Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Conjugated Molecules for Colourimetric and Fluorimetric Sensing of Sodium and Potassium

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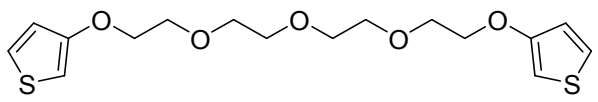
Materials

All reagents were purchased from Sigma Aldrich, Tokyo Chemicals Industry and Fluorochem, solvents were purchased from VWR and dry solvents were purchased from Acros Organics and used without further purification. Deuterated 1,1,2,2-tetrachloroethane and chloroform were purchased from Cambridge Isotopes.

Characterisation

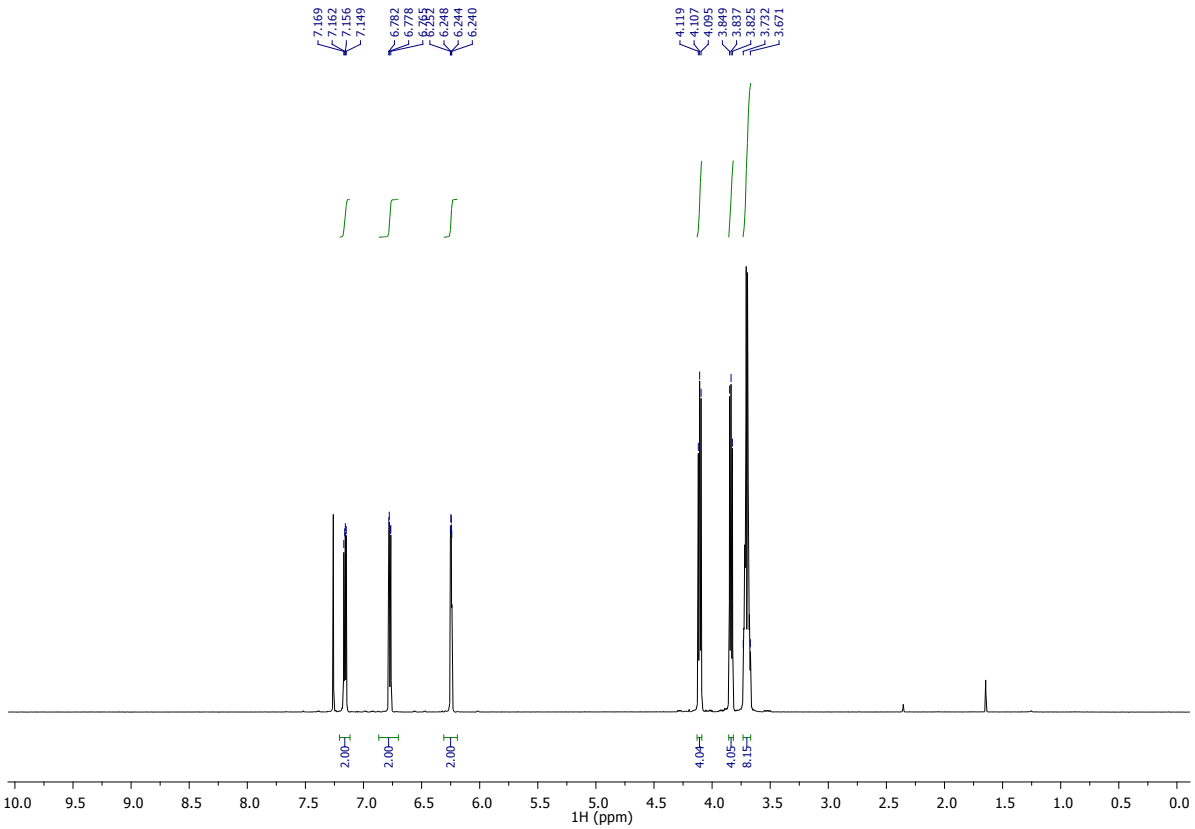
^{1}H and ^{13}C NMR spectroscopy was carried out on a Bruker AV400 or Bruker AVIII400 spectrometer or Bruker AV600 spectrometer. UV-Vis spectroscopy was carried out using a Shimadzu UV3600 UV-Vis-nIR spectrometer. Fluorescence measurements were carried out using an Agilent Cary Eclipse fluorimeter; all fluorescence data were recorded at room temperature with 5 nm excitation and emission slit widths with excitation wavelength set at the isosbestic point of the UV-absorbance spectrum. GCMS was carried out using an Agilent 6890N GC/5973 Mass selective detector. LCMS was carried out using an Agilent 1100 series LCMS. The Bruker Autoflex Maldi-TOF has a resolution of 10,000 – 22,000 FWHM in reflection mode for the analysis of small molecules, and a mass accuracy of 2 ppm with internal calibration. The software used for the analysis and data processing is Flex Analysis 3.0. Samples were acquired in reflection positive mode using a range m/z 100 to m/z 800. Exact molecular weight of the compound was obtained using an Acquity H Class UPLC instrument interfacing though an electrospray ionization (ESI) LockSpray source to a High Definition Mass Spectrometer Synapt G2Si, both from Waters Corporation (Milford, MA, USA). Data were acquired and analysed using MassLynx v4.1 (Waters, MA, USA).

Synthesis



1. 3,3'-((((Oxybis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl))bis(oxy))dithiophene

In a dry degassed RBF was added toluene (200 ml), 3-methoxythiophene (5.6 g, 49.0 mmol, 2 equivalents) and 2,2'-((oxybis(ethane-2,1-diyl))bis(oxy))bis(ethan-1-ol) (4.76g, 24.5 mmol, 1 equivalent) and *p*-toluene sulfonic acid monohydrate (466 mg, 2.4 mmol, 0.1 equivalent). The reaction was fitted with fractional distillation apparatus and heated to vigorous reflux to azeotropically distil off by products. A further portion of dry toluene (100 ml) was added after 4 hours and the reaction was refluxed for a total of 6 hours after which a dark brown solution was observed. The reaction was cooled to room temperature and quenched with deionised water (200 ml) and extracted with ethyl acetate (3 x 100 ml). The combine organic phases were washed with 0.1 M NaOH (50 ml) and brine (50 ml) and dried over $MgSO_4$ and solvent removed in vacuo. The resulting dark brown residue was purified by column chromatography eluting with 4:1:0.03 toluene:EtOAc:triethylamine affording the title compound as a brown oil. Yield 7.21 g, 83 % HRMS (ESI/TOF) m/z+H^+ Calculated 359.0987 found 359.0895, ^{1}H (400 MHz, $CDCl_3$) δ 7.16 (dd, 2H, J_1 = 2.8, J_2 = 5.6 Hz), 6.77 (dd, 2H, J_1 = 1.4 J_2 = 5.2 Hz), 6.25 (dd, 2H, J_1 = 1.6, J_2 = 3.2 Hz), 4.12-4.10 (m, 4H), 3.84 (m, 4H), 3.70 (m ,8H), ^{13}C{^{1}H} (101 MHz, $CDCl_3$) δ 157.7, 124. 8, 119.7, 97.6, 70.9, 70.8, 69.8, 69.7.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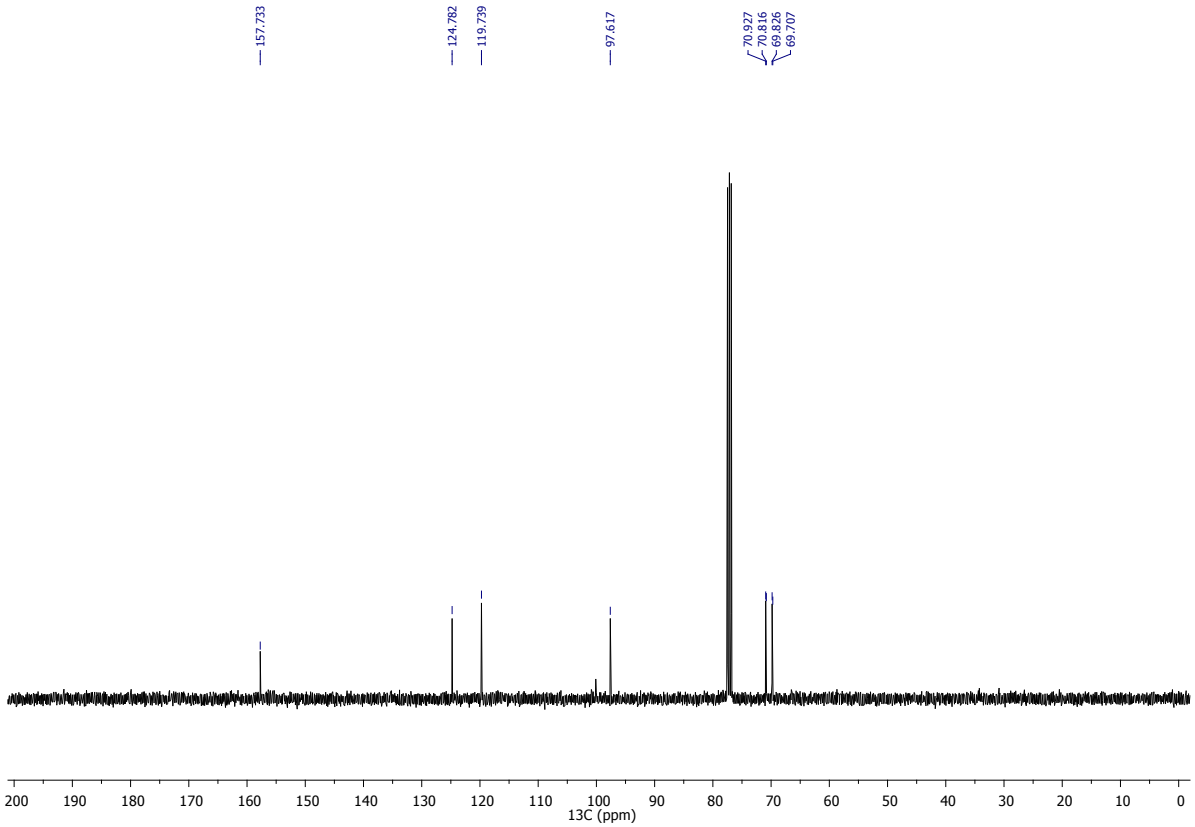
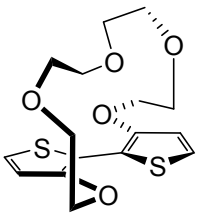
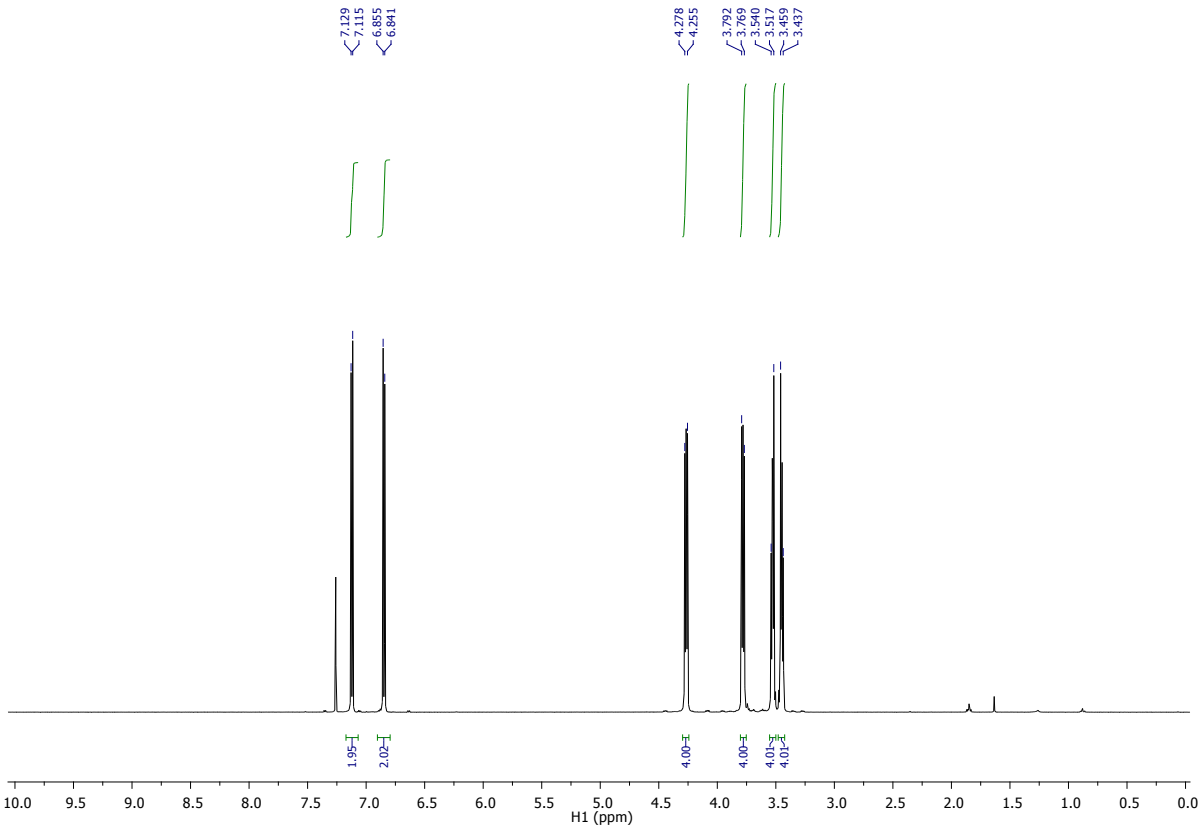
7.156
7.149
6.782
6.778
6.252
6.248
6.244
6.240
4.119
4.107
4.095
3.849
3.837
3.825
3.732
3.671
2.00
2.00
2.00
4.04
4.05
8.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
1H (ppm)


157.733
124.782
119.739
97.617
70.927
70.816
69.826
69.707
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
13C (ppm)



2. 5,6,8,9,11,12,14,15-Octahydrodithieno[3,2-*n*:2',3'-*p*][1,4,7,10,13]pentaoxacycloheptadecine

In a dry degassed RBF was added 3,3'-((((oxybis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl))bis(oxy))dithiophene (7.16 g, 20 mmol, 1 equivalent) and dry dimethoxyethane, (100 ml) and cooled to -78 °C and freshly titrated n-butyl lithium (2.13 M in hexane, 19.6 ml, 42 mmol 2.1 equivalents) was added dropwise. The solution was warmed to -20 ^{o}C and stirred for1 h after which the solution was cooled to -78 °C again. In a second dry RBF was added $CuCl_2$ (5.62 g, 42 mmol, 2.1 equivalents) and dry dimethoxyethane (100 ml) and cooled to 0. The lithiated 3,3'-((((oxybis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl))bis(oxy))dithiophene solution was added dropwise to the copper chloride suspension at 0 °C via cannula and stirred while warming to room for 48 h after which the solution appeared dark red. The solution was filtered through celite, and the celite pad was washed thoroughly with ethyl acetate. The organic washings were extracted with deionised water (3 x 200 ml). The combined organic phase was dried over $MgSO_4$ and concentrated in vacuo. The resulting black oil was subject to a short silica plug which was eluted with ethyl acetate thoroughly which was concentrated and purified by column chromatography eluting with 2:1 toluene:ethyl acetate. The off brown clear oil was recrystallised from 5:1 diethyl ether:THF affording the title compound as pale yellow crystals. Yield 1.8 g, 26 %, mp 106 °C. HRMS (ESI/TOF) m/z+H^+ Calculated for $C_{16}H_{19}O_5S_2Na$ 379.0650 Found 379.0678 ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, 2H, *J* = 5.6 Hz), 6.85 (d, 2H, *J* = 5.6 Hz), 4.27-4.25 (m 4H), 3.79-3.77 (m, 4H), 3.54-3.51 (m, 4H), 3.48-3.44 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.2, 122.98, 118.1, 113.7, 71.65, 71.1, 70.7, 70.6.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6.855
6.841
4.278
4.255
3.792
3.769
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3.459
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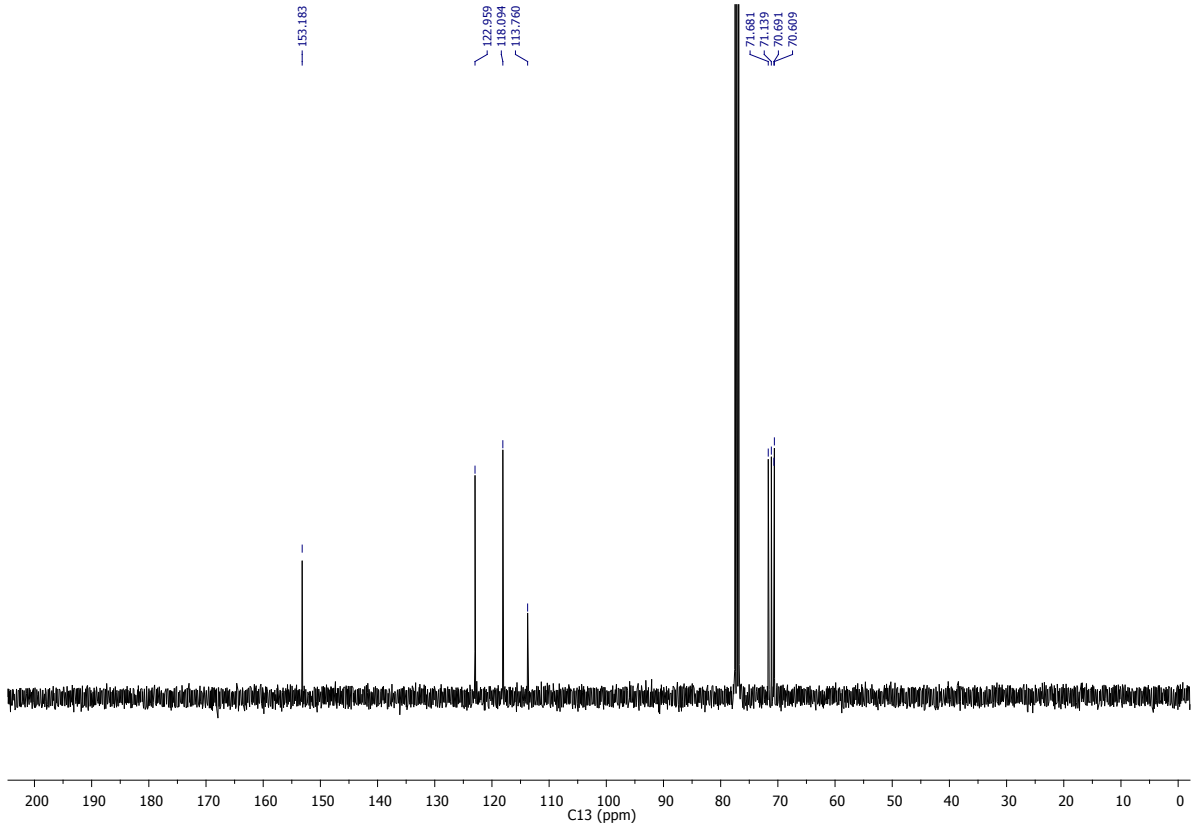
2.02
4.00
4.00
4.01
4.01
H1 (ppm)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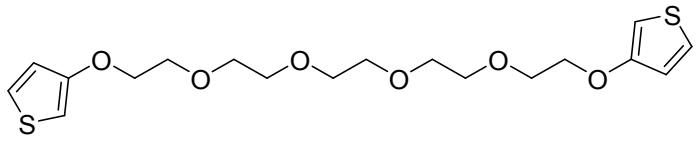
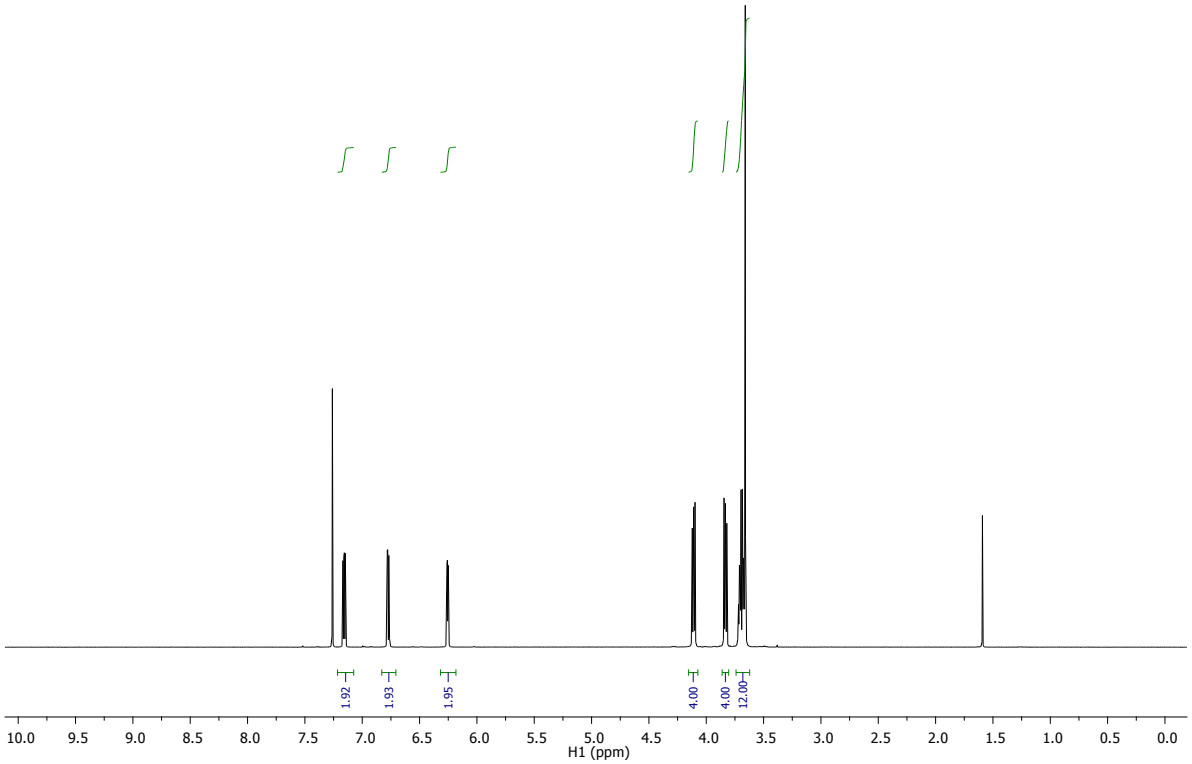
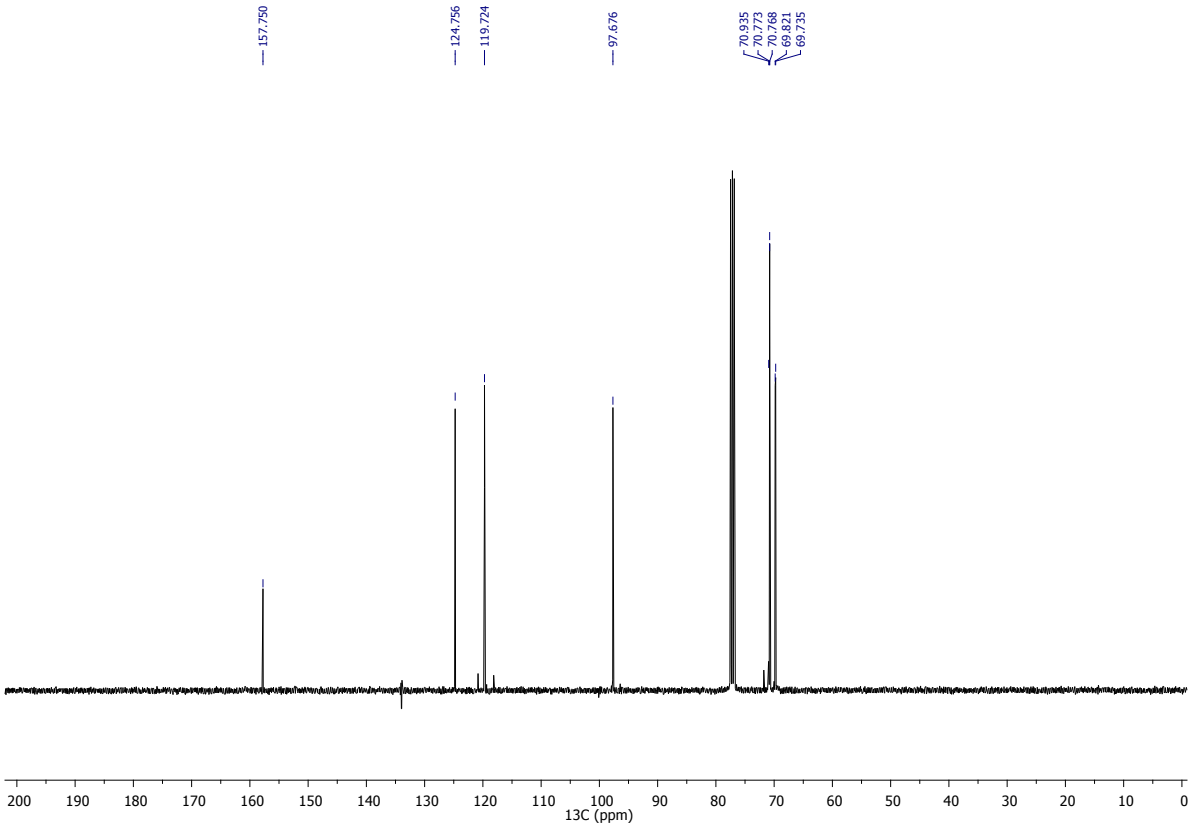
71.681
71.139
70.691
70.609
C13 (ppm)



3. 5,6,8,9,11,12,14,15,17,18-Decahydrodithieno[3,2-*q*:2',3'-*s*][1,4,7,10,13,16]hexaoxacycloicosine

In a dry degassed RBF was added 1,14-bis(thiophen-3-yloxy)-3,6,9,12-tetraoxatetradecane toluene (200 ml) (9.0 g, 37.7 mmol, 1 equivalent), 3-methoxythiophene (8.61 g, 75.5 mmol, 2 equivalents) and *p*-toluene sulfonic acid monohydrate (703 mg, 3.7 mmol, 0.1 equivalent). The reaction was fitted with fractional distillation apparatus and heated to vigorous reflux to azeotropically distil off by-products. A further portion of dry toluene (100 ml) was added after 4 hours and the reaction was refluxed for a total of 6 hours. The reaction was cooled to room temperature and quenched with deionised water (200 ml) and extracted with ethyl acetate (3 x 100 ml). The combine organic phases were washed with 0.1 M NaOH (50 ml) and brine (50 ml) and dried over $MgSO_4$ and solvent removed in vacuo. The resulting dark brown residue was purified by column chromatography eluting with 19:1 dichloromethane:acetone affording the title compound as a brown oil. Yield 9.93 g, 65%. HRMS (ESI/TOF) m/z+H^+ Calculated for 403.1249 found 403.1294, ^{1}H (400 MHz, $CDCl_3$) δ 7.16 (dd, 2H, J_1 = 3.2 Hz, J_2 = 5.2 Hz), 6.78 (dd, 2H, J_1 = 1.2 Hz, J_2 = 5.2 Hz), 6.26 (dd, 2H, J_1 = 1.6 Hz, J_2 = 3.2 Hz) 4.12-4.10 (m, 4H), 3.84-3.82 (m, 4H), 3.72-3.66 (m, 12H). ^{13}C{^{1}H} (101 MHz, $CDCl_3$) δ 157.8, 124.8, 119.7, 97.7, 70.9, 70.8, 69.8, 69.7


1.92
1.93
1.95
4.00
4.00
12.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
H1 (ppm)


157.750
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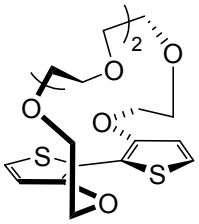
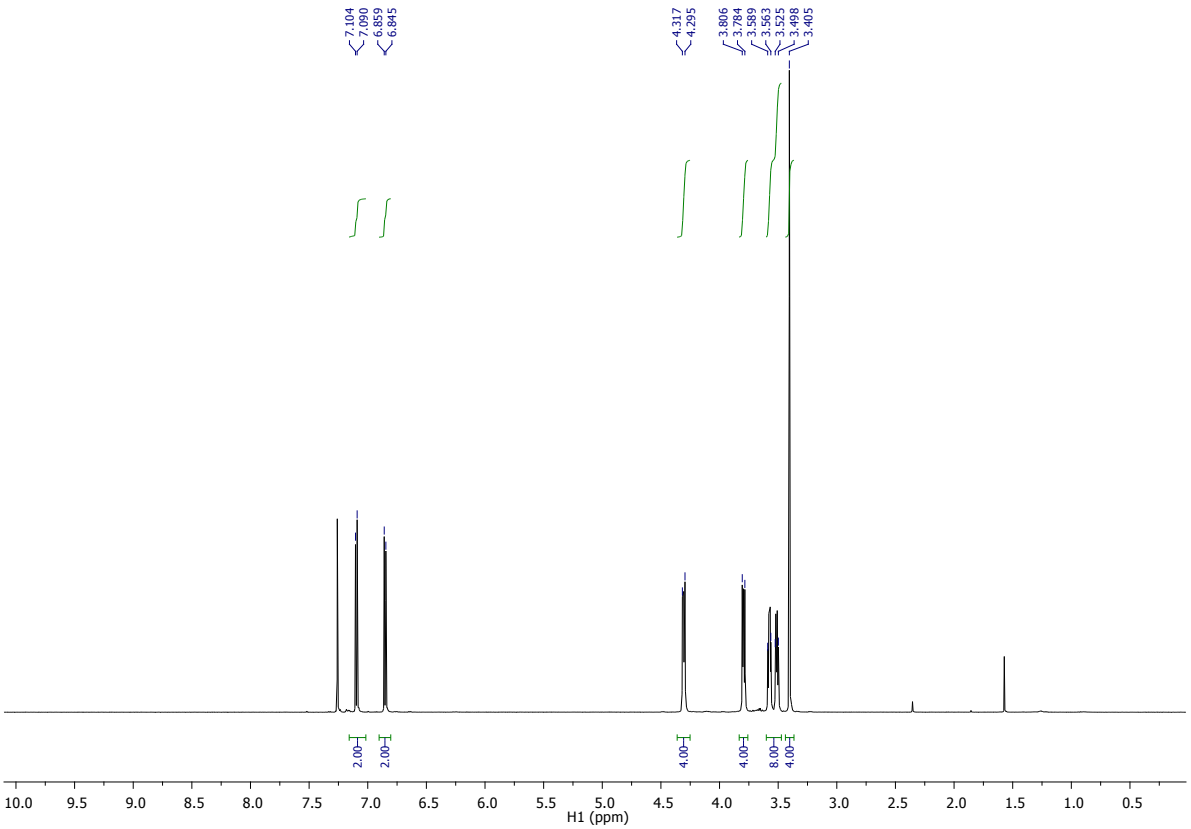
119.724
97.676
70.935
70.773
70.768
69.821
69.735
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
13C (ppm)



4. 5,6,8,9,11,12,14,15,17,18-Decahydrodithieno[3,2-*q*:2',3'-*s*][1,4,7,10,13,16]hexaoxacycloicosine

In a dry degassed RBF was added 5,6,8,9,11,12,14,15,17,18-decahydrodithieno[3,2-*q*:2',3'-*s*][1,4,7,10,13,16]hexaoxacycloicosine (9.93 g, 24.7 mmol, 1 equivalent) and dry dimethoxyethane, (100 ml) and cooled to -78 °C and freshly titrated n-butyl lithium (2.5 M in hexane, 20.8 ml, 52 mmol 2.1 equivalents) was added dropwise. The solution was warmed to -20 °C and stirred for1 h after which the solution was cooled to -78 °C again. In a second dry RBF was added $CuCl_2$ (6.64 g, 49.4 mmol, 2 equivalents) and dry dimethoxyethane (100 ml) and cooled to 0 °C. The lithiated 5,6,8,9,11,12,14,15,17,18-decahydrodithieno[3,2-*q*:2',3'-*s*][1,4,7,10,13,16]hexaoxacycloicosine solution was added dropwise to the copper chloride suspension at 0 °C via cannula and stirred while warming to room temperature for 48 h after which the solution appeared dark red. The solution was filtered through celite, and the celite pad was washed thoroughly with ethyl acetate. The organic washings were extracted with deionised water (3 x 200 ml). The combined organic phase was dried over $MgSO_4$ and concentrated in vacuo. The resulting black oil was subject to a short silica plug which was eluted with ethyl acetate thoroughly which was concentrated and purified by column chromatography eluting with 2:1 toluene:ethyl acetate. The off brown clear oil was recrystallised from 5:1 diethyl ether:THF affording the title compound as yellowish crystals. Yield 0.7289 g, 7 %, mp 105-106 °C HRMS (ESI/TOF) m/z+H^+ Calculated for $C_{18}H_{24}O_6S_2$ 401.1093 Found 401.1070 ^1H (400 MHz, $CDCl_3$) $^{13}C\{1H\}$ (101 MHz, $CDCl_3$) δ 167.7, 152.4, 122.3, 117.0, 114.0, 71.6, 71.3, 70.7, 70.5, 70.5.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6.845
4.317
4.295
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3.784
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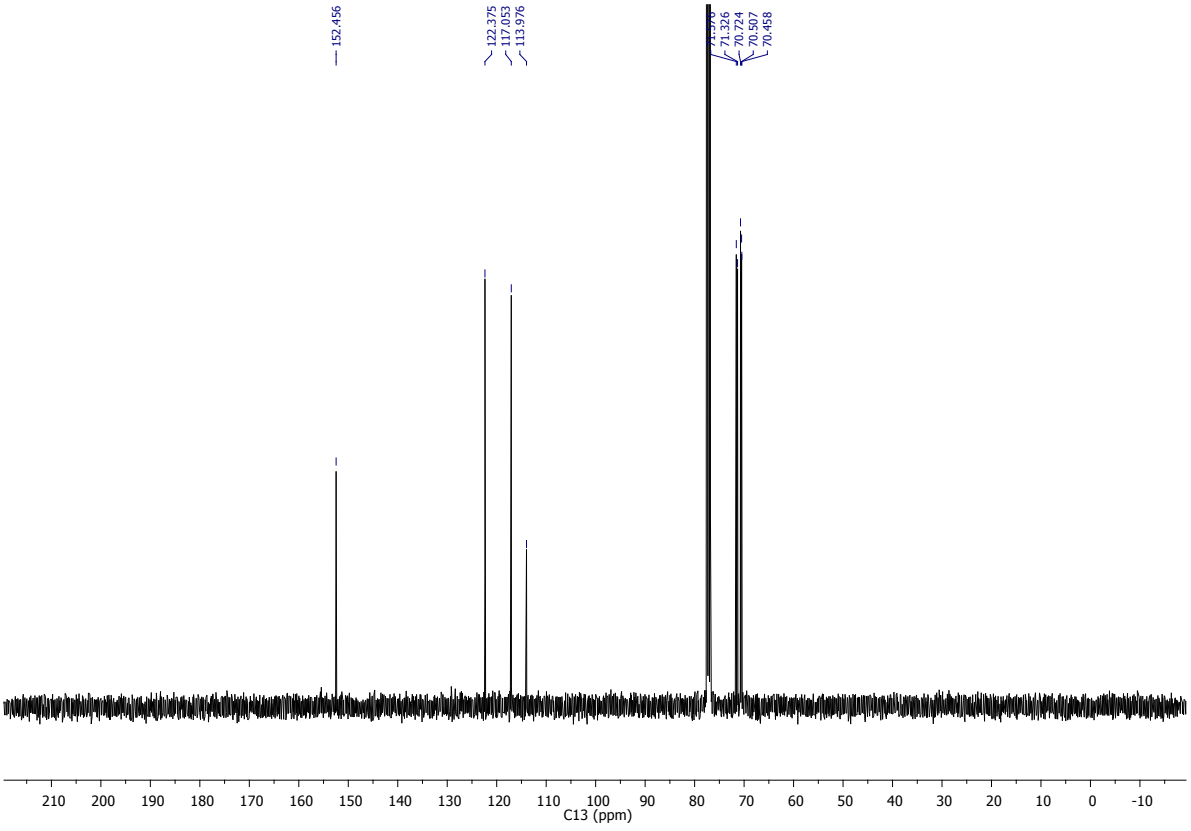
3.405
2.00
2.00
4.00
4.00
8.00
4.00
H1 (ppm)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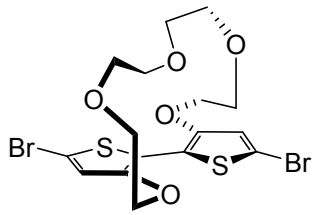
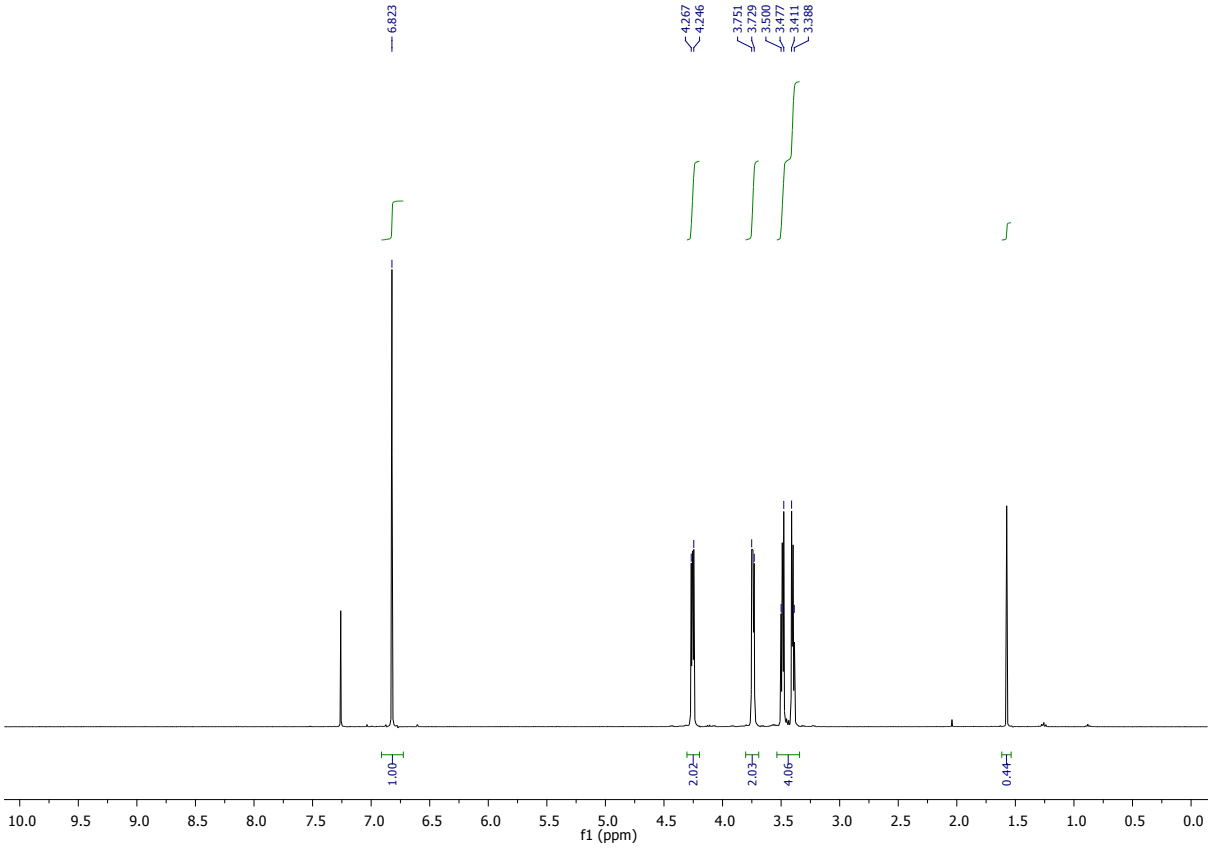
70.458
C13 (ppm)



5. 2,18-Dibromo-5,6,8,9,11,12,14,15-octahydrodithieno[3,2-*n*:2',3'-*p*][1,4,7,10,13]pentaoxacyclo-heptadecine

5,6,8,9,11,12,14,15,17,18-decahydrodithieno[3,2-*q*:2',3'-*s*][1,4,7,10,13,16]hexaoxacycloicosine (345 mg, 0.96 mmol, 1 equivalent) was dissolved in dry chloroform (10 ml) and cooled to -20 °C. *N*-bromosuccinimide (0.335 g, 1.88 mmol 2 equivalents) was added in one portion to the solution in the absence of light. The solution was stirred at -20 °C for 40 minutes. The reaction was quenched with 50 ml deionised water and extracted with chloroform (3 x 30 ml) which were combined and washed with a further portion of water. The combined organic phases were dried over $MgSO_4$ and the solvent removed *in vacuo*. The crude material was purified by column chromatography eluting with petroleum ether (b.p. 40-60 °C): ethyl acetate 3:2. The material was further recrystallised from 50:50 petroleum ether (b.p. 40-60 °C) affording grey crystals. Yield, 247.7 mg, 50.2 % mp 133-135 °C (decomp) HRMS (ESI/TOF) m/z+H^+ Calculated for $C_{16}H_{18}Br_2O_5S_2$ 514.9020 found 514.9010 ^1H (400 MHz, $CDCl_3$) δ 6.82 (s, 2H), 4.27-4.25 (m, 4H), 3.75-3.73 (m, 4H), 3.50-3.48 (m, 4H), 3.41-3.39 (m, 4H). $^{13}C\{^1H\}$ (101 MHz, $CDCl_3$) δ 151.7, 121.1, 116.0, 110.2, 72.4, 71.5, 70.9, 70.6.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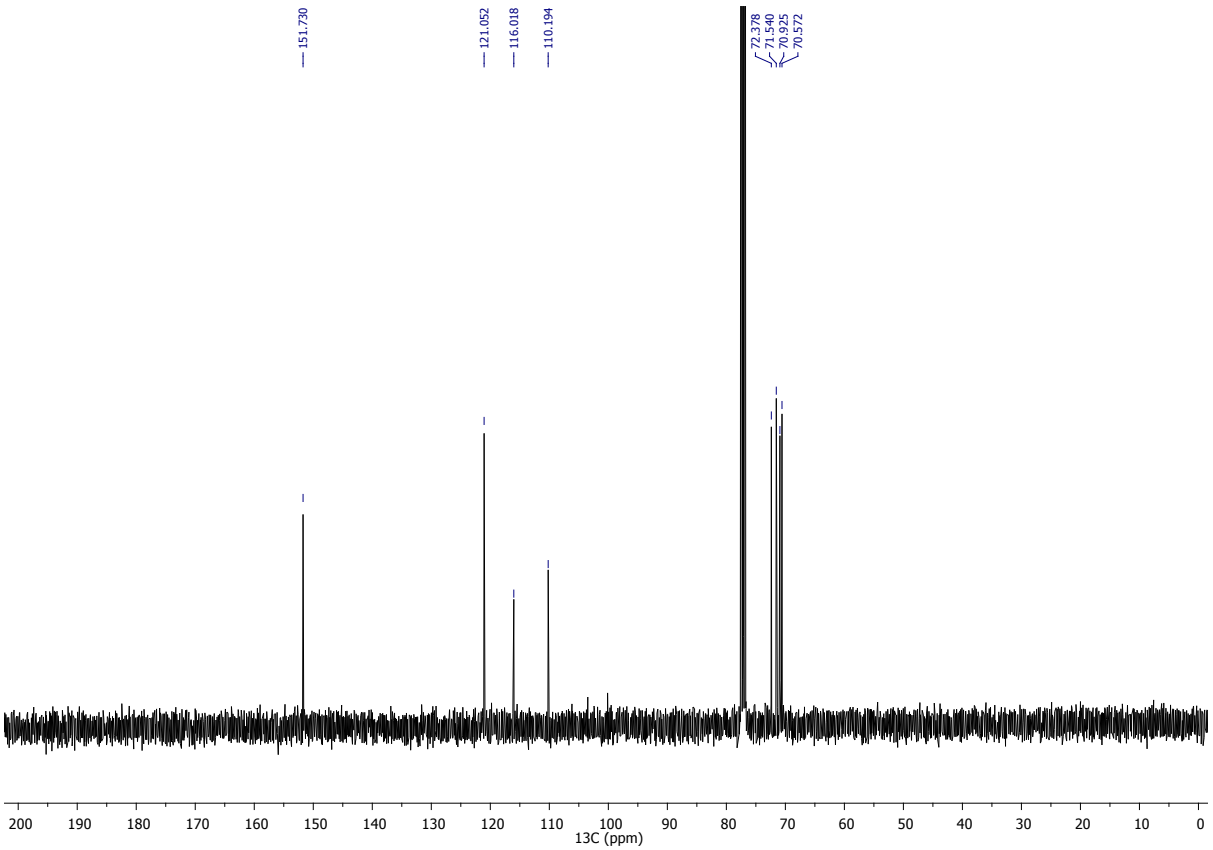
2.02
2.03
4.06
0.44
f1 (ppm)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110.194
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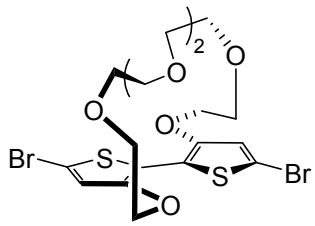
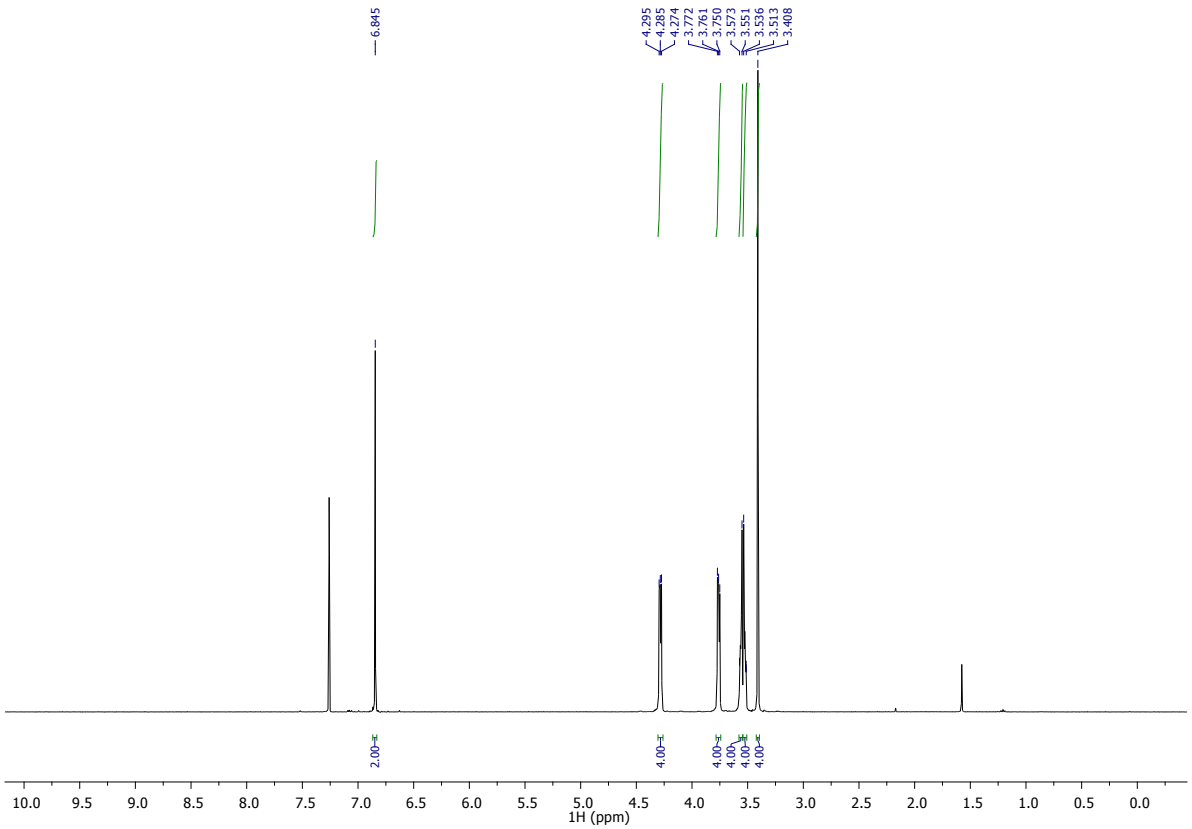
70.572
13C (ppm)



6. 2,21-Dibromo-5,6,8,9,11,12,14,15,17,18-decahydrodithieno[3,2-*q*:2',3'-*s*][1,4,7,10,13,16]hexa-oxacycloicosine

5,6,8,9,11,12,14,15,17,18-Decahydrodithieno[3,2-*q*:2',3'-*s*][1,4,7,10,13,16]hexaoxacycloicosine (200 mg, 0.5 mmol, 1 equivalent) was dissolved in dry DMF (10 ml) and cooled to -20 °C. *N*-bromosuccinimide (0.182 g, 1.05 mmol 2.05 equivalents) was added in one portion to the solution in the absence of light. The solution was stirred at -20 °C for 3 hours minutes. The reaction was quenched with 50 ml deionised water/ice mixture and extracted with diethyl ether (3 x 30 ml) which were combined and washed with a further portion of water (50 ml). The combined organic phases were dried over $MgSO_4$ and the solvent removed in vacuo. The crude material was purified by column chromatography eluting with toluene:ethyl acetate 1:1 with 3 vol% triethylamine. The material was further recrystallised from diethyl ether affording grey crystals. Yield 155 mg, 55 %. ^{1}H (400 MHz, $CDCl_3$) δ 6.85 (s, 2H), 4.30-4.28 (m, 4H), 4.27-4.77 (m, 4H), 3.77-3.75, 3.57-3.51 (m, 8H), 3.41 (s, 4H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 167.8, 150.7, 119.9, 115.4, 110.0, 71.9, 71.5, 70.9, 70.5.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3.772
3.761
3.750
3.573
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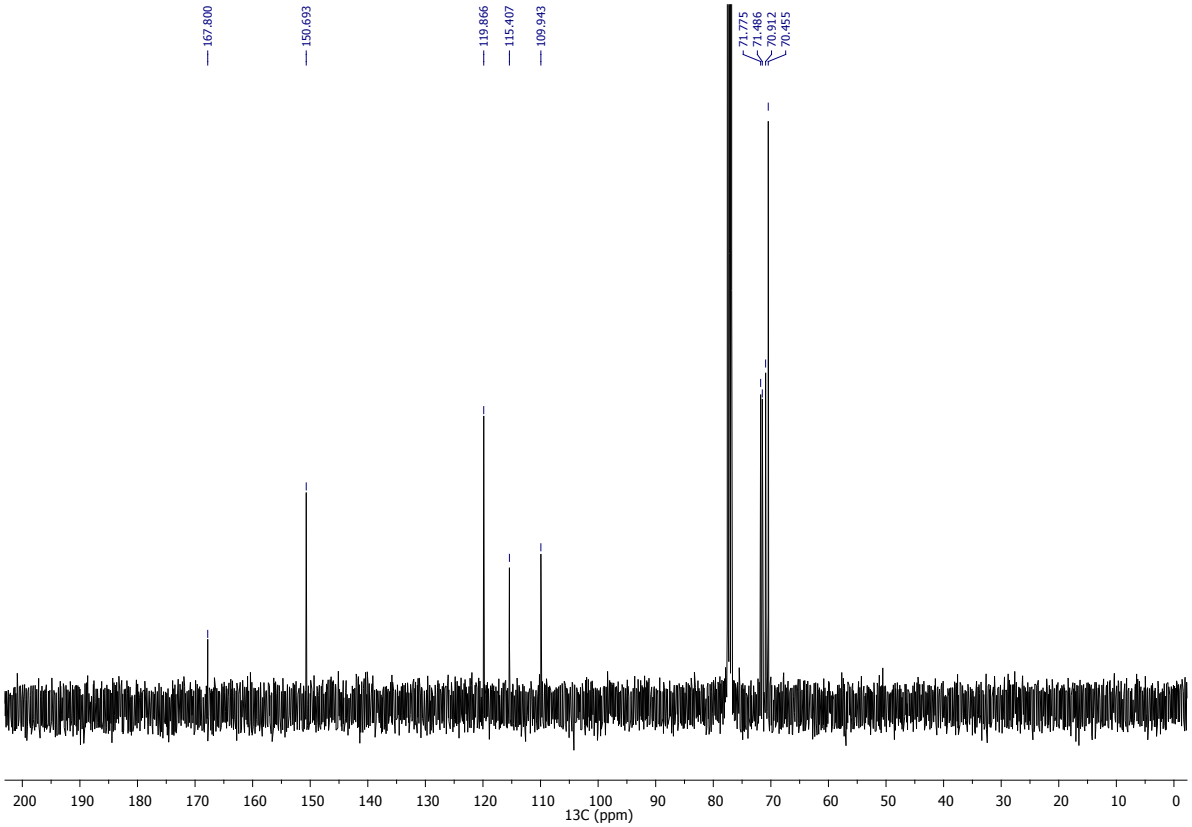
4.00
4.00
4.00
1H (ppm)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71.775
71.486
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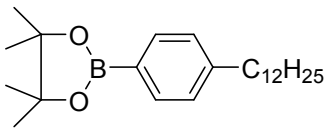
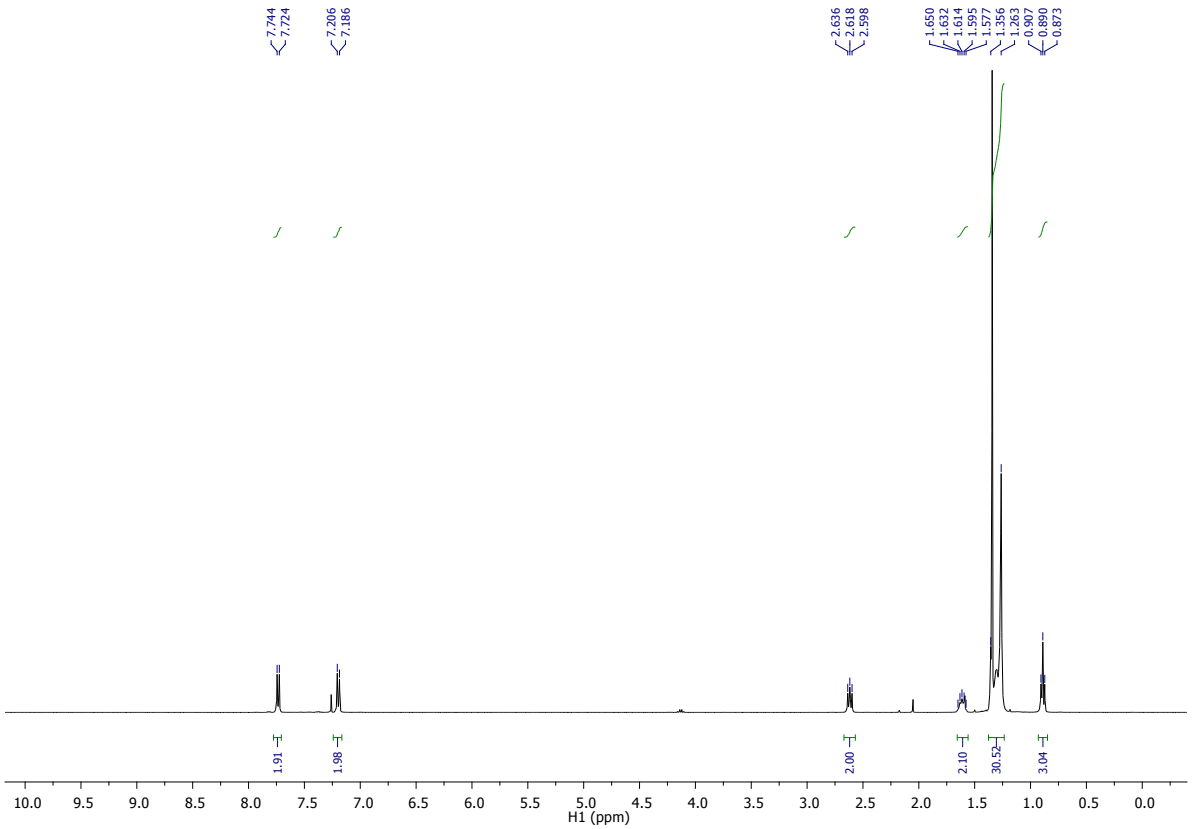
70.455
13C (ppm)



7. 2-(4-Dodecylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

In a dried round bottom flask was added 1-bromo-4-dodecylbenzene (1.33 g, 4.07 mmol, 1 equivalent) and dry DMF (35 ml). 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (2.06 g, 8.15 mmol 2 equivalents) and potassium acetate (1.20 g, 12.3 mmol, 3 equivalents) and 1,1'-bis(diphenylphosphino)ferrocene dichloropalladium(II) (14.8 mg, 0.020 mmol, 5 mol%) were added and the solution degassed by the freeze-pump-thaw-cycles in liquid nitrogen. The solution was heated to 90 °C for 18 hours. The solution was concentrated *in vacuo* to approximated 5 ml and diluted with DCM (30 ml) and extracted with ice cold deionised water (3 x 30 ml), the organic phase was dried over $MgSO_4$ and the solvent removed *in vacuo*. The brownish residue was purified by column chromatography eluting with petroleum ether (b.p. 40-60 °C) ethyl acetate 9:1 affording the title compound as a clear oil. Yield 1.36 g, 90 %. LR-GCMS calculated m/z 372.32 found 372.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, 2H, *J* = 8 Hz), 7.20 (d, 2H, *J* = 8 Hz), 2.62 (t, 2H, *J* = 7. 2 Hz), 1.65-1.58 (m, 2H), 1.36-1.26 (m, 30H), 0.89 (t, 3H, 6.8 Hz). ^{13}C{^{1}H} (101 MHz, $CDCl_3$) δ 146.6, 135.0, 83.7, 36.3, 32.1, 31.5, 29.8, 29.8, 29.8, 29.7, 29.7, 29.5, 29.5, 25.0, 22.8, 14.3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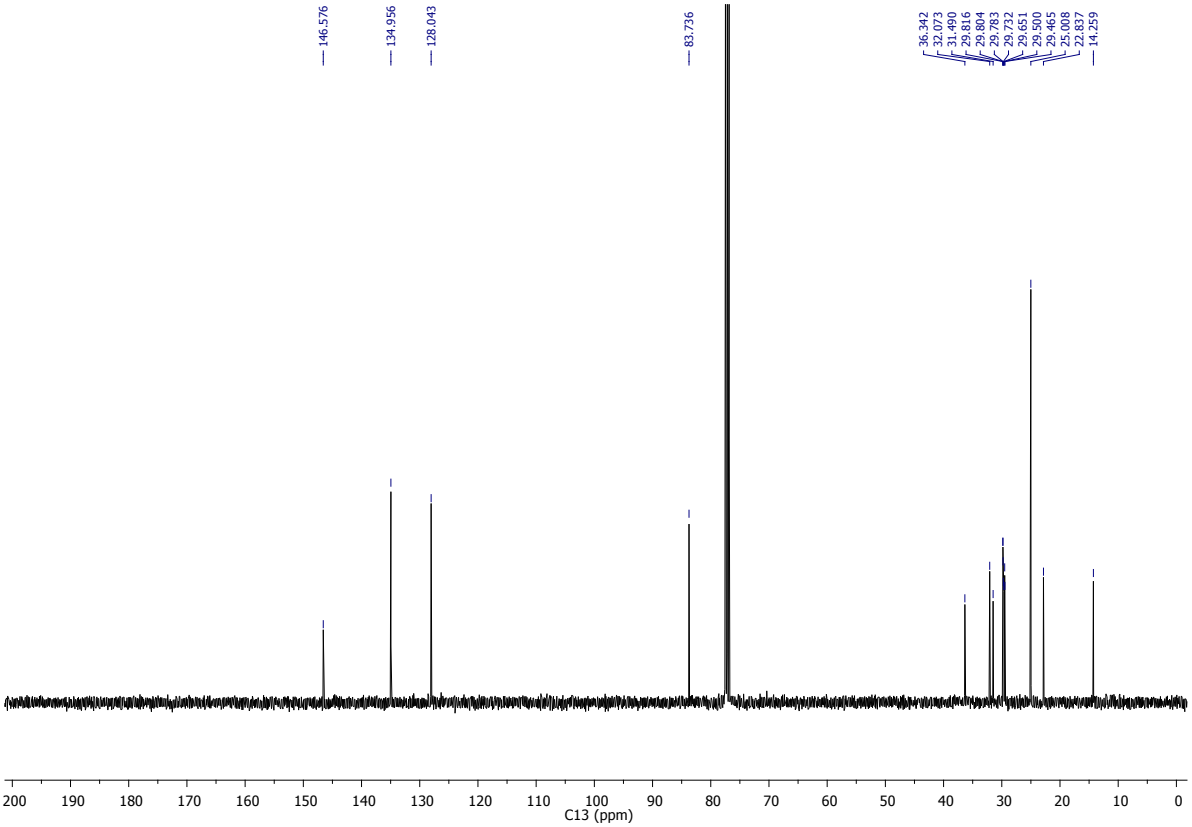
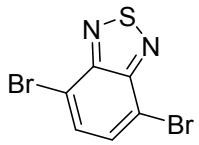
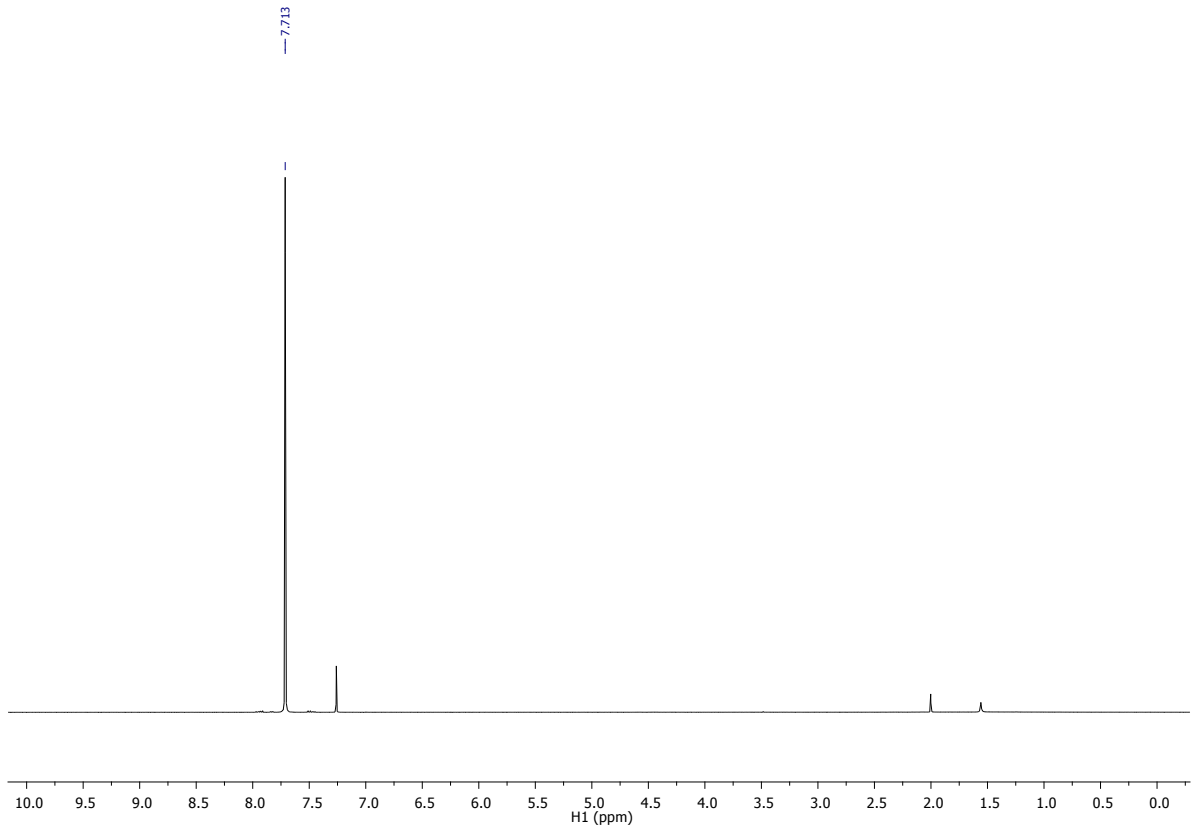
7.724
7.206
7.186
2.636
2.618
2.598
1.650
1.632
1.614
1.595
1.577
1.356
1.263
0.907
0.890
0.873
1.91
1.98
2.00
2.10
30.52
3.04
H1 (ppm)

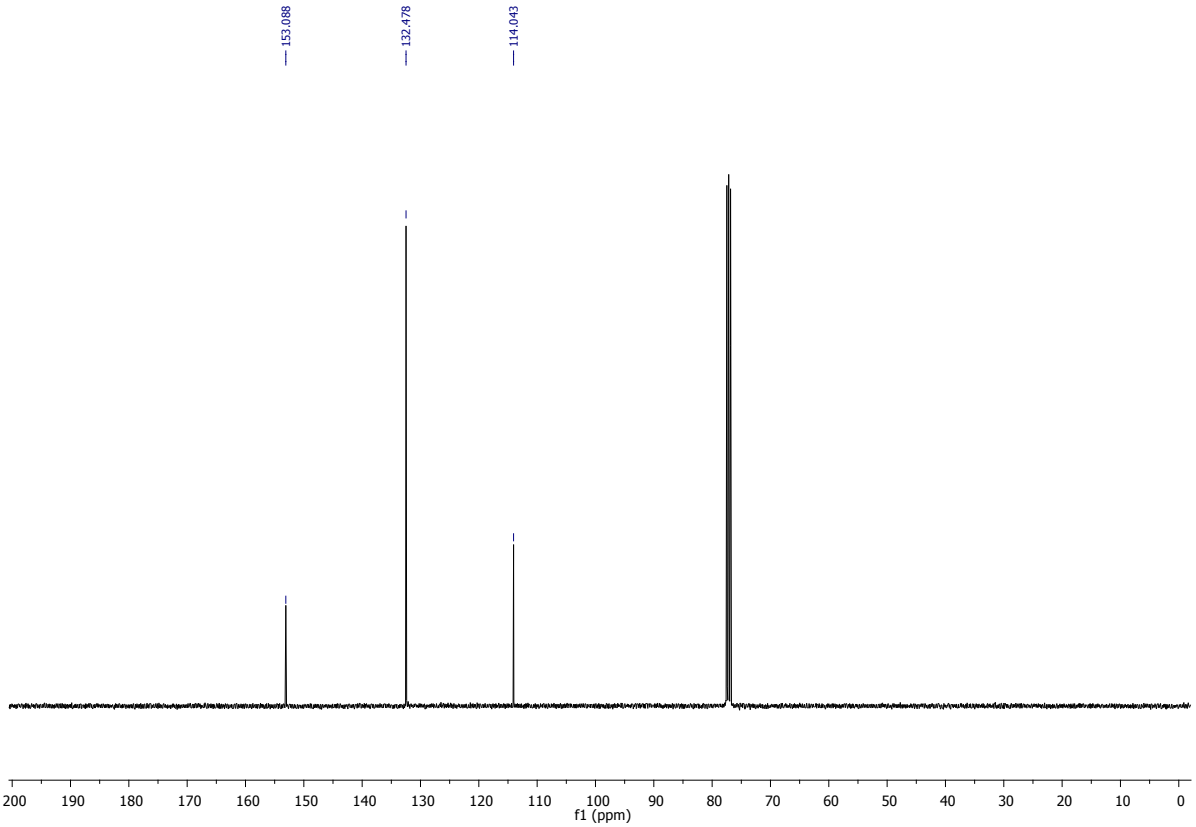

146.576
134.956
128.043
83.736
36.342
32.073
31.490
29.816
29.804
29.783
29.732
29.651
29.500
29.465
25.008
22.837
14.259
C13 (ppm)

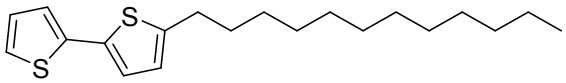


8. 4,7-Dibromobenzo[*c*][1,2,5]thiadiazole

Synthesised according to literature procedure.[1] In a 250 ml 3 neck round bottom flask was added 2,1,3-benzothiadiazole (13.6 g, 100 mmol, 1 equivalent) in 45 ml of 45% hydrobromic acid in acetic acid. The solution was stirred at reflux while bromine (48 ml, 300 mmol, 3 equivalents) was added portion wise over the course of 30 minutes. The solution became dark brown and formed a solid yellow precipitate was formed. A further portion of 15 ml 45% bromine in acetic acid was added and the solution refluxed for 6 hours. The reaction was cooled and quenched via slow addition to saturated $Na_2S_2O_3$ solution until pH 7 was achieved and brown colour had been dissipated. The solution was extracted with chloroform repeatedly (5x500 ml) and the organic phase dried and concentrated upon which a yellow precipitate was observed the resulting solid was purified by crystallisation from boiling chloroform. The title compound was isolated as needle like crystals. Yield 2.36 g, 8 %, mp 156 °C LR-GCMS calculated m/z 293.96 found 293.80. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71. $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) δ 153.1, 122.5 114.4.

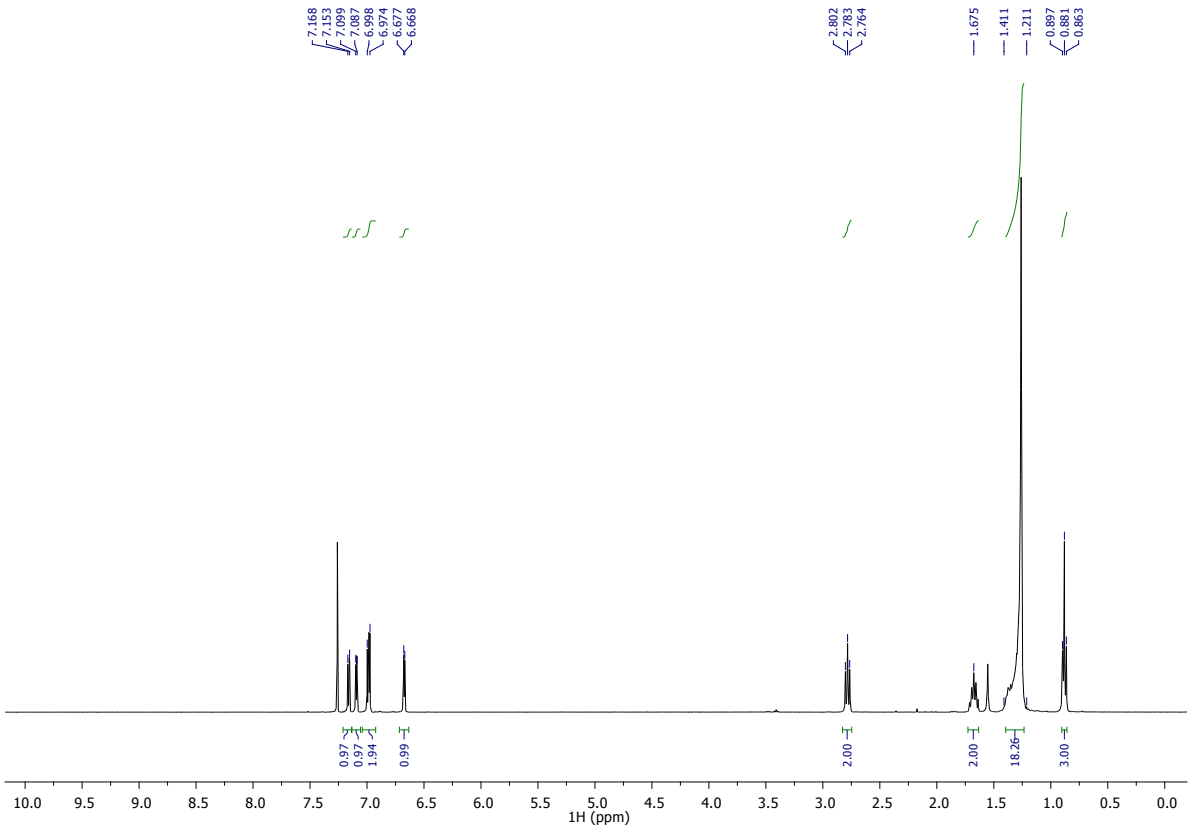

7.713
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
H1 (ppm)

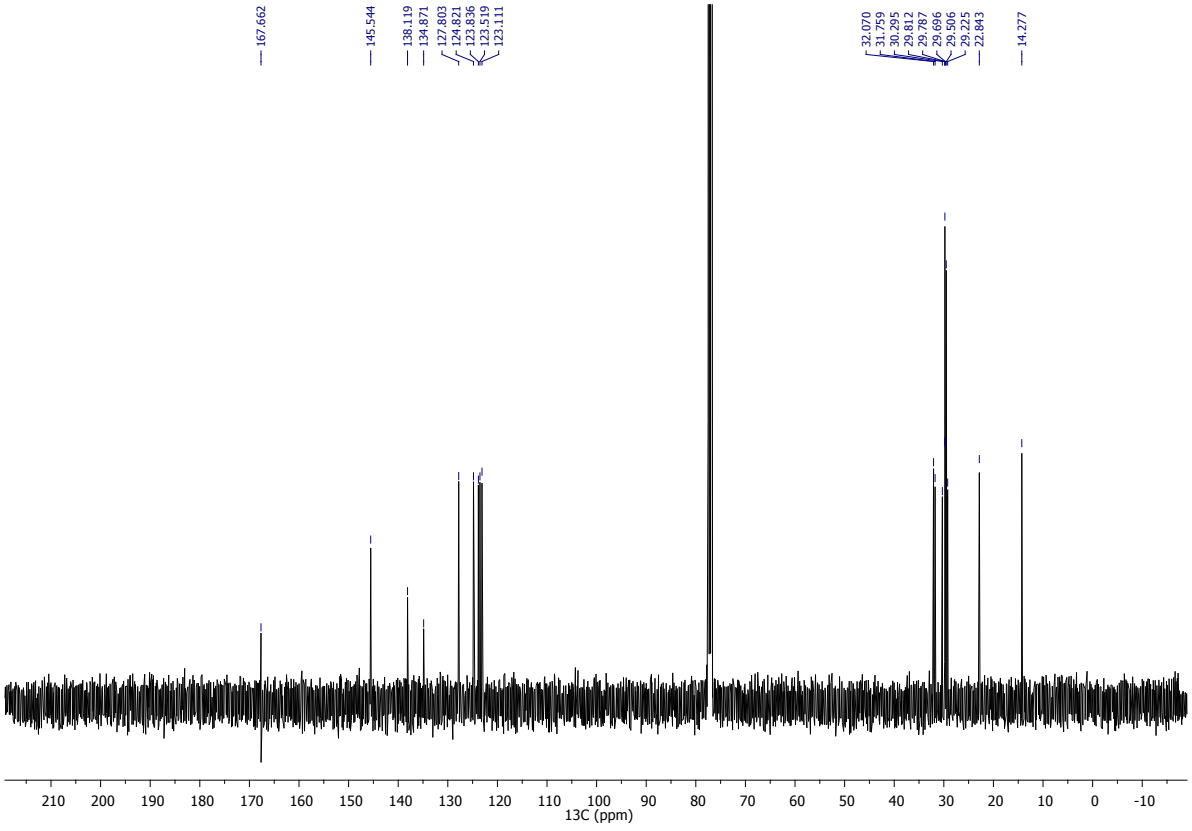

153.088
132.478
114.043
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

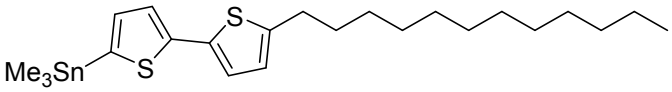


9. 5-Dodecyl-2,2'-bithiophene

Synthesised according to procedure adapted from literature.[2] In a dry degassed 3-neck round bottom flask was dissolved 2,2'-bithiophene (3.00 g, 18 mmol, 1 equivalent) and dissolved in anhydrous THF (30 ml) and the solution cooled to -78 °C and *n*-BuLi 2.5 M in hexanes) (7.2 ml, 18 mmol, 1 equivalent) was added dropwise and the solution stirred for 1 h at -78 °C. 1-Bromo-n-dodecane (4.5 g, 18 mmol, 1 equivalent) was added dropwise at -78 °C. The solution was stirred for 16 h warming to room temperature, when a reddish solution was observed. The reaction mixture was quenched by addition of 100 ml deionised water and extracted with diethyl ether (3x100 ml), the combined organic phases were washed with brine (200 ml) dried over $MgSO_4$ and concentrated *in vacuo.* The greenish residue was run through a short silica plug eluting with hexane initially, followed by hexanes:EtOAc 50:50 v/v and concentrated *in vacuo*. The residue was subject to silica column with hexane:EtOAc 95:5 v/v. The title compound was isolated as yellow crystals. Yield 2.37 g, 39 % mp 39-39 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.15 (m, 1H), 7.10-7.09 (m 1H), 7.00-6.97 (m, 2H), 6.68-6.67 (m, 1H), 2.78 (t, 2H *J* = 7.6 Hz), 1.71-1.64 (m, 2H), 1.41-1.21 (m, 18H), 0.88 (t, 3H, *J* = 6.4 Hz). ^{13}C{^{1}H} (101 MHz, $CDCl_3$) δ 167.7, 145.5, 138.1, 134.9, 127.8, 124.8, 123.8, 123.5, 123.1, 32.1, 31.8, 30.3, 29.8, 29.8, 29.7, 29.5, 29.2, 22.8, 14.3.

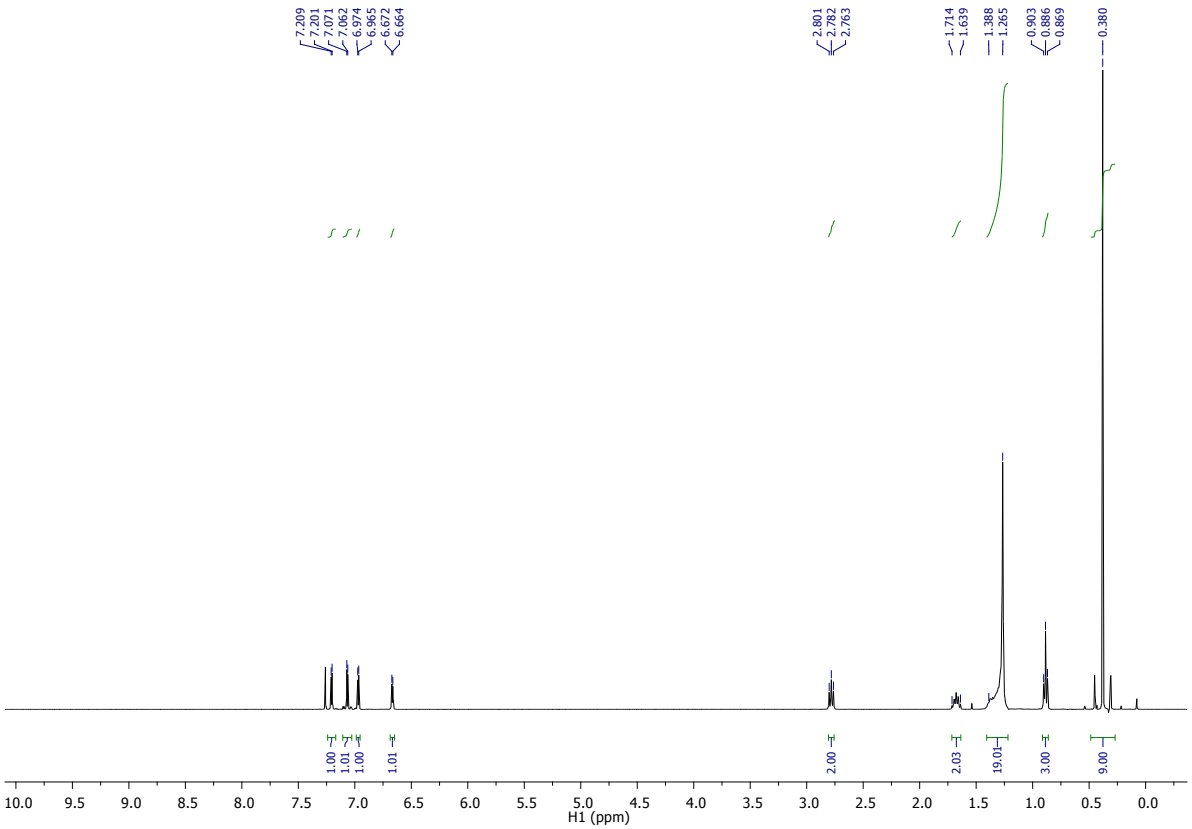

7.168
7.153
7.099
7.087
6.998
6.974
6.677
6.668
2.802
2.783
2.764
1.675
1.411
1.211
0.897
0.881
0.863
0.97
0.97
1.94
0.99
2.00
2.00
18.26
3.00
1H (ppm)

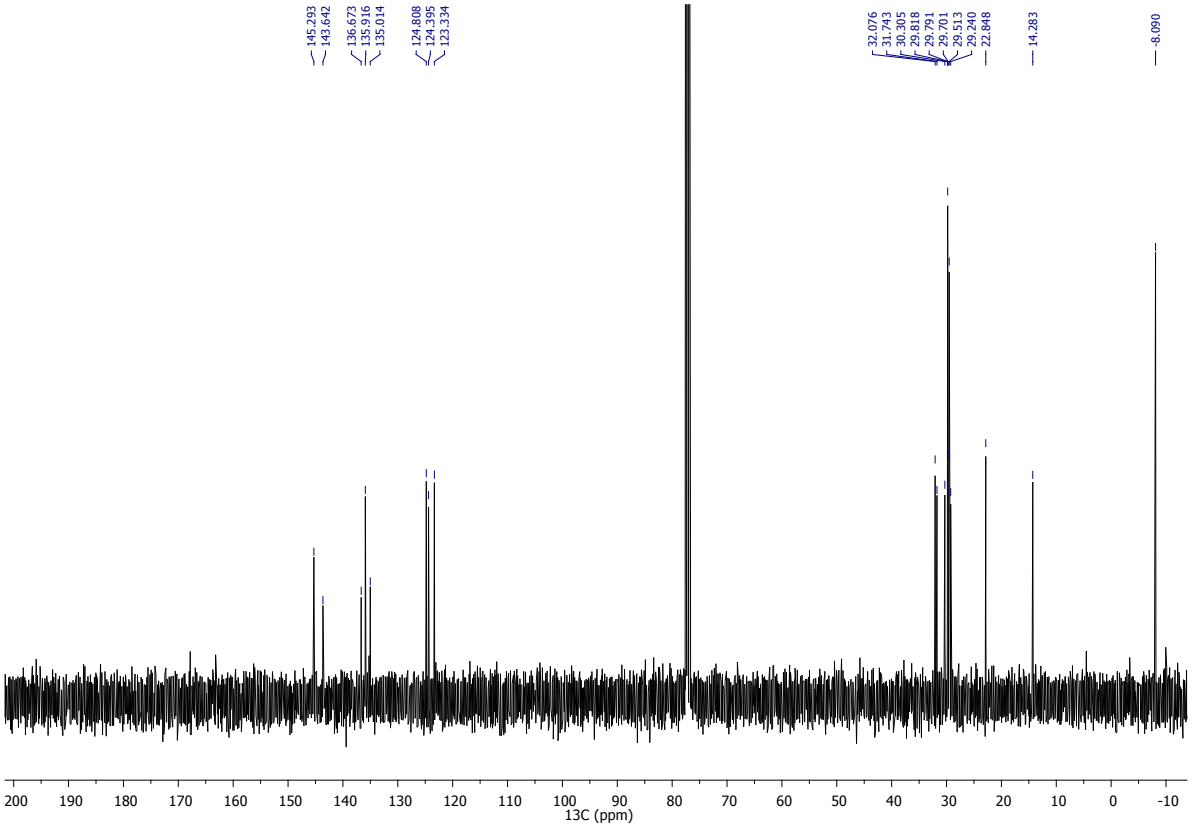

167.662
145.544
138.119
134.871
127.803
124.821
123.836
123.519
123.111
32.070
31.759
30.295
29.812
29.787
29.696
29.506
29.225
22.843
14.277
13C (ppm)

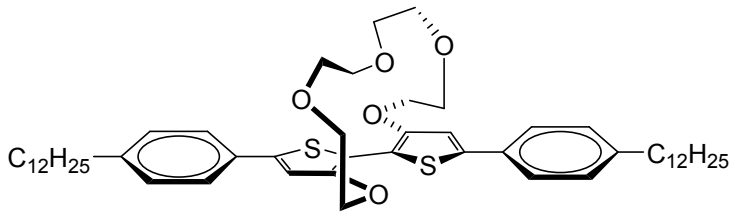


10. (5'-Dodecyl-[2,2'-bithiophen]-5-yl)trimethylstannane

A dried degassed round bottom flask was charged with 5-dodecyl-2,2'-bithiophene (1.0 g, 3.0 mmol, 1 equivalent) and was dissolved in dry THF (5 ml) and cooled to -78 °C. *n*-BuLi 2.5 M in hexanes (1.43 ml, 3.6 mmol, 1.2 equivalents) and the solution was stirred for 1 hour at -78 °C, after which a cloudy off-white suspension was observed. Trimethyltin chloride 1.0 M in hexanes (3.6 ml, 3.6 mmol, 1.2 equivalents) was added dropwise and the solution raised slowly to room temperature over 1 h and stirred at room temperature for 18 h. The solution was quenched with deionised water (100 ml) and extracted with diethyl ether (3x50 ml), dried over $MgSO_4$ and the solvent removed in vacuo and dried under high vacuum overnight affording the title compound as white crystals. Yield 1.12 g, 75 %. MALDI TOF m/z 498.14 calculated for $C_{23}H_{38}S_2Sn$ found 497.97, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, 1H, *J* = 3.2 Hz) , 7.06 (d, 1H, *J* = 3.6 Hz) , 6.97 (d, 1H, *J* = 3.6 Hz), 6.66 (d, 1H, *J* = 3.2 HZ), 2.78 (t, 2H, *J* = 7.6 Hz), 1.71-1.64 (m, 2H), 1.41-1.21 (m, 18H), 0.89 (t, 3H, *J* = 6.8), 0.38 (s, 9H) $^{13}C\{^1H\}$ (101 MHz, $CDCl_3$) δ 145.3, 143.64, 136.7, 135.9, 135.0, 124.8, 124.4, 123.3, 32.1, 31.7, 30.3, 29.8, 29.8, 29.7, 29.5, 29.2, 22.9, 14.3, -8.1.

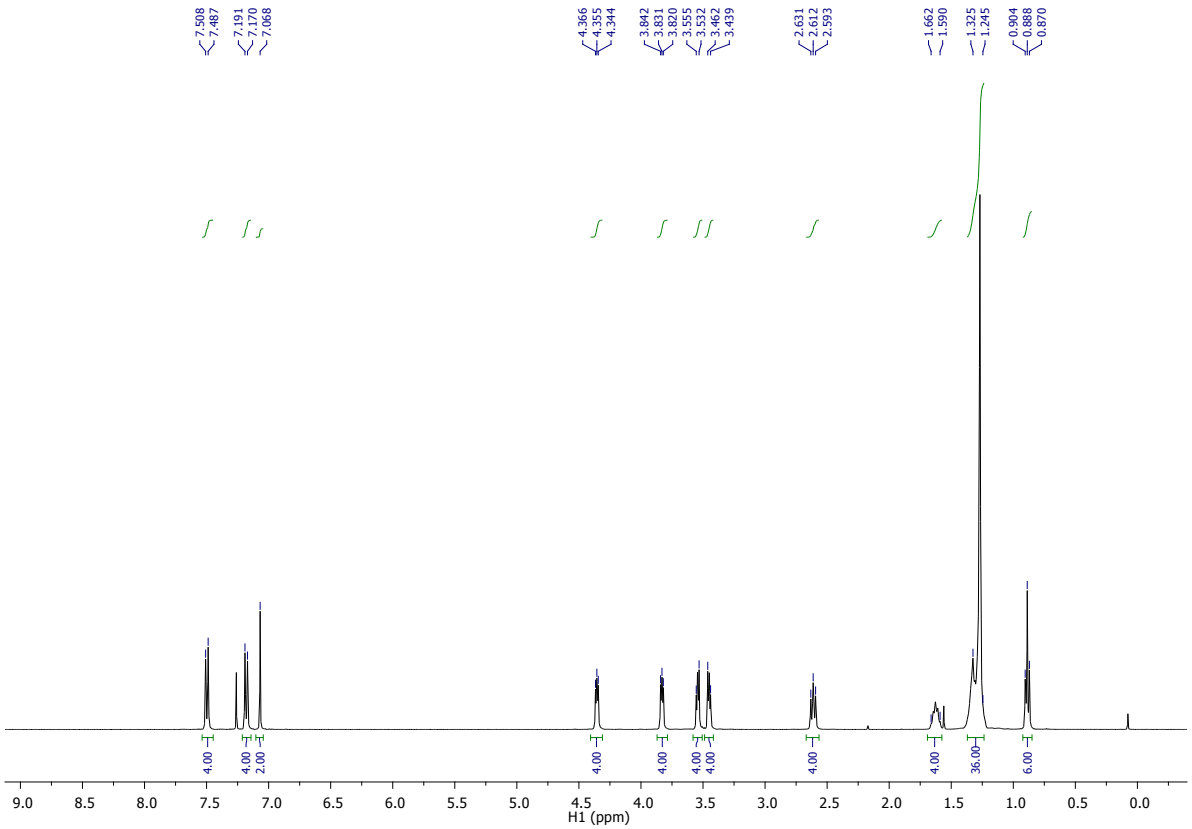

7.209
7.201
7.071
7.062
6.974
6.965
6.672
6.664
2.801
2.782
2.763
1.714
1.639
1.388
1.265
0.903
0.886
0.869
0.380
1.00
1.01
1.00
1.01
2.00
2.03
19.01
3.00
9.00
H1 (ppm)

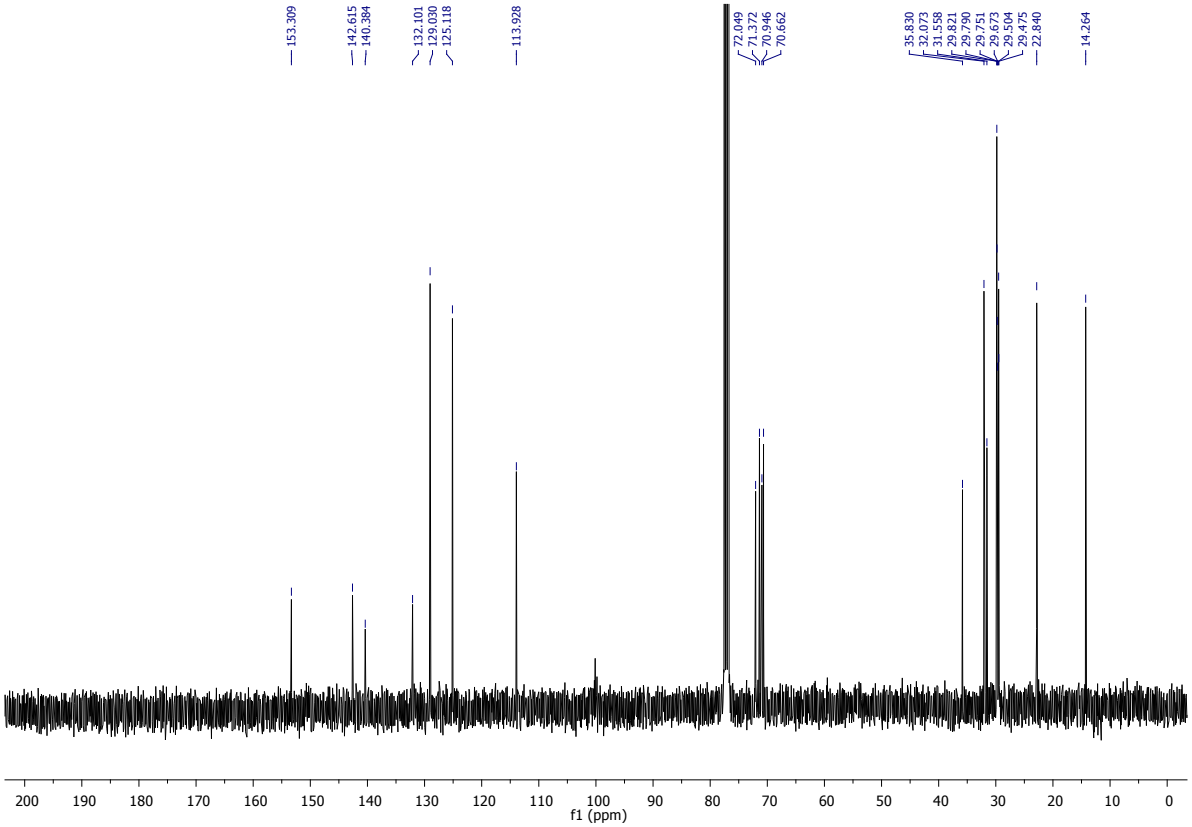

145.293
143.642
136.673
135.916
135.014
124.808
124.395
123.334
32.076
31.743
30.305
29.818
29.791
29.701
29.513
29.240
22.848
14.283
-8.090
13C (ppm)



11. 2,18-Bis(4-dodecylphenyl)-5,6,8,9,11,12,14,15-octahydrodithieno[3,2-*n*:2',3'-*p*][1,4,7,10,13]-pentaoxacycloheptadecine (M1)

In a 3-neck round bottom flask 5,6,8,9,11,12,14,15,17,18-decahydrodithieno[3,2-*q*:2',3'-*s*]-[1,4,7,10,13,16]hexaoxacycloicosine (100 mg, 0.19 mmol, 1 equivalent) and 2-(4-dodecylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (152 mg, 2.1 equivalents) were dissolved in toluene 5 ml and 2 M K_2CO_3 (4 ml) was added. The solution was degassed via N_2 bubbling for 30 minutes after which tetrakis(triphenylphosphine)palladium(0) (20 mg, 0.02 mmol, 0.1 equivalents) was added. The solution was heated to 100 °C for 18 hours, after which a brownish solution was observed. The mixture was cooled and extracted with toluene (50 ml) and washed with deionised water (3 x 20 ml) the organic phase was dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography eluting with petroleum ether(60:40 °C):toluene:ethyl acetate 6:1:3 v/v. the resulting yellow solid was suspended in boiling hexane and acetone added gradually until dissolution. The title compound was afforded as a yellow powder and dried under vacuum. Yield 95 mg 57% MP 98-99 °C, MALDI TOF m/z 844.51 calculated for $C_{52}H_{76}O_5S_2$ found 844.1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, 4H, *J* = 8.4 Hz), 7.18 (d, 4H, *J* = 8.4 Hz) 7.07 (d, 2H), 4.37-4.34 (m, 4H), 3.84-3.82 (m, 4H), 3.56-3.53 (m, 4H), 3.60-3.44 (m, 4H), 2.61 (t, 4H, *J* = 7.6 Hz), 1.66-1.59 (m, 4H), 1.32-1.24 (m 36H), 0.89 (t, 6H, *J* =6.4 Hz). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.3, 142.6, 140.4, 132.1, 129.0, 125.1, 113.9, 72.1, 71.4, 71.0, 70.7, 35.8, 32.1, 31.6, 29.8, 29.8, 29.8, 29.7, 29.5, 29.5, 22.8, 14.3


7.508
7.487
7.191
7.170
7.068
4.366
4.355
4.344
3.842
3.831
3.820
3.555
3.532
3.462
3.439
2.631
2.612
2.593
1.662
1.590
1.325
1.245
0.904
0.888
0.870
4.00
4.00
2.00
4.00
4.00
4.00
4.00
4.00
4.00
36.00
6.00
H1 (ppm)


153.309
142.615
140.384
132.101
129.030
125.118
113.928
72.049
71.372
70.946
70.662
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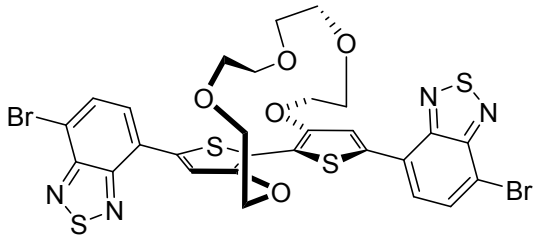
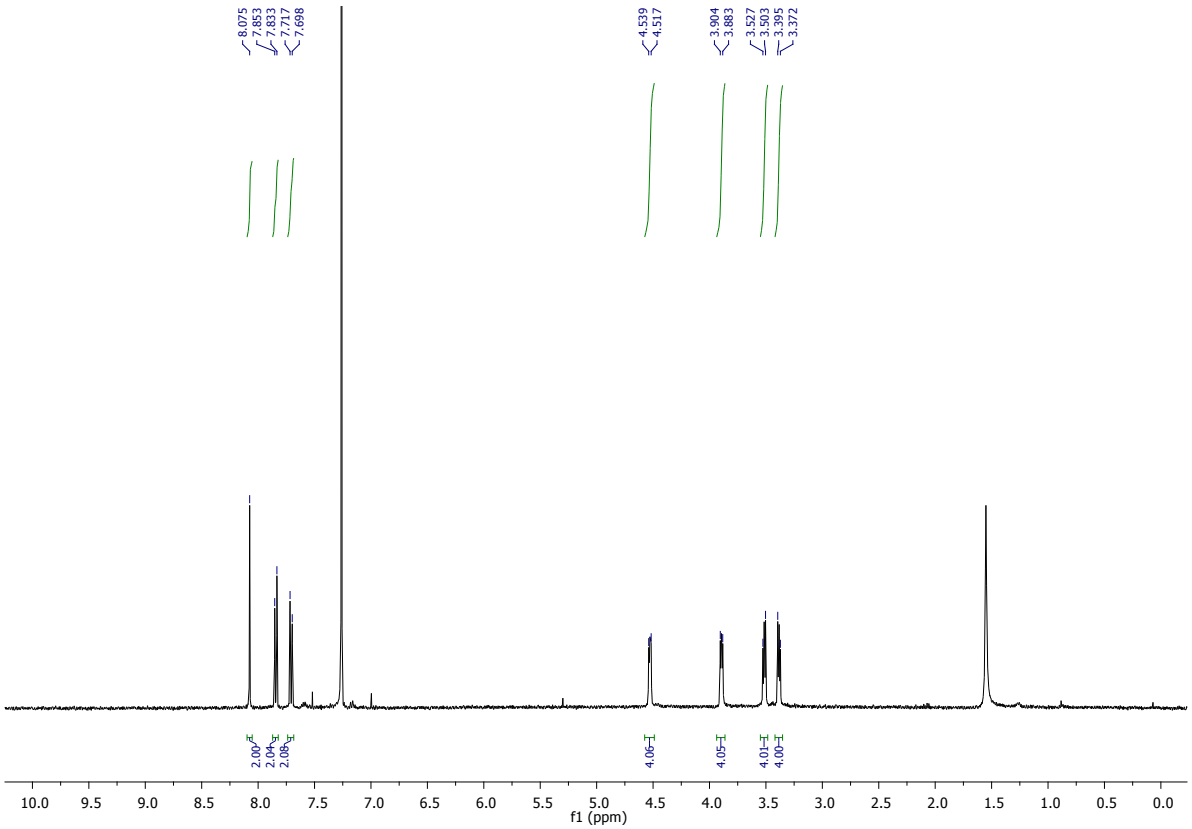
29.673
29.504
29.475
22.840
14.264
f1 (ppm)



12 2,18-Bis(7-bromobenzo[*c*][1,2,5]thiadiazol-4-yl)-5,6,8,9,11,12,14,15-octahydrodithieno[3,2-*n*:2',3'-*p*][1,4,7,10,13]pentaoxacycloheptadecine (M4)

In a dried degassed 3-neck round bottom flask was added 5,6,8,9,11,12,14,15-octahydrodithieno[3,2-*n*:2',3'-*p*][1,4,7,10,13]pentaoxacycloheptadecine (250 mg, 0.7 mmol, 1 equivalent) and dry THF (70 ml) and tetramethylethylenediamine (245 mg, 2.1 mmol, 3 equivalents) and the solution cooled to -78 °C and *n*-BuLi 2.5 M in hexanes wad added dropwise at -78 °C and the solution turned reddish and was stirred at room temperature for 20 minutes. The solution was cooled to -78 °C and trimethyltin chloride (1.0 M in hexanes, 1. 75 ml, 2.5 equivalents). The solution was warmed to room temperature and stirred for 18 h. The mixture was quenched with deionised water (20 ml) and extracted with dichloromethane (3 x 20 ml), dried over $MgSO_4$ and the DCM removed *in vacuo* and dried under high vacuum for 1 h in a tared microwave vial. The stannylated intermediate (0.53 g, 0.78 mmol, 1 equivalent) was then dissolved in toluene and 4,7-dibromo-2,1,3-benzothiadiazole (0.70 g, 2.35 mmol, 3 equivalents) and tetrakis(triphenylphosphine)palladium(0) (18 mg, 0.015 mmol, 0.02 equivalents) were added. The solution was degassed by N_2 bubbling for 30 minutes before being heated to 100 °C for 24 h after which a purple solution was observed. The solution was poured onto a short silica plug and the plug eluted with chloroform:acetone 9:1 v/v until the coloured fraction had ceased to elute. The fraction was concentrated *in vacuo* and the residue purified by column chromatography eluting with DCM:acetone 95:5 v/v. The title compound was afforded as a dark purple powder. Yield 0.138 g, 25.1 % mp >250 °C. HRMS (ESI/TOF) m/z+H^+ calculated for $C_{28}H_{21}Br_2N_4O_5S_4Na$ 804.8718 found 804.8580. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 2H), 7.84 (d, 2H, *J* = 8 Hz), 7.71 (d, 2H, *J* = 8 Hz), 4.54-4.52 (m, 4H), 3.90-3.88 (m, 4H), 3.53-3.50 (m, 4H), 3.40-3.37 (m, 4H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 132.3, 124.5, 119.5, 100.0, 72.4, 71.4, 71.0, 70.4.


8.075
7.853
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7.717
7.698
4.539
4.517
3.904
3.883
3.527
3.503
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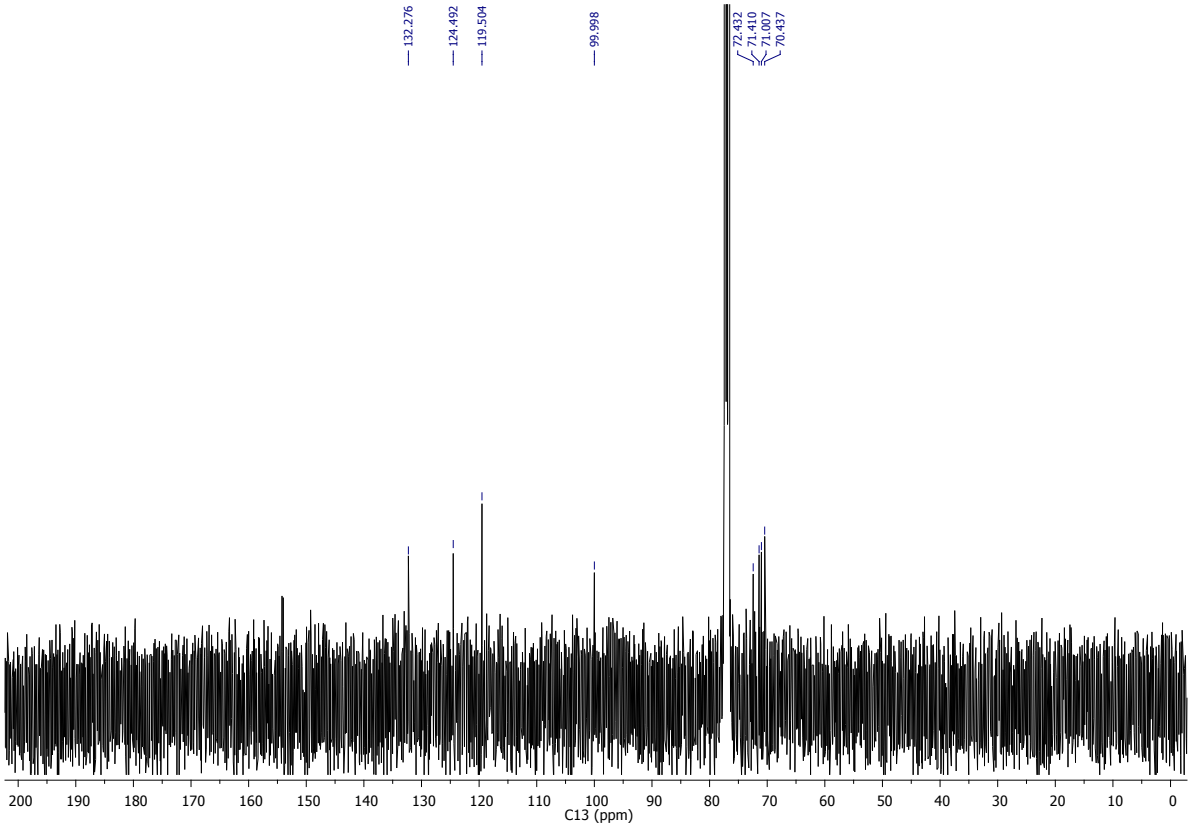
2.08
4.06
4.05
4.01
4.00
f1 (ppm)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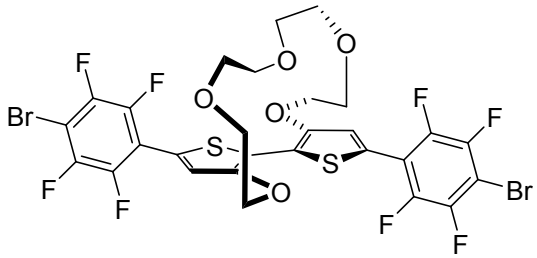
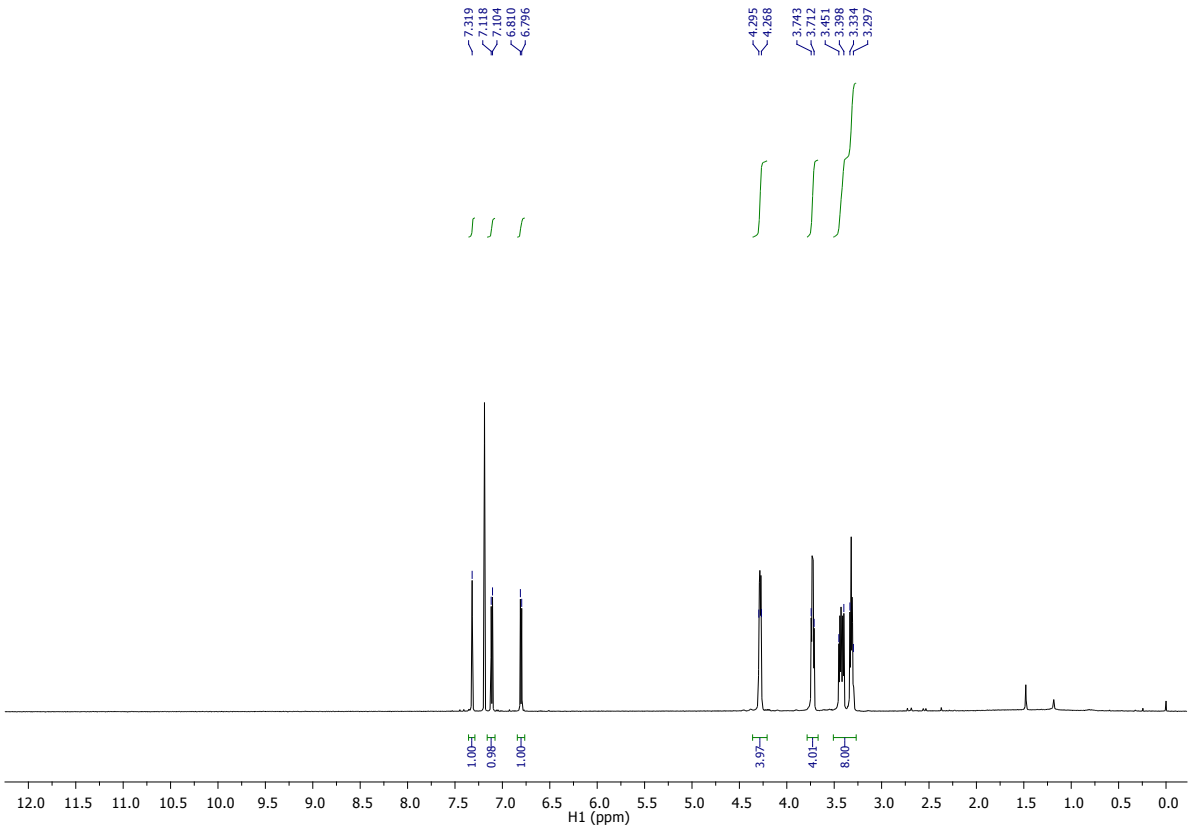
119.504
99.998
72.432
71.410
71.007
70.437
C13 (ppm)



13 2,18-Bis(4-bromo-2,3,5,6-tetrafluorophenyl)-5,6,8,9,11,12,14,15-octahydrodithieno[3,2-*n*:2',3'-*p*][1,4,7,10,13]pentaoxacycloheptadecine (M3)

In a dried degassed 3-neck round bottom flask was added 5,6,8,9,11,12,14,15-octahydrodithieno[3,2-*n*:2',3'-*p*][1,4,7,10,13]pentaoxacycloheptadecine (300 mg, 0.85 mmol, 1 equivalent) and dry THF (5 ml) and tetramethylethylenediamine (297 mg, 2.6 mmol, 3 equivalents) and the solution cooled to -78 °C and *n*-BuLi 2.5 M in hexanes was added dropwise at -78 °C and the solution turned reddish and was stirred at room temperature for 20 minutes. The solution was cooled to -78 °C and trimethyltin chloride (1.0 M in hexanes, 1.70 ml, 2.0 equivalents). The solution was warmed to room temperature and stirred for 18 h. The mixture was quenched with deionised water (20 ml) and extracted with dichloromethane (3 x 20 ml), dried over $MgSO_4$ and the DCM removed *in vacuo* and dried under high vacuum for 1 h in a tared microwave vial. The stannylated intermediate (1.05 g, 0.575 mmol, 1 equivalent) was then dissolved in toluene and 1,4-dibromo-2,3,5,6-tetrafluorobenzene (1.05 g, 2.35 mmol, 6 equivalents) and tetrakis(triphenylphosphine)palladium(0) (13 mg, 0.015 mmol, 0.02 equivalents) were added. The solution was degassed by N_2 bubbling for 30 minutes before being heated to 100 °C for 24 h after which a light green solution was observed. The solution was poured onto a short silica plug and the plug eluted with chloroform:acetone 9:1 v/v until the coloured fraction had ceased to elute. The fraction was concentrated *in vacuo* and the residue purified by column chromatography eluting with DCM:acetone 95:5 v/v with 1 vol% triethylamine. The title compound was afforded as a yellow powder. Yield 84 mg, 12.2 % mp 199-201 °C. HRMS (ESI/TOF) m/z+H^+ calculated for $C_{28}H_{17}Br_2F_8O_5S_2Na$ 832.8713 found 832.8685. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 2H), 4.44-4.42 (m, 4H), 3.83-3.81 (m, 4H), 3.49-3.46 (m, 4H), 3.35-3.33 (m, 4H) $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 153.8, 124.1, 121.1, 119.0, 114.3, 111.7, 105.2, 100.1, 73.0, 71.7, 71.3, 70.5.


7.319
7.118
7.104
6.810
6.796
4.295
4.268
3.743
3.712
3.451
3.398
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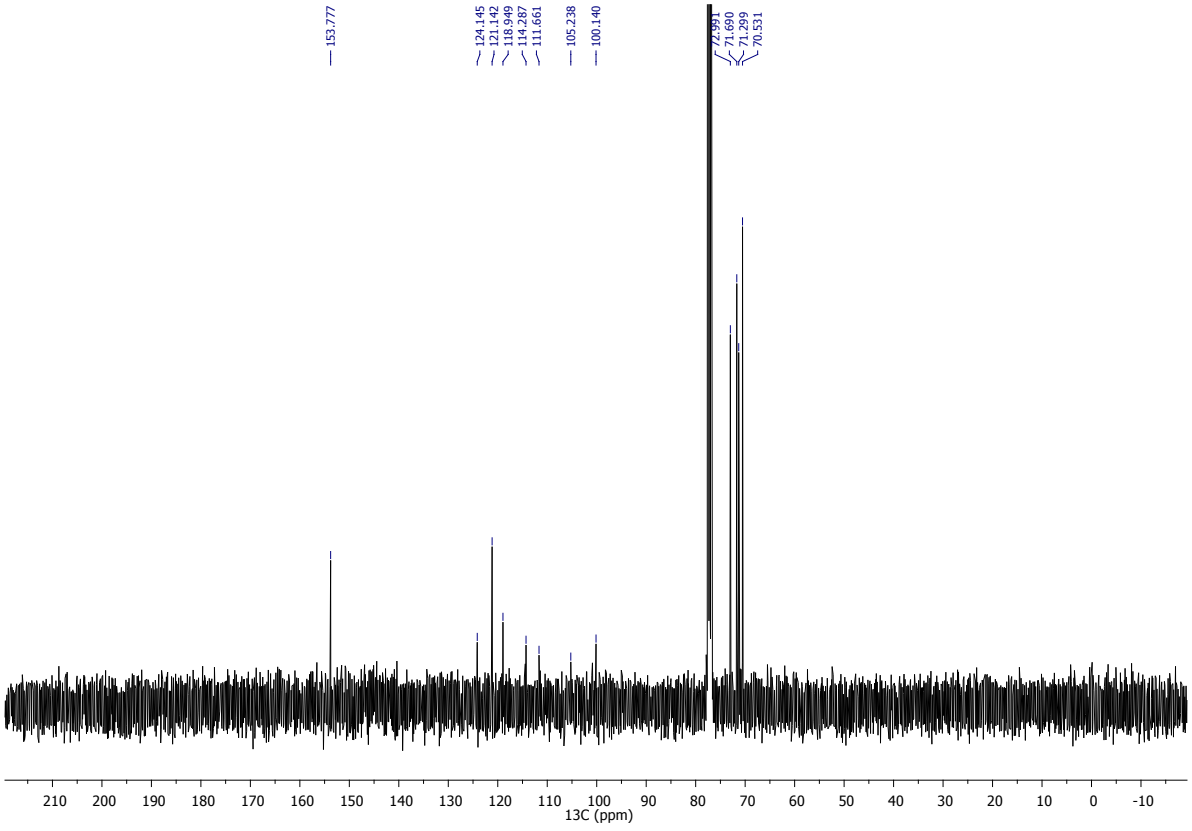
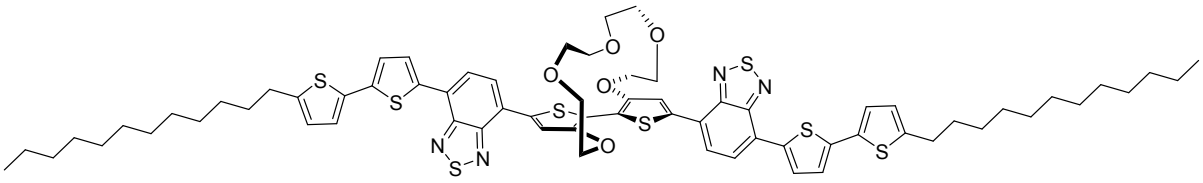
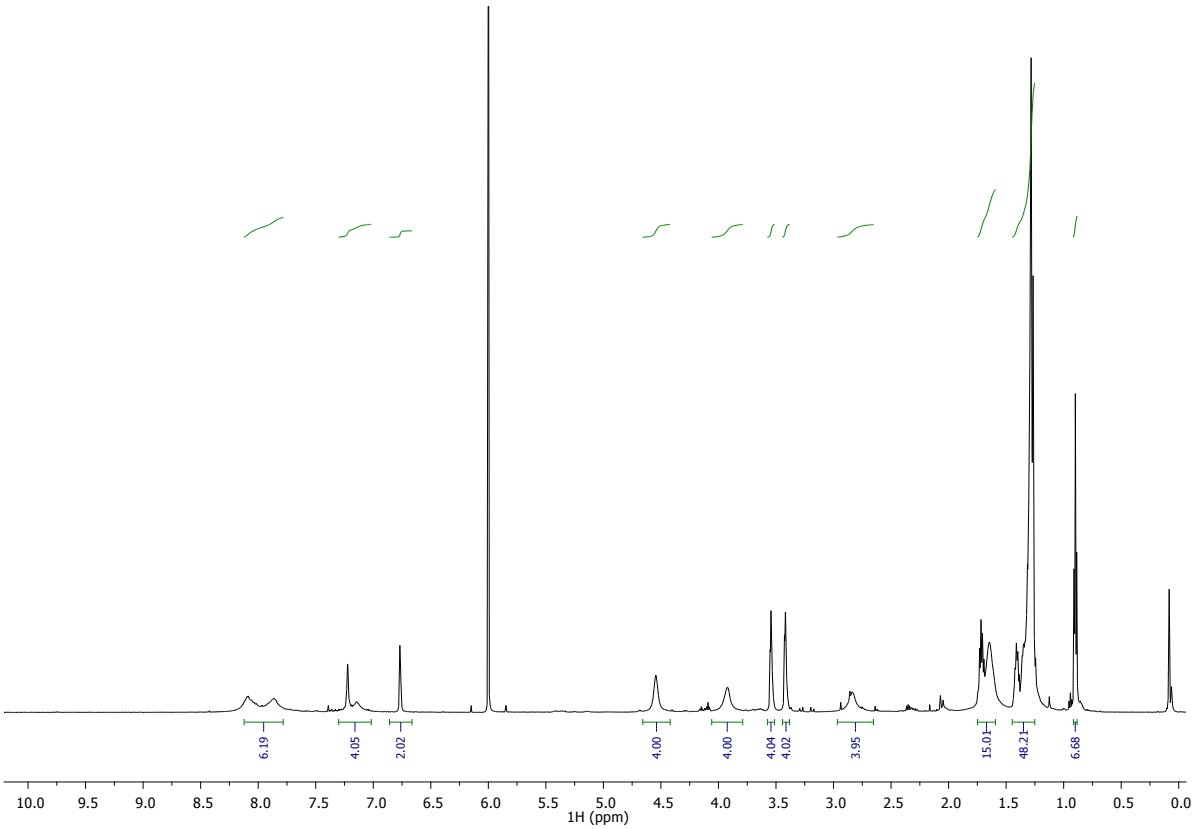
3.297
1.00
0.98
1.00
3.97
4.01
8.00
H1 (ppm)


153.777
124.145
121.142
118.949
114.287
111.661
105.238
100.140
72.991
71.690
71.299
70.531
13C (ppm)



14 2,18-Bis(7-(5'-dodecyl-[2,2'-bithiophen]-5-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)-5,6,8,9,11,12,14,15-octahydrodithieno[3,2-*n*:2',3'-*p*][1,4,7,10,13]pentaoxacycloheptadecine (M6)

In a dried degassed microwave vial 2,18-bis(7-bromobenzo[*c*][1,2,5]thiadiazol-4-yl)-5,6,8,9,11,12,14,15-octahydrodithieno[3,2-*n*:2',3'-*p*][1,4,7,10,13]pentaoxacycloheptadecine (30.0 mg, 0.038 mmol, 1 equivalent) and (5'-dodecyl-[2,2'-bithiophen]-5-yl)trimethylstannane (38.2 mg, 0.076 mmol, 2 equivalents) and tetrakis(triphenylphosphine)palladium (0) (0.8 mg, 0.00076 mmol, 0.02 equivalents) were dissolved in dry toluene (1.5 ml) and the solution degassed by N_2 bubbling for 30 minutes. The solution was heated to 100 °C for 24 h after which a dark blue solution was observed. The solution was poured onto a short silica plug eluting with 98:2 DCM:acetone v/v until the coloured fraction ceased eluting followed by column chromatography eluting with chloroform:methanol 98:2 v/v. The title compound was isolated as a dark blue solid. Yield 48.6 mg, 99 % yield, mp 135-140 °C. MALDI-TOF m/z calculated $C_{68}H_{80}N_4O_5S_8$ 1288.39 found 1288.22. ^{1}H NMR (600 MHz, TCE-d_2) δ 8.18-7.76 (m, 6H), 7.26-7.07 (m, 4H), 6.78-6.75 (m, 2H), 4.58-4.50 (m, 4H), 3.98-3.87 (m, 4H), 3.56-3.54 (m, 4H), 3.43-3.41 (m, 4H), 2.88-2.78 (m, 4H) 1.74-1.69 (m, 6H), 1.43-1.24 (m, 48H), 0.90 (t, 6H, *J* = 7.2 Hz).^{13}C {^{1}H} NMR (151 MHz, TCE-d_2) δ 71.4, 70.5, 32.1, 29.9, 29.8, 29.8, 29.7, 29.5, 29.3, 22.9, 14.4.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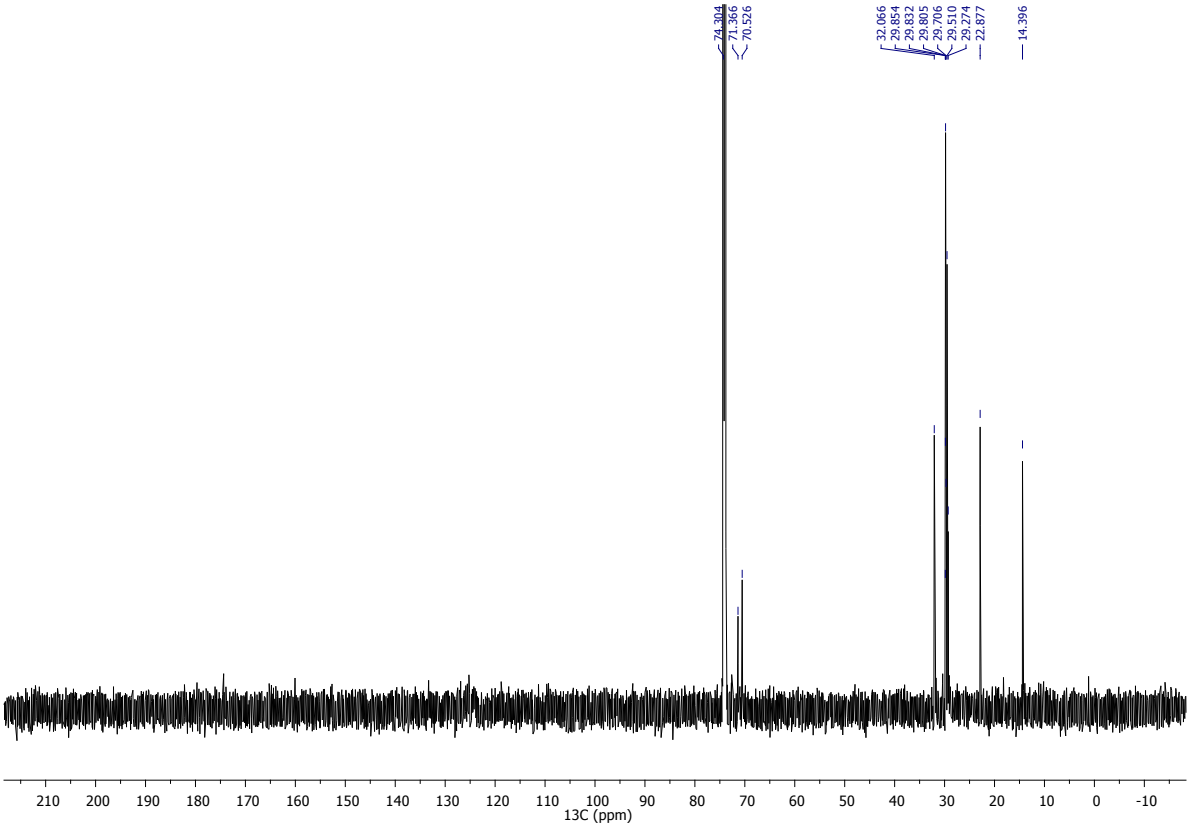
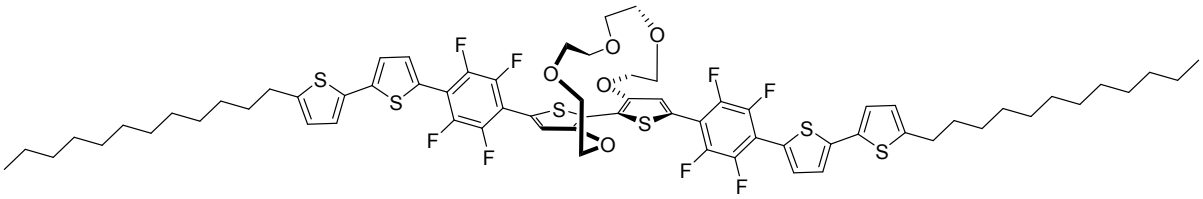
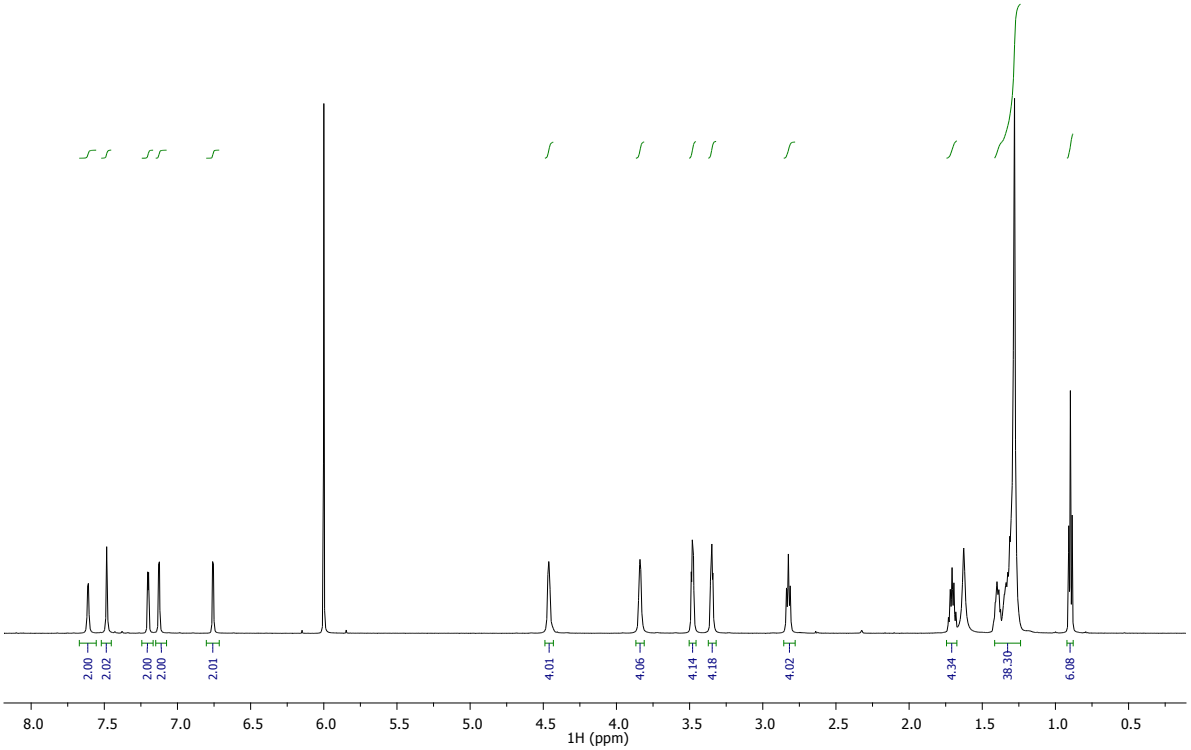
4.05
2.02
4.00
4.00
4.04
4.02
3.95
15.01
48.21
6.68
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
1H (ppm)

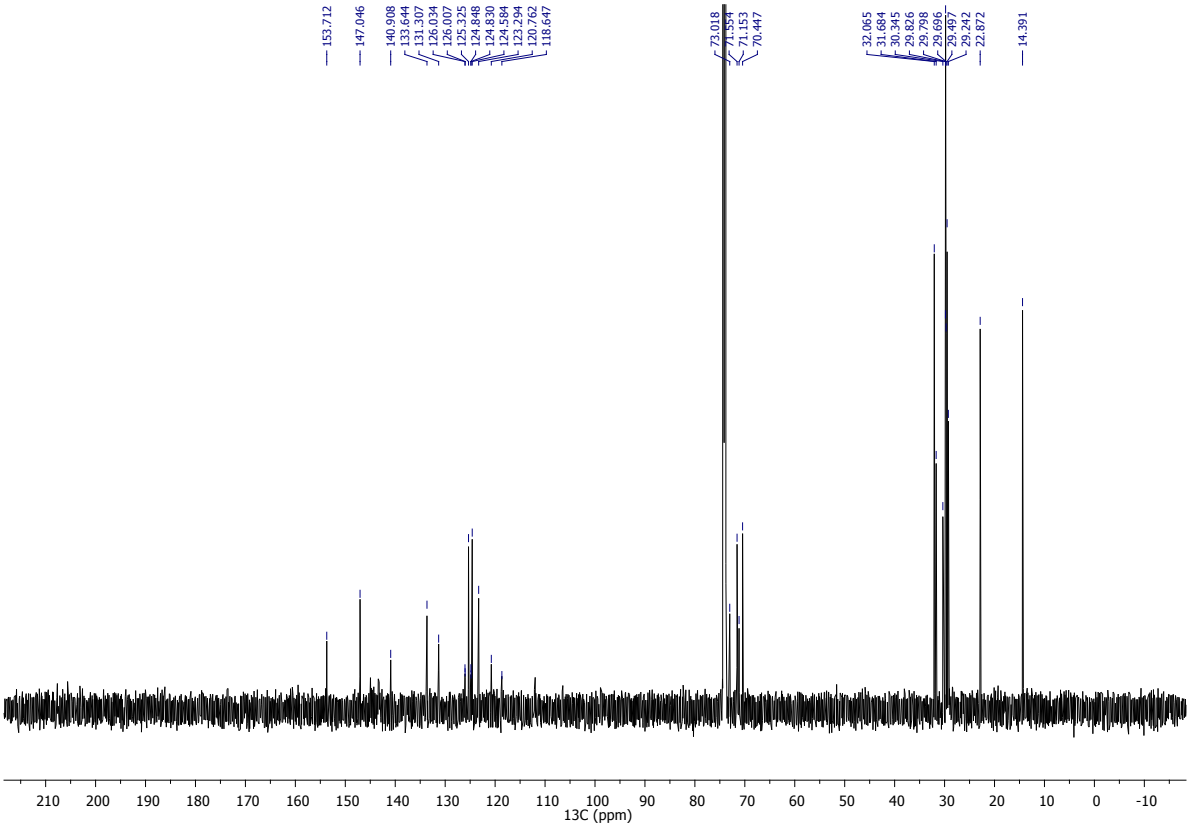

74.304
71.366
70.526
32.066
29.854
29.832
29.805
29.706
29.510
29.274
22.877
14.396
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
13C (ppm)



15 2,18-Bis(4-(5'-dodecyl-[2,2'-bithiophen]-5-yl)-2,3,5,6-tetrafluorophenyl)-5,6,8,9,11,12,14,15-octahydrodithieno[3,2-*n*:2',3'-*p*][1,4,7,10,13]pentaoxacycloheptadecine (M6)

In a dried degassed microwave vial 2,18-bis(4-bromo-2,3,5,6-tetrafluorophenyl)-5,6,8,9,11,12,14,15-octahydrodithieno[3,2-*n*:2',3'-*p*][1,4,7,10,13]pentaoxacycloheptadecine (50.0 mg, 0.062 mmol, 1 equivalent) and (5'-dodecyl-[2,2'-bithiophen]-5-yl)trimethylstannane (61.4 mg, 0.124 mmol, 2 equivalents) and Pd_2dba_3 (2.3 mg, 0.00025 mmol, 0.02 equivalents) and P-(*o*-tolyl)$_3$ (1.5 mg, 0.0050 mmol, 0.08 equivalents) were dissolved in dry toluene (2 ml) and the solution degassed by N_2 bubbling for 30 minutes. The solution was heated to 100 °C for 24 h after which a red solution was observed, which formed an orange precipitate on cooling. The solution was poured onto a short silica plug eluting with 90:10 chloroform:acetone v/v until the coloured fraction ceased eluting followed by column chromatography eluting with chloroform:ethyl acetate 99:1 v/v. the resulting solid was recrystallised from DCM. The title compound was isolated as an orange solid. Yield 72.6 mg, 89 % yield, mp 158-159 °C. MALDI-TOF m/z calculated for $C_{68}H_{76}F_8O_5S_6$ 1317.70 found 1316.13. ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (600 MHz, TCE-d_2) δ 7.61 (d, 2H, 3.6 Hz) , 7.48 (s, 2H), 7.20 (d, 2H, *J* = 4.2 Hz), 7.13 (d, 2H, *J* = 3.6 Hz, 6.76 (d, 2H, *J* = 3.6 Hz), 4.93-4.15 (m, 4H), 3.71-3.80 (m, 4H), 3.51, 3.45 (m, 4H), 3.37-3.33 (m, 4H), 2.83 (t, 4H, *J* = 7.8 Hz), 1.73- 1.68 (m, 4H), 1.42-1.23 (m, 38H),0.90 (t, 6H, *J* = 6.6 Hz). ^{13}C {^{1}H} NMR (151 MHz, TCE-d_2) δ 153.7, 147.1, 140.9, 133.6, 131.3, 126.0, 126.0, 125.3, 124.9, 124.8, 124.6, 123.3, 120.7, 118.7, 73.0, 71.6, 71.2, 70.5, 32.1, 31.7, 30.3, 29.8, 29.8, 29.7, 29.5, 29.2, 22.9, 14.4.


2.00
2.02
2.00
2.00
2.01
4.01
4.06
4.14
4.18
4.02
4.34
38.30
6.08
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
1H (ppm)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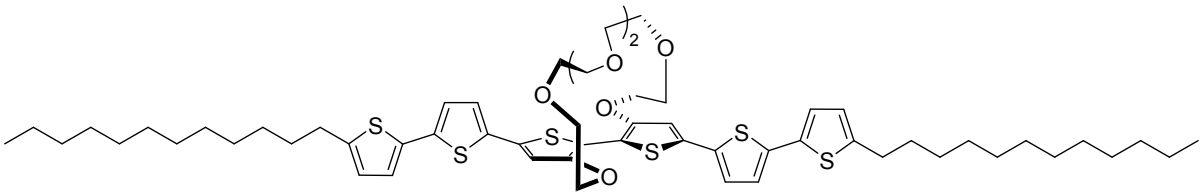
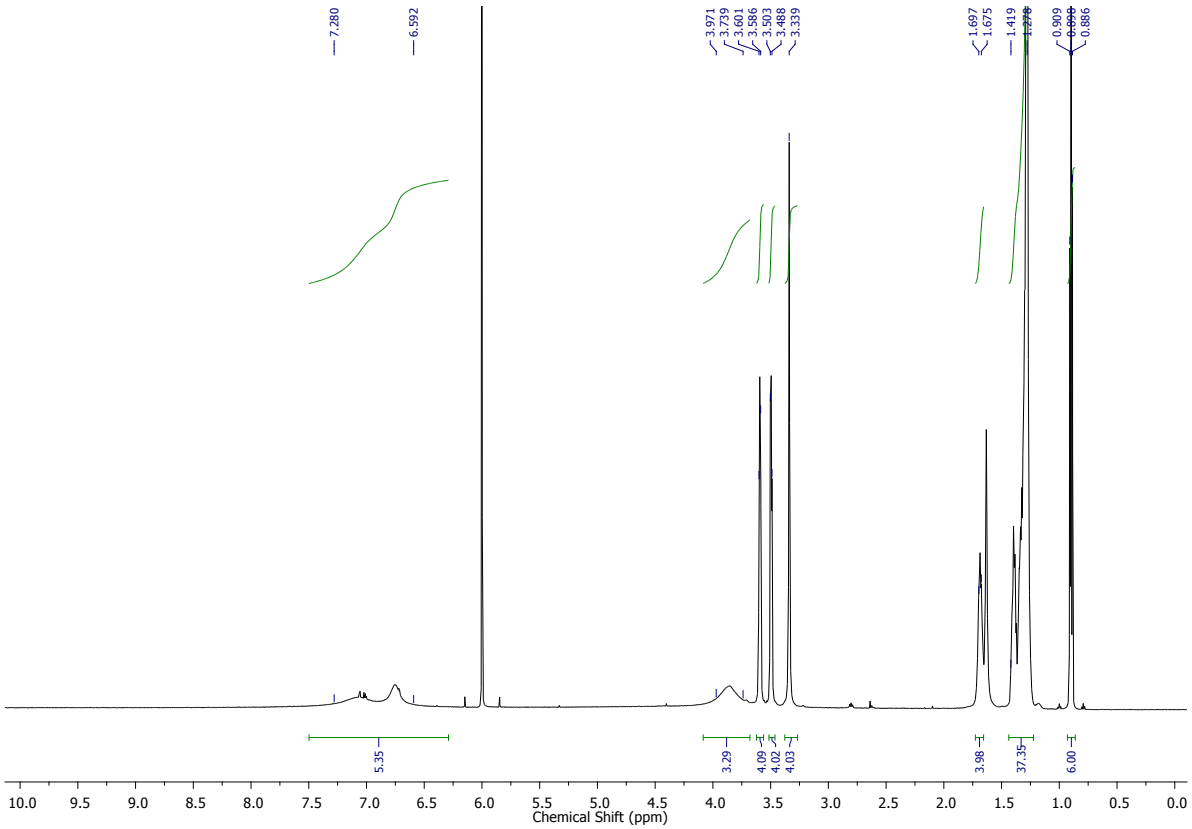
140.908
133.644
131.307
126.034
126.007
125.325
124.848
124.830
124.584
123.294
120.762
118.647
73.018
71.554
71.153
70.447
32.065
31.684
30.345
29.826
29.798
29.696
29.497
29.242
22.872
14.391
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
13C (ppm)



16 2,21-Bis(5'-dodecyl-[2,2'-bithiophen]-5-yl)-5,6,8,9,11,12,14,15,17,18-decahydrodithieno[3,2-*q*:2',3'-*s*][1,4,7,10,13,16]hexaoxacycloicosine (M2)

In a dried degassed microwave vial 2,21-dibromo-5,6,8,9,11,12,14,15,17,18-decahydrodithieno[3,2-*q*:2',3'-*s*][1,4,7,10,13,16]hexaoxacycloicosine (115 mg, 0.21 mmol, 1 equivalent) and (5'-dodecyl-[2,2'-bithiophen]-5-yl)trimethylstannane (205 mg, 0.4.12 mmol, 2 equivalents) were dissolved in dry toluene (2 ml) and the solution degassed by N_2 bubbling for 30 minutes. Tetrakis(triphenylphosphine) palladium(0) was added and the solution further degassed for 10 minutes. The solution was heated to 100 °C for 24 h after which a colour change from yellow to orange was observed. The solution was poured directly onto a column and the column eluted with toluene:ethyl acetate 7:3 v/v. The title compound was isolated as a bright orange solid yield 127 mg, 58 % yield, mp 103-105 °C MALDI-TOF m/z 1064.43 calculated for $C_{58}H_{80}O_6S_6$ found 1066.10. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.05-6.95 (m, 8H), 6.68 (d, 2H, *J* = 3 HZ), 4.40-4.37 (m, 4H), 3.85-3.83 (m, 4H), 3.60-3.58 (m, 4H) 3.52-3.51 (m, 4H), 3.37 (s, 4H), 2.85-2.75 (m, 4H), 1.71-1.66 (m, 4H), 1.41-1.21 (m, 36H), 0.88 (t, 3H, *J* = 5.4 Hz). ^{13}C{^{1}H} NMR (151 MHz, TCE-d_2) δ 71.6, 70.5, 70.2, 32.1, 29.8, 29.8, 29.7, 29.5, 29.3, 22.9, 14.4.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6.592
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3.739
3.601
3.586
3.503
3.488
3.339
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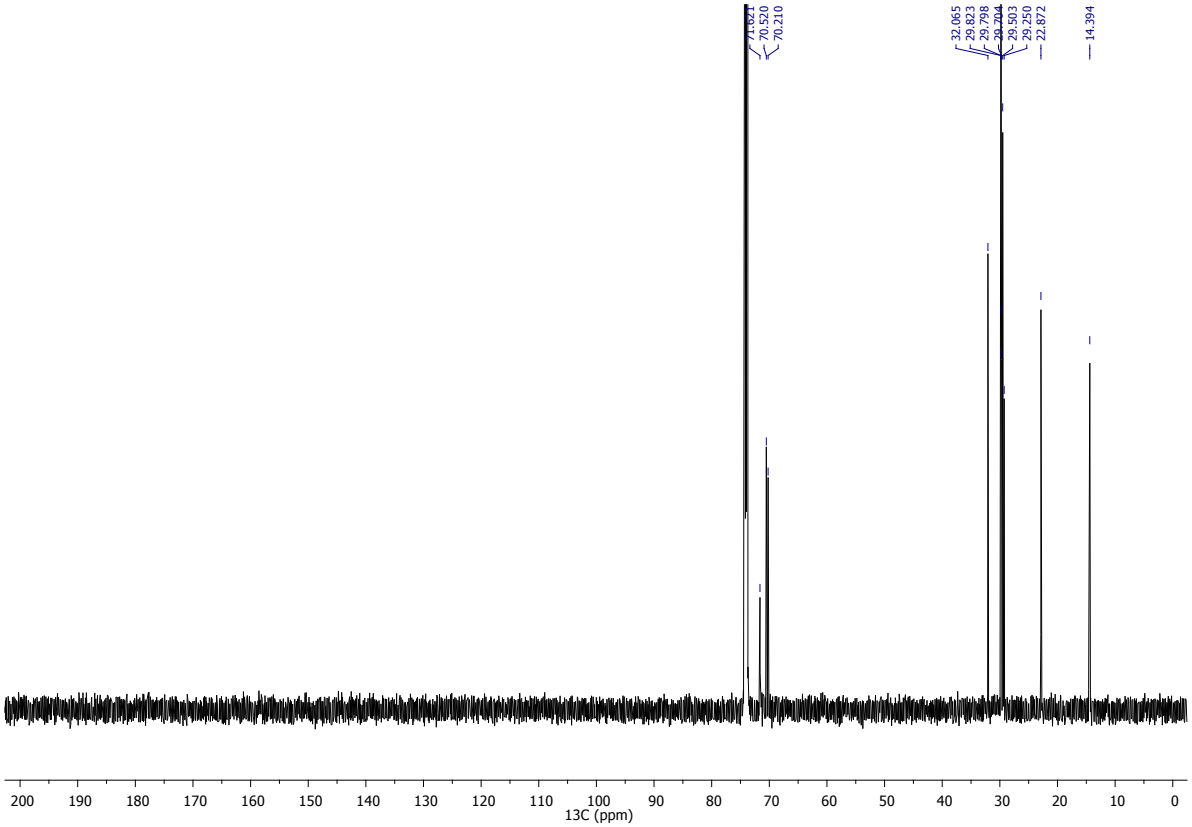
1.675
1.419
1.278
0.909
0.898
0.886
5.35
3.29
4.09
4.02
4.03
3.98
37.35
6.00
Chemical Shift (ppm)


71.824
70.520
70.210
32.065
29.823
29.798
29.503
29.250
22.872
14.394
13C (ppm)

UV-Vis

M1

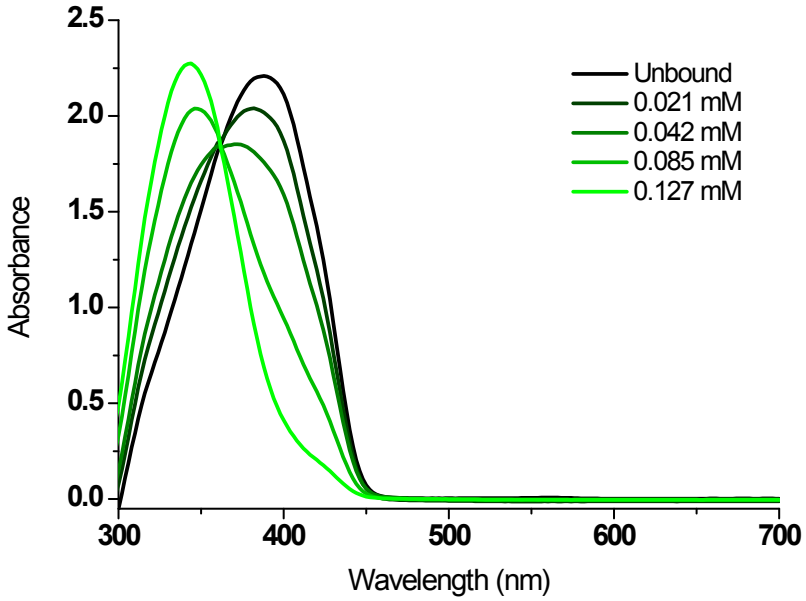


Figure S1 UV-Vis titration experiment at room temperature for **M1** (8.8×10^{-5} M in chloroform) upon addition of $NaBPh_4$ aliquots in chloroform.

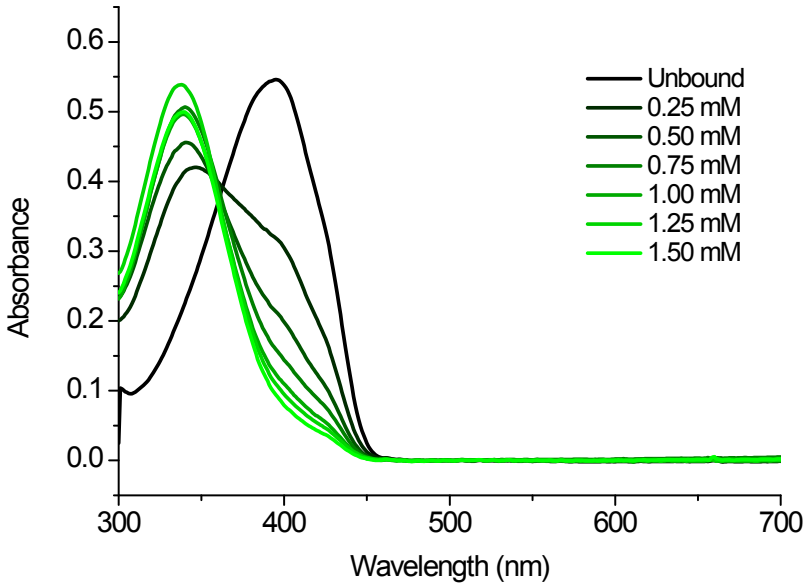


Figure S2 UV-Vis titration experiment at room temperature for **M1** (1.7×10^{-5} M in THF) upon addition of $NaBPh_4$ aliquots in THF.

M2

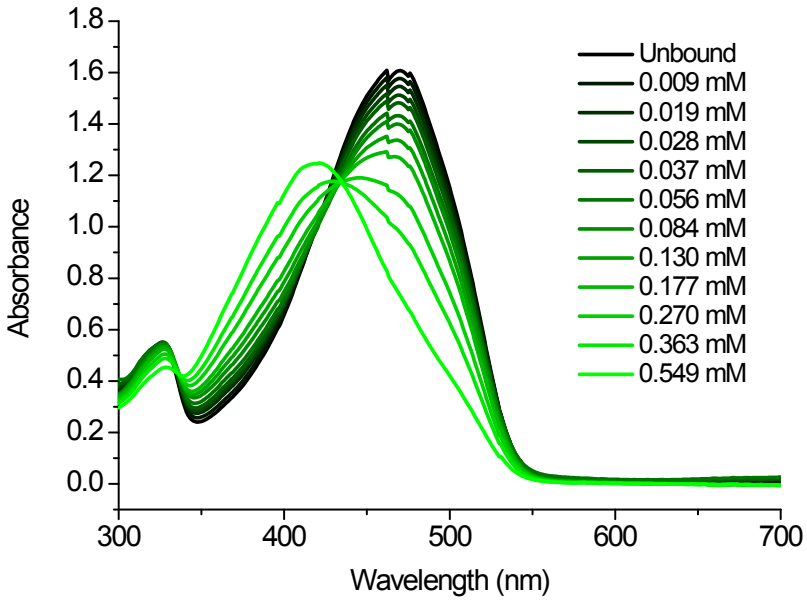


Figure S3 UV-Vis titration experiment at room temperature for **M2** (6.1 x 10^{-6} M in chloroform) upon addition of $KBPh_4$ aliquots in chloroform.

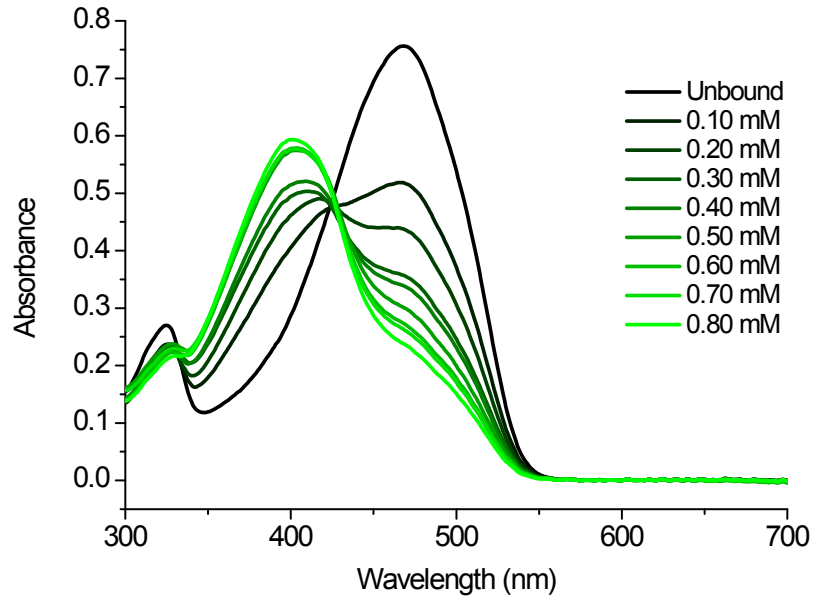


Figure S4 UV-Vis titration experiment at room temperature for **M2** (1.38 x 10^{-5} M in THF) upon addition of $KBPh_4$ aliquots in THF.

M3

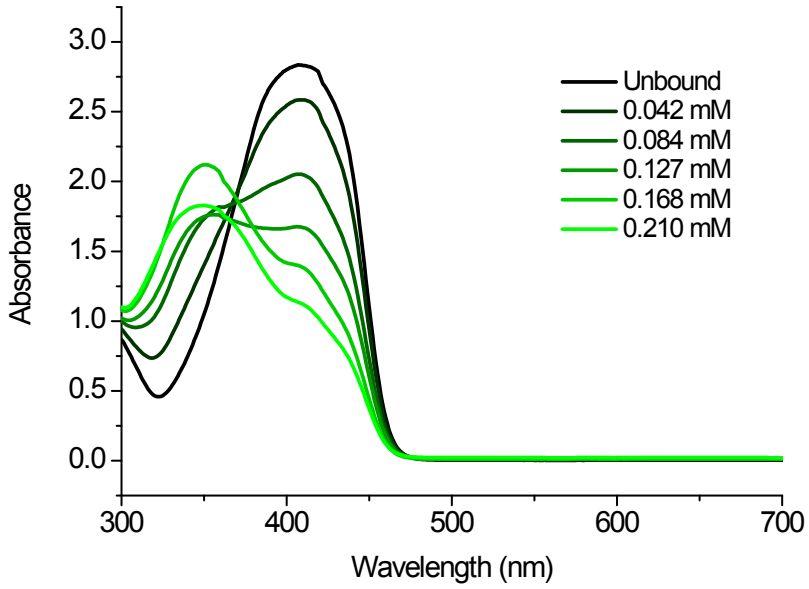


Figure S5 UV-Vis titration experiment at room temperature for **M3** (9.9 x 10^{-5} M in chloroform) upon addition of $NaBPh_4$ aliquots in chloroform.

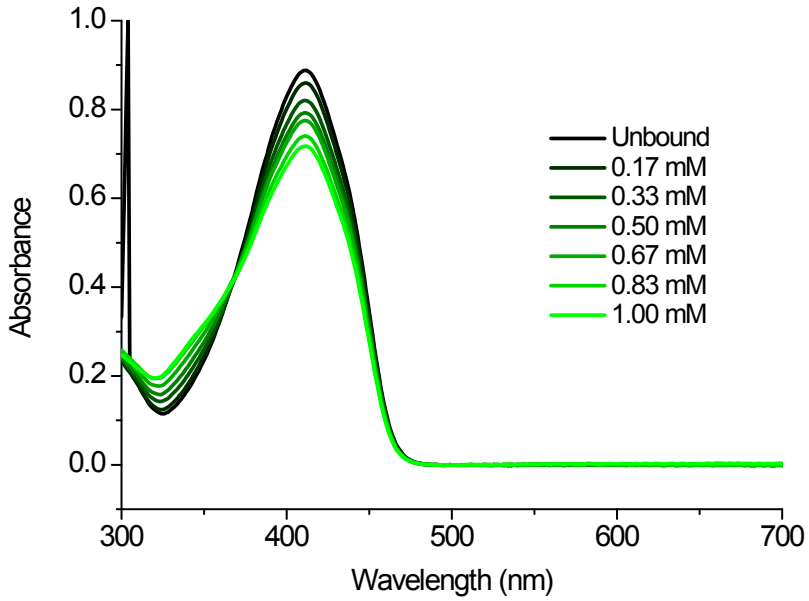


Figure S6 M3 UV-Vis titration experiment at room temperature for **M3** (1.8 x 10^{-5} M in THF) upon addition of $NaBPh_4$ aliquots in THF.

M4

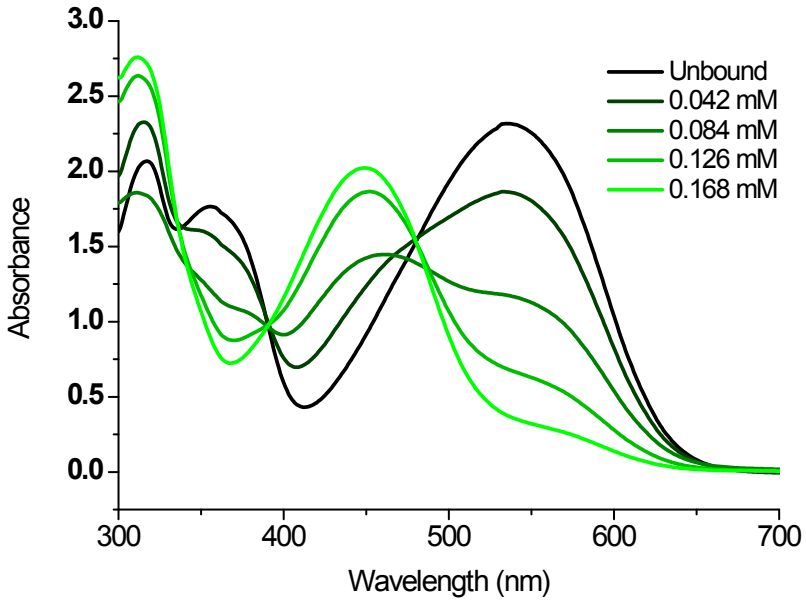


Figure S7 UV-Vis titration experiment at room temperature for **M4** (10.0 x 10^{-5} M in chloroform) upon addition of $NaBPh_4$ aliquots in chloroform.

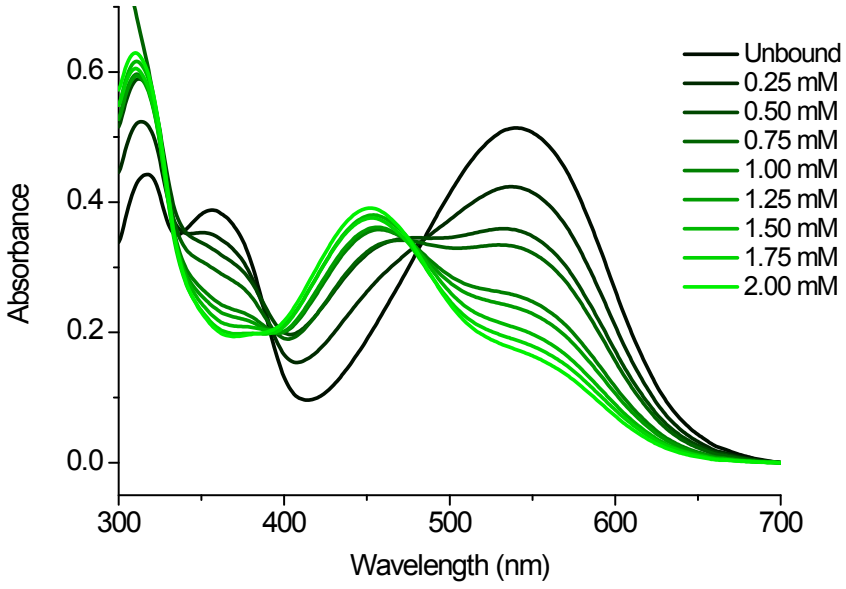


Figure S8 UV-Vis titration experiment at room temperature for **M4** (1.8 x 10^{-5} M in THF) upon addition of $NaBPh_4$ aliquots in THF.

M5

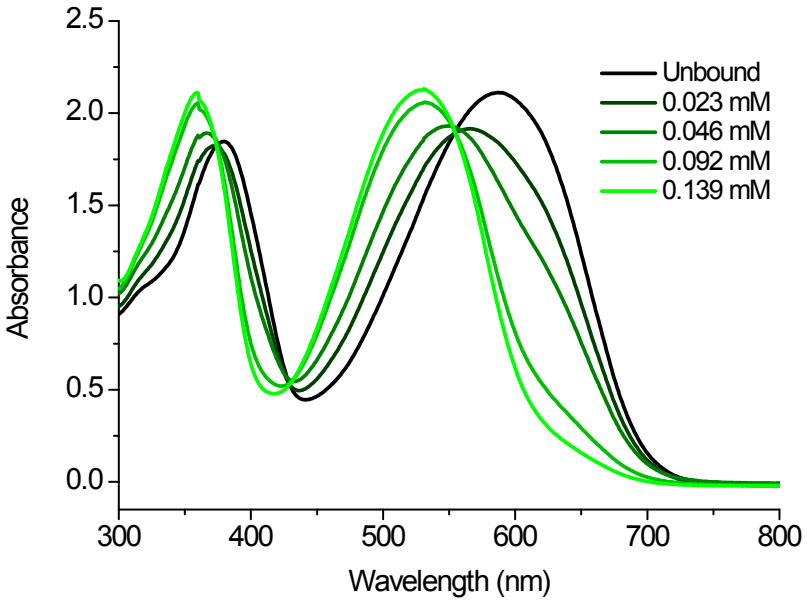


Figure S9 UV-Vis titration experiment at room temperature for **M5** (4.4 x 10^{-5} M in chloroform) upon addition of $NaBPh_4$ aliquots in chloroform.

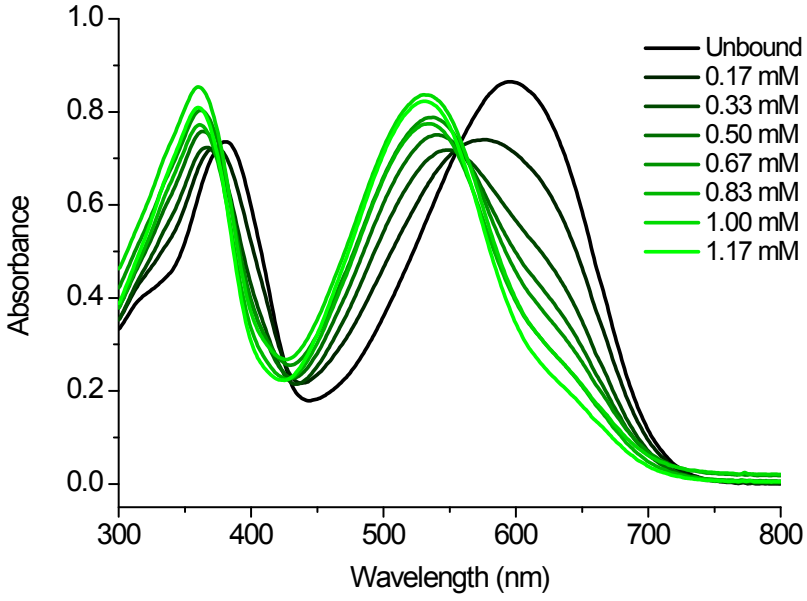


Figure S10 UV-Vis titration experiment at room temperature for **M5** (1.1 x 10^{-5} M in THF) upon addition of $NaBPh_4$ aliquots in THF.

M6

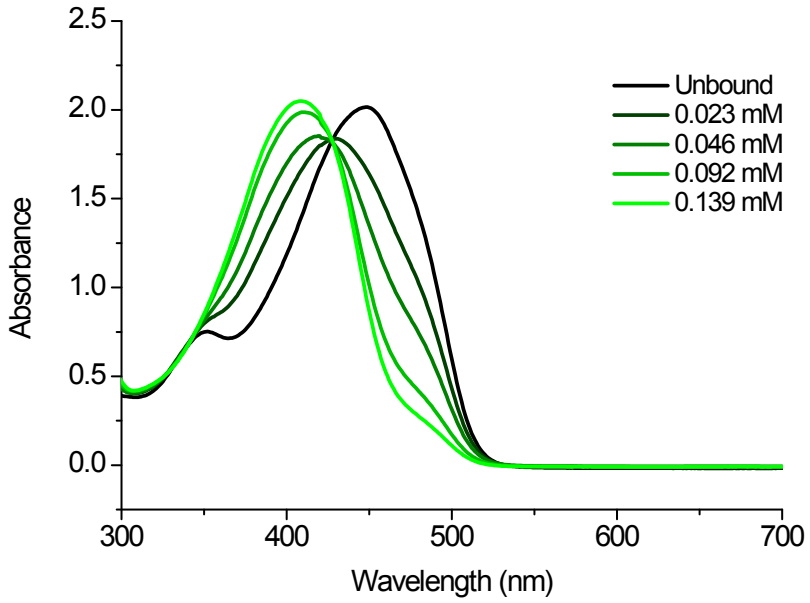


Figure S11 UV-Vis titration experiment at room temperature for **M6** (2.8 x 10^{-5} M in chloroform) upon addition of $NaBPh_4$ aliquots in chloroform.

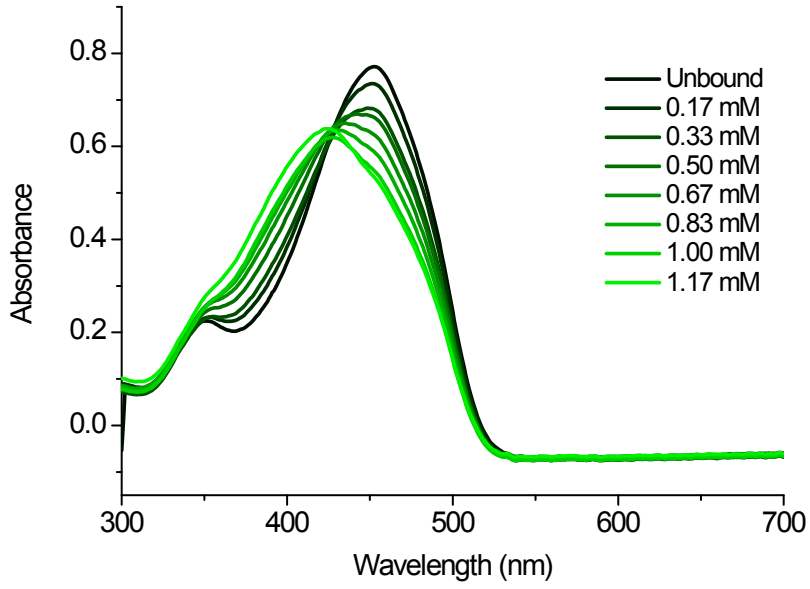


Figure S12 UV-Vis titration experiment at room temperature for **M6** (1.0 x 10^{-5} M in THF) upon addition of $NaBPh_4$ aliquots in THF.

Benesi Hildebrand plots

All binding constants were calculated from the UV-Vis titration experiments in the previous section at the stated concentration and temperature.

Binding constant (K_d) was calculated via previously reported methods, using equation S1.[3]

$$\frac{1}{(A - A_0)} = \frac{1}{K_a(A_{max} - A_0)[G]} + \frac{1}{(A_{max} - A_0)}$$

Where A is the absorbance of the molecule in the presence of the guest, A_0 is the absorbance recorded in the maximum guest concentration, and [G] is the guest concentration and K_a is the association constant.

A plot of:

$$\frac{1}{[G]} \; versus \; \frac{1}{(A - A_0)}$$

Yields a straight line where:

$$Gradient = \frac{1}{K_a(A_{max} - A_0)}$$

Which can be solved for K_a:

$$K_a = \frac{1}{Gradient(A_{max} - A_0)}$$

K_d was then calculated from

$$K_d = \frac{1}{K_a}$$

M1

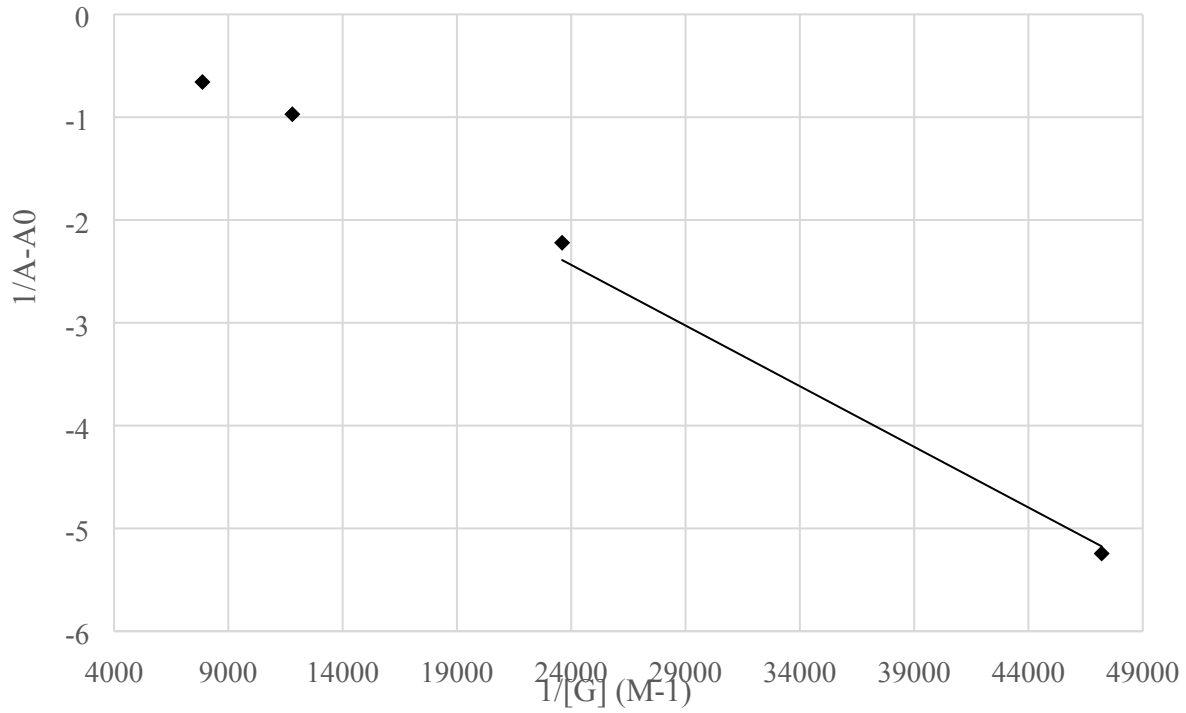


Figure S12 Benesi-Hildebrand plot of **M1** at 8.8 x 10^{-5} M in chloroform titrated with $NaBPh_4$ aliquots at room temperature.

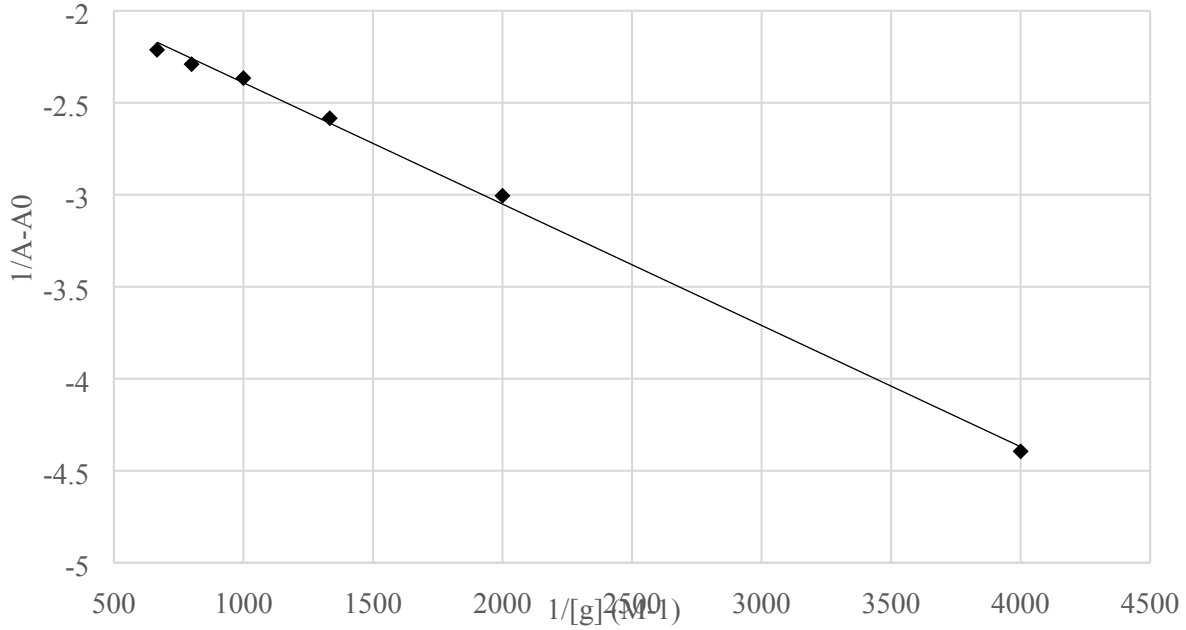


Figure S13 Benesi-Hildebrand plot of **M1** at 1.7 x 10^{-5} M in THF titrated with $NaBPh_4$ aliquots at room temperature.

M2

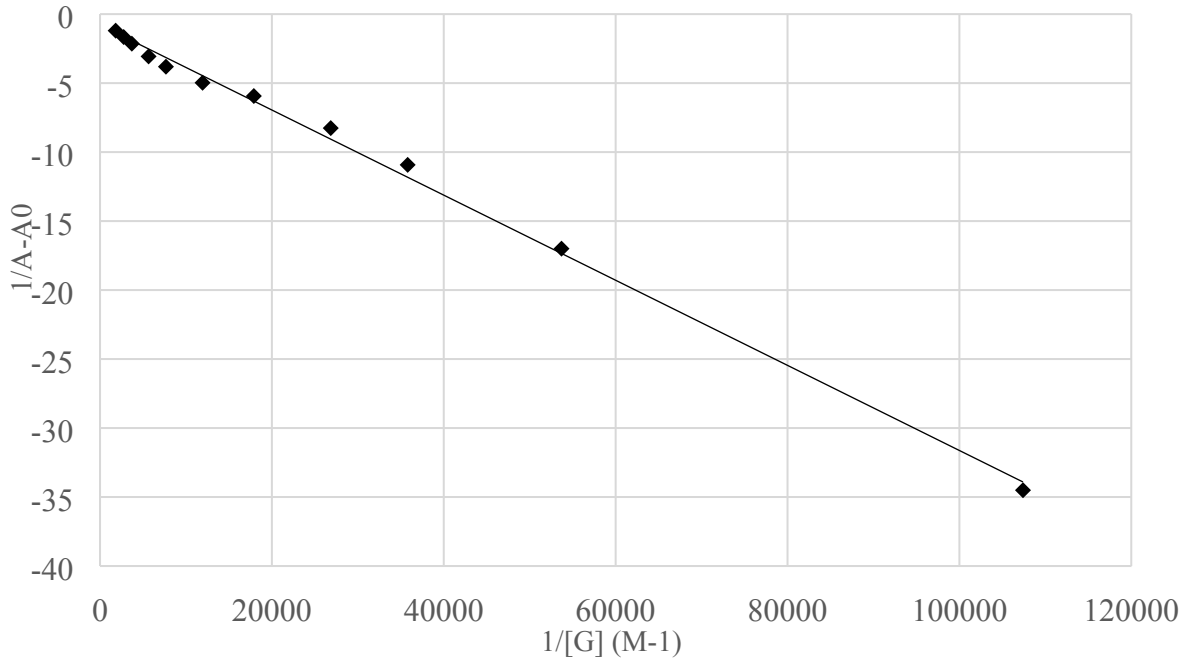


Figure S14 Benesi-Hildebrand plot of **M2** at 6.1 x 10^{-6} M in chloroform titrated with $KBPh_4$ aliquots at room temperature.

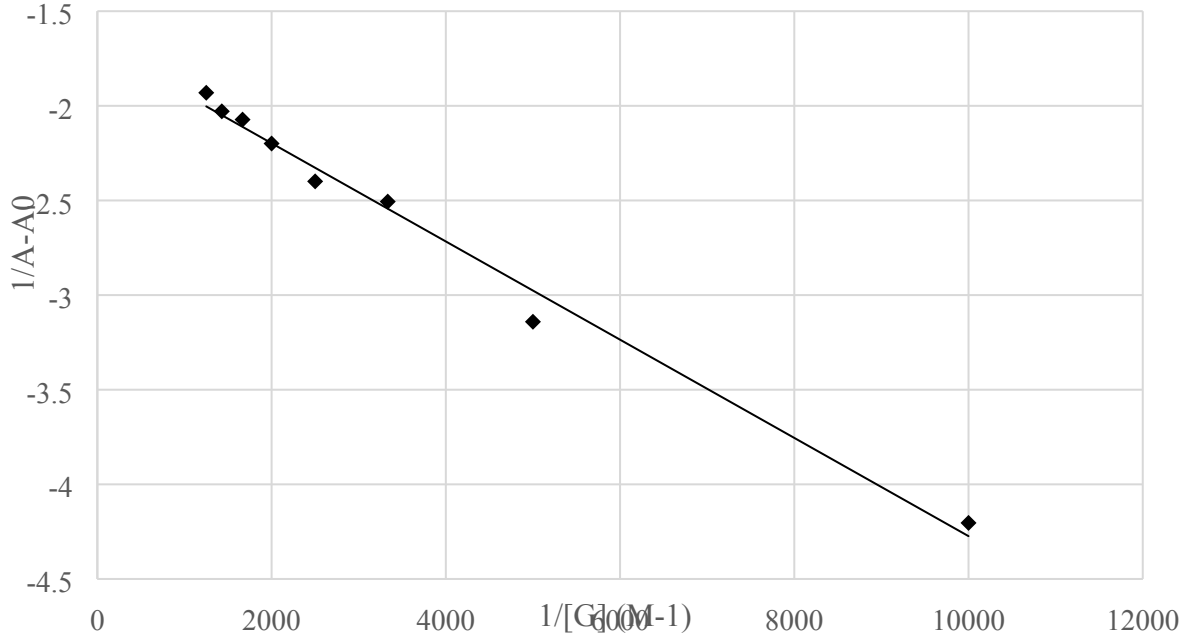


Figure S15 Benesi-Hildebrand plot of **M2** at 1.38 x 10^{-5} M in THF titrated with $KBPh_4$ aliquots at room temperature.

M3

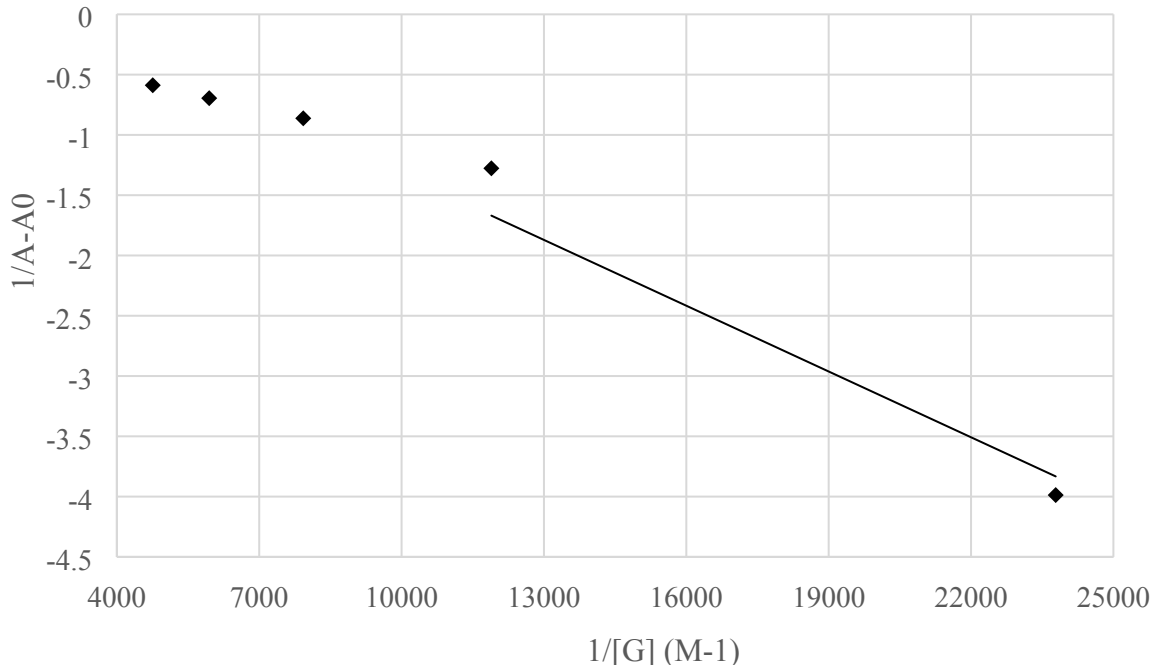


Figure S16 Benesi-Hildebrand plot of **M3** at 9.9 x 10^{-5} M in chloroform titrated with $NaBPh_4$ aliquots at room temperature.

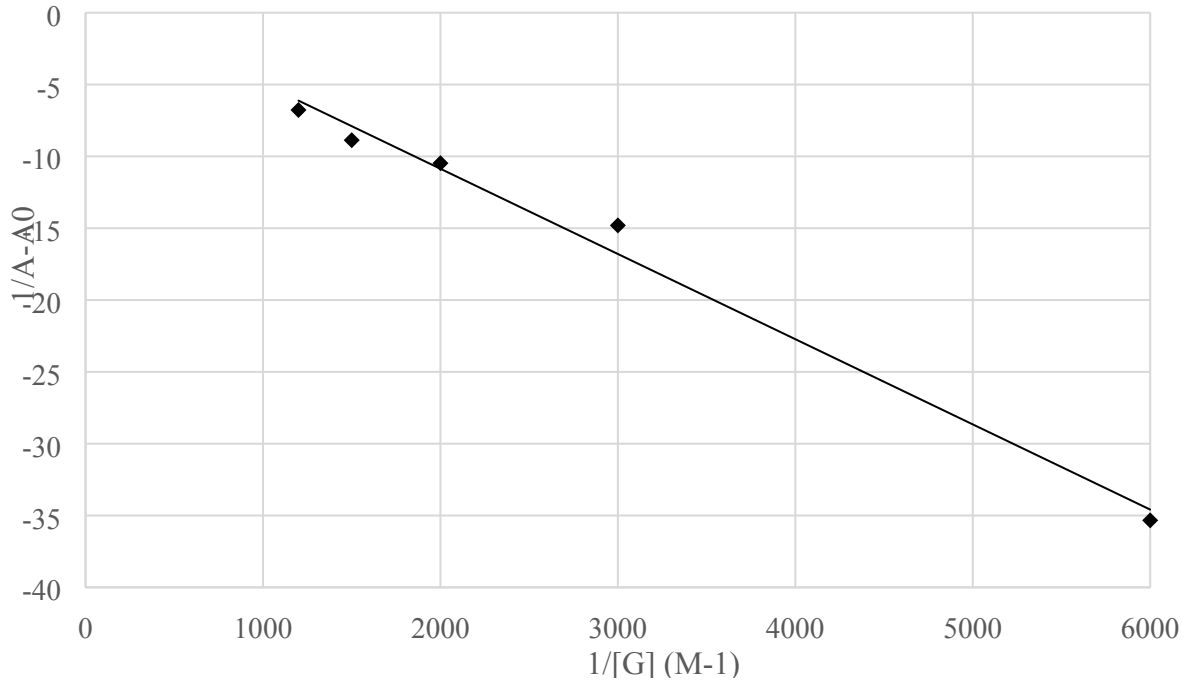


Figure S17 Benesi-Hildebrand plot of **M3** at 1.8 x 10^{-5} M in THF titrated with $NaBPh_4$ aliquots at room temperature.

M4

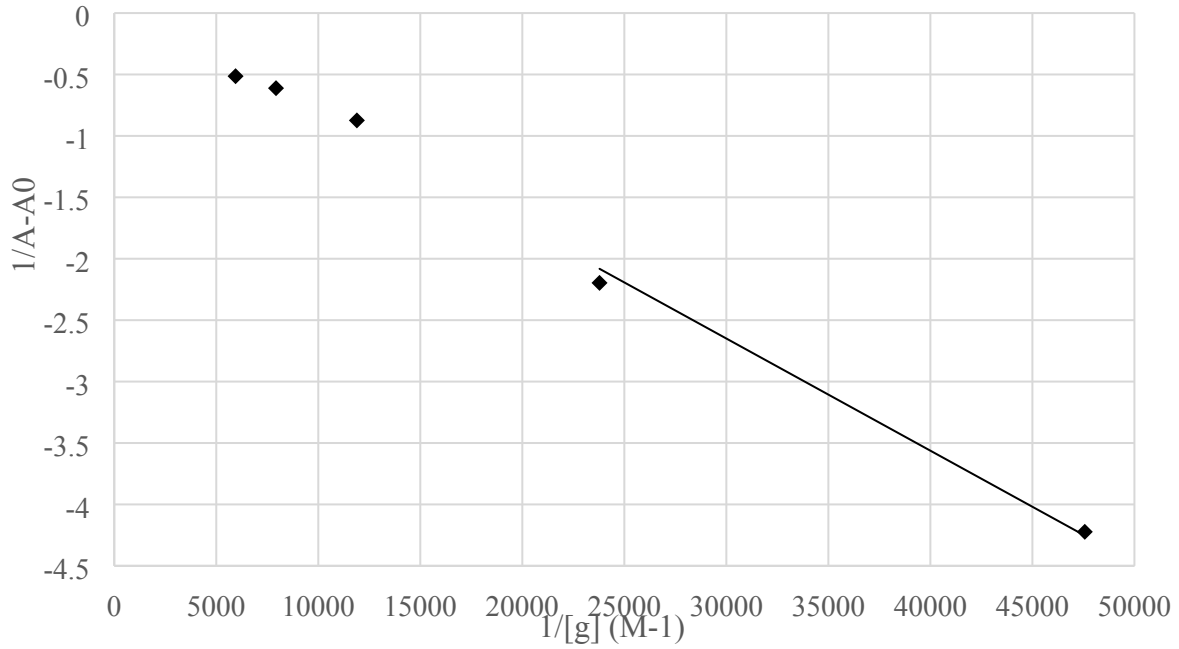


Figure S18 Benesi-Hildebrand plot of **M4** at 10.0 x 10^{-5} M in chloroform titrated with $NaBPh_4$ aliquots at room temperature.

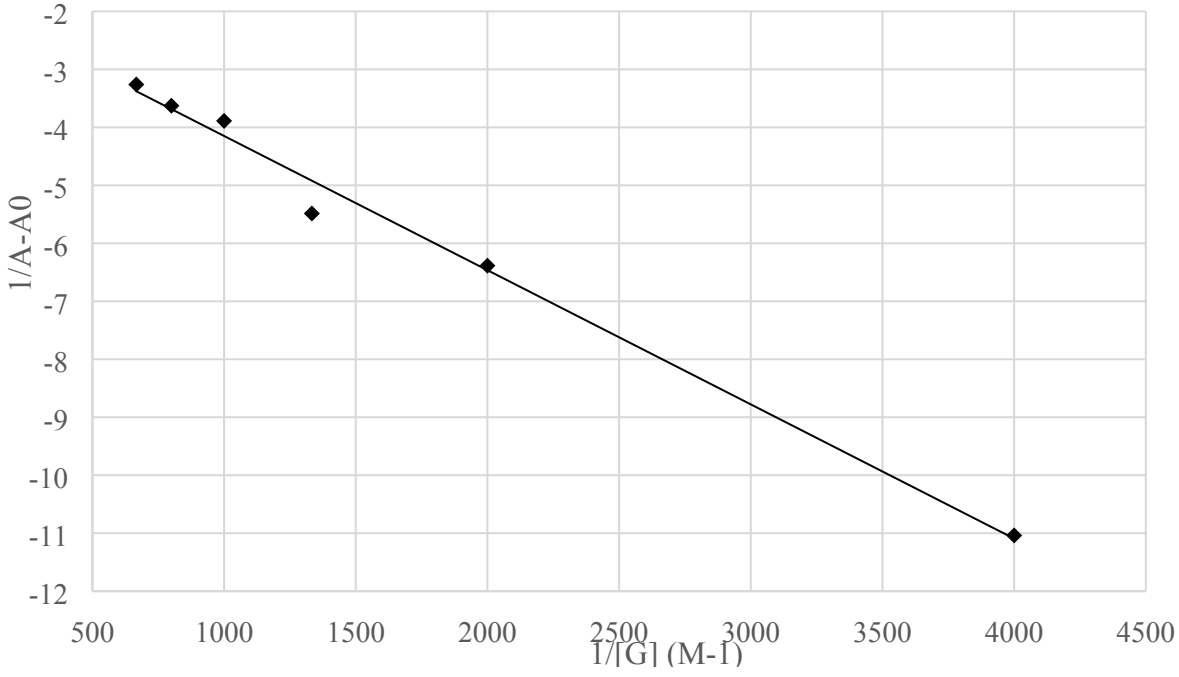


Figure S19 Benesi-Hildebrand plot of **M4** at 1.8 x 10^{-5} M in THF titrated with $NaBPh_4$ aliquots at room temperature.

M5

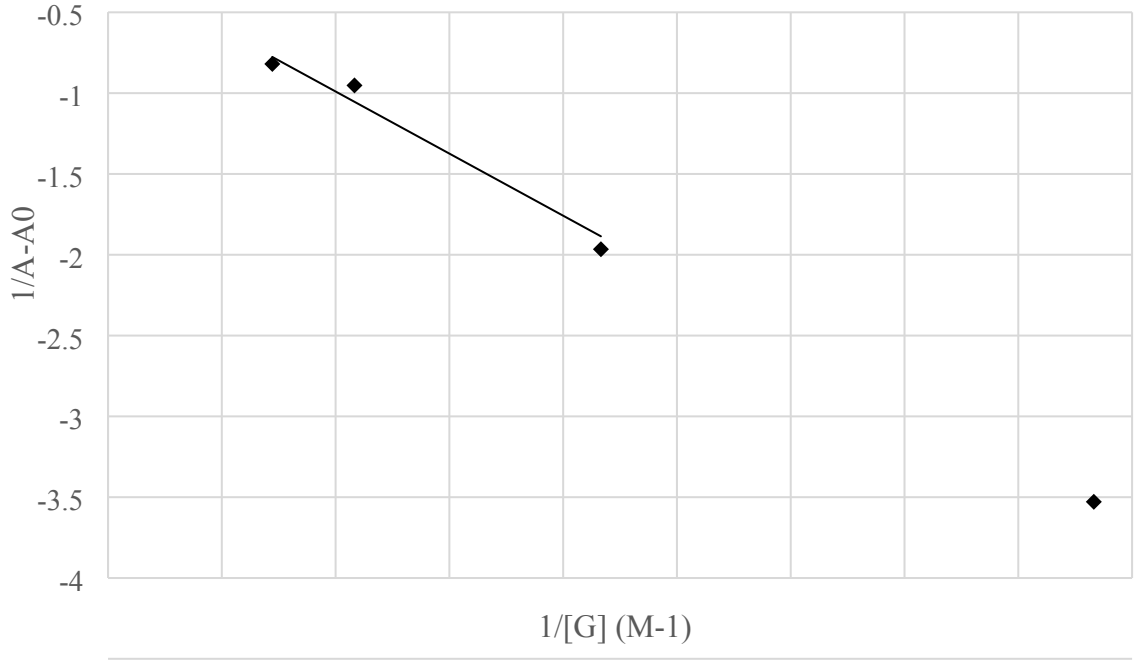


Figure S20 Benesi-Hildebrand plot of **M5** at 4.4 x 10^{-5} M in chloroform titrated with $NaBPh_4$ aliquots at room temperature.

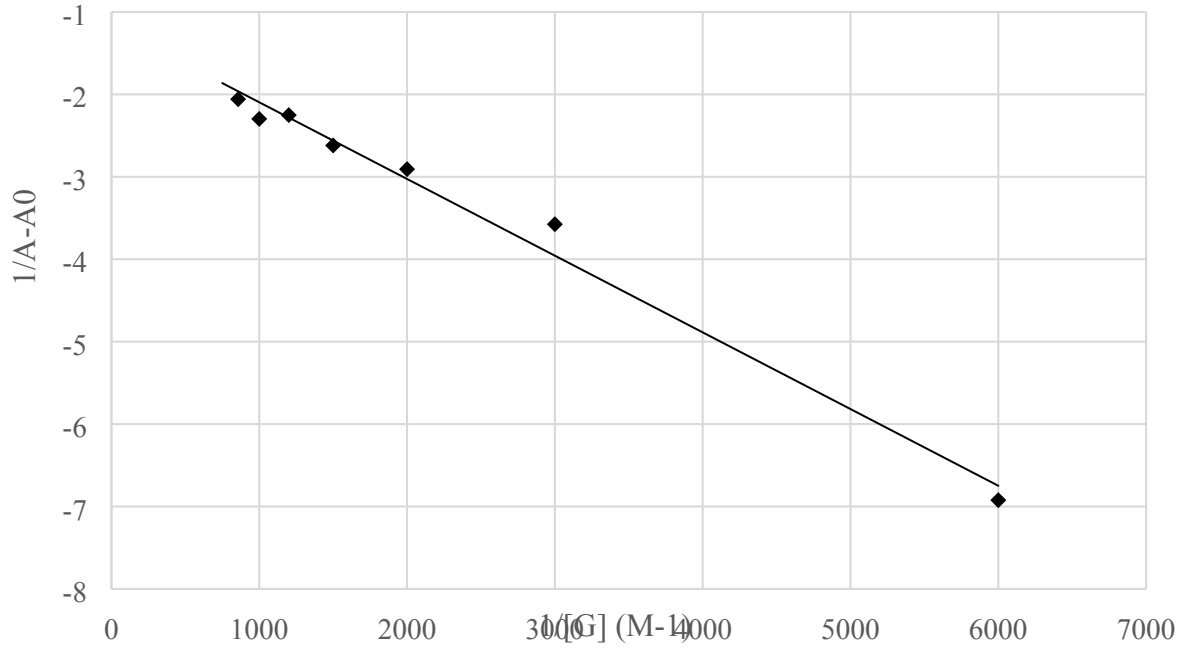


Figure S21 Benesi-Hildebrand plot of **M5** at 1.1 x 10^{-5} M in THF titrated with $NaBPh_4$ aliquots at room temperature.

M6

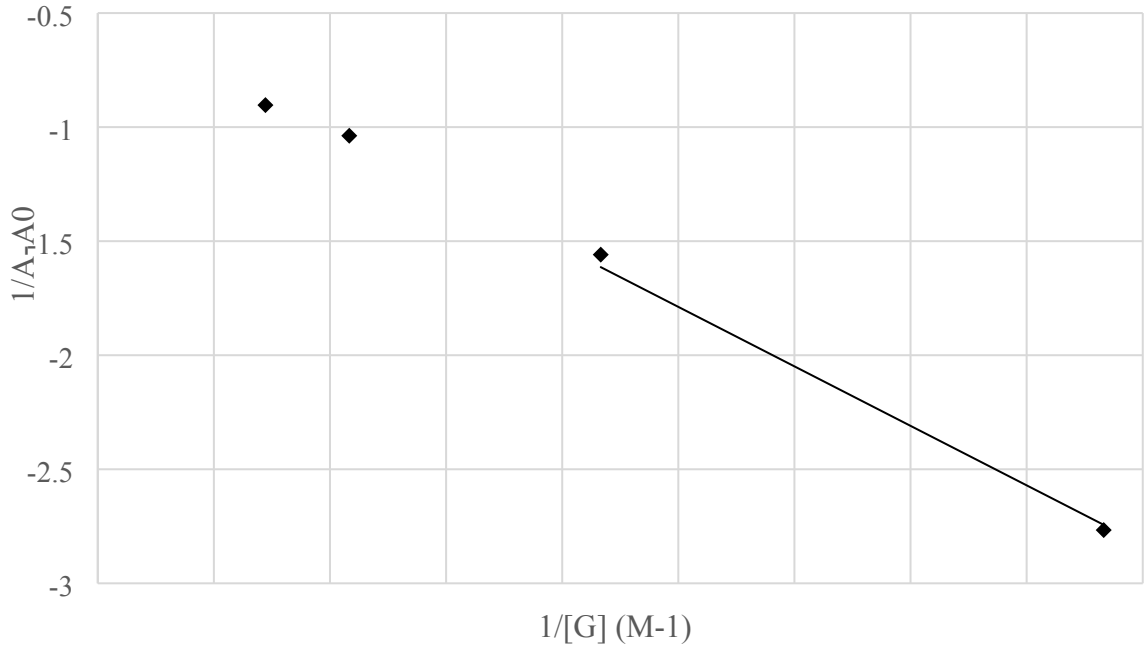


Figure S22 Benesi-Hildebrand plot of **M6** at 2.8 x 10^{-5} M in chloroform titrated with $NaBPh_4$ aliquots at room temperature.

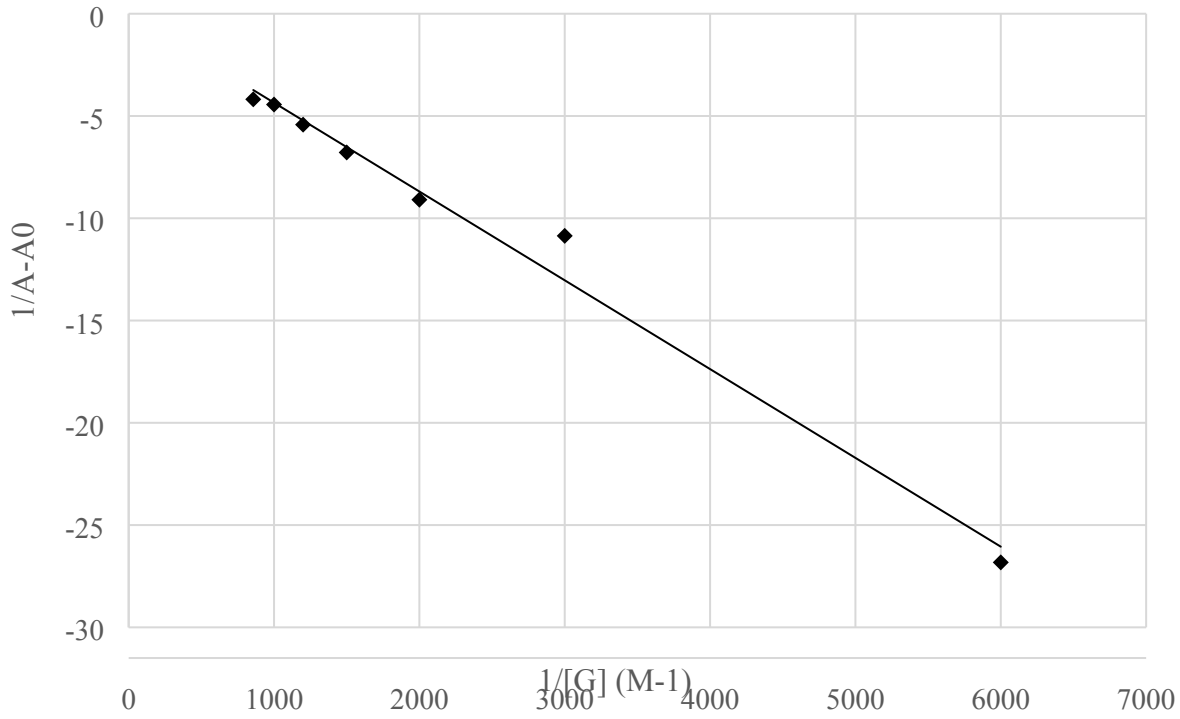


Figure S23 Benesi-Hildebrand plot of **M6** at 1.0 x 10^{-5} M in THF titrated with $NaBPh_4$ aliquots at room temperature.

Limit of Detection Calculation

Limit of detection (LOD) and limit of quantification (LOQ) were calculated according to reported methods.[4]

$$LOD = \frac{3\sigma}{m}$$

$$LOQ = \frac{10\sigma}{m}$$

Where *LOD* is the limit of detection, LOQ is limit of quantification σ is the standard deviation of the baseline, and *m* is the gradient of the calibration curve.

In this case the calibration curve (*m*):

$$m = \frac{Absorbance\ intensity\ of\ molecule\ cation\ complex}{Absorbance\ intensity\ of\ neutral\ molecule}$$

M1

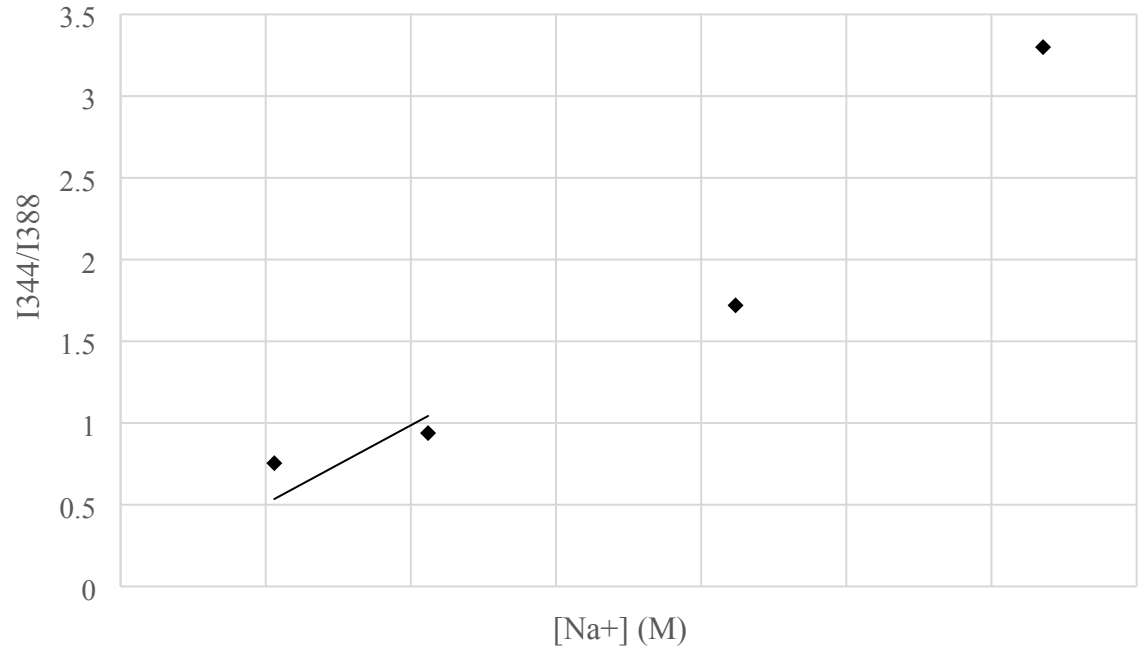


Figure S24 Ratiometric response of **M1** to Na^+ at unbound (388 nm) and bound (344 nm) absorption maxima in chloroform at room temperature.

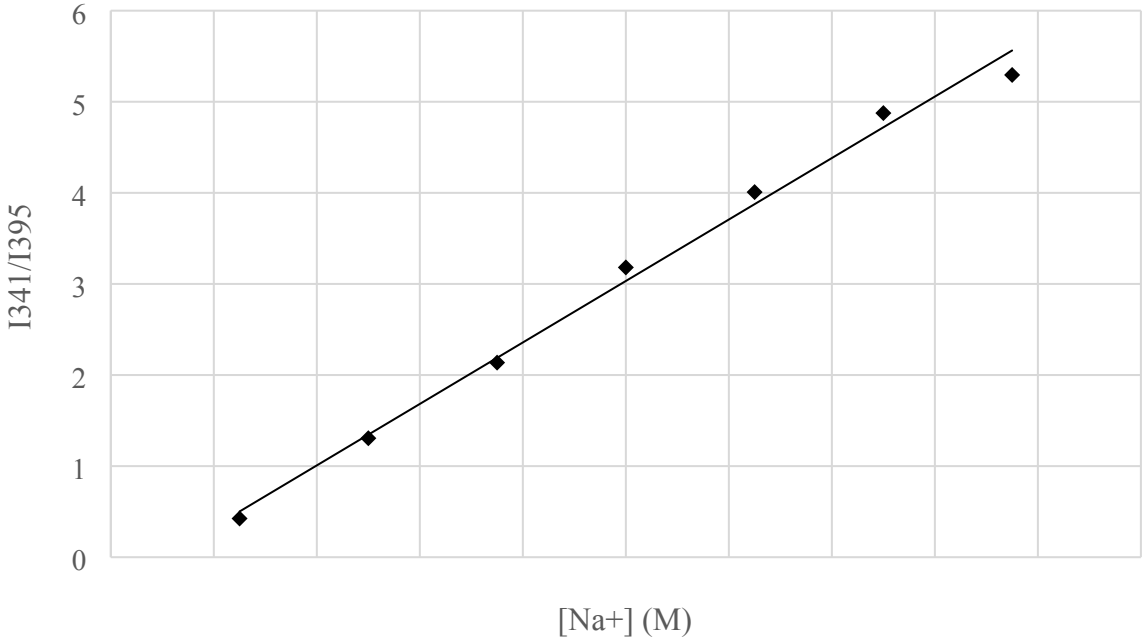


Figure S25 Ratiometric response of **M1** to Na^+ at unbound (395 nm) and bound (341 nm) absorption maxima in chloroform at room temperature.

M2

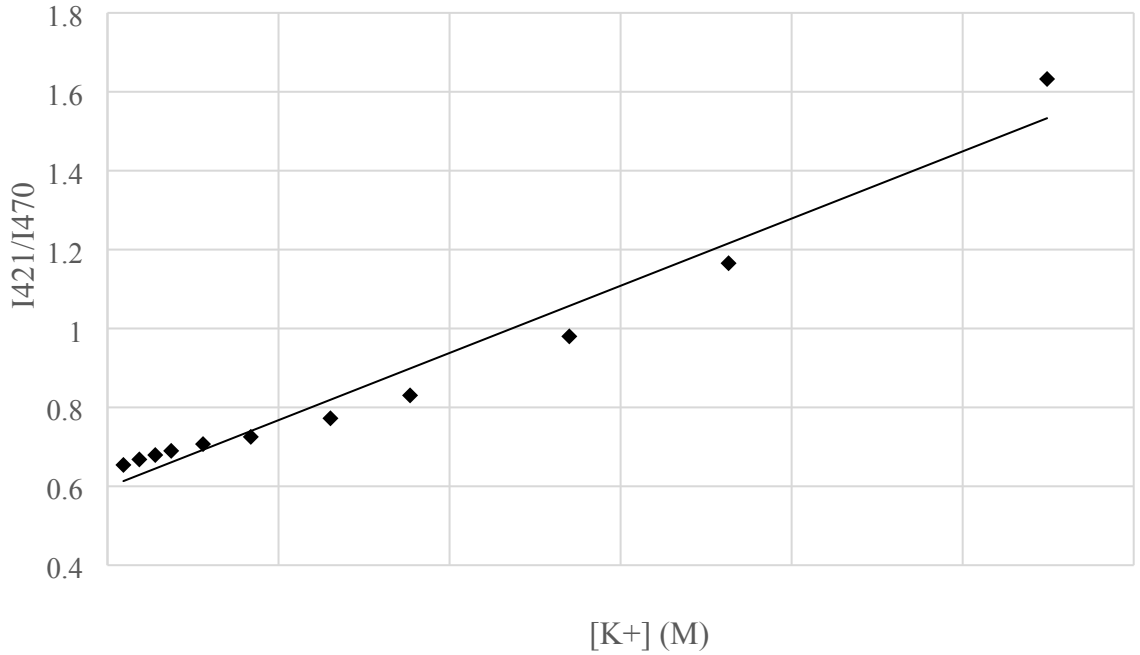


Figure S26 Ratiometric response of **M2** to K^+ at unbound (470 nm) and bound (421 nm) absorption maxima in chloroform at room temperature.

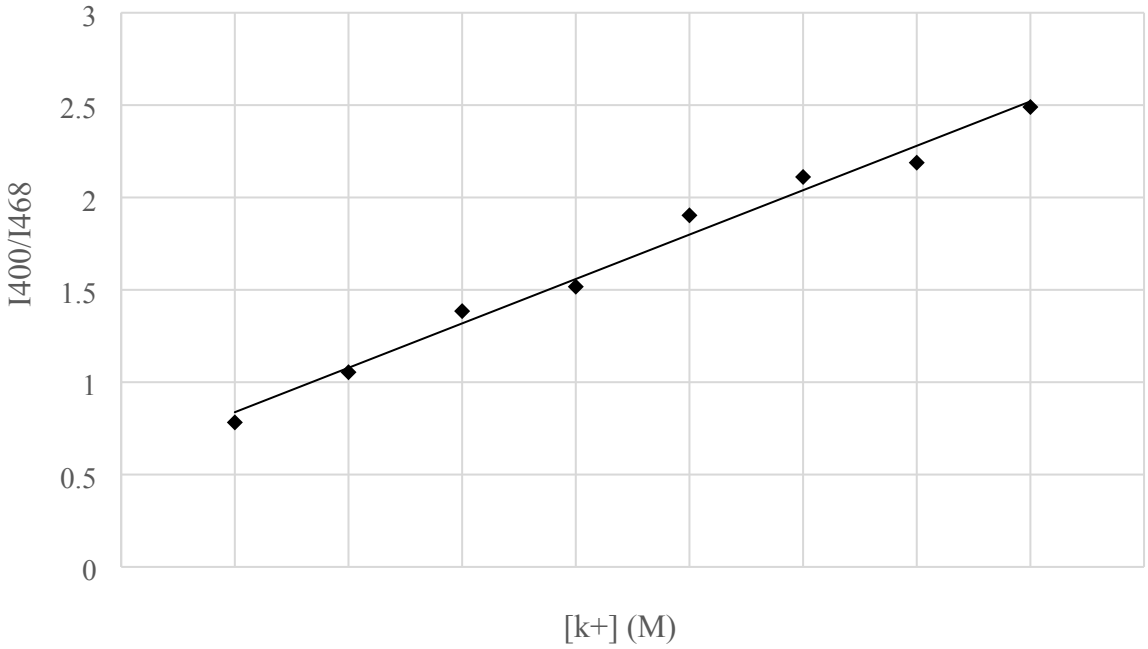


Figure S27 Ratiometric response of **M2** to K^+ at unbound (468 nm) and bound (400 nm) absorption maxima in THF at room temperature.

M3

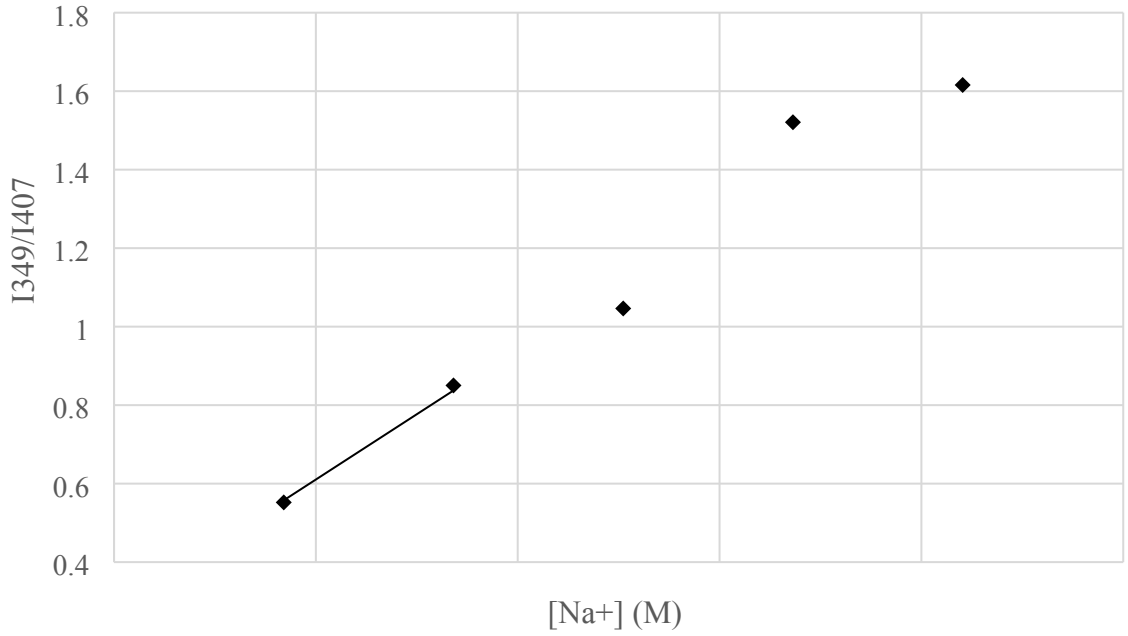


Figure S28 Ratiometric response of **M3** to Na^+ at unbound (407 nm) and bound (349 nm) absorption maxima in chloroform at room temperature.

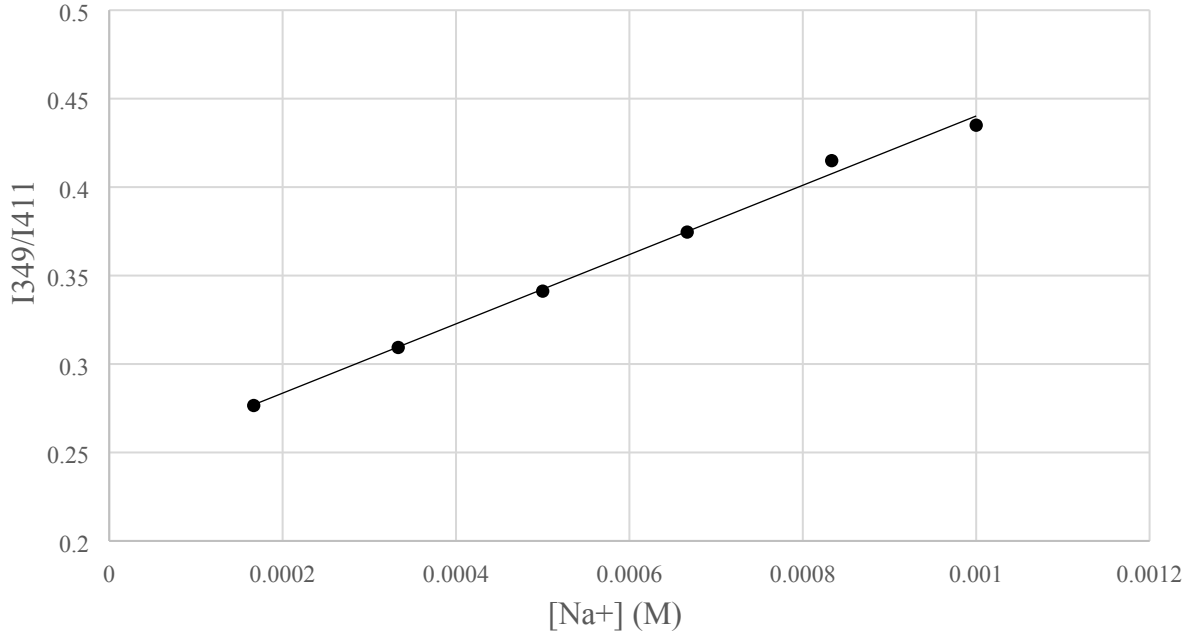


Figure S28 Ratiometric response of **M3** to Na^+ at unbound (411 nm) and bound (349 nm) absorption maxima in THF at room temperature.

M4

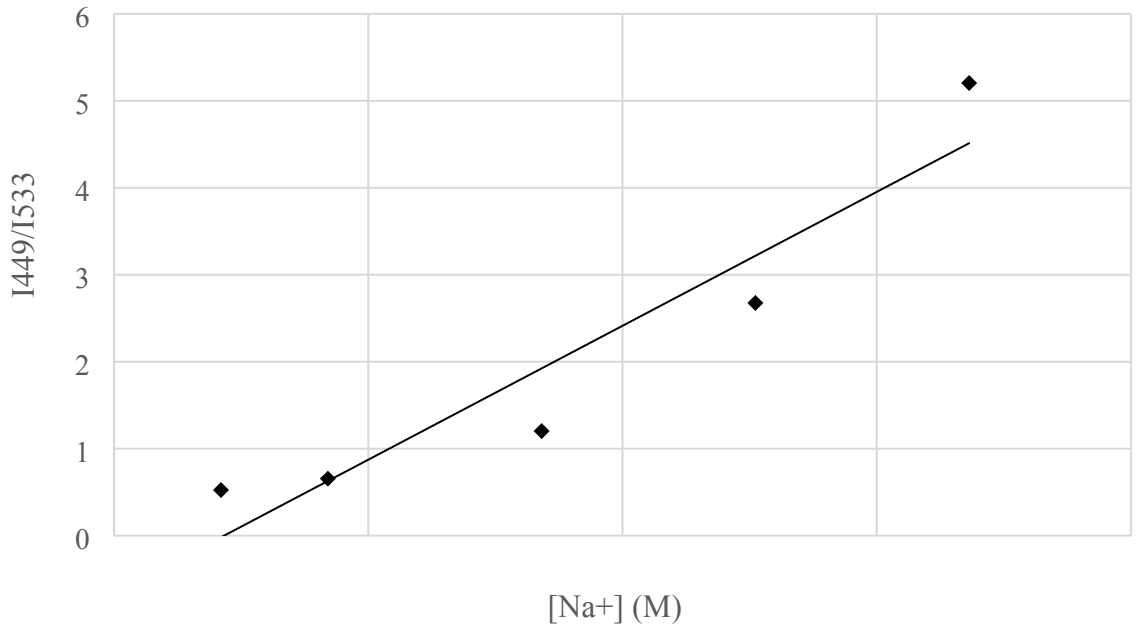


Figure S29 Ratiometric response of **M4** to Na^+ at unbound (533 nm) and bound (449 nm) absorption maxima in chloroform at room temperature.

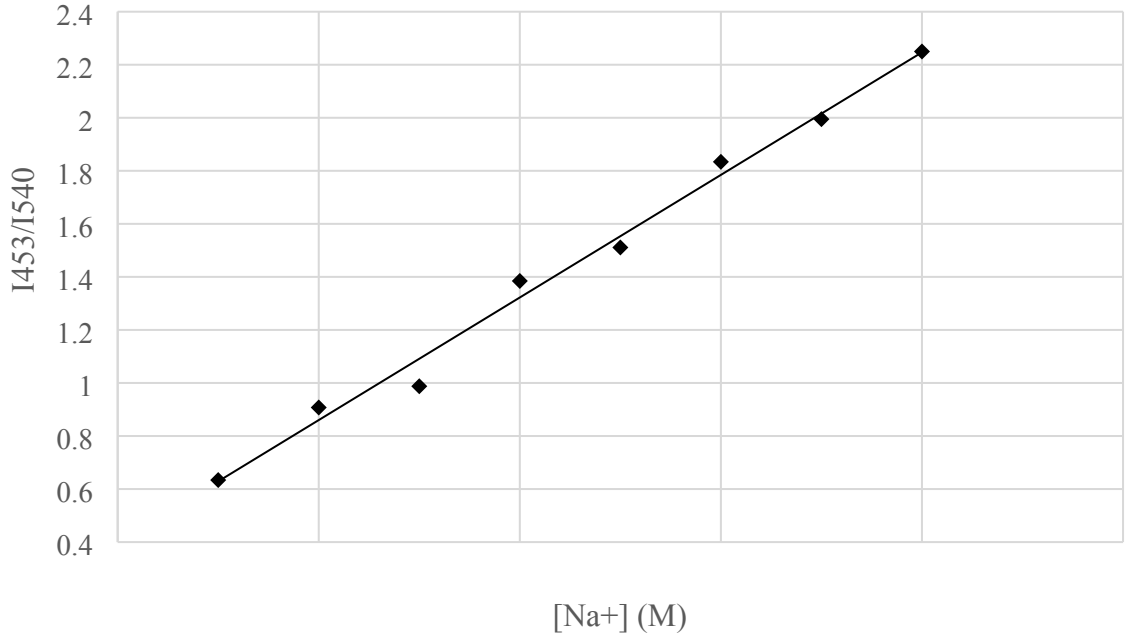


Figure S30 Ratiometric response of **M4** to Na^+ at unbound (540 nm) and bound (453 nm) absorption maxima in THF at room temperature.

M5

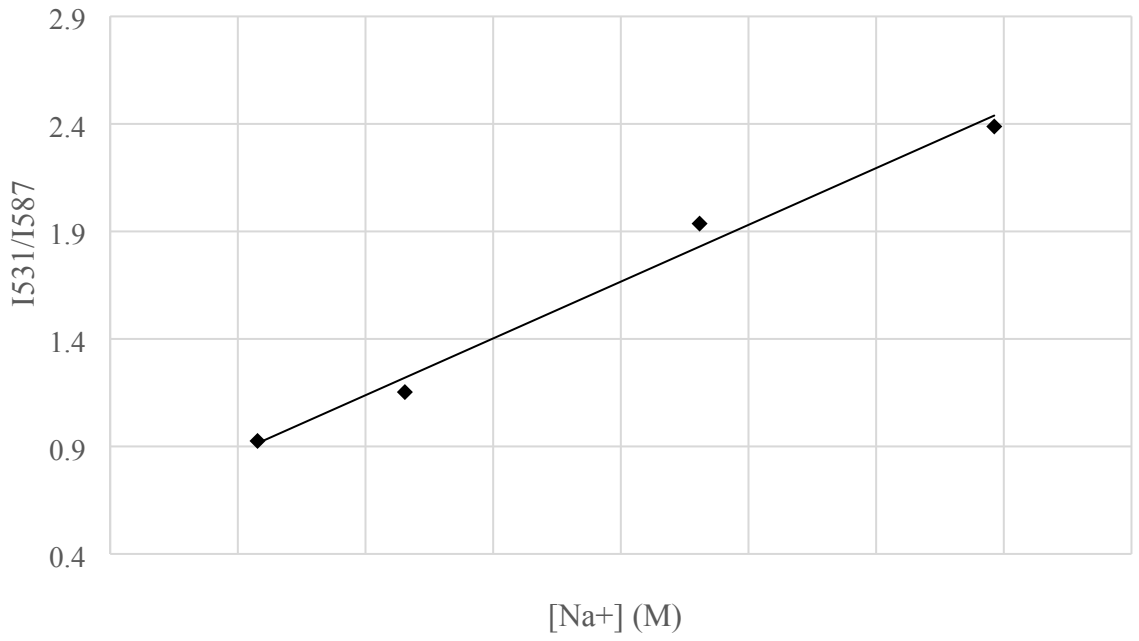


Figure S31 Ratiometric response of **M5** to Na^+ at unbound (587 nm) and bound (531 nm) absorption maxima in chloroform at room temperature.

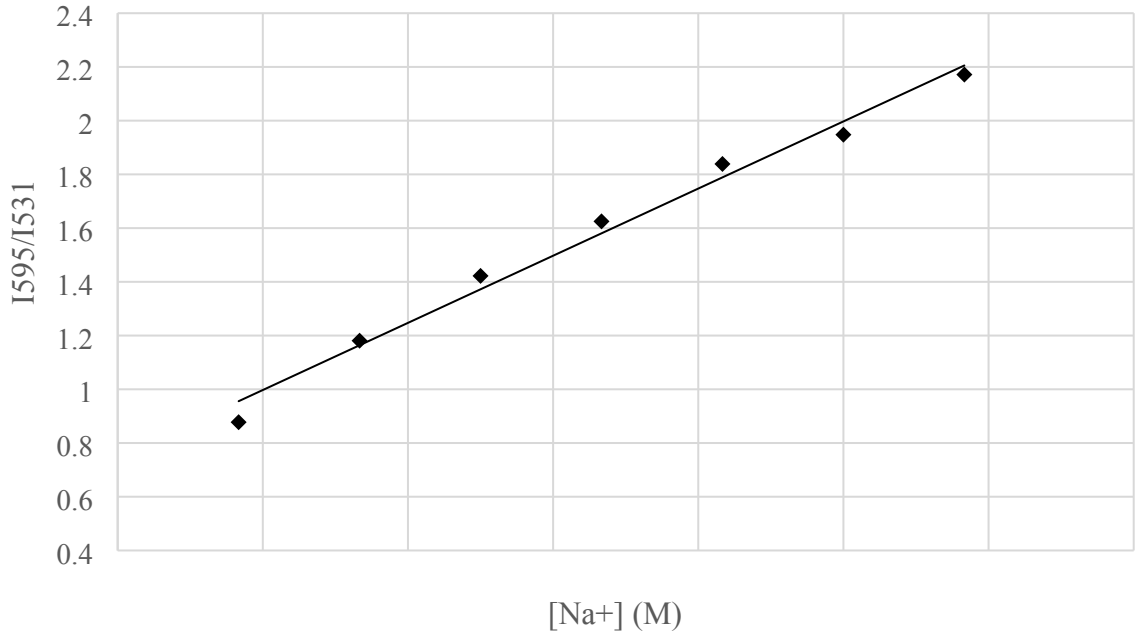


Figure S32 Ratiometric response of **M5** to Na^+ at unbound (595 nm) and bound (531 nm) absorption maxima in THF at room temperature.

M6

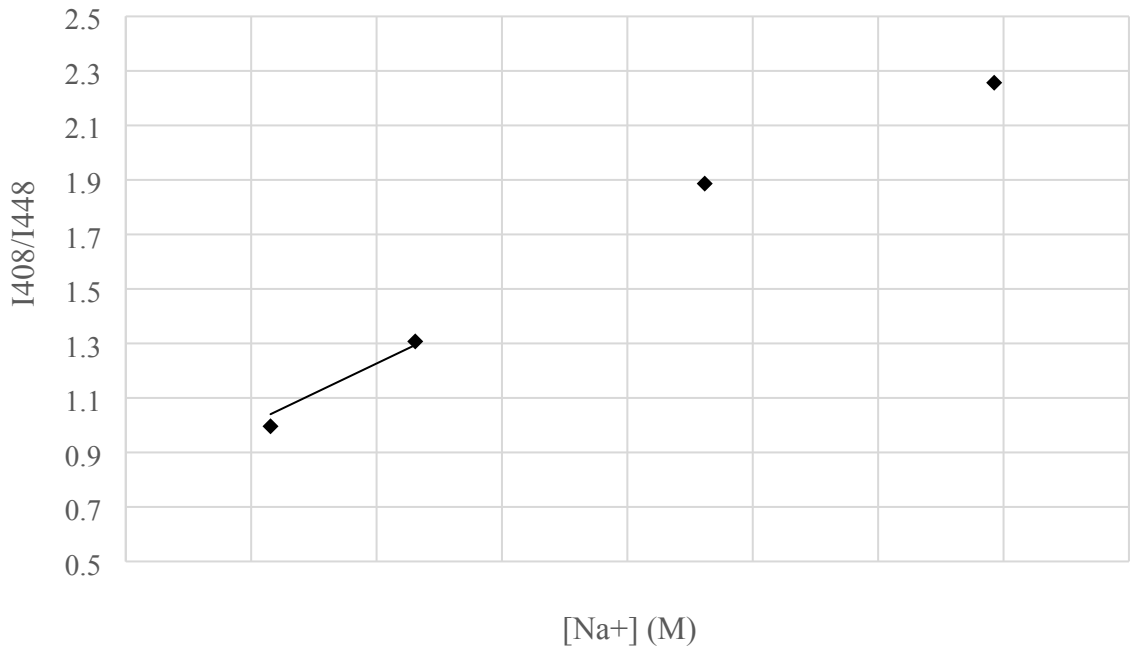


Figure S33 Ratiometric response of **M6** to Na^+ at unbound (448 nm) and bound (408 nm) absorption maxima in chloroform at room temperature.

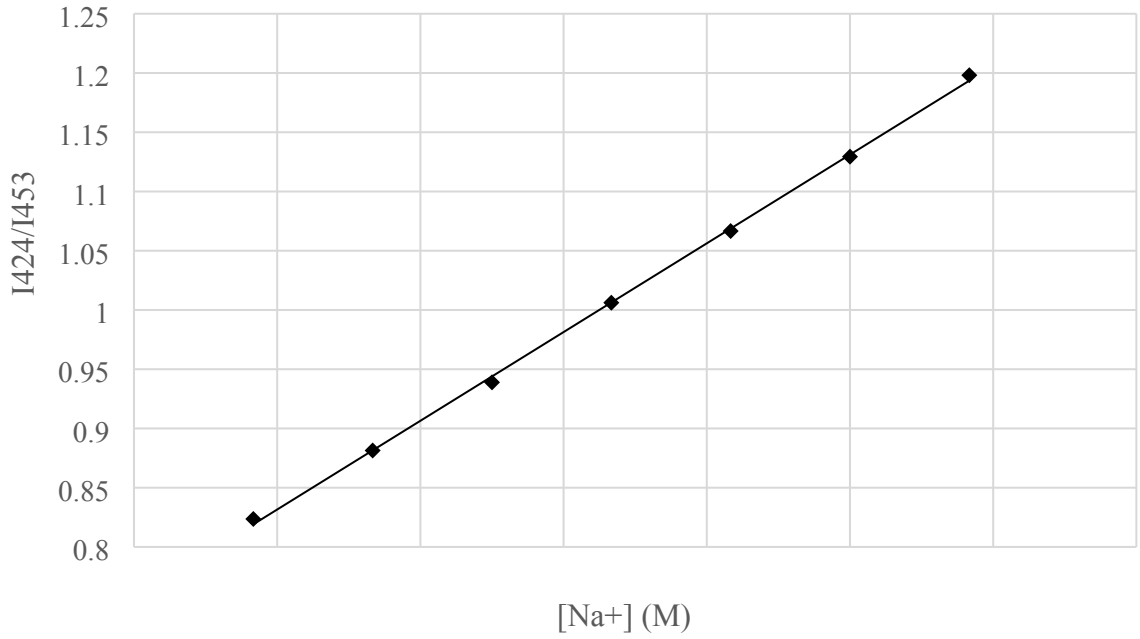


Figure S34 Ratiometric response of **M6** to Na^+ at unbound (453 nm) and bound (424 nm) absorption maxima in THF at room temperature.

Stability Tests

M1

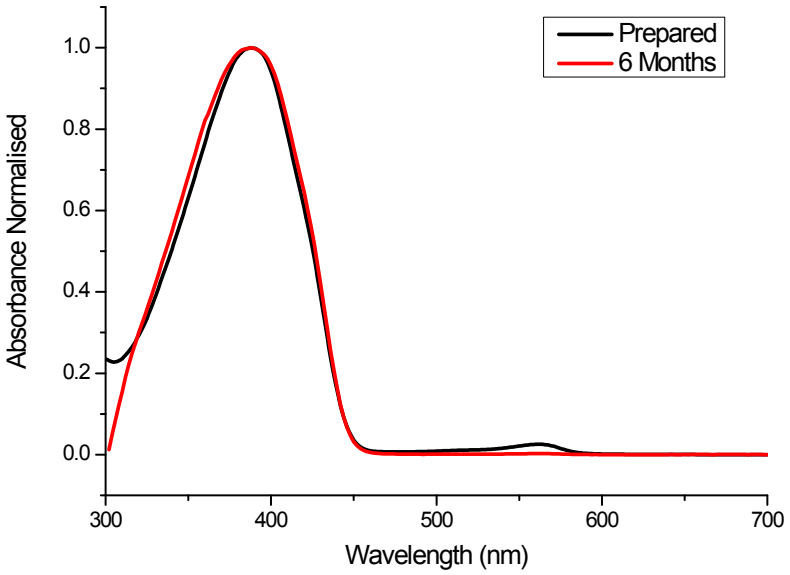


Figure S35 Stability of **M1** in chloroform when first prepared and 6 months later stored in dark under atmospheric conditions at room temperature.

M2

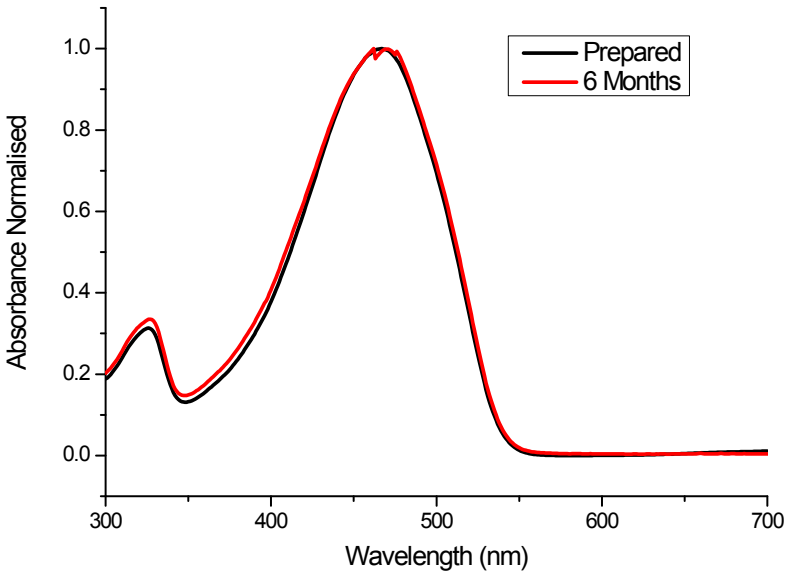


Figure S36 Stability of **M2** in chloroform when first prepared and 6 months later stored in dark under atmospheric conditions at room temperature.

M3

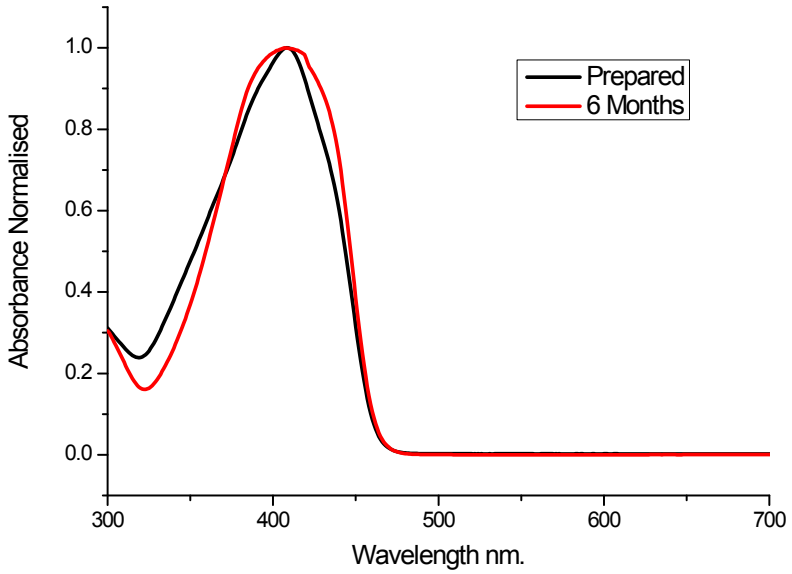


Figure S37 Stability of **M3** in chloroform when first prepared and 6 months later stored in dark under atmospheric conditions at room temperature.

M4

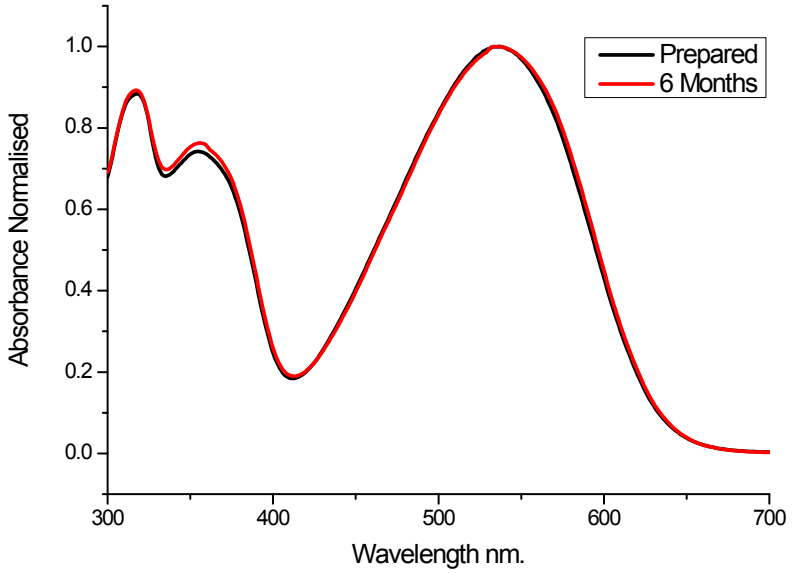


Figure S38 Stability of **M4** in chloroform when first prepared and 6 months later stored in dark under atmospheric conditions at room temperature.

M5

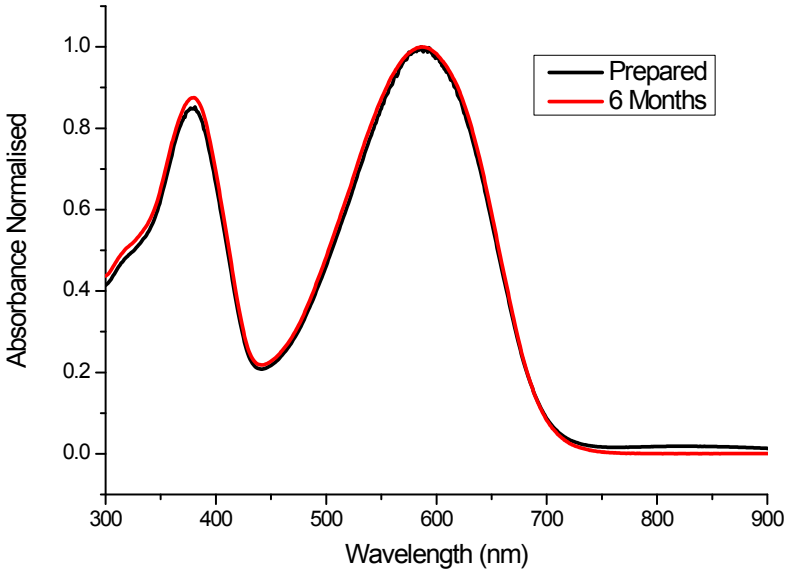


Figure S39 Stability of **M5** in chloroform when first prepared and 6 months later stored in dark under atmospheric conditions at room temperature.

M6

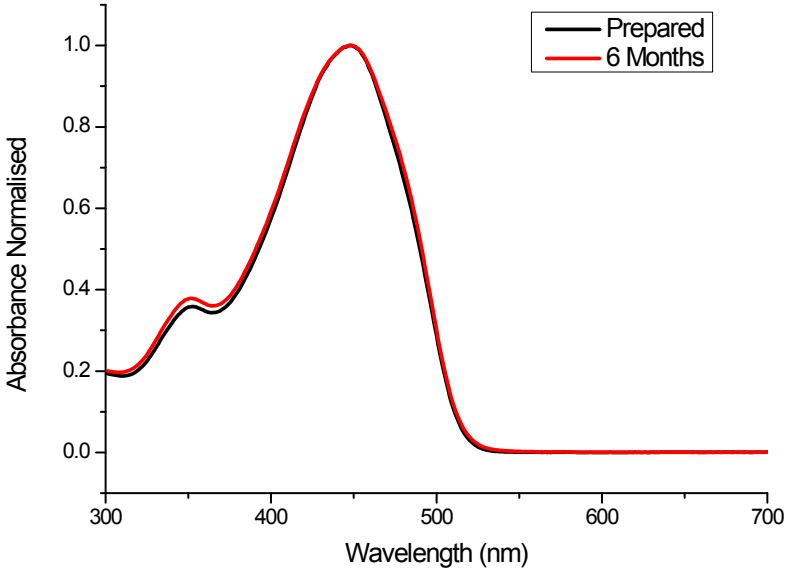


Figure S40 Stability of **M6** in chloroform when first prepared and 6 months later stored in dark under atmospheric conditions at room temperature.

Fluorescence

All fluorescence data were recorded at room temperature with 5 nm excitation and emission slit widths with excitation set at the isosbestic point of the UV-absorbance spectrum.

M1

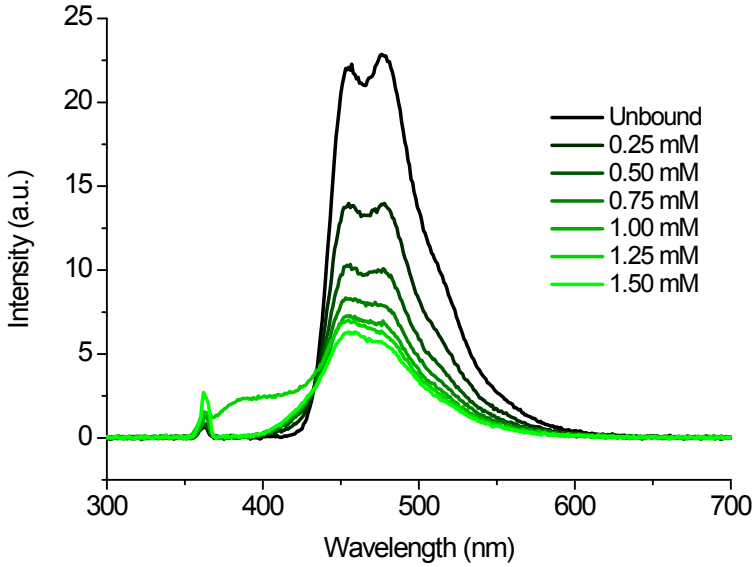


Figure S41 Fluorescence titration experiment at room temperature for **M1** (1.7 x 10^{-5} M in THF) upon addition of $NaBPh_4$ aliquots in THF.

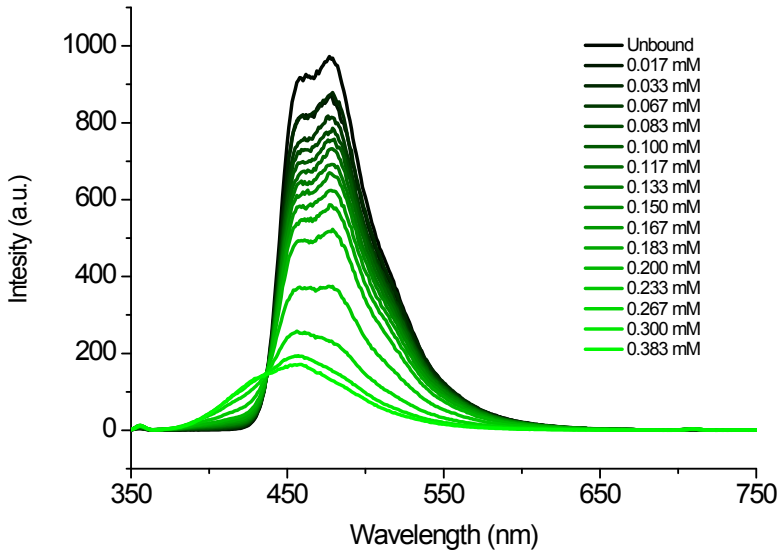


Figure S42 Fluorescence titration experiment at room temperature for **M1** (10 x 10^{-5} M in chloroform) upon addition of $NaBPh_4$ aliquots in chloroform.

M2

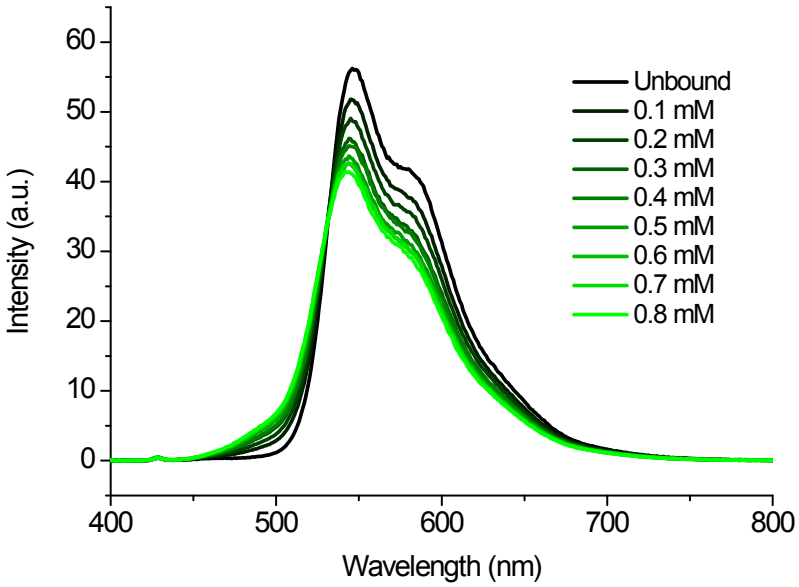


Figure S43 Fluorescence titration experiment at room temperature for **M2** (1.38 x 10^{-5} M in THF) upon addition of $KBPh_4$ aliquots in THF.

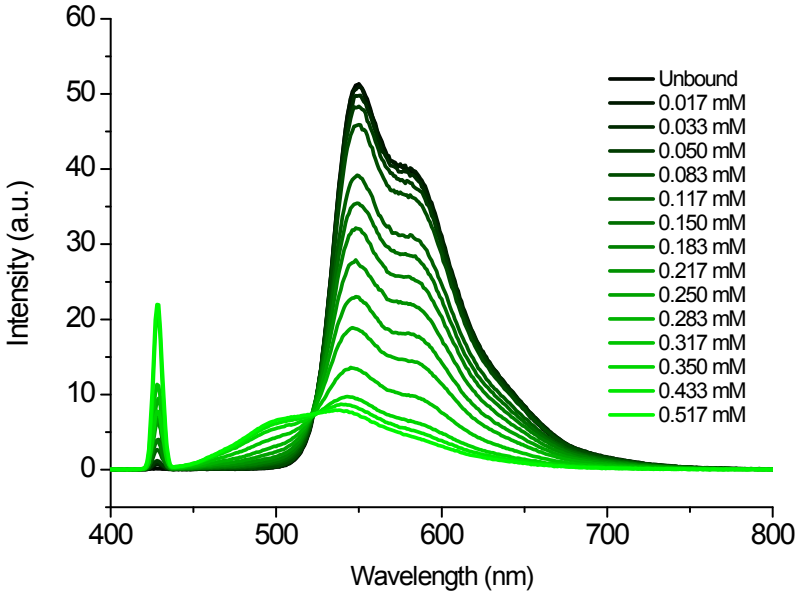


Figure S44 Fluorescence titration experiment at room temperature for **M2** (1.78 x 10^{-5} M in chloroform) upon addition of $KBPh_4$ aliquots in chloroform.

M4

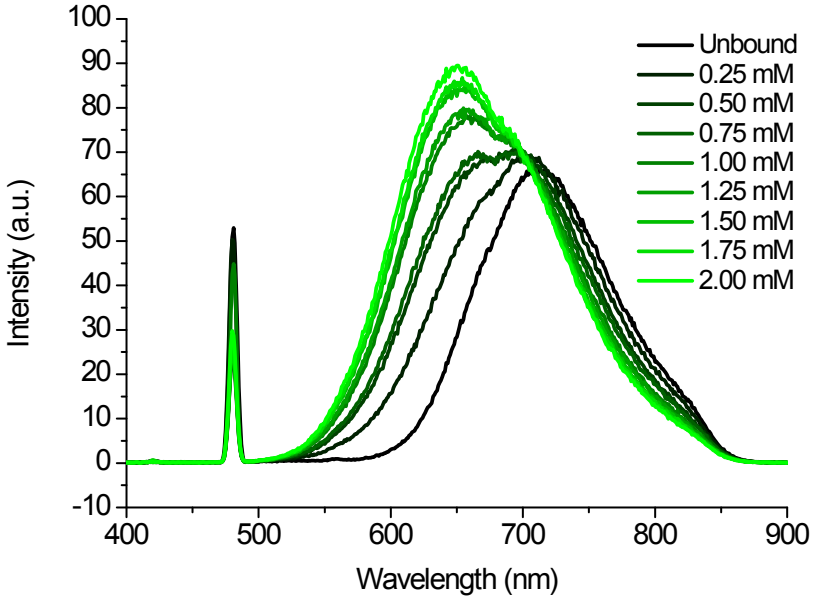


Figure S45 Fluorescence titration experiment at room temperature for **M4** (1.8 x 10^{-5} M in THF) upon addition of $NaBPh_4$ aliquots in THF.

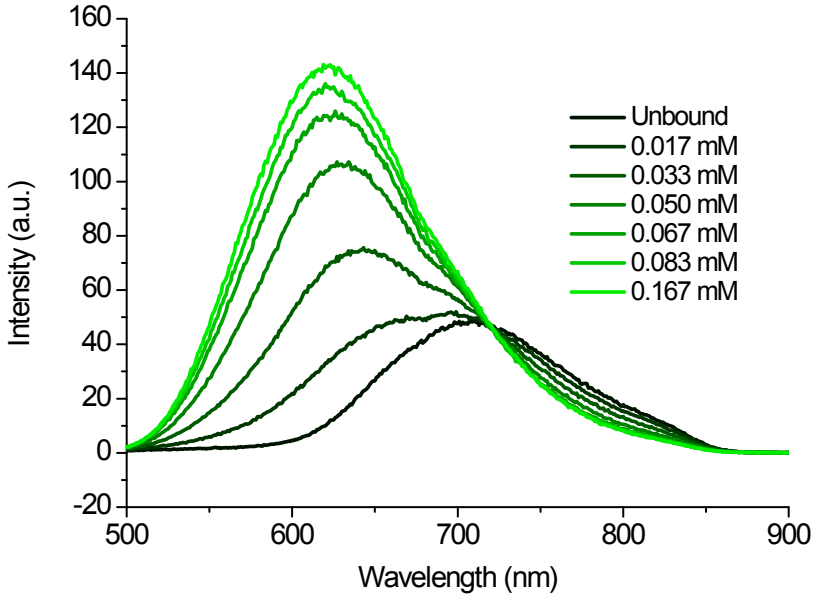


Figure S46 Fluorescence titration experiment at room temperature for **M4** (5.2 x 10^{-5} M in chloroform) upon addition of $NaBPh_4$ aliquots in chloroform.

M5

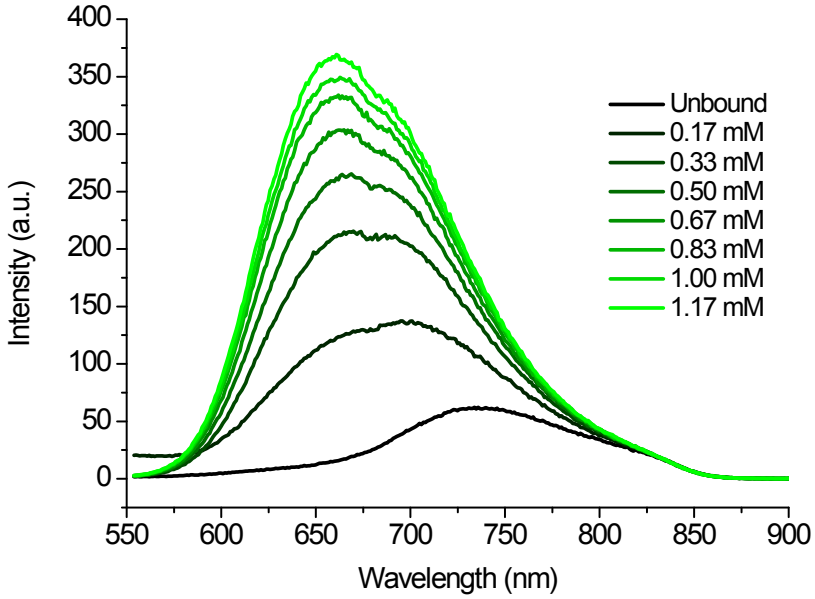


Figure S47 Fluorescence titration experiment at room temperature for **M5** (1.1 x 10^{-5} M in THF) upon addition of $NaBPh_4$ aliquots in THF.

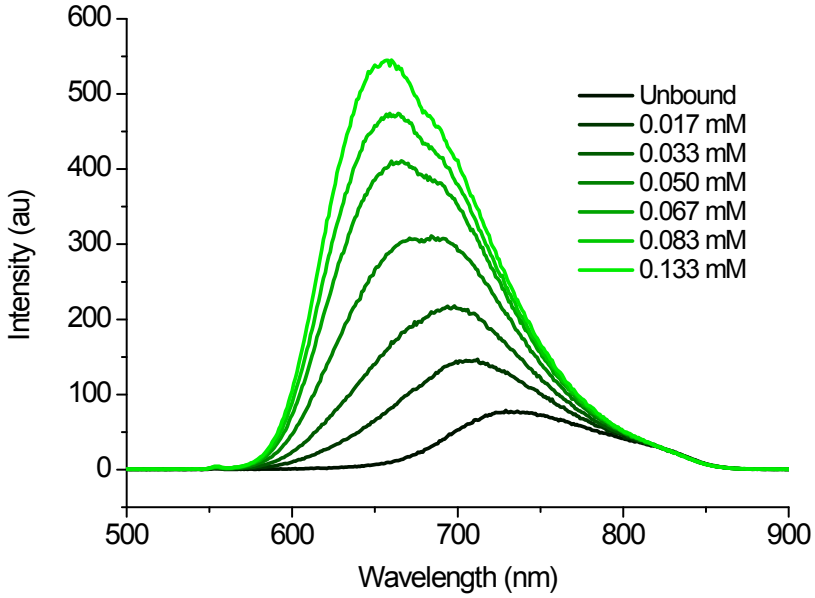


Figure S48 Fluorescence titration experiment at room temperature for **M5** (7.1 x 10^{-5} M in chloroform) upon addition of $NaBPh_4$ aliquots in chloroform.

M6

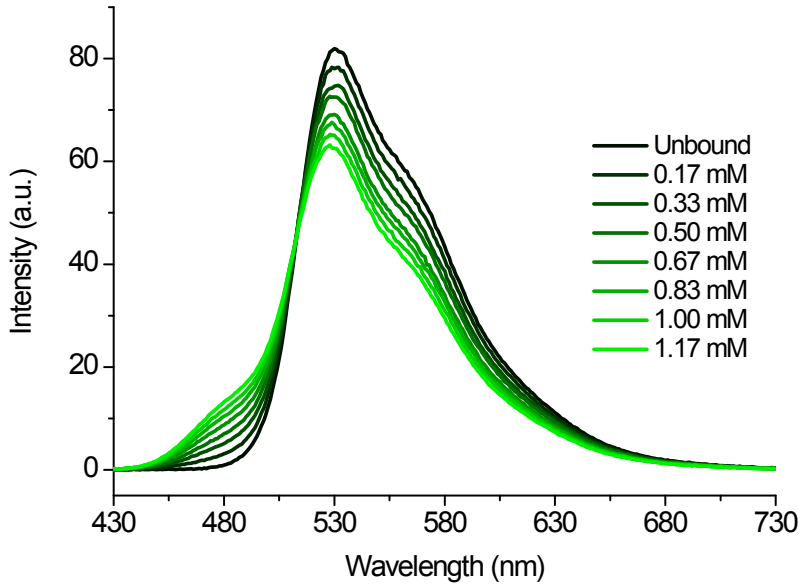


Figure S49 Fluorescence titration experiment at room temperature for **M6** (1.0 x 10^{-5} M in THF) upon addition of $NaBPh_4$ aliquots in THF.

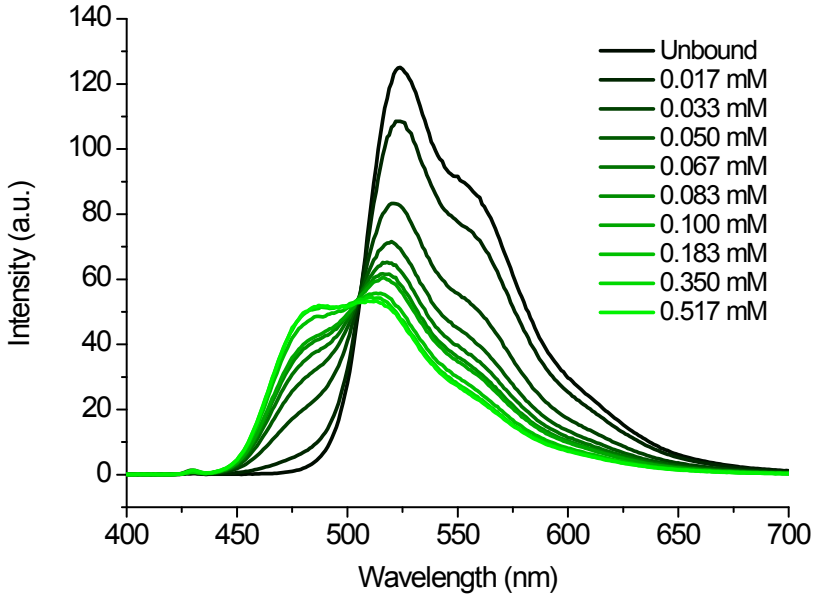


Figure S50 Fluorescence titration experiment at room temperature for **M4** (2.3 x 10^{-5} M in chloroform) upon addition of $NaBPh_4$ aliquots in chloroform.

Quantum Yield Calculations

All quantum yield calculations were carried out at room temperature in degassed solvent with a PMT voltage of 400 V and excitation and emission slit widths of 5 nm with excitation at λ_{max} absorbance in the UV-Vis spectrum. Concentration of the materials was approximately 10^{-6} M. Quantum yield was calculated according to the reported method using either anthracene, rubrene or coumarin-6 as standards[5] according to the following equation:

$$\Phi_m = \Phi_{standard} \left(\frac{Grad_m}{Grad_{Standard}}\right)\left(\frac{\eta_m}{\eta_{standard}}\right)^2$$

Where Φ_m is the quantum yield of the molecule, $\Phi_{standard}$ is literature quantum yield of the standard, $Grad_m$ is the gradient of integrated fluorescence intensity versus absorption of the molecule, $Grad_{standard}$ is the gradient of integrated fluorescence intensity versus absorption of the molecule, η_m is the refractive index of the solvent of the molecule and η_m is the refractive index of the solvent used for the standard.[6]

Anthracene

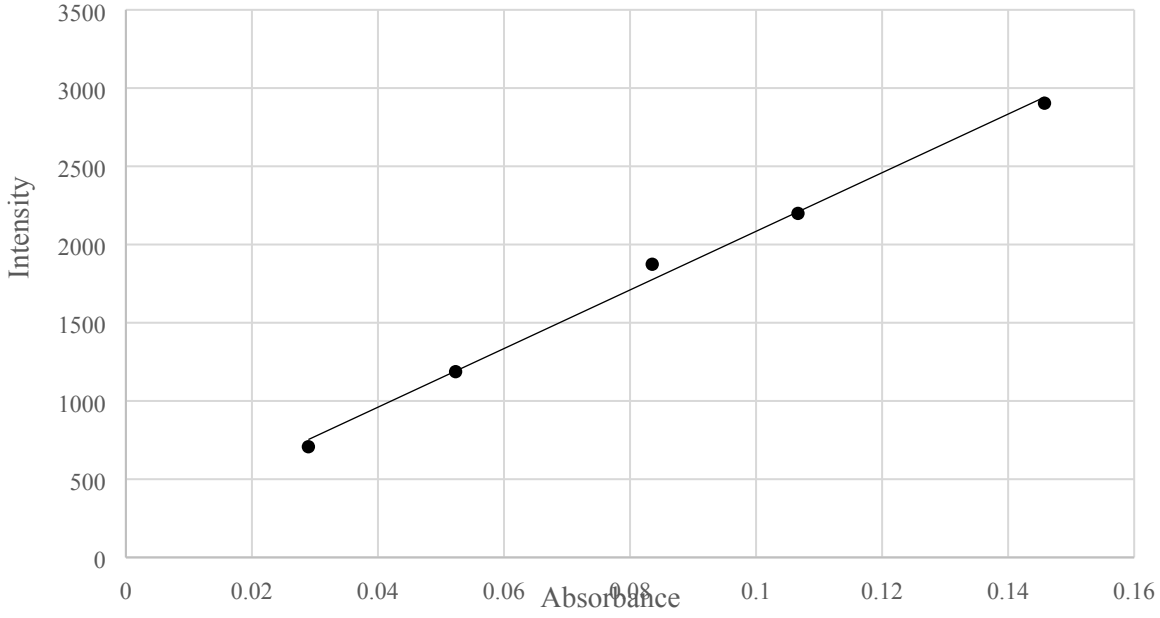


Figure S51 Anthracene standard dilution series at room temperature in degassed cyclohexane for quantum yield calculations.

Rubrene

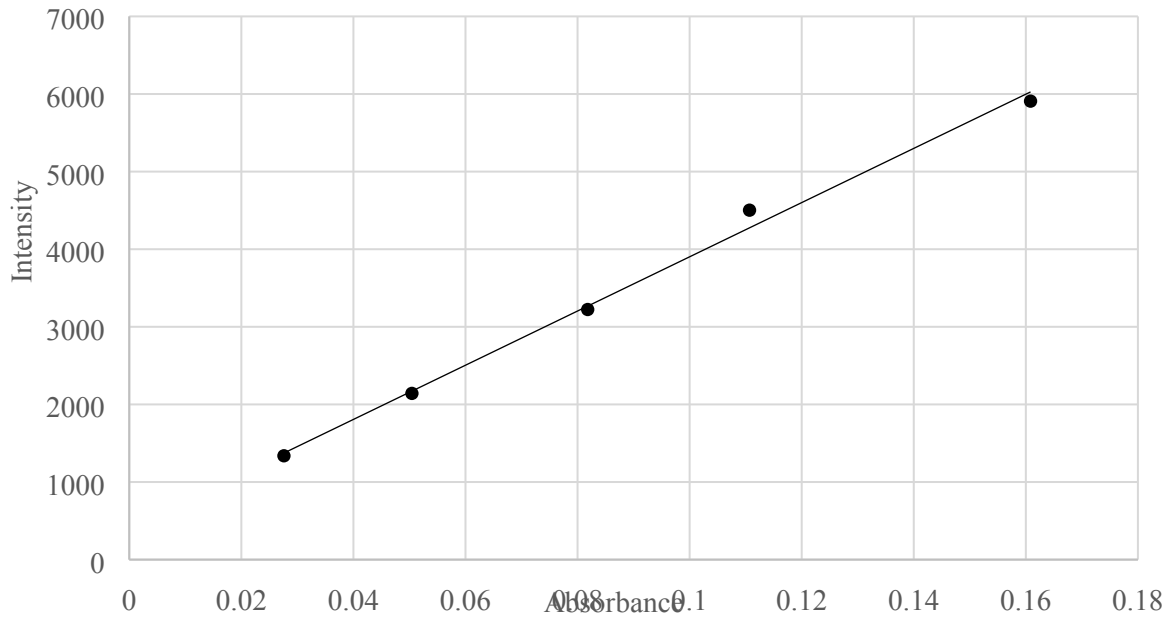


Figure S52 Rubrene standard dilution series at room temperature in degassed chloroform for quantum yield calculations.

Coumarin 6

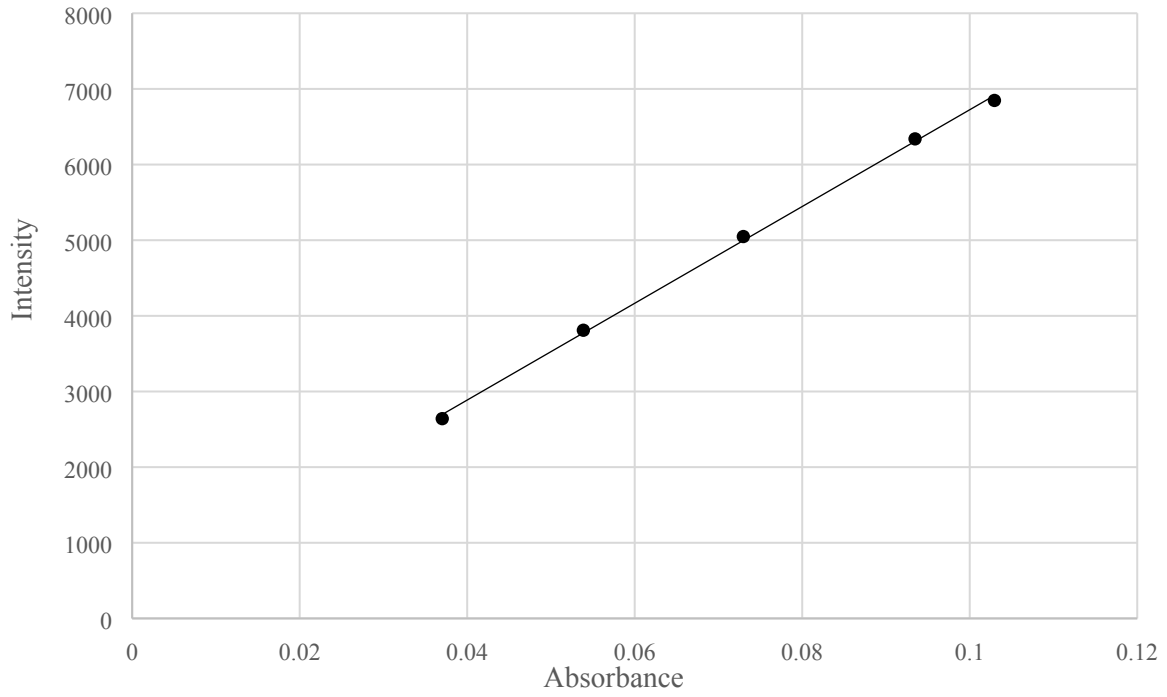


Figure S53 Coumarin 6 standard dilution series at room temperature in degassed ethanol for quantum yield calculations.

M1

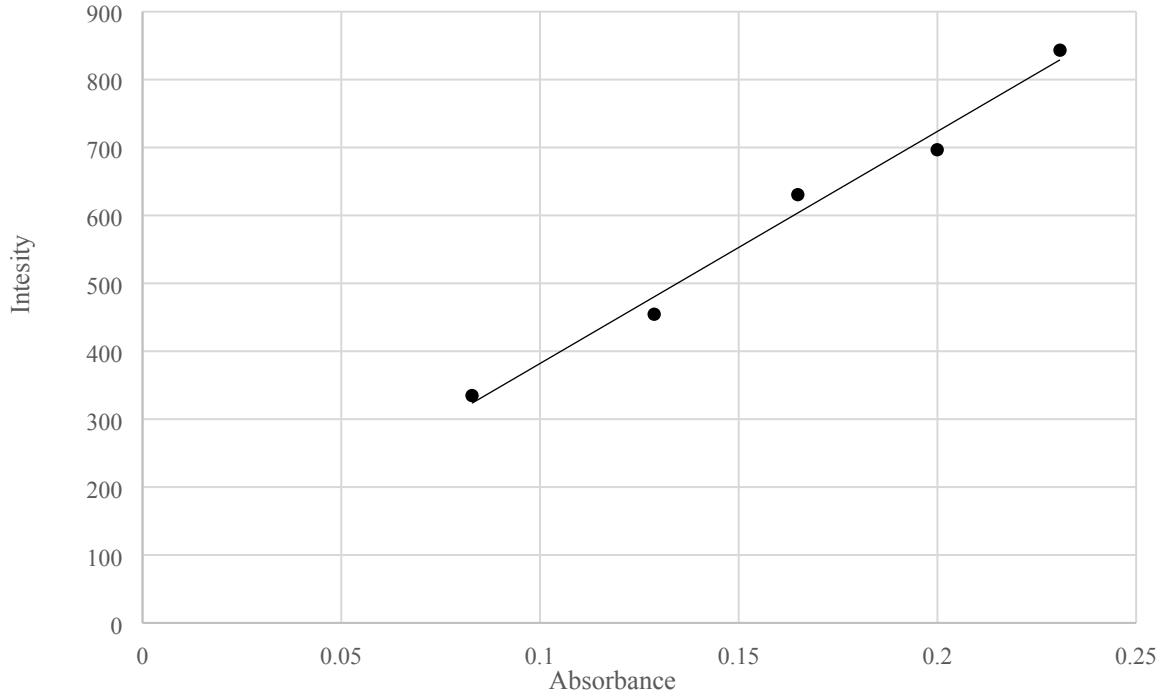


Figure S54 Fluorescence dilution series in chloroform for **M1** in the unbound state for quantum yield calculations.

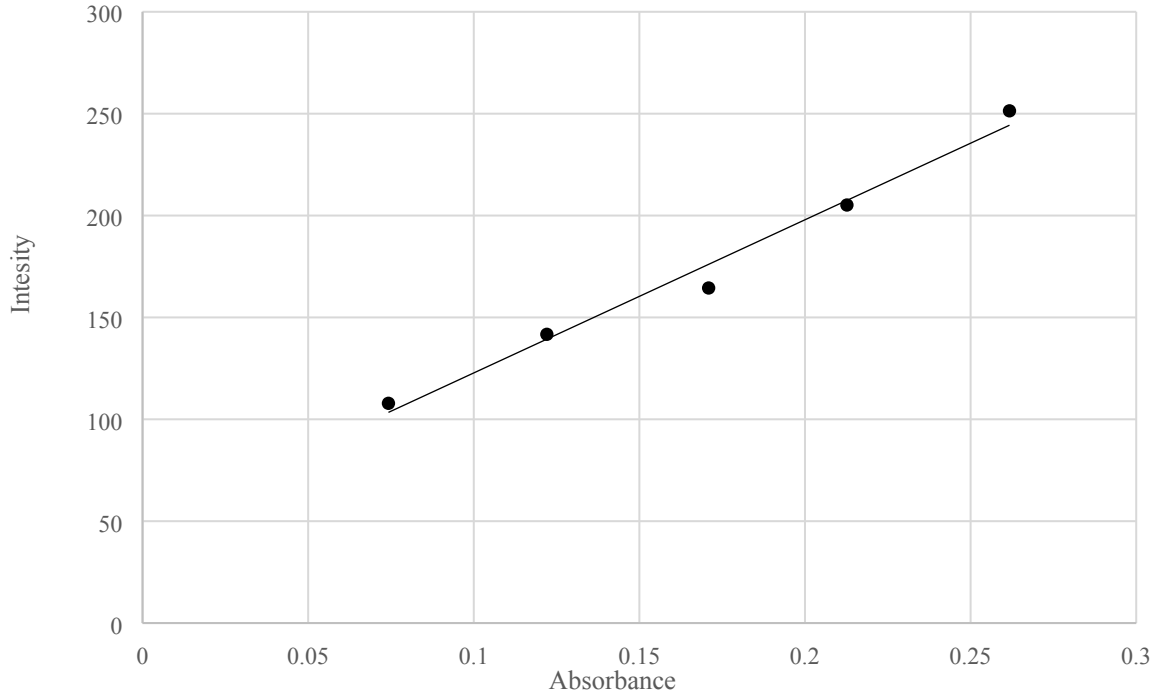


Figure S55 Fluorescence dilution series in chloroform for the **M1-Na**$^{+}$ complex for quantum yield calculations.

M2

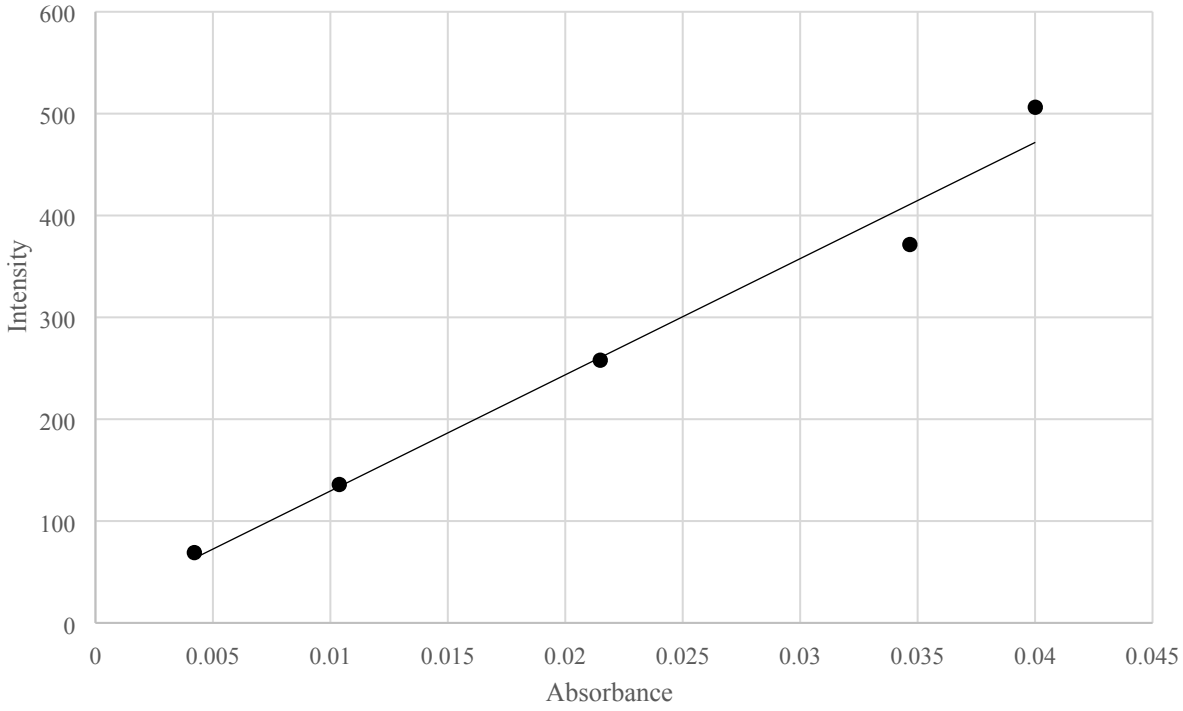


Figure S56 Fluorescence dilution series in dichloromethane for **M2** in the unbound state for quantum yield calculations.

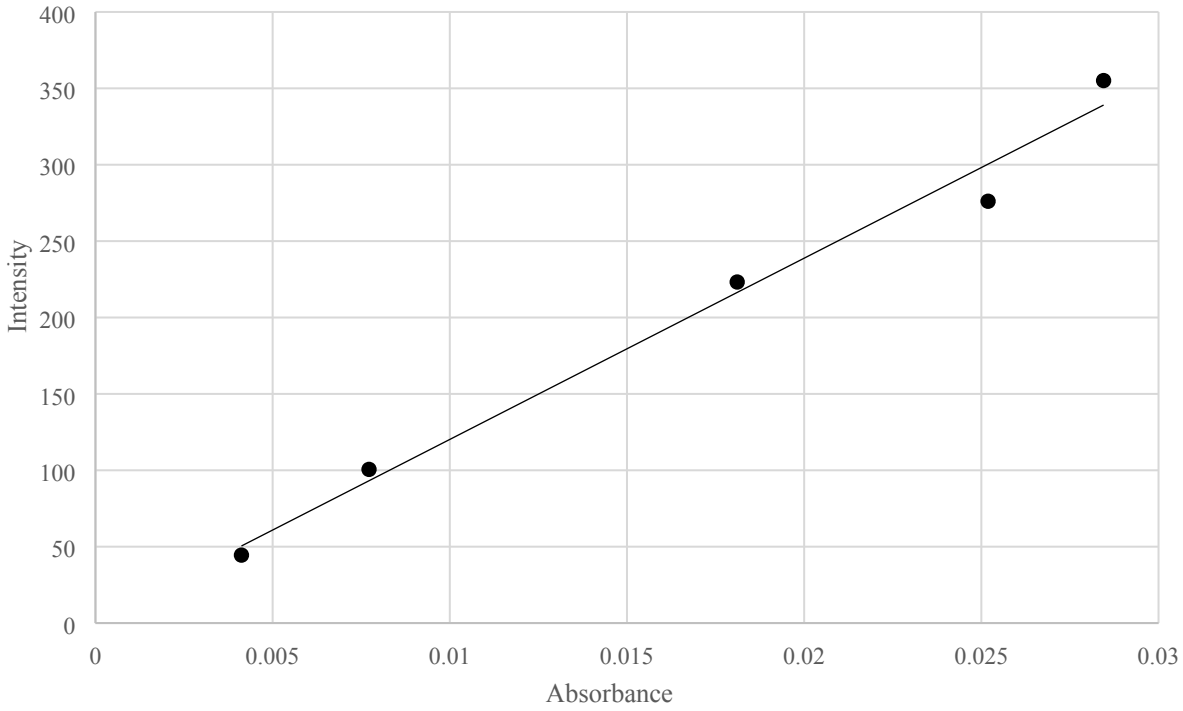


Figure S57 Fluorescence dilution series in dichloromethane for the **M2-Na$^+$** complex for quantum yield calculations.

M4

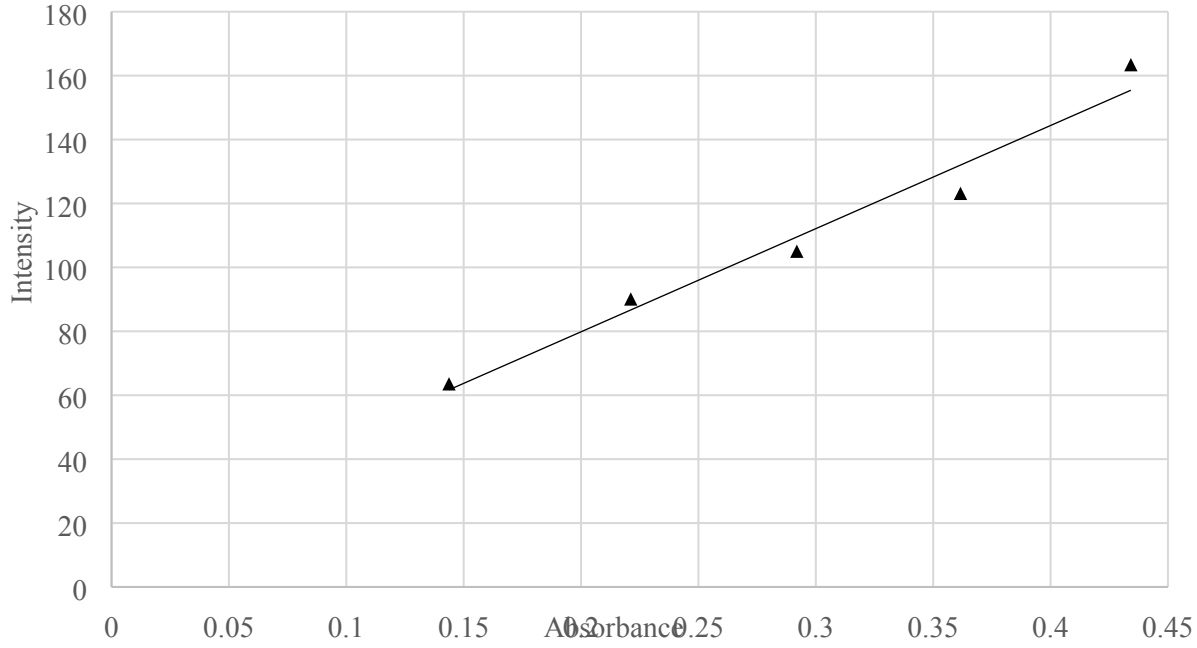


Figure S58 Fluorescence dilution series in chloroform for **M4** in the unbound state for quantum yield calculations.

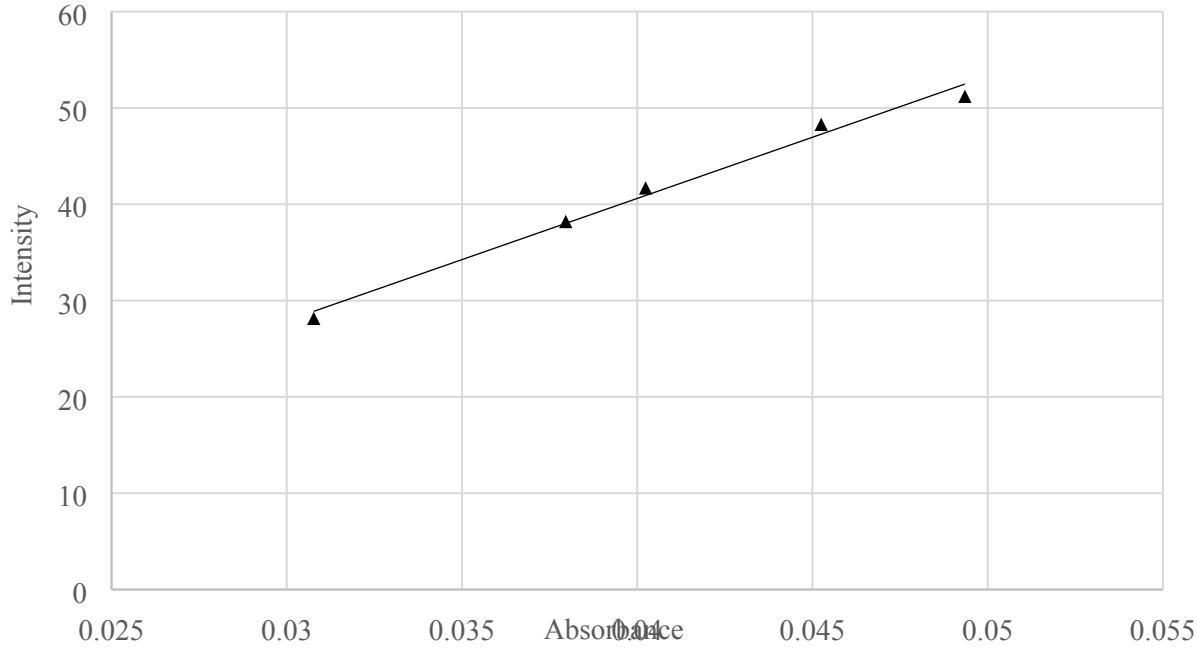


Figure S59 Fluorescence dilution series in chloroform for the **M4-Na$^+$** complex for quantum yield calculations.

M5

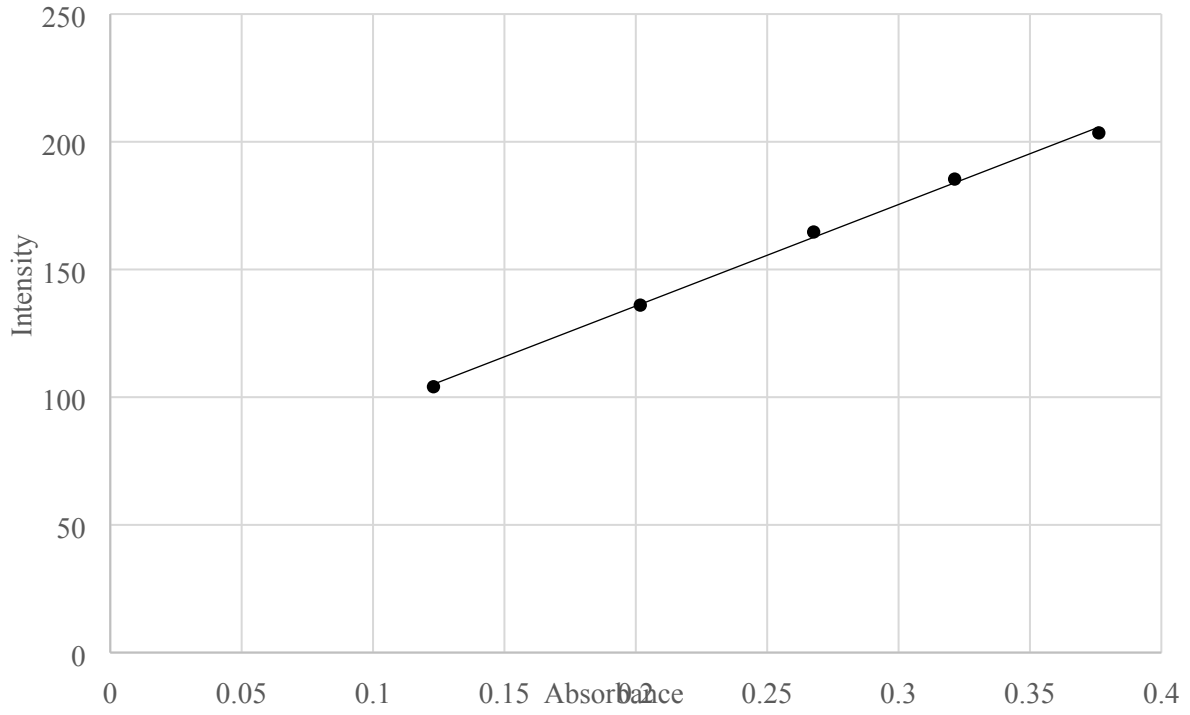


Figure S60 Fluorescence dilution series in chloroform for **M5** in the unbound state for quantum yield calculations.

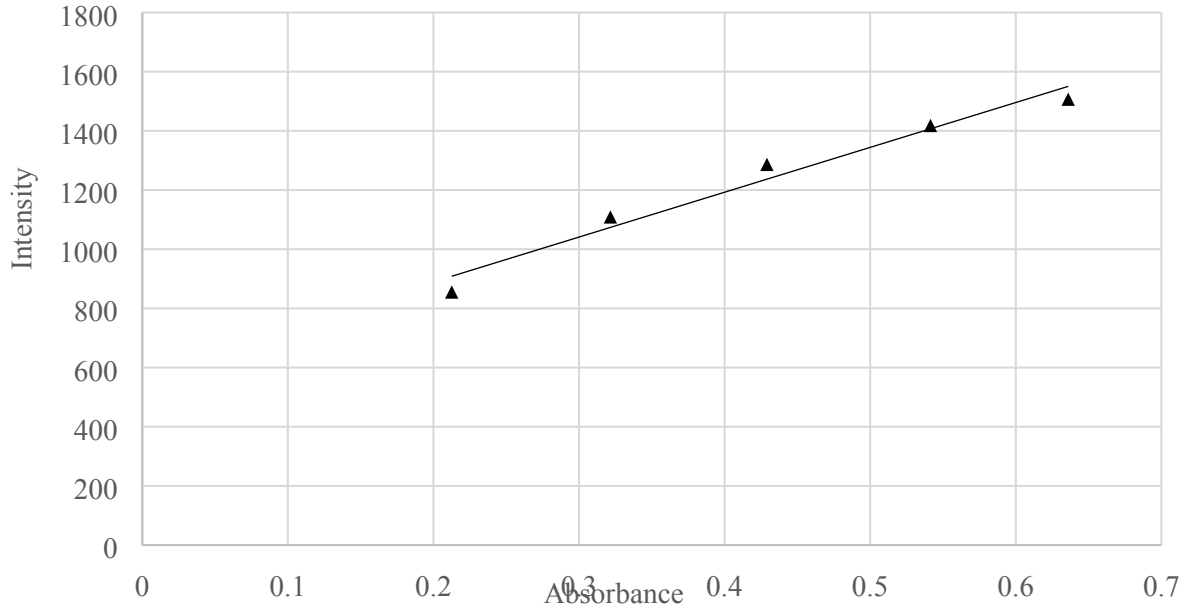


Figure S61 Fluorescence dilution series in chloroform for the **M5-Na$^+$** complex for quantum yield calculations.

M6

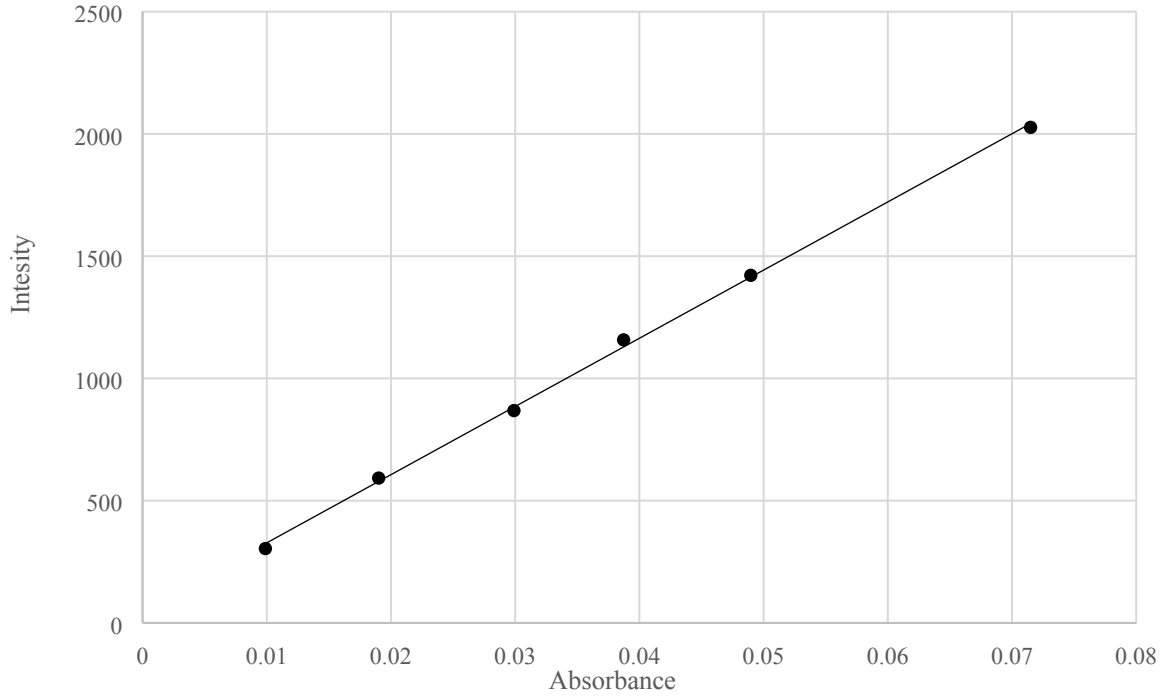


Figure S62 Fluorescence dilution series in chloroform for **M6** in the unbound state for quantum yield calculations.

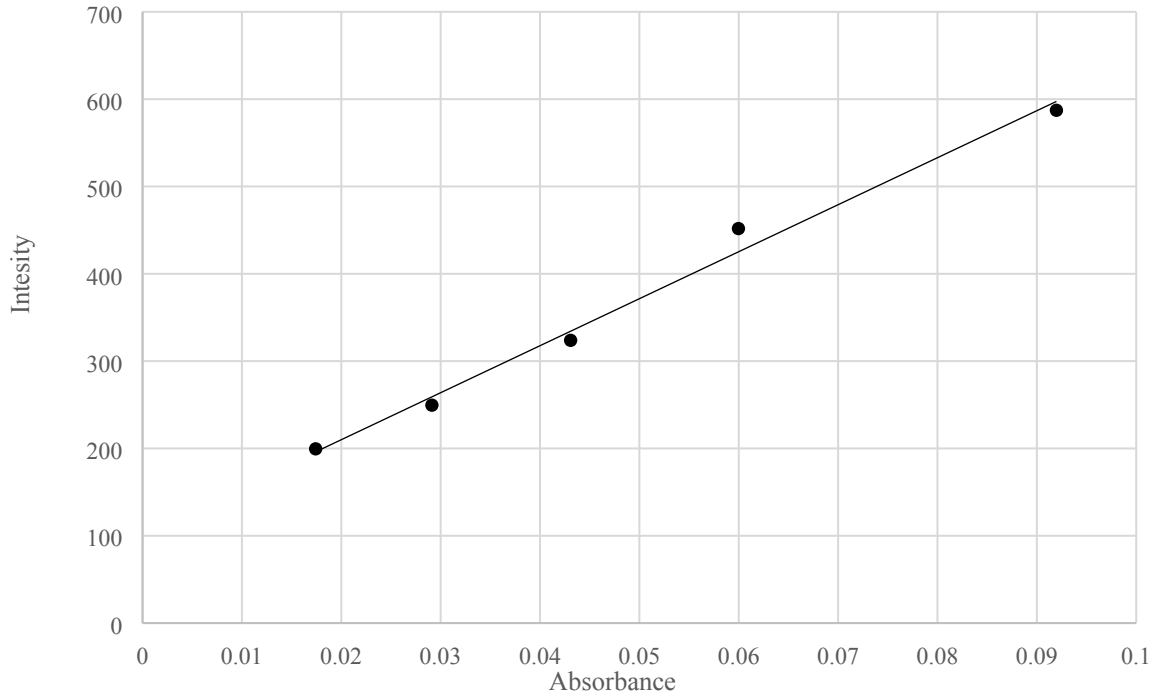


Figure S63 Fluorescence dilution series in chloroform for the **M6-Na$^+$** complex for quantum yield calculations.

Tabulated Additional Optical Data

SI Table 1

	λ_{max} (nm) unbound (chloroform)	λ_{max} (nm) bound (chloroform)	$\Delta\lambda_{max}$ (nm) complexation (chloroform)	ε ($M^{-1}cm^{-1}$) (chloroform)	K_d (mM) (chloroform)	LOD (nM) (chloroform)	λ_{em}(max) (nm) (chloroform)	Stokes shift (nm) unbound/bound (chloroform)	$\Phi_{Unbound}$	Φ_{bound}
M1	388	344	44	32600	0.078	10	478	90/114	0.06	0.01
M2	470	421	49	72800	0.029	129	550	80/117	0.12†	0.12†
M3	407	351	44		0.107	33	-	-	-	-
M4	536	449	87	43000	0.047	7	712	171/201	0.005	0.02
M5	588	531	57	83500	0.022	58	733	148/126	0.006	0.02
M6	448	409	39	123000	0.047	20	524	76/101	0.36	0.07

†Data recorded in dichloromethane; remaining quantum yields recorded in chloroform.

Selectivity Tests

M1

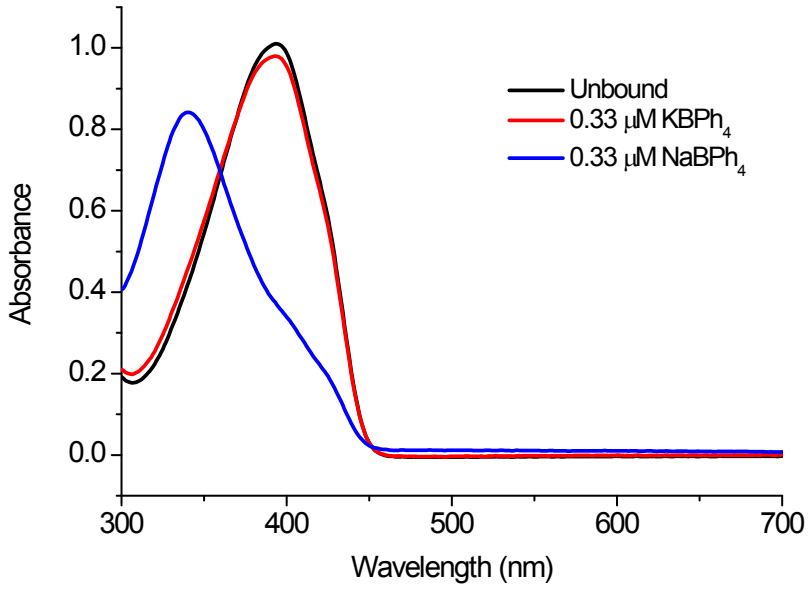


Figure S64 UV-Vis spectrum of **M1** at 3.1 x 10^{-5} M in THF at room temperature in response to an identical concentration of $NaBPh_4$ or $KBPh_4$.

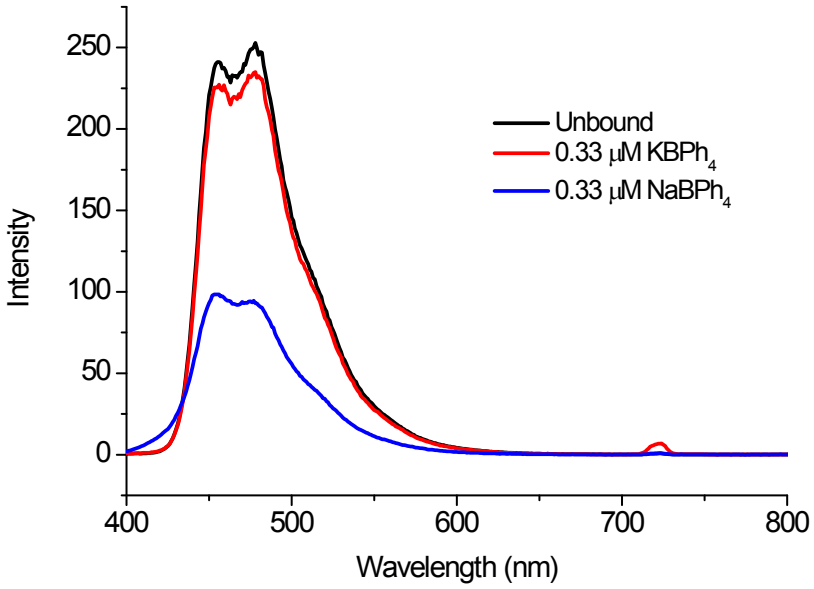


Figure S65 Fluorescence spectrum of **M1** at 3.1 x 10^{-5} M in THF at room temperature in response to an identical concentration of $NaBPh_4$ or $KBPh_4$.

M2

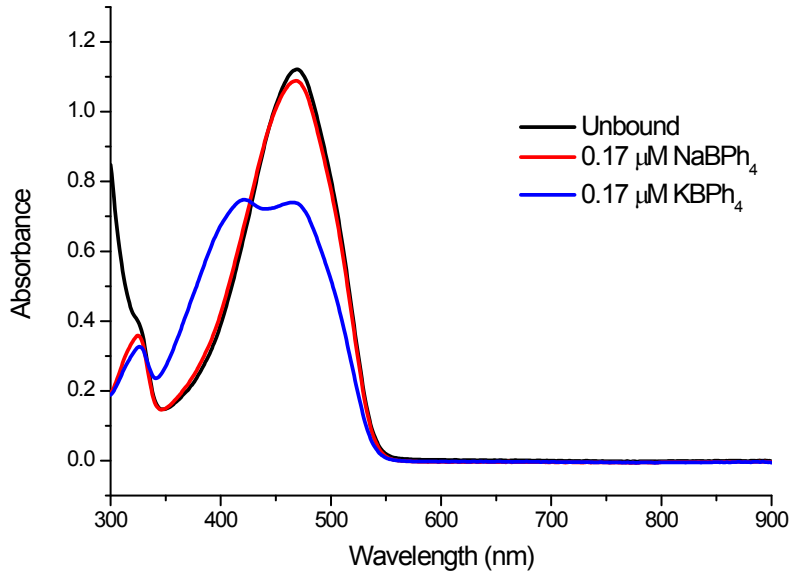


Figure S66 UV-Vis spectrum of **M2** at 1.5 x 10^{-5} M in THF at room temperature in response to an identical concentration of $NaBPh_4$ or $KBPh_4$.

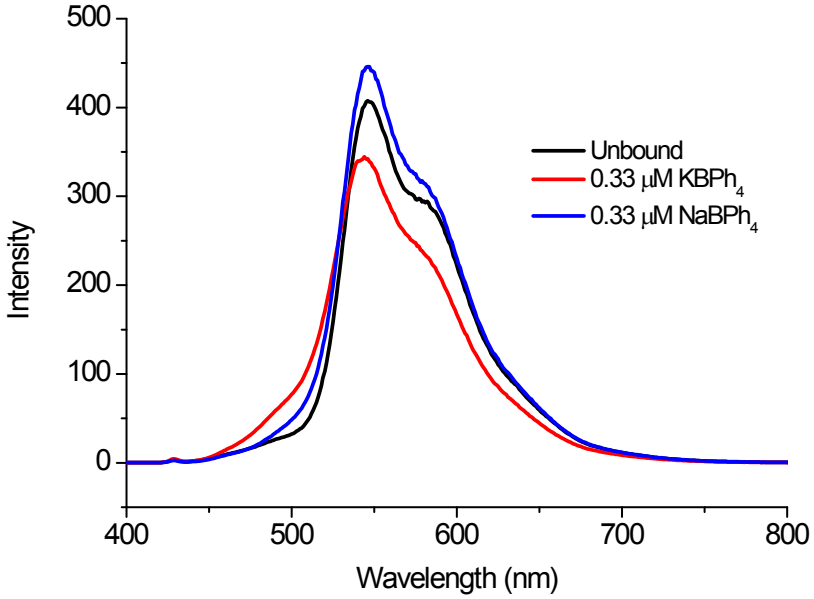


Figure S67 Fluorescence spectrum of **M2** at 1.5 x 10^{-5} M in THF at room temperature in response to an identical concentration of $NaBPh_4$ or $KBPh_4$.

M3

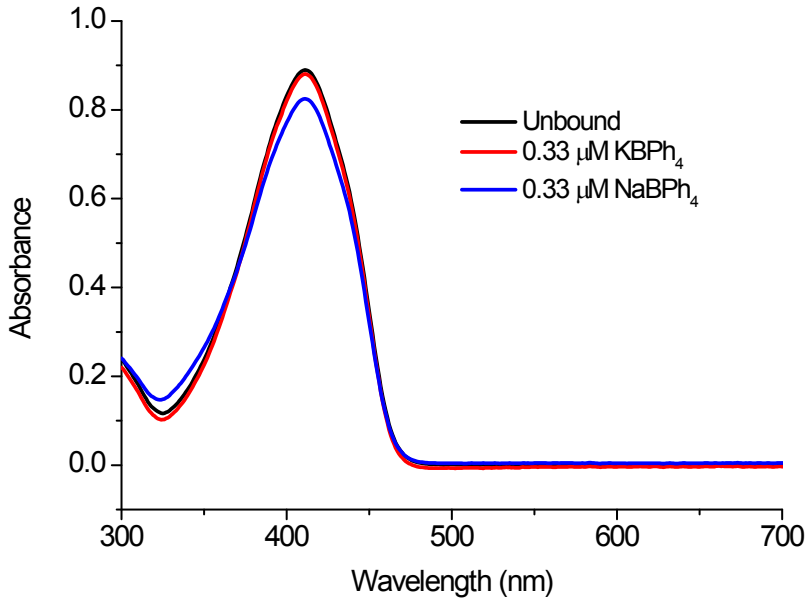


Figure S68 UV-Vis spectrum of **M3** at 2.8 x 10^{-5} M in THF at room temperature in response to an identical concentration of $NaBPh_4$ or $KBPh_4$.

M4

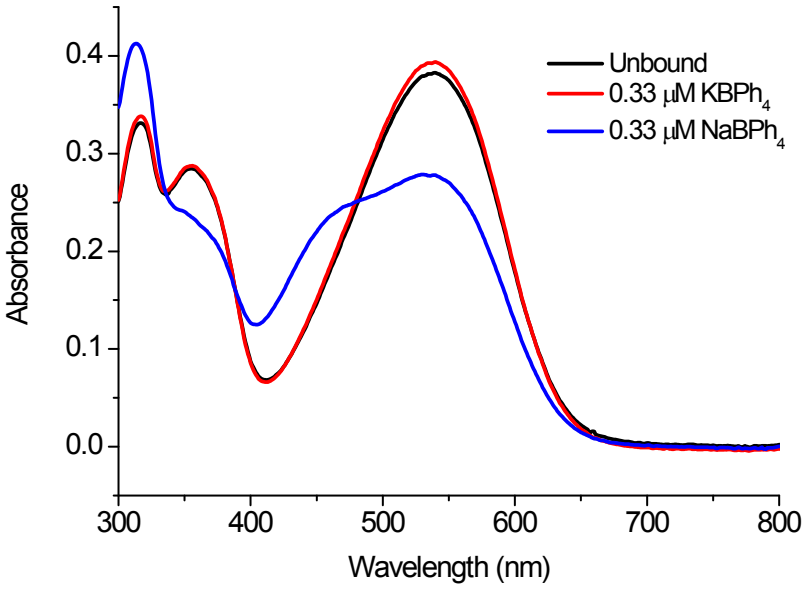


Figure S69 UV-Vis spectrum of **M4** at 8.9 x 10^{-6} M in THF at room temperature in response to an identical concentration of $NaBPh_4$ or $KBPh_4$.

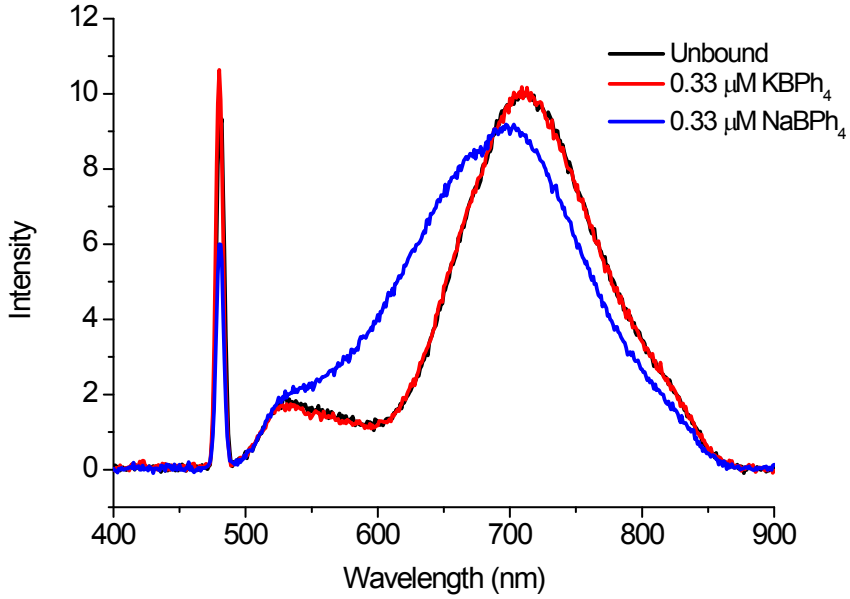


Figure S70 Fluorescence spectrum of **M4** at 8.9 x 10^{-6} M in THF at room temperature in response to an identical concentration of $NaBPh_4$ or $KBPh_4$.

M5

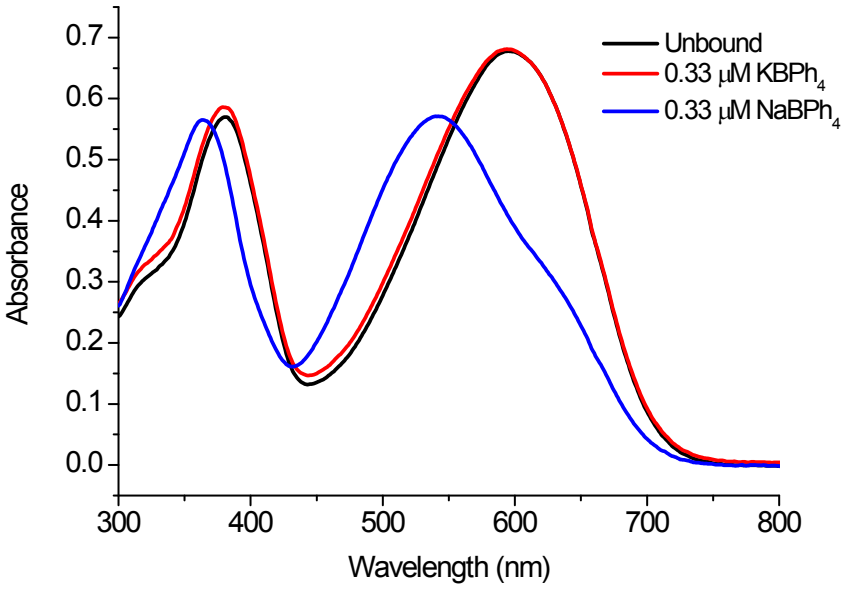


Figure S71 UV-Vis spectrum of **M5** at 8.1 x 10^{-6} M in THF at room temperature in response to an identical concentration of $NaBPh_4$ or $KBPh_4$.

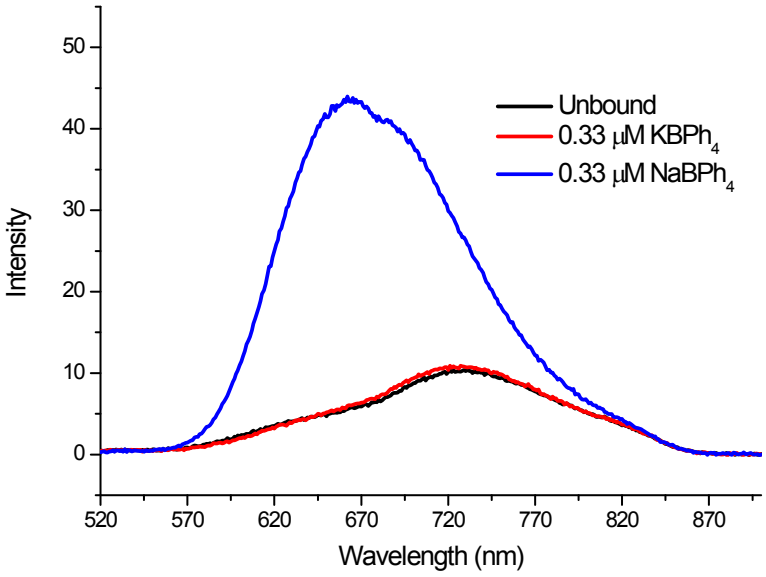


Figure S72 Fluorescence spectrum of **M5** at 8.1 x 10^{-6} M in THF at room temperature in response to an identical concentration of $NaBPh_4$ or $KBPh_4$.

M6

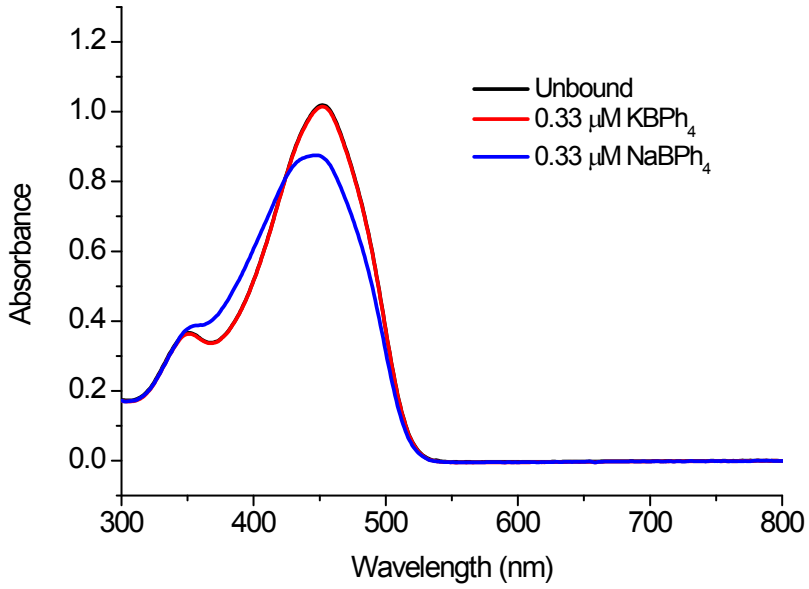


Figure S73 UV-Vis spectrum of **M6** at 8.3 x 10^{-6} M in THF at room temperature in response to an identical concentration of $NaBPh_4$ or $KBPh_4$.

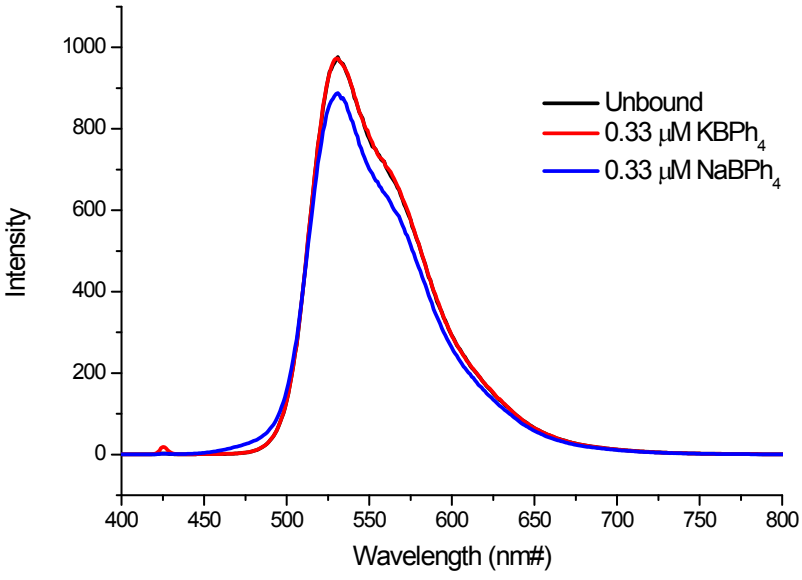


Figure S74 Fluorescence spectrum of **M6** at 8.3 x 10^{-6} M in THF at room temperature in response to an identical concentration of $NaBPh_4$ or $KBPh_4$.

Competitive Binding study

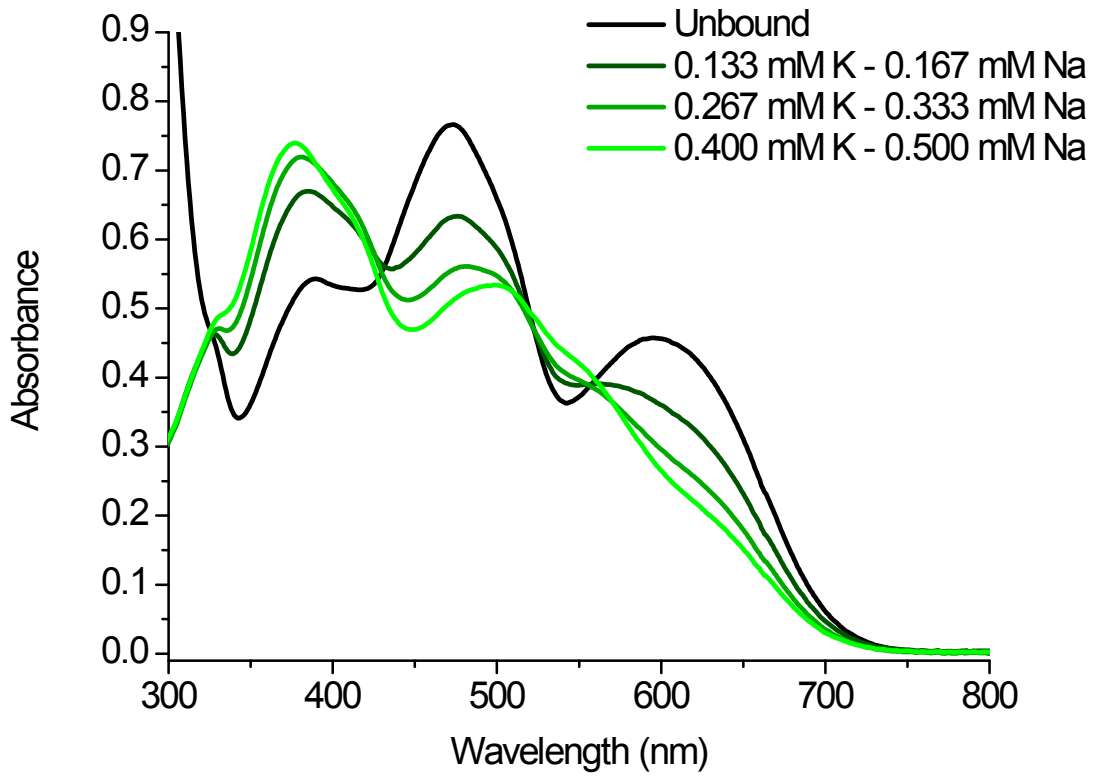


Figure S75 UV-Vis spectra of a blend of **M2** and **M5** at 3.1 x 10^{-5} M in THF at room temperature titrated with 0.002 M $KBPh_4$ in THF and 0.005 M $NaBPh_4$ in THF simultaneously.

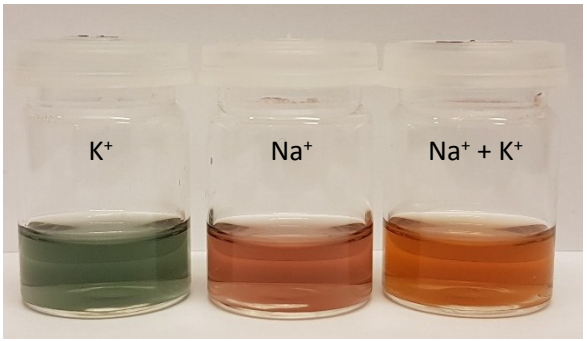


Figure S76 Photograph of end point of titrations of blended **M2** and **M5** with $KBPh_4$ (left) and $NaBPh_4$ (middle) and both $NaBPh_4$ and $KBPh_4$ (right). Data obtained in THF at room temperature with 0.005 M $NaBPh_4$ and 0.002 M $KBPh_4$ solutions.

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