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).
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(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 MgSO₄ 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, ¹H (400 MHz, CDCl₃) δ 7.16 (dd, 2H, J₁ = 2.8, J₂ = 5.6 Hz), 6.77 (dd, 2H, J₁ = 1.4, J₂ = 5.2 Hz), 6.25 (dd, 2H, J₁ = 1.6, J₂ = 3.2 Hz), 4.12-4.10 (m, 4H), 3.84 (m, 4H), 3.70 (m,8H), ¹³C{¹H} (101 MHz, CDCl₃) δ 157.7, 124.8, 119.7, 97.6, 70.9, 70.8, 69.8, 69.7.
2. 5,6,8,9,11,12,14,15-Octahydridithieno[3,2-\textit{n} :2',3'-\textit{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 °C and stirred for 1 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$_5$S$_2$Na 379.0650 Found 379.0678 1H NMR (400 MHz, CDCl$_3$) $\delta$ 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). 13C(1H) NMR (101 MHz, CDCl$_3$) $\delta$ 153.2, 122.98, 118.1, 113.7, 71.65, 71.1, 70.7, 70.6.
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 MgSO₄ 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, 1H (400 MHz, CDCl₃) δ 7.16 (dd, 2H, J₁ = 3.2 Hz, J₂ = 5.2 Hz), 6.78 (dd, 2H, J₁ = 1.2 Hz, J₂ = 5.2 Hz), 6.26 (dd, 2H, J₁ = 1.6 Hz, J₂ = 3.2 Hz) 4.12-4.10 (m, 4H), 3.84-3.82 (m, 4H), 3.72-3.66 (m, 12H). 13C{¹H} (101 MHz, CDCl₃) δ 157.8, 124.8, 119.7, 97.7, 70.9, 70.8, 69.8, 69.7
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 for 1 h after which the solution was cooled to -78 °C again. In a second dry RBF was added CuCl₂ (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 MgSO₄ 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 C₁₈H₂₄O₆S₂ 401.1093 Found 401.1070 ¹H (400 MHz, CDCl₃) δ 167.7, 152.4, 122.3, 117.0, 114.0, 71.6, 71.3, 70.7, 70.5, 70.5.
5. 2,18-Dibromo-5,6,8,9,11,12,14,15-octahydrodithieno[3,2-\textit{n}:2',3'-p][1,4,7,10,13]pentaacycloheptadecine

5,6,8,9,11,12,14,15,17,18-decahydrodithieno[3,2-\textit{q}:2',3'-s][1,4,7,10,13,16]hexaacycloicosine (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 \textit{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$_2$O$_5$S$_2$ 514.9020 found 514.9010

$^1$H (400 MHz, CDCl$_3$) $\delta$ 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($^1$H) (101 MHz, CDCl$_3$) $\delta$ 151.7, 121.1, 116.0, 110.2, 72.4, 71.5, 70.9, 70.6.
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]hexaoxacycloicosine**

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.
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 MgSO₄ 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. ¹H NMR (400 MHz, CDCl₃) 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). ¹³C(¹H) (101 MHz, CDCl₃) 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
8. 4,7-Dibromobenzo[c][1,2,5]thiadiazole

Synthesised according to literature procedure. 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$_2$S$_2$O$_3$ 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$_3$) $\delta$ 7.71. $^{13}$C($^1$H) (101 MHz, CDCl$_3$) $\delta$ 153.1, 122.5 114.4.
9. 5-Dodecyl-2,2′-bithiophene

Synthesised according to procedure adapted from literature. 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 MgSO₄ 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. ¹H NMR (400 MHz, CDCl₃) 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). ¹³C{¹H} (101 MHz, CDCl₃) 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.
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$_2$Sn found 497.97, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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($^1$H) (101 MHz, CDCl$_3$) $\delta$ 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.
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 \(\text{K}_2\text{CO}_3\) (4 ml) was added. The solution was degassed via \(\text{N}_2\) 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 \(\text{MgSO}_4\) 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 \(\text{C}_{52}\text{H}_{76}\text{O}_{5}\text{S}_{2}\) found 844.1.

**\(^1\)H NMR** (400 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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, 29.7, 29.5, 29.5, 22.8, 14.3
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 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, 1.75 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 MgSO₄ 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 N₂ 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 C₉₂H₇₁Br₂N₄O₅S₄Na 804.8718 found 804.8580. ¹H NMR (400 MHz, CDCl₃) 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). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 132.3, 124.5, 119.5, 100.0, 72.4, 71.4, 71.0, 70.4.
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\textsubscript{4} and the DCM removed \textit{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\textsubscript{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 \textit{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\textsuperscript+ calculated for C\textsubscript{28}H\textsubscript{17}Br\textsubscript{2}F\textsubscript{8}O\textsubscript{5}S\textsubscript{2}Na 832.8713 found 832.8685. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 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) \textsuperscript{13}C\textsuperscript{1}H NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 153.8, 124.1, 121.1, 119.0, 114.3, 111.7, 105.2, 100.1, 73.0, 71.7, 71.3, 70.5.
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 N₂ 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 C₆₈H₈₀N₄O₅S₈ 1288.39 found 1288.22. ¹H NMR (600 MHz, TCE-d₂) 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).¹³C {¹H} NMR (151 MHz, TCE-d₂) δ 71.4, 70.5, 32.1, 29.9, 29.8, 29.7, 29.5, 29.3, 22.9, 14.4.
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$_2$dba$_3$ (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$_8$O$_5$S$_6$ 1317.70 found 1316.13. $^1$H NMR (400 MHz, CDCl$_3$) 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.
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 N₂ 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_{6}S_{6} found 1066.10. ^1H NMR (600 MHz, CDCl₃) 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). ^13C(^1H) NMR 
(151 MHz, TCE-d₂) δ 71.6, 70.5, 70.2, 32.1, 29.8, 29.8, 29.7, 29.5, 29.3, 22.9, 14.4.
**Figure S1** UV-Vis titration experiment at room temperature for **M1** (8.8 x 10^{-5} M in chloroform) upon addition of NaBPh₄ aliquots in chloroform.

**Figure S2** UV-Vis titration experiment at room temperature for **M1** (1.7 x 10^{-5} M in THF) upon addition of NaBPh₄ aliquots in THF.
Figure S3 UV-Vis titration experiment at room temperature for M2 (6.1 x 10^{-6} M in chloroform) upon addition of KBPh₄ 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 KBPh₄ aliquots in THF.
Figure S5 UV-Vis titration experiment at room temperature for M3 (9.9 x 10^-5 M in chloroform) upon addition of NaBPh₄ 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 NaBPh₄ aliquots in THF.
**Figure S7** UV-Vis titration experiment at room temperature for M4 (10.0 x 10^{-5} M in chloroform) upon addition of NaBPh₄ 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 NaBPh₄ aliquots in THF.
**Figure S9** UV-Vis titration experiment at room temperature for M5 (4.4 x 10^{-5} M in chloroform) upon addition of NaBPh₄ 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 NaBPh₄ aliquots in THF.
Figure S11 UV-Vis titration experiment at room temperature for M6 (2.8 x 10^{-5} M in chloroform) upon addition of NaBPh₄ 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 NaBPh₄ 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

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

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:

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

Yields a straight line where:

\[\text{Gradient} = \frac{1}{K_a(A_{\text{max}} - A_0)}\]

Which can be solved for $K_a$:

\[K_a = \frac{1}{\text{Gradient}(A_{\text{max}} - A_0)}\]

$K_a$ was then calculated from

\[K_d = \frac{1}{K_a}\]
**Figure S12** Benesi-Hildebrand plot of M1 at $8.8 \times 10^{-5}$ M in chloroform titrated with NaBPh$_4$ aliquots at room temperature.

**Figure S13** Benesi-Hildebrand plot of M1 at $1.7 \times 10^{-5}$ M in THF titrated with NaBPh$_4$ aliquots at room temperature.
Figure S14 Benesi-Hildebrand plot of M2 at $6.1 \times 10^{-6}$ M in chloroform titrated with KBPh4 aliquots at room temperature.

Figure S15 Benesi-Hildebrand plot of M2 at $1.38 \times 10^{-5}$ M in THF titrated with KBPh4 aliquots at room temperature.
**Figure S16** Benesi-Hildebrand plot of M3 at 9.9 x 10^{-5} M in chloroform titrated with NaBPh₄ aliquots at room temperature.

**Figure S17** Benesi-Hildebrand plot of M3 at 1.8 x 10^{-5} M in THF titrated with NaBPh₄ aliquots at room temperature.
Figure S18 Benesi-Hildebrand plot of M4 at 10.0 x 10^{-5} M in chloroform titrated with NaBPh₄ aliquots at room temperature.

Figure S19 Benesi-Hildebrand plot of M4 at 1.8 x 10^{-5} M in THF titrated with NaBPh₄ aliquots at room temperature.
Figure S20 Benesi-Hildebrand plot of M5 at 4.4 x 10^-5 M in chloroform titrated with NaBPh₄ aliquots at room temperature.

Figure S21 Benesi-Hildebrand plot of M5 at 1.1 x 10^-5 M in THF titrated with NaBPh₄ aliquots at room temperature.
**Figure S22** Benesi-Hildebrand plot of M6 at $2.8 \times 10^{-5}$ M in chloroform titrated with NaBPh$_4$ aliquots at room temperature.

**Figure S23** Benesi-Hildebrand plot of M6 at $1.0 \times 10^{-5}$ 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 \(\sigma\) is the standard deviation of the baseline, and \(m\) is the gradient of the calibration curve.

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

\[
m = \frac{\text{Absorbance intensity of molecule cation complex}}{\text{Absorbance intensity of neutral molecule}}
\]
**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.
**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.
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.
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.
**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.
**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**

![Graph](image1)

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

**M2**

![Graph](image2)

**Figure S36** Stability of M2 in chloroform when first prepared and 6 months later stored in dark under atmospheric conditions at room temperature.
Figure S37 Stability of M3 in chloroform when first prepared and 6 months later stored in dark under atmospheric conditions at room temperature.

Figure S38 Stability of M4 in chloroform when first prepared and 6 months later stored in dark under atmospheric conditions at room temperature.
Figure S39 Stability of M5 in chloroform when first prepared and 6 months later stored in dark under atmospheric conditions at room temperature.

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.

**Figure S41** Fluorescence titration experiment at room temperature for M1 \((1.7 \times 10^{-5} \text{ M in THF})\) upon addition of NaBPh₄ aliquots in THF.

**Figure S42** Fluorescence titration experiment at room temperature for M1 \((10 \times 10^{-5} \text{ M in chloroform})\) upon addition of NaBPh₄ aliquots in chloroform.
**Figure S43** Fluorescence titration experiment at room temperature for M2 ($1.38 \times 10^{-5} \text{ M}$ in THF) upon addition of KBPh₄ aliquots in THF.

**Figure S44** Fluorescence titration experiment at room temperature for M2 ($1.78 \times 10^{-5} \text{ M}$ in chloroform) upon addition of KBPh₄ aliquots in chloroform.
**Figure S45** Fluorescence titration experiment at room temperature for M4 \( (1.8 \times 10^{-5} \text{ M in THF}) \) upon addition of NaBPh₄ aliquots in THF.

**Figure S46** Fluorescence titration experiment at room temperature for M4 \( (5.2 \times 10^{-5} \text{ M in chloroform}) \) upon addition of NaBPh₄ aliquots in chloroform.
Figure S47 Fluorescence titration experiment at room temperature for M5 (1.1 x 10^{-5} M in THF) upon addition of NaBPh₄ aliquots in THF.

Figure S48 Fluorescence titration experiment at room temperature for M5 (7.1 x 10^{-5} M in chloroform) upon addition of NaBPh₄ aliquots in chloroform.
**Figure S49** Fluorescence titration experiment at room temperature for **M6** (1.0 x 10^{-5} M in THF) upon addition of NaBPh₄ aliquots in THF.

**Figure S50** Fluorescence titration experiment at room temperature for **M4** (2.3 x 10^{-5} M in chloroform) upon addition of NaBPh₄ 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 $\lambda_{\text{max}}$ 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 according to the following equation:

$$\Phi_m = \Phi_{\text{standard}} \left( \frac{\text{Grad}_m}{\text{Grad}_{\text{standard}}} \right) \left( \frac{\eta_m}{\eta_{\text{standard}}} \right)^2$$

Where $\Phi_m$ is the quantum yield of the molecule, $\Phi_{\text{standard}}$ is literature quantum yield of the standard, $\text{Grad}_m$ is the gradient of integrated fluorescence intensity versus absorption of the molecule, $\text{Grad}_{\text{standard}}$ is the gradient of integrated fluorescence intensity versus absorption of the molecule, $\eta_m$ is the refractive index of the solvent of the molecule and $\eta_{\text{standard}}$ is the refractive index of the solvent used for the standard.

**Anthracene**

![Anthracene standard dilution series at room temperature in degassed cyclohexane for quantum yield calculations.](Figure S51)
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.
**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.
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.
**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.
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.
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\textsuperscript{+} complex for quantum yield calculations.
Tabulated Additional Optical Data

**SI Table 1**

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<th>ε (M&lt;sup&gt;-1&lt;/sup&gt;cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>K&lt;sub&gt;d&lt;/sub&gt; (mM)</th>
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†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 NaBPh₄ or KBPh₄.

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 NaBPh₄ or KBPh₄.
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.
Figure S68 UV-Vis spectrum of M3 at 2.8 x 10^{-5} \text{ M} in THF at room temperature in response to an identical concentration of NaBPh\textsubscript{4} or KBPh\textsubscript{4}.
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.
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 NaBPh₄ or KBPh₄.

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 NaBPh₄ or KBPh₄.
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 NaBPh₄ or KBPh₄.

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 NaBPh₄ or KBPh₄.
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 KBPh₄ in THF and 0.005 M NaBPh₄ in THF simultaneously.

**Figure S76** Photograph of end point of titrations of blended M2 and M5 with KBPh₄ (left) and NaBPh₄ (middle) and both NaBPh₄ and KBPh₄ (right). Data obtained in THF at room temperature with 0.005 M NaBPh₄ and 0.002 M KBPh₄ solutions.
References


