 117.44, 114.28, 110.50, 106.55, 73.37, 72.10, 70.85, 70.76, 70.72, 70.64, 69.97, 69.73, 59.52, 59.17, 39.36, 36.89, 34.38, 32.27, 30.66, 30.40, 30.04, 29.62, 26.39, 21.41, 21.33, 19.64, 14.35. MALDI-ToF (m/z): calc. for C₁₄₈H₂₂₂N₆O₃₂S₂ [M] 2659.54; observed [M+H]⁺ 2660.56.

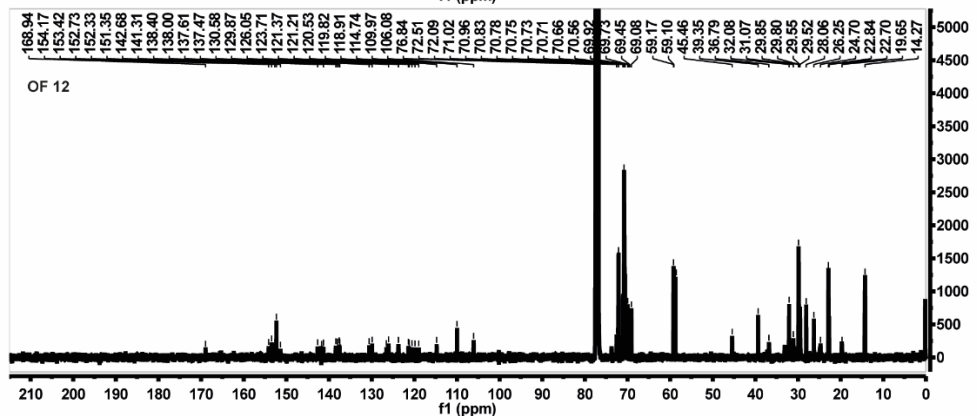
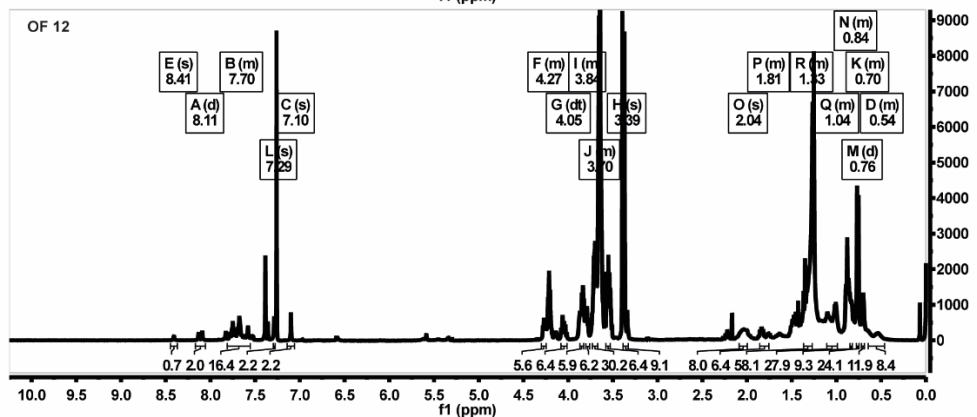
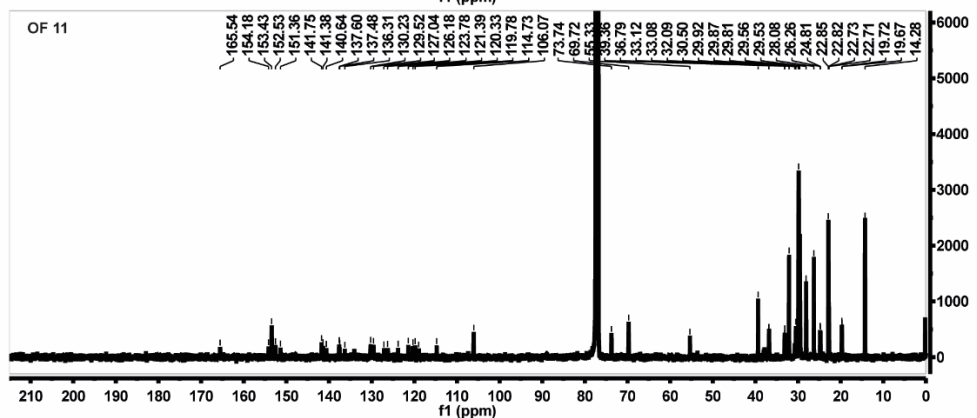
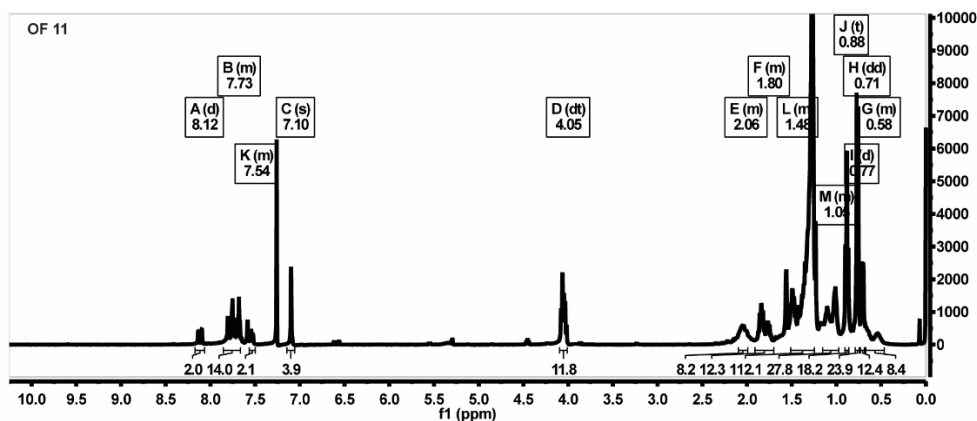
General procedure for the synthesis of OF 20 – 22 | The pH of a solution of **8** (59.8 mg, 54.0 μmol) in dry methylene chloride (1.0 ml) was adjusted to 8 using a few drops of triethylamine. Methyl-PEG₄-NHS (36.0 mg, 108.0 μmol) and lauric acid-NHS (32.1 mg, 108.0 μmol) dissolved in dry methylene chloride (0.5 mL) were added dropwise and the reaction continued overnight at room temperature under an inert atmosphere. The crude reaction mixture was purified by column chromatography (silica, methylene chloride + 1% methanol) to yield red solids.

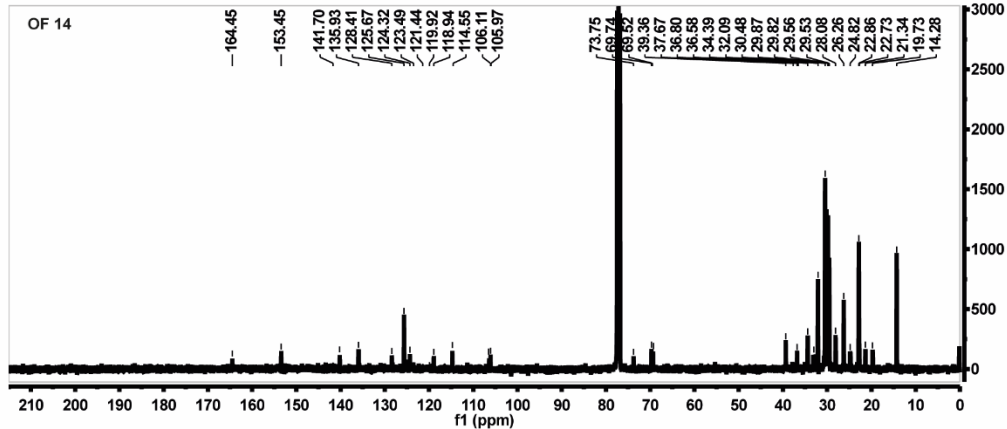
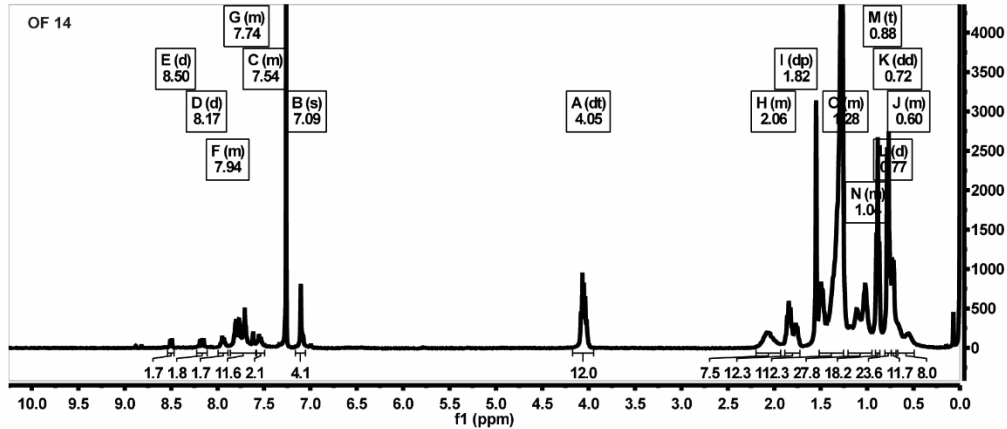
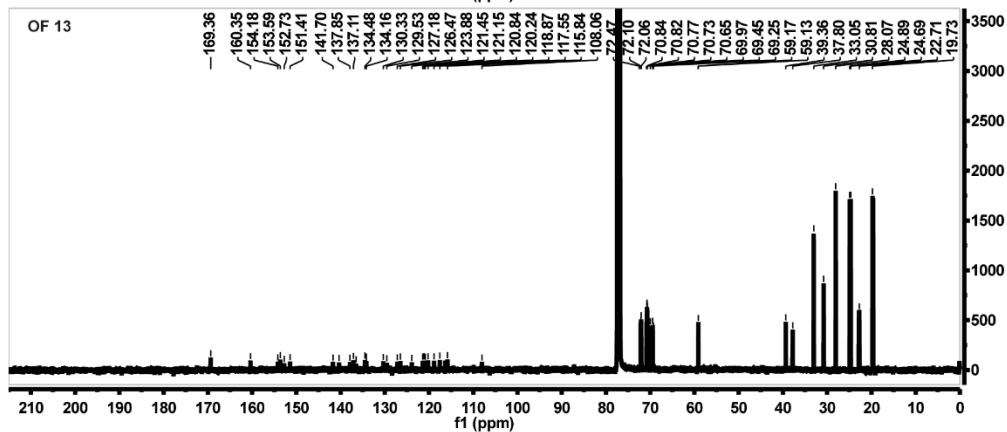
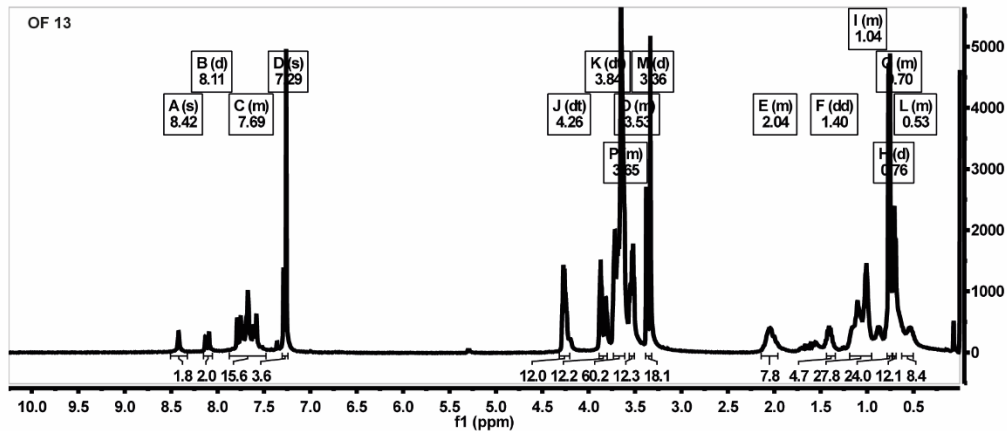
OF **20** | Y = 22%; ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, *J* = 16.2 Hz, 2H), 7.77 – 7.54 (m, 14H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.19 (s, 2H), 2.39 (t, *J* = 7.6 Hz, 4H), 2.14 – 1.90 (m, 8H), 1.84 – 1.69 (m, 4H), 1.47 – 1.23 (m, 28H), 1.19 – 0.96 (m, 28H), 0.93 – 0.83 (m, 14H), 0.80 – 0.75 (m, 24H), 0.73 – 0.67 (m, 12H), 0.65 – 0.46 (m, 8H). ¹³C NMR (100 MHz, CDCl₃) δ 169.75, 154.17, 152.42, 151.28, 141.75, 137.59, 136.41, 134.88, 134.04, 128.49, 126.95, 126.16, 122.01, 121.33, 120.30, 119.69, 118.48, 114.31, 55.26, 39.36, 36.77, 33.05, 32.07, 30.67, 29.86, 29.80, 29.78, 29.66, 29.58, 29.50, 28.08, 25.72, 24.80, 24.71, 22.85, 22.82, 22.71, 19.67, 14.28. MALDI-ToF (m/z): calc. for C₁₀₀H₁₅₀N₄O₂S [M] 1472.39; observed [M]⁺ 1472.15.

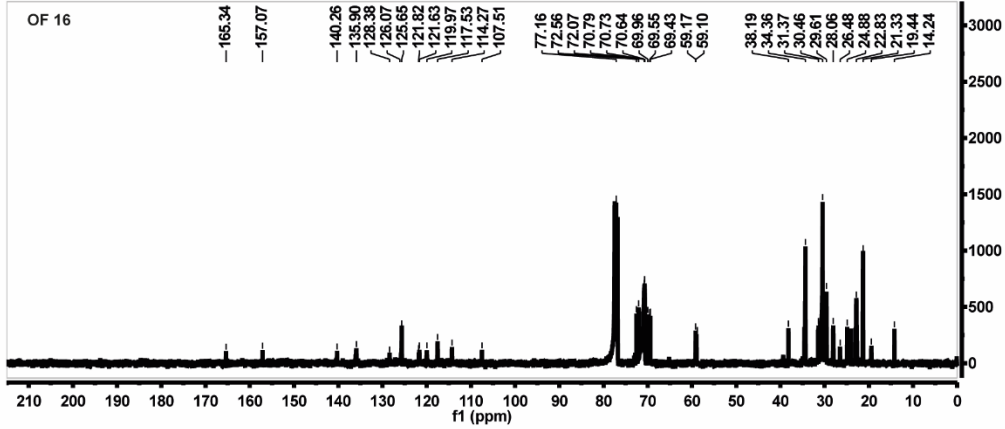
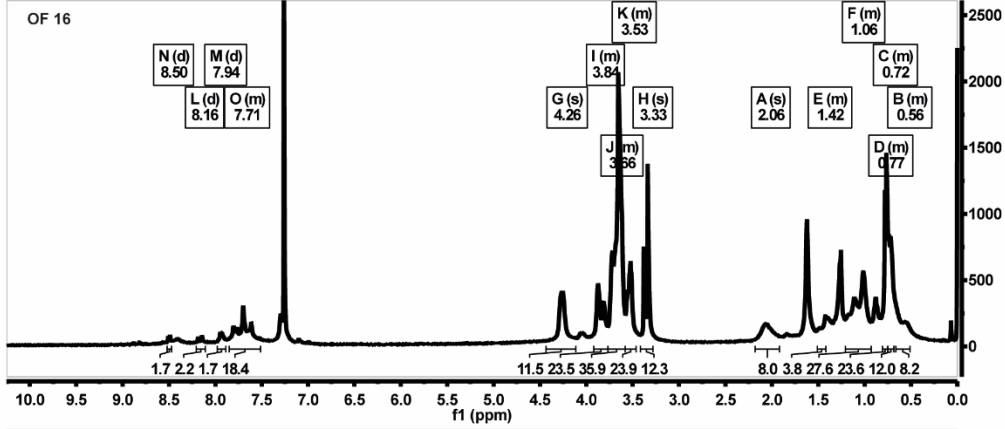
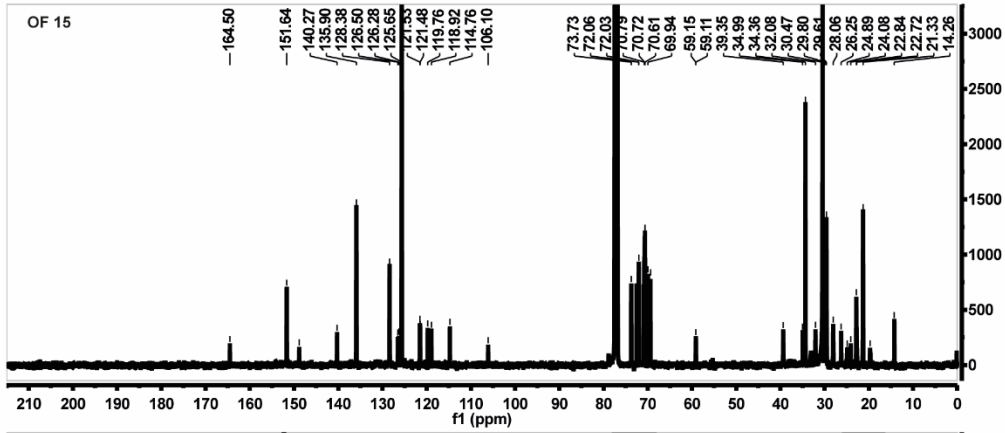
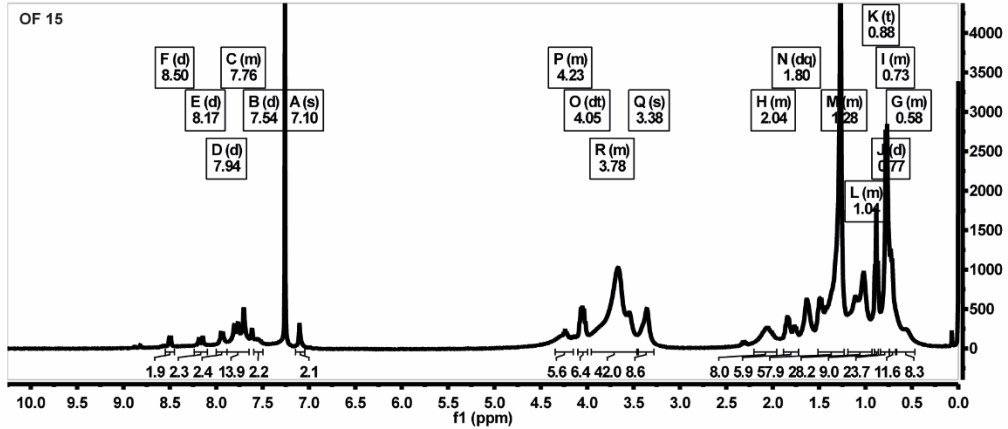
OF **21** | Y = 47%; ¹H NMR (400 MHz, CDCl₃) δ 8.72 (s, 1H), 8.10 (d, *J* = 16.2 Hz, 2H), 7.90 – 7.54 (m, 16H), 7.48 (s, 1H), 3.88 (t, *J* = 5.6 Hz, 2H), 3.75 – 3.62 (m, 10H), 3.56 – 3.53 (m, 2H), 3.37 (s, 3H), 2.69 (t, *J* = 5.6 Hz, 2H), 2.11 – 1.94 (m, 8H), 1.44 – 1.25 (m, 24H), 1.19 – 0.95 (m, 28H), 0.89 – 0.87 (m, 3H), 0.77 (dd, *J* = 6.6, 2.6 Hz, 24H), 0.72 – 0.67 (m, 12H), 0.64 – 0.43 (m, 8H). ¹³C NMR (100 MHz, CDCl₃) δ 169.92, 154.17, 152.29, 151.33, 141.59, 138.12, 136.84, 136.04, 134.10, 129.47, 126.94, 126.13, 123.58, 121.34, 120.06, 119.57, 118.75, 114.60, 72.06, 70.79, 70.67, 70.55, 70.48, 67.37, 59.15, 55.25, 55.22, 39.35, 38.30, 37.95, 37.81, 36.82, 36.77, 33.14, 33.05, 32.06, 30.70, 29.79, 29.76, 29.65, 29.57, 29.51, 29.49, 28.06, 24.88, 24.79, 24.69, 22.83, 22.81, 22.72, 22.70, 19.69, 19.61, 14.26. MALDI-ToF (m/z): calc. for C₉₈H₁₄₆N₄O₆S [M] 1508.33; observed [M]⁺ 1508.08.

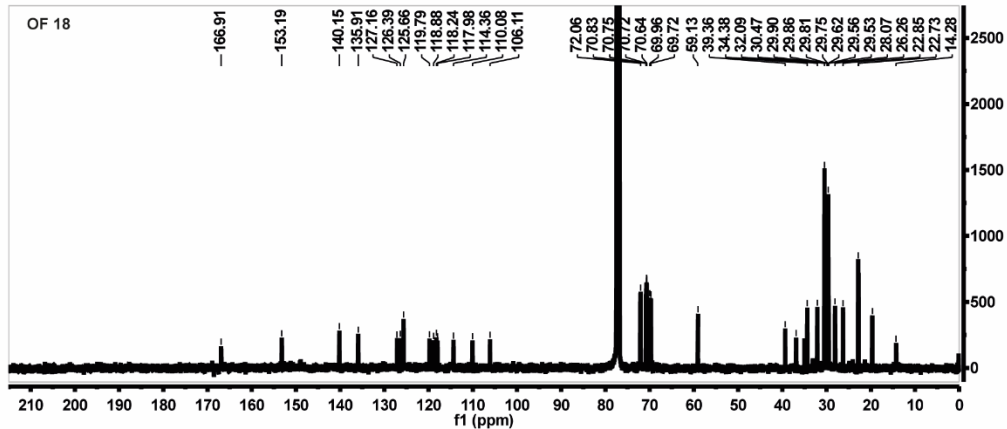
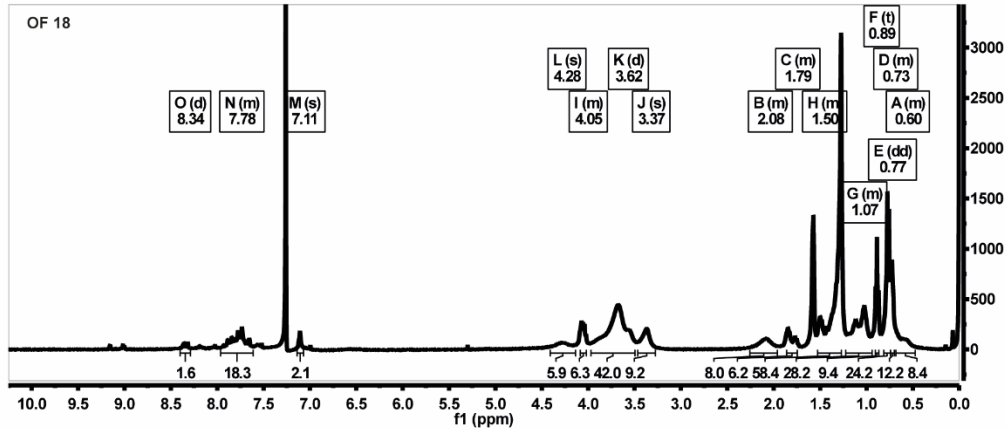
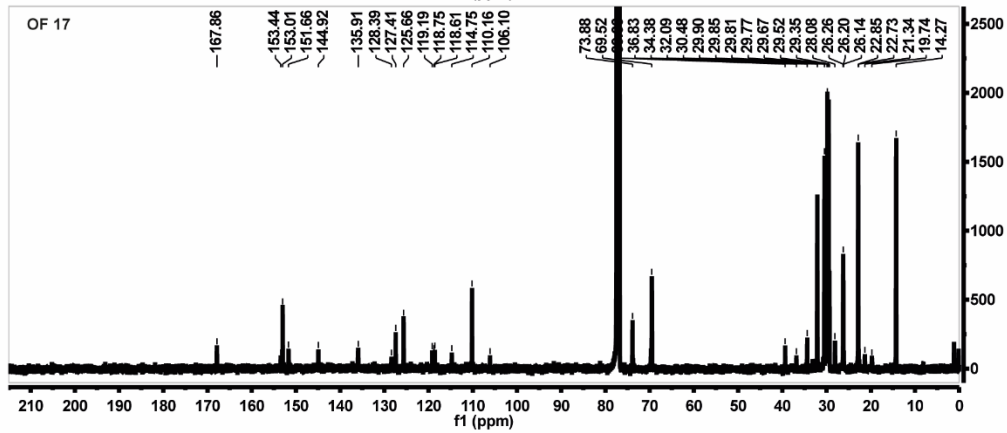
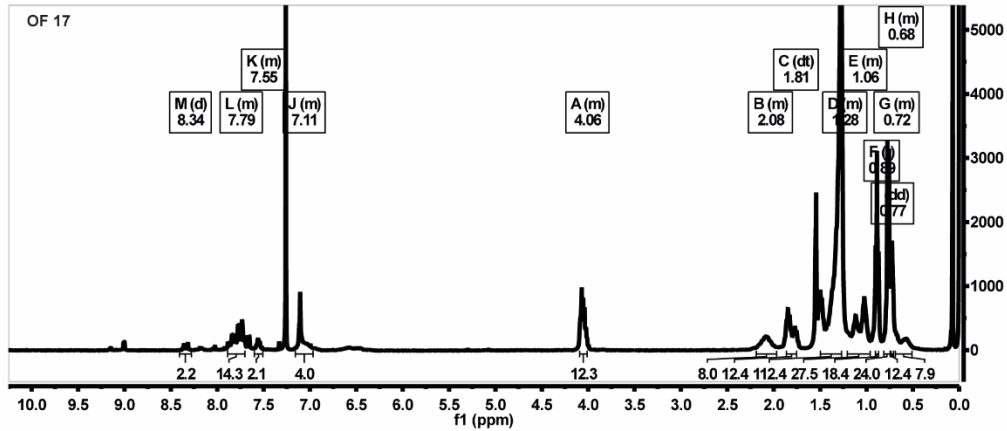
OF **22** | Y = 19%; ¹H NMR (400 MHz, CDCl₃) δ 8.73 (s, 2H), 8.09 (d, *J* = 16.2 Hz, 2H), 7.82 – 7.54 (m, 14H), 7.46 – 7.36 (m, 2H), 3.87 (t, *J* = 5.7 Hz, 4H), 3.74 – 3.62 (m, 20H), 3.56 – 3.52 (m, 4H), 3.37 (s, 6H), 2.69 (t, *J* = 5.6 Hz, 4H), 2.11 – 1.91 (m, 8H), 1.47 – 1.35 (m, 4H), 1.18 – 0.93 (m, 25H), 0.89 – 0.84 (m, 4H), 0.77 (dd, *J* = 6.6, 2.6 Hz, 24H), 0.72 – 0.67 (m, 12H), 0.63 – 0.42 (m, 8H). ¹³C NMR (100 MHz, CDCl₃) δ 169.94, 154.14, 152.26, 151.30, 141.56, 138.09, 136.82, 136.02, 134.04, 129.47, 126.94, 126.09, 123.56, 121.31, 120.04, 119.56, 118.72, 114.56, 72.03, 70.76, 70.64, 70.53, 70.45, 67.36, 59.14, 55.20, 39.33, 38.27, 38.01, 37.74, 36.79, 33.12, 33.03, 30.75, 28.04, 24.87, 24.67, 22.82, 22.80, 22.70, 22.68, 19.67, 19.59, 14.25. MALDI-ToF (m/z): calc. for C₉₆H₁₄₂N₄O₁₀S [M] 1544.27; observed [M]⁺ 1544.03.

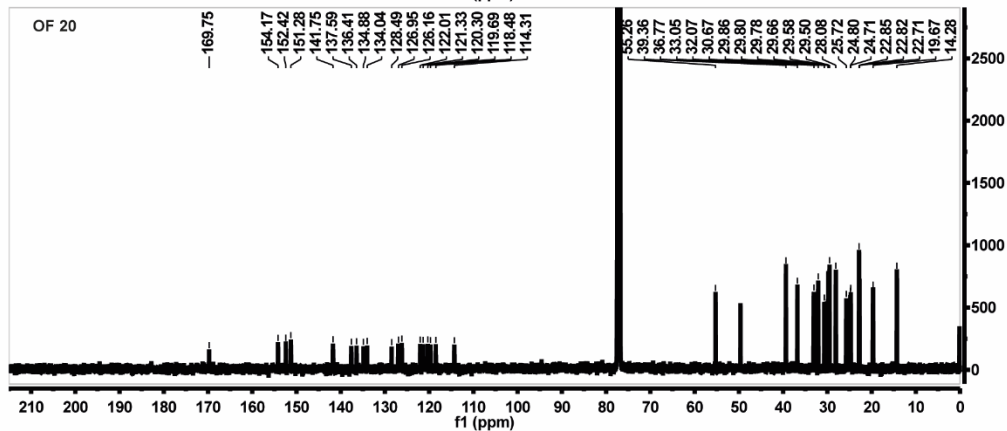
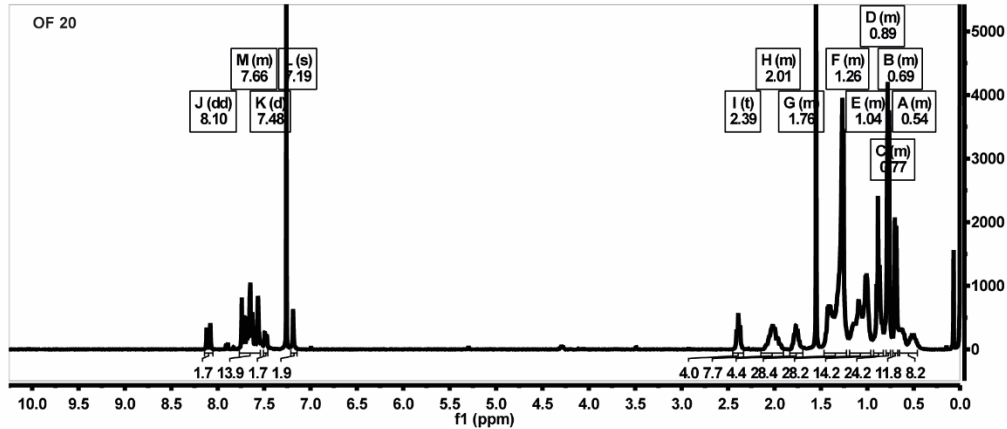
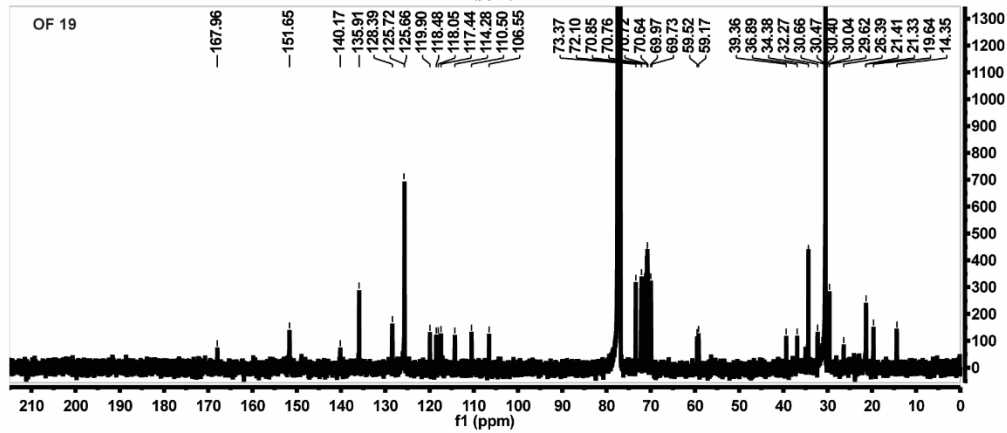
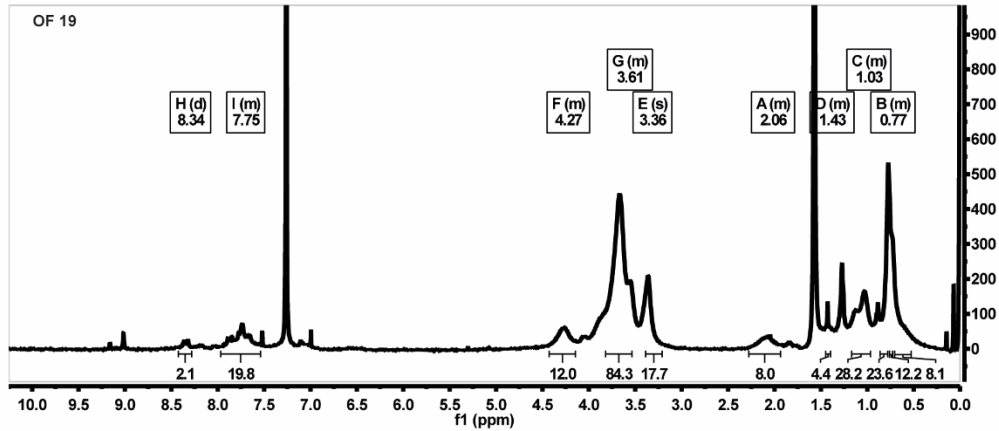
¹H- and ¹³C-NMR spectra

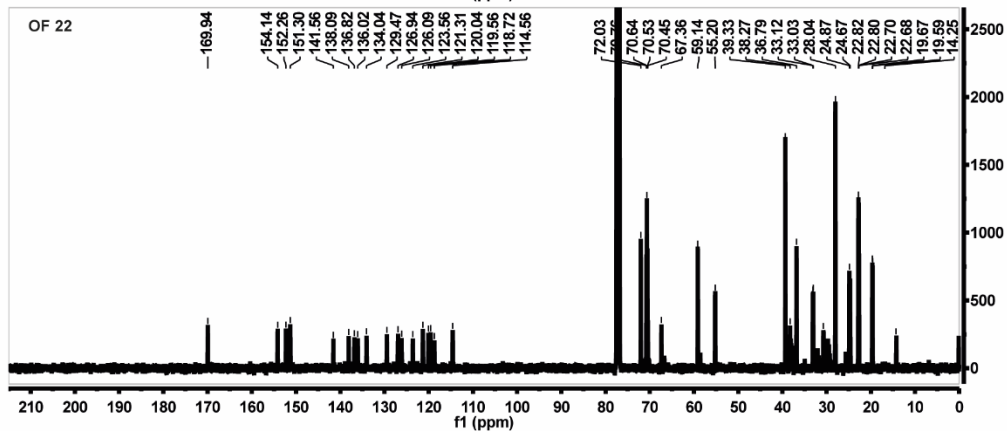
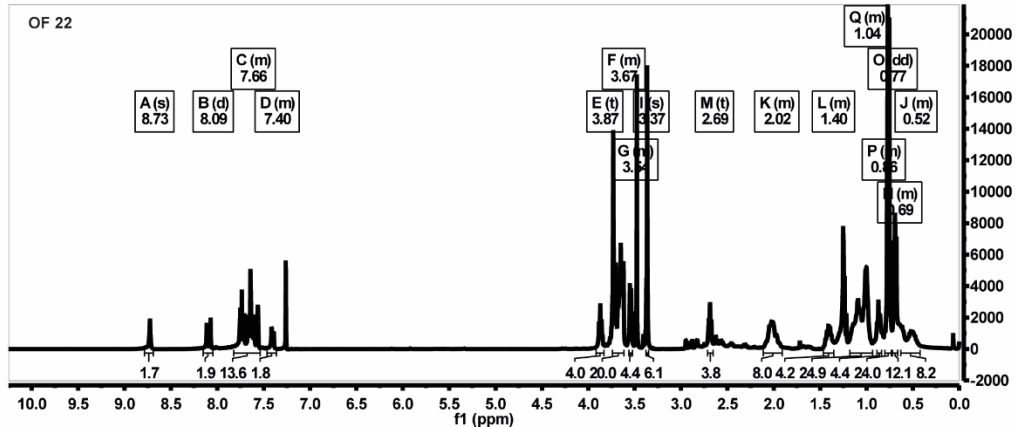
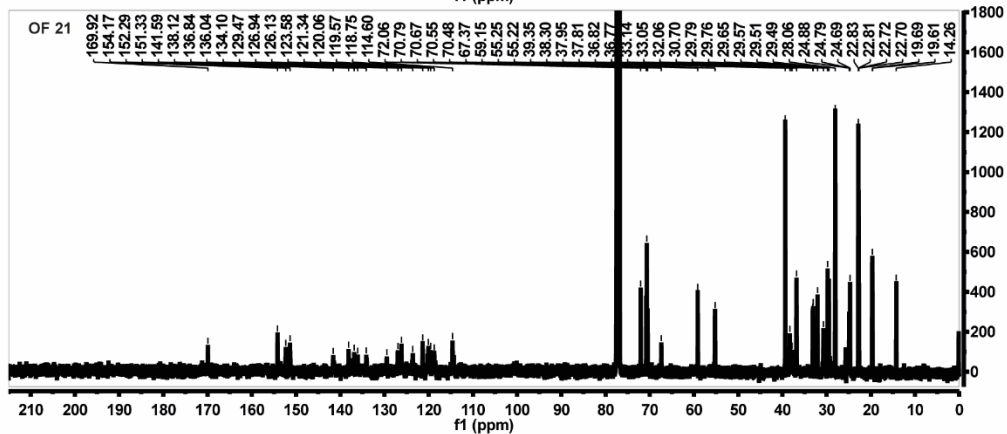
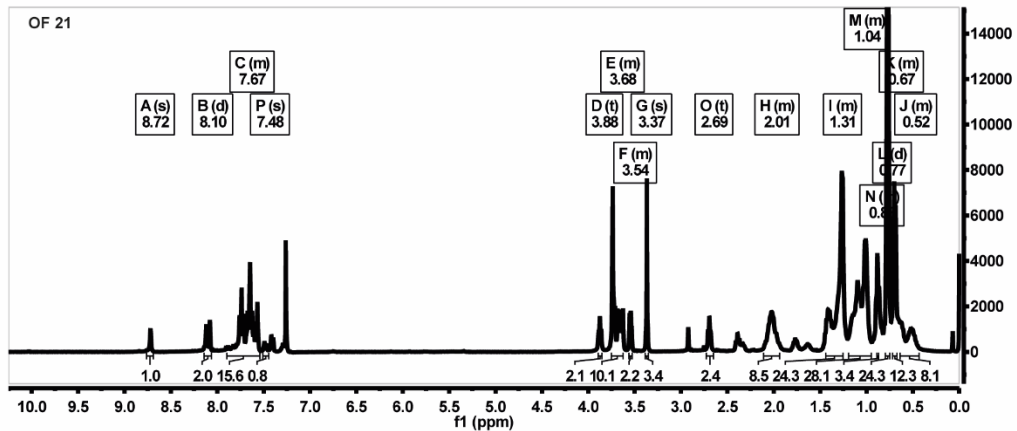












Supplementary figures

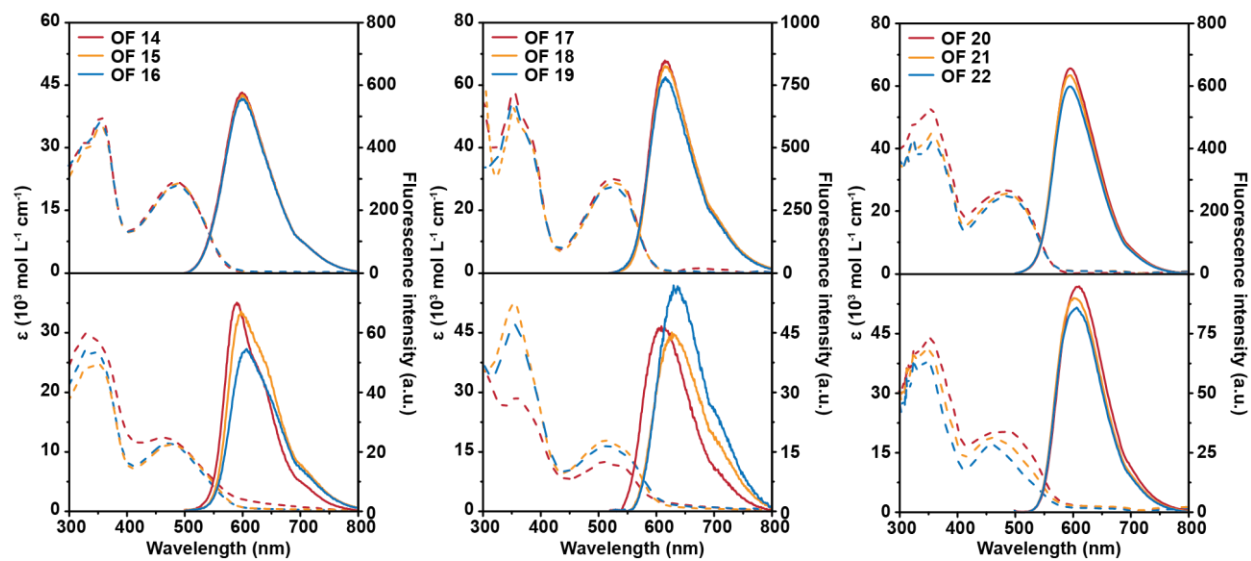


Figure S1 | Optical properties of core-extended fluorene co-oligomers. UV-Vis absorption spectra (dashed lines) and corresponding fluorescence spectra (solid lines) in THF (top) and water (bottom) of OFs **14** – **22** ($c = 1.5 \times 10^{-5} \text{ M}$, $\lambda_{\text{exc}} = 480 \text{ nm}$).

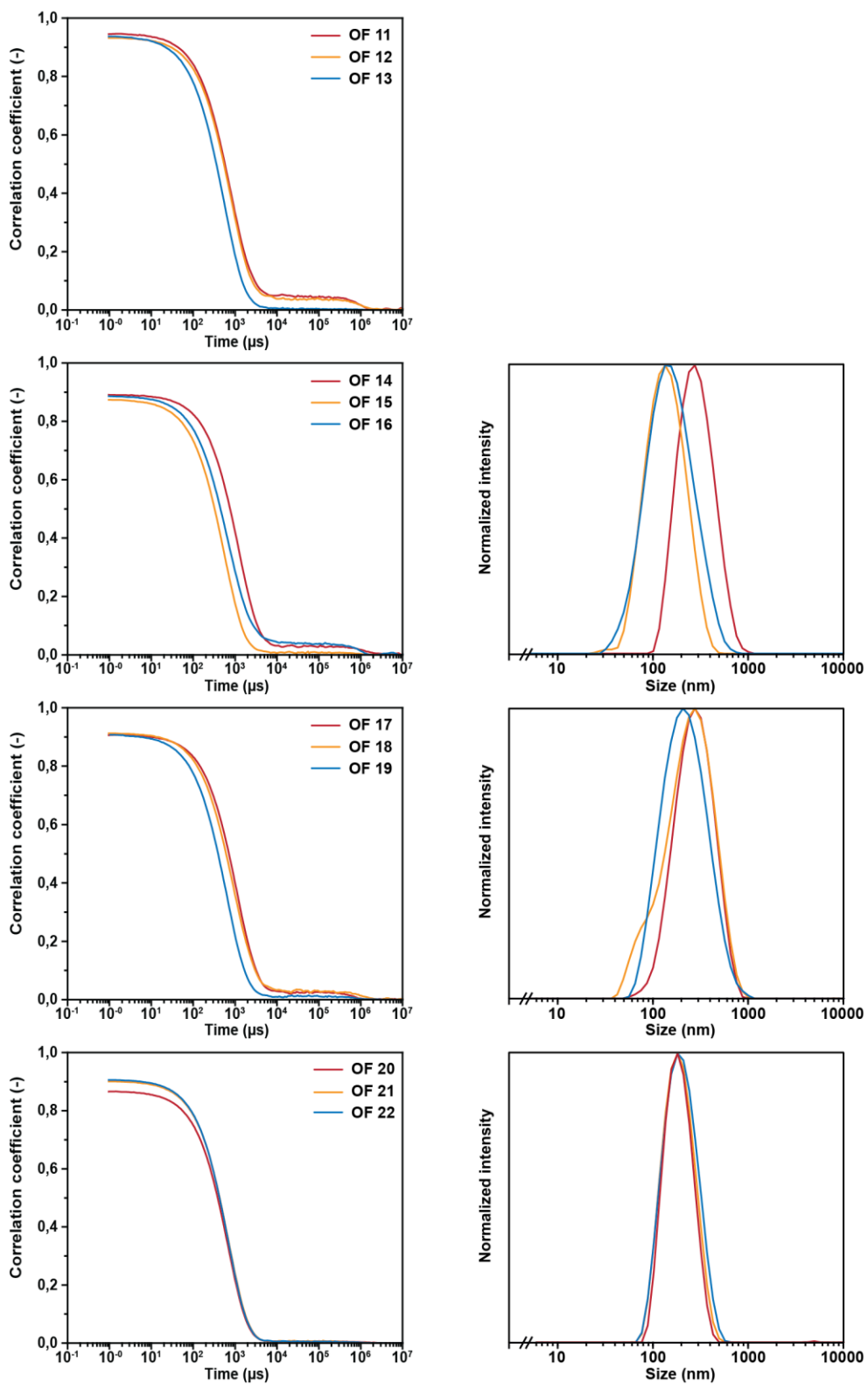


Figure S2 | Hydrodynamic diameter of unimolecular assemblies. Dynamic light scattering correlogram (left) and normalized fits of the scattering intensity distribution (right) indicating diameters of unimolecular nanoparticles self-assembled from OF **11 – 22** in water ($c = 1.5 \times 10^{-5}$ M).

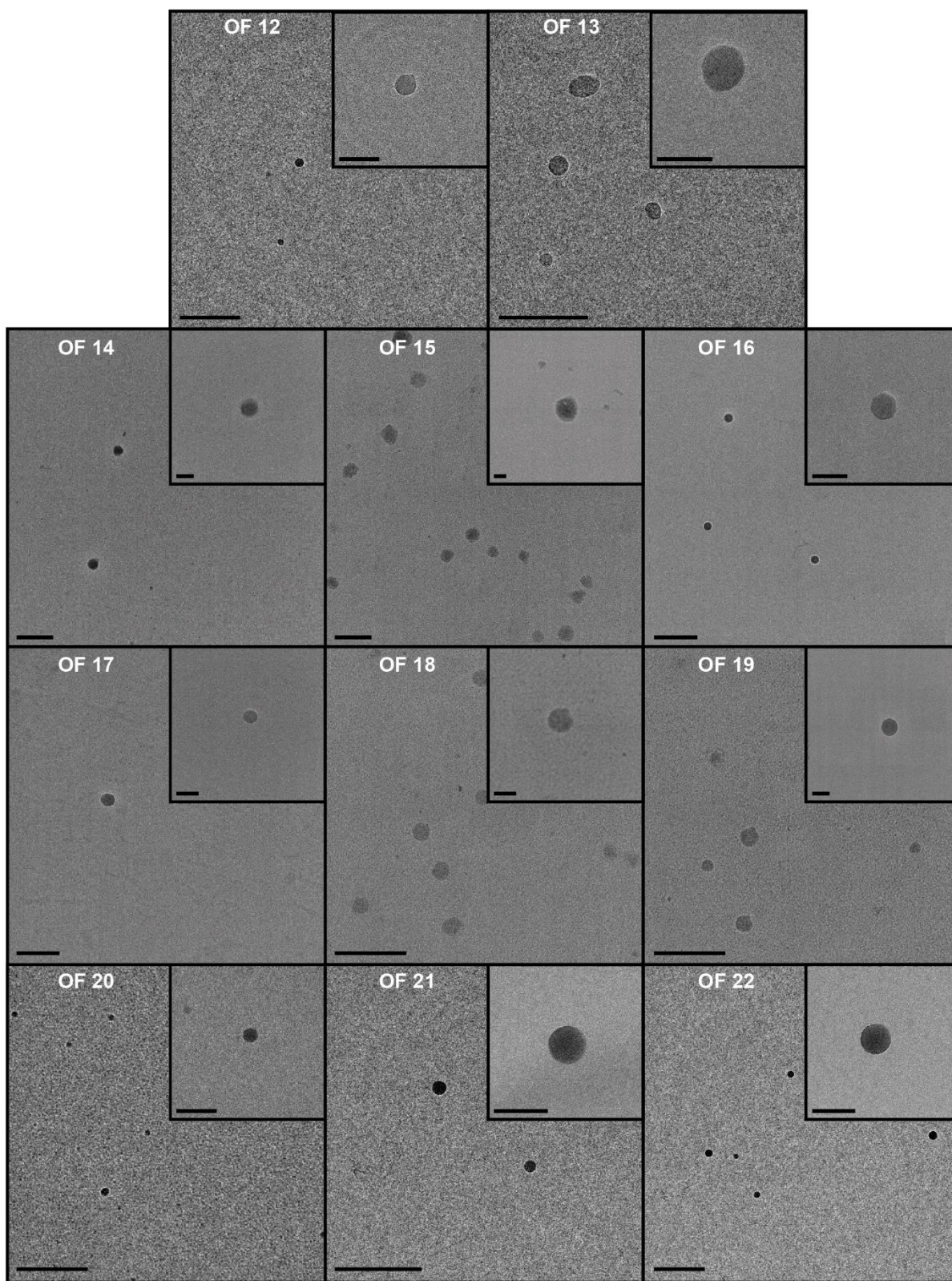


Figure S3 | Electron microscopy images of unimolecular assemblies. Transmission electron microscopy images of unimolecular nanoparticles self-assembled from OF 11 – 22 in water ($c = 1.5 \times 10^{-5}$ M, scale bar: 0.5 μ m). Insets: magnified TEM image of the same sample (scale bar: 200 nm).