Electronic Supplementary Material (ESI) for Chemical Communications

Utilizing Electronic Effects in the Modulation of BTPhen Ligands with Respect to the Partitioning of Minor Actinides from Lanthanides

Ashfaq Afsar,[a] Dominic L. Laventine,[a] Laurence M. Harwood,[a] Michael J. Hudson[a] and Andreas Geist[b]*

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1.0 Experimental Procedures

General procedure

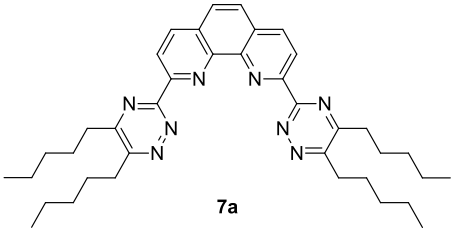
NMR spectra were recorded using either a Bruker AMX400 or an Avance DFX400 instrument. Deuterated chloroform ($CDCl_3$) and Deuterated DMSO (dimethyl sulfoxide-d_6) were used as solvents. Chemical shifts (δ values) were reported in parts per million (ppm) with the abbreviations s, d, t, q, qn, sx, dd, ddd and br denoting singlet, doublet, triplet, quartet, quintet, sextet, double doublets, doublet of doublets of doublets and broad resonances respectively. Coupling constants (*J*) are quoted in Hertz.

IR spectra were recorded as Nujol® mulls (N) on a Perkin Elmer RX1 FT-IR instrument.

All the melting points were determined on a Gallenkamp melting point apparatus.

Mass spectra ($^m/z$) were recorded under conditions of electrospray ionisation (ESI). The ions observed were quasimolecular ions created by the addition of a hydrogen ion denoted as $[MH]^+$ or of sodium ion, [M + Na]. The instrument used was Xcalibur Tune 2.1 (SP1).

2,9-Bis(5,6-dipentyl-1,2,4-triazin-3-yl)-1,10-phenanthroline (7a)

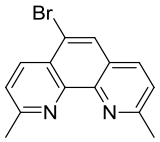


7a

To a suspension of **6a** (0.50 g, 1.7 mmol) in THF (50 mL) was added dodecane-6,7-dione (0.76 g, 3.8 mmol, 2.2 eq). Et_3N (3 mL, 21.3 mmol) was added and the mixture was heated under reflux for 3 days. After allowing the solution to cool to room temperature, the solvent was evaporated and the remaining semi-solid residue was triturated with ice-cold Et_2O (100 mL). The insoluble solid was filtered and washed with further ice-cold Et_2O (100 mL) and allowed to dry in air to afford the ligand **7a** as a yellow solid (0.27 g, 25 %); Mp (138-141°C); ^{1}H NMR ($CDCl_3$): δ_H = 0.94 (m, 12H), 1.45 (m, 16H), 1.90 (m, 8H), 3.11 (m, 8H), 7.96 (s, 2H), 8.45 (d, *J* = 8.3 Hz, 2H), 8.93 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ_C = 14, 14.1, 22.5,

22.5, 28.2, 28.3, 31.7, 32.1, 32.4, 34.4, 123.1, 127.5, 129.7, 137.2, 146.6, 153.6, 160, 161.6, 162.6; $C_{76}H_{100}N_{16}$ [2M + Na] requires $^{m}/_{z}$ 1259.8209; (FTMS + c ESI) MS found $^{m}/_{z}$ 1259.8235; IR ν_{max} / cm^{-1}= 3511, 2956, 2926, 2858, 2674, 2490, 1622, 1585, 1518, 1496, 1466, 1441.

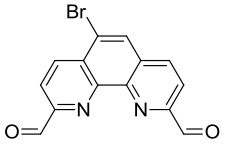
5-Bromo-2,9-dimethyl-1,10-phenonthroline (2)



2

Fuming sulfuric acid (75 mL) was added to 2,9-dimethyl-1,10-phenanthroline **51** (5.11 g, 24.5 mmol). Bromine (0.76 mL, 14.7 mmol, 0.6 eq) was added and the mixture was heated under reflux overnight. The flask was allowed to cool to room temperature and the solution was quenched with water (200 mL). NaOH pellets were added until the pH of the solution was between 7-8. The resulting mixture was extracted with chloroform (2×200 mL) and the combined organic phases were dried over $MgSO_4$, filtered and the solvent removed under vacuum to afford the product **151** as a yellow solid (6.51 g, 93 %); Mp (175-178°C); ^{1}H-NMR ($CDCl_3$): δ_H = 2.94 (s, 3H), 2.98 (s, 3H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 8.03 (s, 1H), 8.04 (d, *J* = 8.2 Hz, 1H), 8.53 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ_C = 25.7, 26.0, 119.7, 124.1, 124.3, 126.0, 127.1, 128.6, 135.4, 136.1, 144.8, 145.8, 160.0, 160.3; $C_{14}H_{11}N_2Br_1$ $[MH]^+$ requires $^{m}/_{z}$ 287.0178; (FTMS + p ESI) MS found $^{m}/_{z}$ 287.0180; IR ν_{max} / cm^{-1}= 3385, 3048, 2916, 2163, 1603, 1589, 1546, 1491, 1435, 1400.

5-Bromo-1,10-phenanthroline-2,9-dicarbaldehyde (4b)

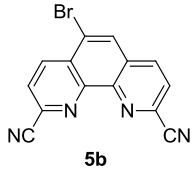


4b

Selenium dioxide (12.34 g, 111.2 mmol, 2.1 eq) dissolved in 1,4-dioxane (250 mL) and water (~ 7mL) was heated to reflux. To this solution was added a solution of **2** (15.08 g, 52.5 mmol) in dioxane (250 mL) dropwise over 30 min. The solution was heated under reflux for 2.5 h.

After allowing the solution to cool to room temperature, the precipitated selenium metal was filtered off. The filtrate was evaporated and the solid was triturated with Et_2O (200 mL). The insoluble solid was filtered, washed with Et_2O (200 mL) and allowed to dry in vacuum oven (40 ^oC) to afford the product **4b** as a dark brown solid (14.94 g, 90 %); Mp (207-210°C); ^{1}H-NMR (DMSO-d_6): δ_H = 8.30 (d, J = 8.3 Hz, 1H), 8.40 (d, J = 8.5 Hz, 1H), 8.70 (d, J = 8.3 Hz, 1H), 8.75 (s, 1H), 8.90 (d, J = 8.5 Hz, 1H), 10.33 (s, 1H, CHO), 10.37 (s, 1H, CHO); ^{13}C NMR (DMSO-d_6) δ_C = 120.7, 121.1, 122.4, 129.9, 131.7, 132.3, 137.7, 137.7, 144.5, 145.5, 152.4, 152.4, 193.1, 193.4; $C_{14}H_7N_2O_2Br$ $[MH]^+$ requires $^m/_z$ 314.9764 and 316.9743; (FTMS + p ESI) MS found $^m/_z$ 314.9764 and 316.9743; IR ν_{max} / cm^{-1}= 3068, 2856, 2191, 1973, 1697, 1598, 1548, 1351, 1237.

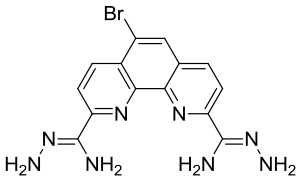
5-Bromo-1,10-phenanthroline-2,9-dicarbonitrile (5b)



5b

To a suspension of **4b** (11.33 g, 36 mmol) in dry MeCN (500 mL) was added hydroxylamine hydrochloride (5.80 g, 83.4 mmol, 2.3 eq) and Et_3N (33.1 mL, 235.5 mmol, 6.5 eq). The solution was heated under reflux for 4 h. After allowing the mixture to cool to room temperature, *p*-toluenesulfonylchloride (22.67 g, 118.9 mmol, 3.3 eq) and pyridine (18 mL, 223.5 mmol, 6.2 eq) were added and the mixture was heated under reflux for 24 h. The mixture was filtered while hot and the solid residue was washed with hot MeCN (40 mL). The filtrate was evaporated to afford a brown semi-solid which was triturated with MeOH (200 mL) and then filtered and washed with MeOH (200 mL) and Et_2O (200 mL) to afford the product **5b** as a brown solid (7.19 g, 65 %); Mp (151-154°C); ^{1}H NMR (DMSO-d_6) δ_H = 8.39 (d, J = 8.3 Hz, 1H), 8.47 (d, J = 8.5 Hz, 1H), 8.70 (s, 1H), 8.73 (d, J = 8.3 Hz, 1H), 8.82 (d, J = 8.5 Hz, 1H); ^{13}C NMR (DMSO-d_6) δ_C = 117, 117.4, 122.3, 126.8, 129.1, 130.4, 132.3, 133.1, 133.4, 137.8, 137.8, 143, 144.9, 145.5; $C_{14}H_5N_4Br$ $[MH]^+$ requires $^m/_z$ 308.9770 and 310.9750; (FTMS + p ESI) MS found $^m/_z$ 308.9773 and 310.9751; IR ν_{max} / cm^{-1}= 3082, 2984, 2238, 1616, 1497, 1366.

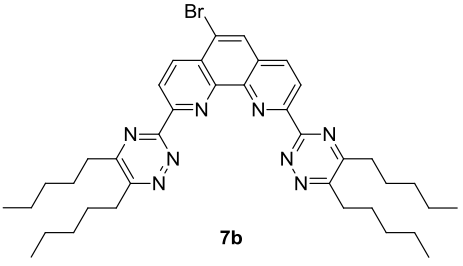
5-Bromo-1,10-phenanthroline-2,9-dicarbohydrazonamide (6b)



6b

To a suspension of **5b** (2.50 g, 8.1 mmol) in EtOH (50 mL) was added hydrazine hydrate (50 mL, 64%). The suspension was stirred at room temperature for 2 days. Et_2O (50 mL) and MeOH (50 mL) were added and the solid was filtered and washed with Et_2O (200 mL) and allowed to dry in a vacuum oven (40 ^oC) to afford the product **6b** as a brown solid (2.10 g, 70 %); Mp (above 335°C); ^1H NMR (DMSO-d_6) δ_H = 5.86 (br s, 4H, NH_2), 6.15 (br s, 4H, NH_2), 8.31 (d, J = 8.3 Hz, 1H), 8.37 (d, J = 8.5 Hz, 1H), 8.41 (d, J = 8.3 Hz, 1H), 8.43 (s, 1H), 8.54 (d, J = 8.5 Hz, 1H); ^{13}C NMR (DMSO-d_6) δ_C = 119.1, 119.7, 120.1, 126.7, 128.4, 129.2, 135.1, 135.3, 142.7, 143, 143.2, 144.2, 151.7, 151.9; $C_{14}H_{13}N_8Br$ $[MH]^+$ requires $^m/_z$ 373.0519 and 375.0499; (FTMS + c ESI) MS found $^m/_z$ 373.0519 and 375.0499; IR ν_{max} / cm^{-1}= 3450, 3339, 3188, 2922, 2853, 1634, 1601, 1581, 1544, 1490, 1448, 1403.

5-Bromo-2,9-bis(5,6-dipentyl-1,2,4-triazin-3-yl)-1,10-phenanthroline (7b)

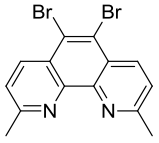


7b

To a suspension of **6b** (0.50 g, 1.3 mmol) in 1,4-dioxane (75 mL) was added dodecane-6,7-dione (0.61 g, 3.1 mmol, 2.4 eq). Triethylamine (2 mL, 14.2 mmol) was added and the mixture was heated under reflux for 3 days. After allowing the solution to cool to room temperature, the solvent was evaporated and the remaining semi-solid residue was triturated with ice-cold Et_2O (200 mL). The insoluble solid was filtered and washed with further ice-cold Et_2O (200 mL) and allowed to dry in air to afford the ligand **7b** as a yellow solid (0.28 g, 30 %); Mp (130-133°C); ^1H NMR ($CDCl_3$) δ_H = 0.93 (m, 12H), 1.44 (m, 16H), 1.90 (m, 8H), 3.09 (m, 8H), 8.30 (s, 1H), 8.39 (d, J = 8.4 Hz, 1H), 8.88 (d, J = 8.6 Hz, 1H), 8.93 (d, J = 8.4 Hz, 1H),

9.01 (d, J = 8.6 Hz, 1H) ; ^{13}C NMR ($CDCl_3$) δ_C = 14, 14.1, 22.5, 22.5, 28.1, 28.3, 31.7, 32.1, 32.5, 34.3, 122.0, 123.7, 123.8, 129.0, 129.8, 130.6, 136.3, 137.3, 146.0, 146.9, 154.0, 154.2, 160.1, 160.3, 161.1, 161.3, 162.6; $C_{38}H_{49}N_8Br$ $[MH]^+$ requires $^m/_z$ 697.3336 and 699.3316; (FTMS + p ESI) MS found $^m/_z$ 697.3335 and 699.3315; IR ν_{max} / cm^{-1}= 3513, 3468, 2959, 2927, 2860, 1604, 1515, 1488, 1466, 1439.

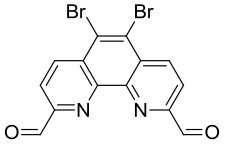
5,6-Dibromo-2,9-dimethyl-1,10-phenonthroline (3)



3

Fuming sulfuric acid (110 mL) was added to **1** (13.12 g, 63 mmol). Bromine (6.5 mL, 252.4 mmol, 4 eq) was added and the mixture was heated under reflux for 3 days. The flask was allowed to cool to room temperature and the solution was quenched with water (500 mL). NaOH pellets were added until the pH of the solution was between7-8. The resulting mixture was extracted with chloroform (10×100 mL) and the combined organic phases were dried over $MgSO_4$, filtered and the solvent removed under vacuum to afford the product **3** as a yellow solid (21.63 g, 94 %); Mp (163-166°C); ^{1}H-NMR ($CDCl_3$): δ_H = 3.00 (s, 6H). 7.57 (d, J = 8.5 Hz, 2H), 8.64 (d, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ_C = 25.7, 124.9, 126.9, 137.4, 145, 160.6; $C_{14}H_{10}N_2Br_2$ $[MH]^+$ requires $^m/_z$ 364.9284, 366.9263 and 368.9243; (FTMS + p ESI) MS found $^m/_z$ 364.9279, 366.9255 and 368.9233; IR ν_{max} / cm^{-1}= 3513, 3410, 1586, 1483, 1434, 1358, 1300, 1201, 1148, 1099.

5,6-Dibromo-1,10-phenanthroline-2,9-dicarbaldehyde (4c)

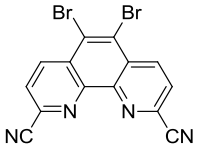


4c

Selenium dioxide (8.64 g, 77.9 mmol, 2.1 eq) dissolved in 1,4-dioxane (250 mL) and water (~ 8 mL) was heated to reflux. To this solution was added a **3** (13.45 g, 36.8 mmol) in dioxane (250 mL) dropwise over 15 min. The solution was heated under reflux for 5 h. After allowing the solution to cool to room temperature, the precipitated selenium metal was filtered off. The

filtrate was left to crystallise overnight and then filtered and washed with Et_2O (200 mL) and allowed to dry in a vacuum oven (40 ^oC) to afford the product **4c** as yellow solid (9.33 g, 64 %); Mp (209-213°C); ^{1}H-NMR ($CDCl_3$): δ_H = 8.40 (d, *J* = 8.5 Hz, 2H), 9.08 (d, *J* = 8.5 Hz, 2H), 10.57 (s, 2H, 2×CHO); ^{13}C NMR ($CDCl_3$) δ_C = 121.7, 127.4, 130.5, 139.1, 144.6, 152.4, 193; $C_{14}H_6N_2O_2Br_2$ $[MH]^+$ requires $^m/_z$ 392.8869 and 394.8848; (FTMS + p ESI) MS found $^m/_z$ 392.8873 and 394.8853; IR ν_{max} / cm^{-1}= 3656, 3080, 2865, 1708, 1245.

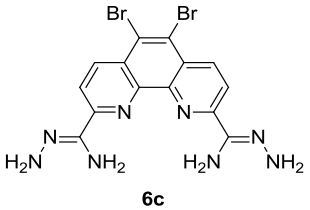
5,6-Dibromo-1,10-phenanthroline-2,9-dicarbonitrile (5c)



5c

To a suspension of **4c** (4.50 g, 11.4 mmol) in dry MeCN (350 mL) was added hydroxylamine hydrochloride (1.75 g, 26 mmol, 2.3 eq) and Et_3N (11 mL, 78.3 mmol, 6.9 eq). The solution was heated under reflux for 24 hours. After allowing the mixture to cool to room temperature, *p*-toluenesulfonyl chloride (7.34 g, 38.5 mmol, 3.4 eq) and pyridine (2.8 mL, 34.76 mmol, 3 eq) were added and the mixture was heated under reflux for 2 days. The mixture was filtered while hot and the solid residue was washed with hot MeCN (20 mL). The filtrate was evaporated to afford a dark brown semi-solid which was triturated with MeOH (100 mL) and then filtered and washed with MeOH (100 mL) and Et_2O (100 mL) to afford the product **5c** as a pale brown solid (2.59 g, 58 %); Mp (135-138°C); ^{1}H NMR (DMSO-d_6) δ_H = 8.38 (d, *J* = 8.5 Hz, 2H), 8.88 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (DMSO-d_6) δ_C = 117, 125.4, 128, 129.1, 133.6, 139.2, 144.1; $C_{14}H_4N_4Br_2$ $[MH]^+$ requires $^m/_z$ 386.8883; (FTMS + p ESI) MS found $^m/_z$ 386.8886; IR ν_{max} / cm^{-1}= 3260, 3083, 2944, 2608, 2241, 1758, 1700, 1571, 1472, 1361, 1209.

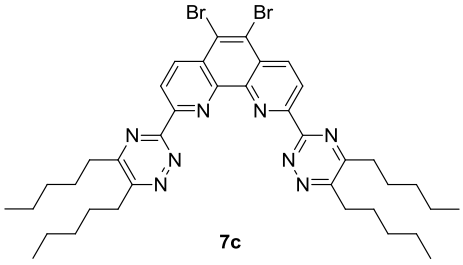
5,6-Dibromo-1,10-phenanthroline-2,9-dicarbohydrazonamide (6c)



6c

To a suspension of **5c** (2.59 g, 6.7 mmol) in EtOH (150 mL) was added hydrazine hydrate (100 mL, 64%). The suspension was stirred at room temperature for 7 days. Et_2O (200 mL) and EtOH (200 mL) were added and the solid was filtered and washed with Et_2O (200 mL) and allowed to dry in a vacuum oven (40 ^oC) to afford the product **6c** as a yellow solid (2.83 g, 94 %); Mp (335-338°C); ^1H NMR (DMSO-d_6) δ_H = 5.80 (br s, 4H, NH_2), 6.11 (br s, 4H, NH_2), 8.37 (d, J = 8.9 Hz, 2H), 8.62 (d, J = 8.5 Hz, 2H); ^{13}C NMR (DMSO-d_6) δ_C = 120.9, 123.7, 127.5, 136.4, 142.7, 143.4, 152.1; $C_{14}H_{12}N_8Br_2$ [M + Na] requires $^m/_z$ 472.9444 and 474.9423; (FTMS + c ESI) MS found $^m/_z$ 472.9450 and 474.9430; IR ν_{max} / cm^{-1}= 3459, 3353, 3190, 1642, 1591, 1490, 1358, 1198.

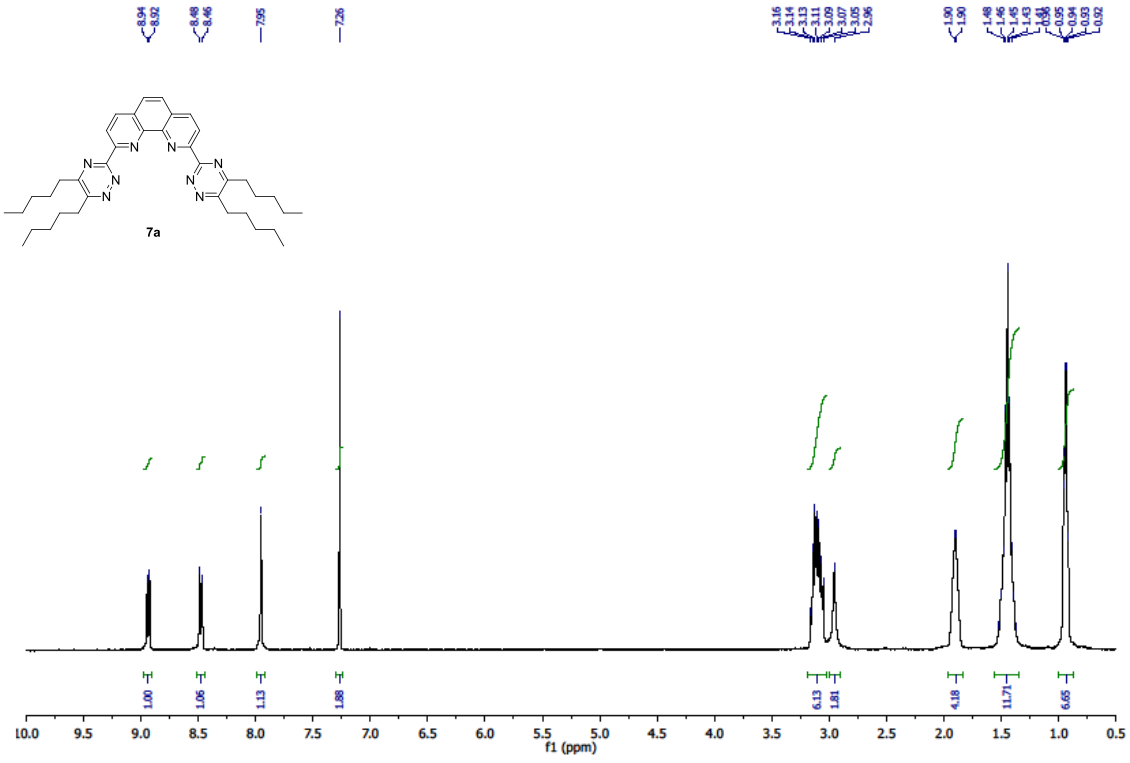
5,6-Dibromo-2,9-bis(5,6-dipentyl-1,2,4-triazin-3-yl)-1,10-phenanthroline (7c)

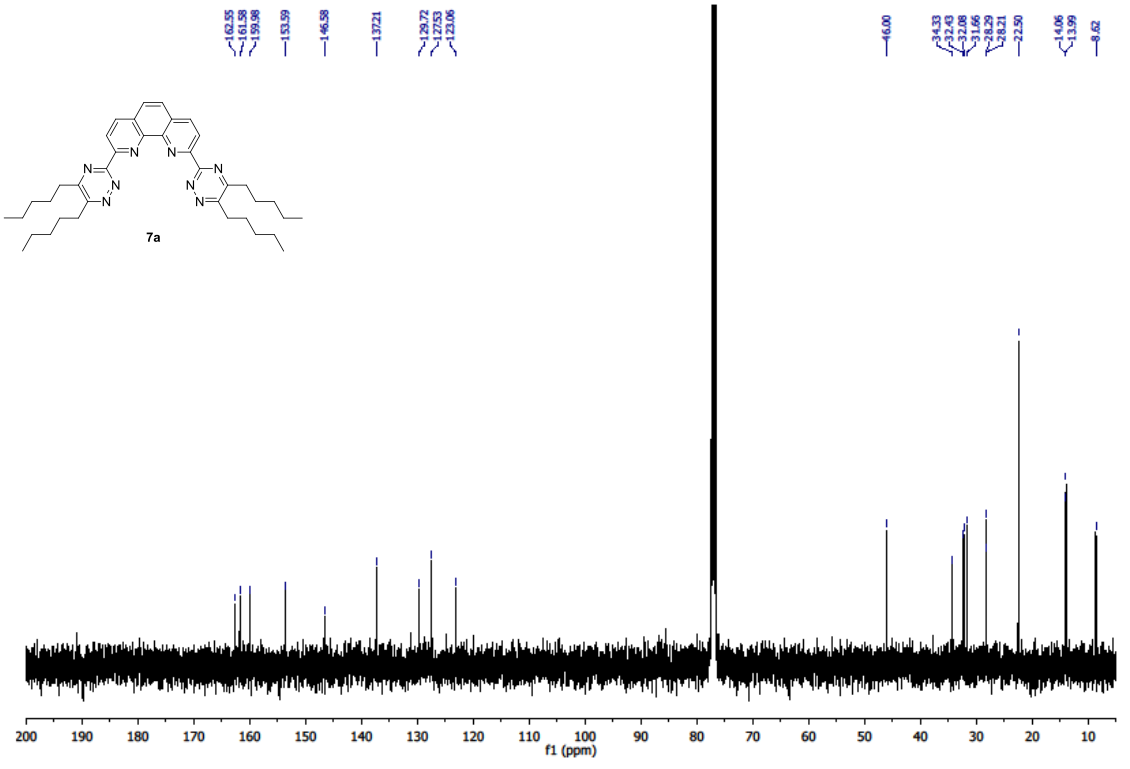


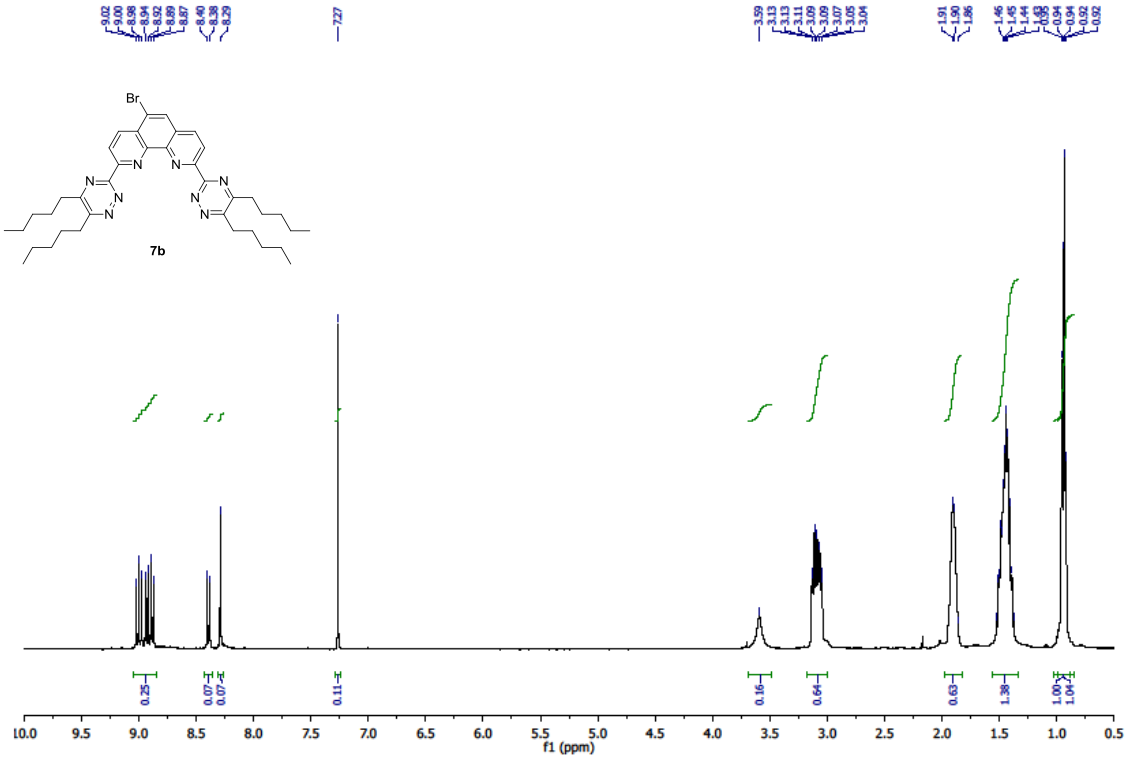
7c

To a suspension of **6c** (0.50 g, 1.1 mmol) in 1,4-dioxane (50 mL) was added dodecane-6,7-dione (0.52 g, 2.6 mmol, 2.4 eq). Triethylamine (2 mL, 14.2 mmol) was added and the mixture was heated under reflux for 3 days. After allowing the solution to cool to room temperature, the solvent was evaporated and the remaining semi-solid residue was triturated with ice-cold Et_2O (100 mL). The insoluble solid was filtered and washed with further ice-cold Et_2O (100 mL) and allowed to dry in air to afford the ligand **7c** as a yellow solid (0.09 g, 11 %); Mp (132-135°C); ^1H NMR ($CDCl_3$) δ_H = 0.94 (m, 12H), 1.45 (m, 16H), 1.90 (m, 8H), 3.07 (t, J = 8.7 Hz, 4H), 3.13 (t, J = 8.7 Hz, 4H), 9.04 (s, 4H, 3-H); ^{13}C NMR ($CDCl_3$) δ_C = 14, 14.1, 22.5, 22.5, 28.1, 28.3, 31.6, 32.1, 32.5, 34.4, 124.4, 126.3, 129.6, 138.5, 146, 154.6, 160.3, 161.6, 162.5; $C_{76}H_{96}N_{16}Br_2{}^{81}Br_2$ [2M + Na] requires $^m/_z$ 1575.4589; (FTMS + c ESI) MS found $^m/_z$ 1575.4639; IR ν_{max} / cm^{-1}= 3512, 3458, 2957, 2925, 2858, 2163, 1628, 1588, 1519, 1479, 1459, 1442.

^{1}H and ^{13}C NMR spectra for ligands



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7b
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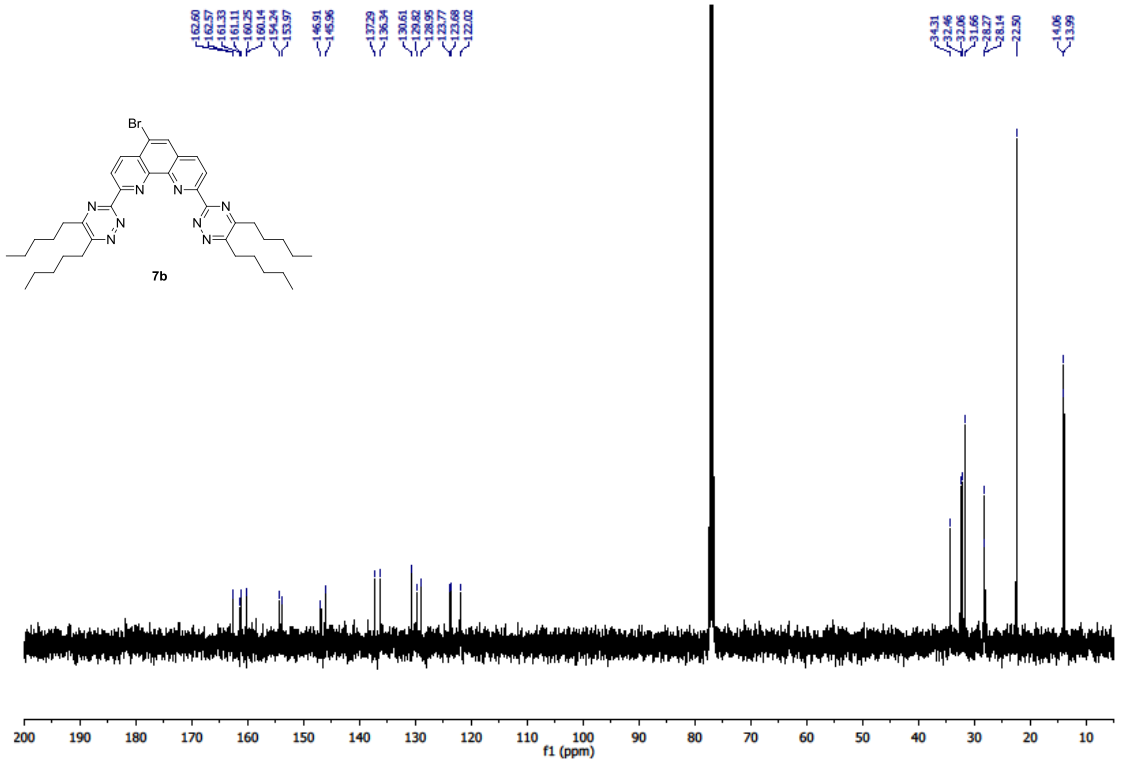
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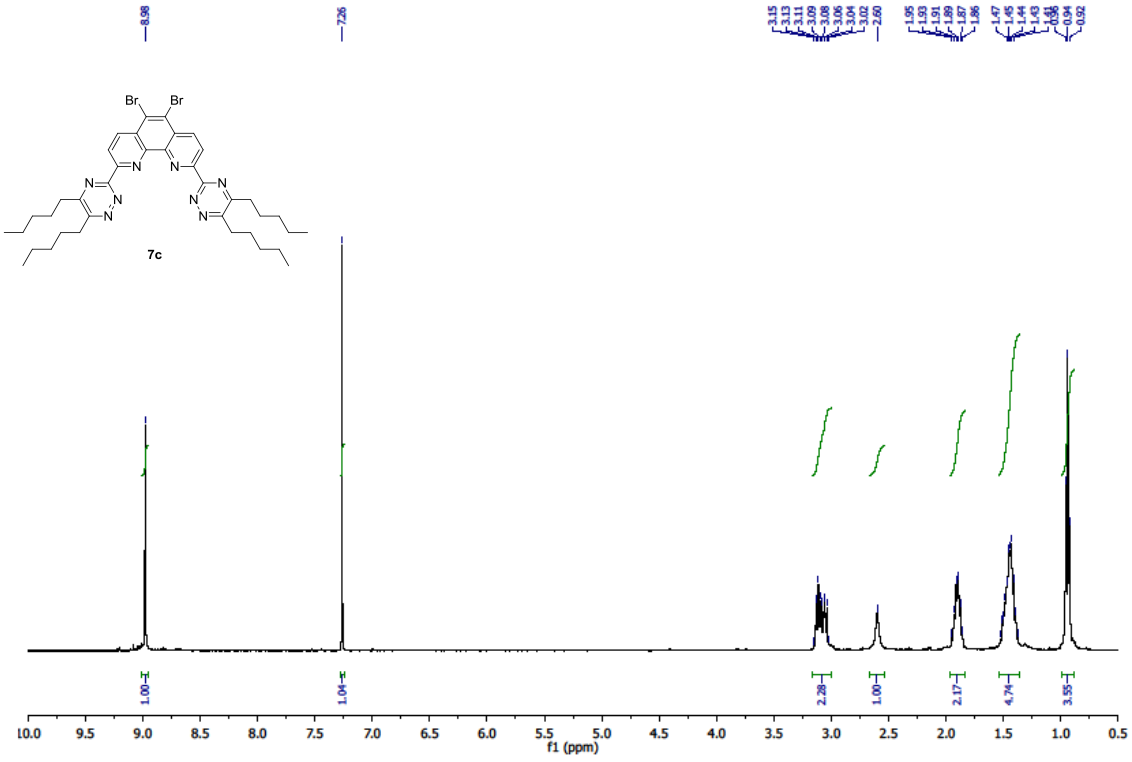
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1.91
1.89
1.87
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1.47
1.45
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0.92
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N
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N
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N
7c
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1.04
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1.00
2.17
4.74
3.55
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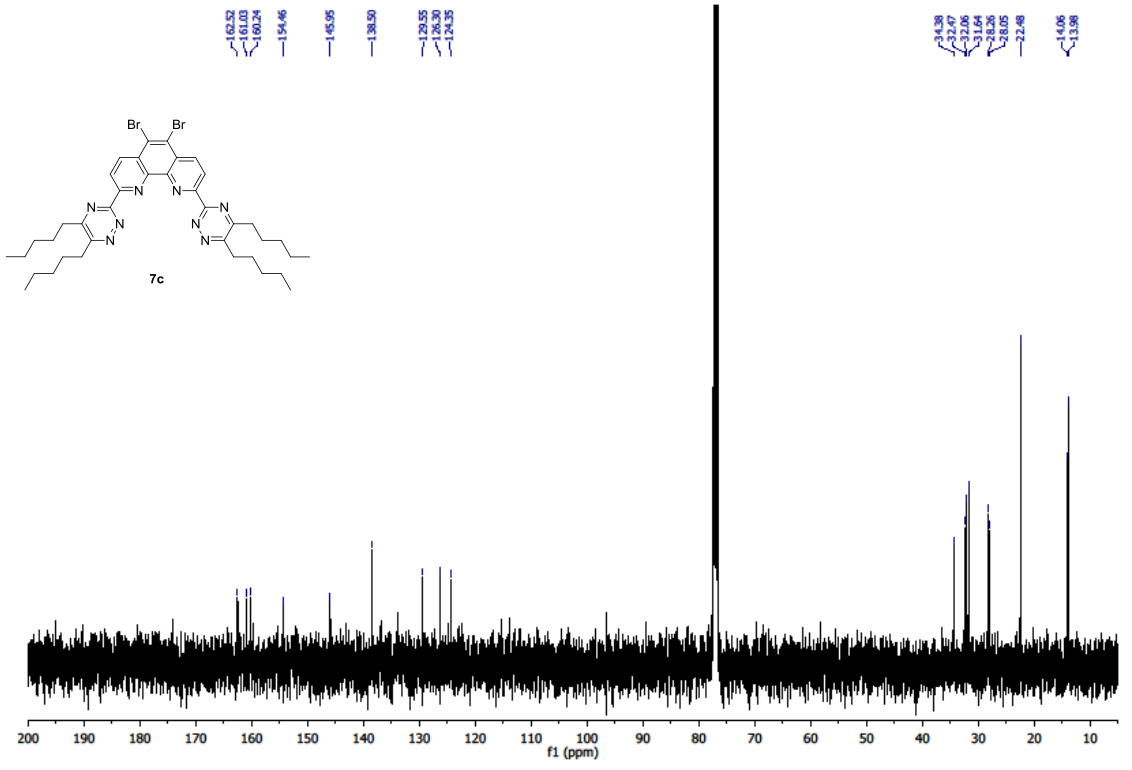
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160.24
154.46
145.05
138.50
129.55
126.30
124.35
34.38
32.47
32.06
31.64
28.26
28.05
22.48
14.06
13.98
Br
Br
N
N
N
N
N
N
7c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

2.0 NMR Spectroscopic Titrations with Lanthanide Salts

General Procedure

A 0.5 mL, 0.01 M solution of C5-BTPhen (**7a**, 5 µmol) in CD_3CN was made up in an NMR tube. A 0.01 M solution of $Ln(NO_3)_3.xH_2O$ was added in 25-50 µL aliquots (0.25-0.5 µmol per aliquot) and the ^1H NMR spectrum was recorded after each addition.

C5-BTPhen: δ_H (CD_3CN) = 0.94 (t, *J* = 6.9 Hz, 6H), 0.95 (t, *J* = 6.9 Hz , 6H) 1.46 (m, 16H), 1.96 (quint, *J* = 4.9 Hz, 8H), 3.00 (t, *J* = 7.3 Hz, 4H), 3.10 (t, *J* = 7.3 Hz, 4H), 8.09 (s, 2H), 8.62 (d, *J* = 8.4 Hz), 8.81 (d, *J* = 8.4 Hz, 2H) ppm.

$La(C5\text{-}BTPhen)_2(NO_3)_x$: δ_H (CD_3CN) = 0.62 (quint, *J* = 7.4 Hz, 4H), 0.70 (t, *J* = 7.2 Hz, 6H), 0.80 (quint, *J* = 7.4 Hz, 4H), 0.89 (t, *J* = 7.2 Hz, 6H), 0.93 (quint, *J* = 7.4 Hz, 4H), 1.33 (m, 8H), 1.76 (quint, *J* = 7.4 Hz, 4H), 2.39 (t, *J* = 7.3 Hz, 4H), 2.74 (t, *J* = 7.3 Hz, 4H), 8.49 (s, 2H), 9.04 (d, *J* = 8.4 Hz, 2H), 9.11 (d, *J* = 8.4 Hz, 2H) ppm.

$Ln(C5\text{-}BTPhen)_2(NO_3)_x$: δ_H (CD_3CN) = 0.52 (quint, *J* = 7.4 Hz, 4H), 0.79 (t, *J* = 7.2 Hz, 6H), 0.80-0.87 (m, 10H), 1.06 (quint, *J* = 7.4 Hz, 4H), 1.30 (m, 8H), 1.69 (quint, *J* = 7.4 Hz, 4H), 2.28 (t, *J* = 7.3 Hz, 4H), 2.72 (t, *J* = 7.3 Hz, 4H), 8.55 (s, 2H), 8.96 (d, *J* = 8.4 Hz, 2H), 9.15 (d, *J* = 8.4 Hz, 2H) ppm.

3.0 Solvent Extraction Properties

General Procedure

500 µL of solutions of BTPhen (10 mmol/L) in 1-octanol and 500 µL of solutions of $^{241}Am(III)$ + $^{152}Eu(III)$ (1 kBq/mL each) in nitric acid of varied concentrations were shaken for 90 minutes on an orbital shaker at 2500/min in 2 mL glass screw-cap vials at *T*= 20 °C. Phases were separated by centrifugation, and 300 µL of each organic and aqueous phase were taken for analysis on a gamma counter (Packard Cobra Auto Gamma 5003).

Distribution ratios D_M were determined from the gamma count rates of both samples,

$D_M = [M]_{org} / [M]_{aq} = (cpm_{org} * V_{aq}) / (cpm_{aq} * V_{org})$

The separation factor is

$SF_{Am/Eu} = D_{Am} / D_{Eu}$

Extraction of Am(III) and Eu(III) into octanol

Table 1. Extraction of Am(III) and Eu(III) into octanol by C5-BTPhen **7a** (0.01 M) as a function of nitric acid concentration

$[HNO_3]$ Initial (mol/L)	D_{Am}	D_{Eu}	$SF_{Am/Eu}$
0.1	66	0.851	77.6
0.2	72.7	1.11	65.8
0.5	69.4	0.914	75.9
0.7	70.7	1.12	63
1	68.4	1.01	67.6
1.5	127	0.831	153
2	115	0.728	158
3	121	0.656	184
4	101	0.567	178

Table 2. Extraction of Am(III) and Eu(III) into octanol by BrC5-BTPhen **7b** (0.01 M) as a function of nitric acid concentration

$[HNO_3]$ Initial (mol/L)	D_{Am}	D_{Eu}	$SF_{Am/Eu}$
0.1	25.1	0.134	187
0.2	63.4	0.257	247
0.5	102	0.479	212
0.7	98.7	0.537	184
1	99.6	0.551	181
1.5	104	0.520	199
2	93.6	0.526	178
3	96.9	0.466	208
4	108	0.434	250

Table 3. Extraction of Am(III) and Eu(III) into octanol by Br_2C5-BTPhen **7c** (0.01 M) as a function of nitric acid concentration

$[HNO_3]$ Initial (mol/L)	D_{Am}	D_{Eu}	$SF_{Am/Eu}$
0.1	1.01	0.00892	114
0.2	8.52	0.0488	175
0.5	9.76	0.0926	105
0.7	23.5	0.131	179
1	57.4	0.143	401
1.5	87.5	0.152	574
2	75.2	0.144	522
3	86.7	0.131	660
4	99.1	0.130	763