ELECTRONIC SUPPLEMENTARY INFORMATION

for the paper entitled

Exploring Electronic Effects on the Partitioning of Actinides(III) from Lanthanides(III) using Functionalised Bis-triazinyl Phenanthroline Ligands

Alyn C. Edwards,† Christoph Wagner,‡,ℓ Laurence M. Harwood,§ Andreas Geist,‡ Neil A. Burton, † Clint A. Sharrad,∆ Ralph W. Adams,† Robin G. Pritchard,† Petra J. Panak,‡,ℓ and Roger C. Whitehead†*

† School of Chemistry, The University of Manchester, Oxford Road, Manchester, M13 9PL, U.K.

‡ Karlsruher Institut für Technologie (KIT-INE), Institut für Nukleare Entsorgung, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany.

ℓ University of Heidelberg, Department of Physical Chemistry, Im Neuenheimer Feld 253, 69120, Germany.

∆ School of Chemical Engineering, The University of Manchester, Oxford Road, Manchester, M13 9PL, U.K.

§ Department of Chemistry, The University of Reading, Reading, RG6 6AD, U.K.

CONTENTS

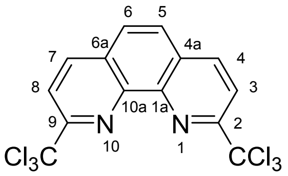
1. Experimental Procedures and Characterization Data

1.1 General Procedures

Flash silica chromatography was performed using technical grade silica gel (pore size: 60 Å 230-240, mesh 40-63 μm). Mass spectra were obtained using: a Waters QTOF (ES), a Waters SQD2 (APCI), a Shimadzu Axima Confidence (MALDI) or a Thermo Finnigan MAT95XP (HRMS) apparatus. Reported mass values fall within ± 10 ppm mass units for electrospray and high resolution mass spectrometry (HRMS). Infrared spectra were recorded on a Thermo Scientific Nicolet iS5 spectrometer. Absorption maxima (ν_{max}) are recorded in wavenumbers (cm^{-1}) with use of the following abbreviations: w, weak; m, medium; s, strong; br, broad. Melting points were recorded on a Sanyo Gallenkamp MPD350 apparatus and readings are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded with B400 Bruker Avance III or B500 Bruker Avance II+ spectrometers. NMR assignments were supported by 2D, ^{1}H-^{1}H COSY and ^{13}C-^{1}H HMQC experiments. Chemical shifts (δ_H) are quoted in parts per million (ppm) to the nearest 0.01 ppm, calibrated to the relevant residual solvent peaks. Coupling constants are reported in Hz. Signal multiplicity is described with the use of the abbreviations: [s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad]. X-Ray crystallography was performed at the University of Manchester by Dr R. Pritchard. All reagents were purchased from Alfa-Aesar, Sigma-Aldrich or Fisher Scientific and used as received.

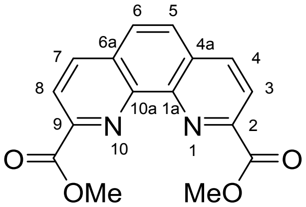
1.1 Synthesis of CyMe$_4$-BTPhen (3)

2,9-bis(trichloromethyl)-1,10-phenanthroline (12)



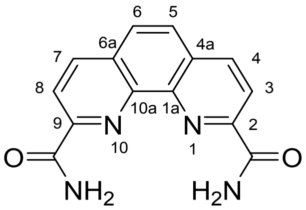
A stirred solution of **11** (2.00 g, 9.60 mmol), *N*-chlorosuccinimide (9.30 g, 69.14 mmol) and benzoyl peroxide (10.00 mg, 0.04 mmol) in $CHCl_3$ (100 mL) was heated at reflux for 72 h. The reaction mixture was washed with a 1M solution of NaOH (5 x 90 mL) followed by a sat. aqueous solution of K_2CO_3 (2 x 90 mL), dried over $MgSO_4$ and concentrated *in vacuo* to afford **15** as a yellow crystalline solid (3.90 g, 99 %). m.p. 210-212 °C [Lit.[1] m.p. 212-214 °C]; ν_{max} / cm^{-1} 1582w (C=C), 1492w (C=C); δ_H (400 MHz; $CDCl_3$) 8.47 (2H, d, *J* 8.5, C(4)$\underline{H}$ and C(7)$\underline{H}$), 8.34 (2H, d, *J* 8.5, C(3)$\underline{H}$ and C(8)$\underline{H}$), 7.99 (2H, s, C(5)$\underline{H}$ and C(6)$\underline{H}$); δ_C (100 MHz; $CDCl_3$) 158.0 ($\underline{C}Cl_3$), 143.2 (Ar-$\underline{C}$), 138.2 ($\underline{C}$(4)H and $\underline{C}$(7)H), 129.2 (Ar-$\underline{C}$), 127.6 ($\underline{C}$(5)H and $\underline{C}$(6)H), 120.6 ($\underline{C}$(3)H and $\underline{C}$(8)H); *m/z* (+ES) 413 ([M{$^{35}Cl_6$}+H]$^+$, 85 %), 415 ([M{$^{35}Cl_5{}^{37}Cl$}+H]$^+$, 100 %), 417 ([M{$^{35}Cl_4{}^{37}Cl_2$}+H]$^+$, 89 %), 419 ([M{$^{35}Cl_3{}^{37}Cl_3$}+H]$^+$, 52 %).

Dimethyl 1,10-phenanthroline-2,9-dicarboxylate (16)



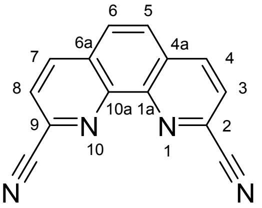
A stirred suspension of **12** (2.00 g, 0.49 mmol) in H_2SO_4 (95 %, 2.0 mL) was heated at 95^{0}C for 4 h. The resulting solution was cooled to ambient temperature and CH_3OH (2.2 mL) added dropwise. The mixture was heated at reflux for 1.5 h, allowed to cool and neutralized through the addition of a sat. solution of $NaHCO_3$ (30 mL). The precipitate was filtered, washed with H_2O (3 x 30 mL) and Et_2O (3 x 50 mL) and dried *in vacuo* to yield **16** (1.42 g, 98 %) as a light tan solid. m.p. 208-211 °C [Lit.[1] m.p. 190-200 °C]; ν_{max} / cm^{-1} 1723s (ester, C=O), 1445m (C=C); δ_H (400 MHz; DMSO) 8.74 (2H, d, *J* 8.4, C(4)$\underline{H}$ and C(7)$\underline{H}$), 8.42 (2H, d, *J* 8.4, C(3)$\underline{H}$ and C(8)$\underline{H}$), 8.22 (2H, s, C(5)$\underline{H}$ and C(6)$\underline{H}$); δ_C (100 MHz; DMSO) 165.6 ($\underline{C}$=O), 147.7 (Ar-$\underline{C}$), 145.1 (Ar-$\underline{C}$), 138.2 ($\underline{C}$(4)H and $\underline{C}$(7)H), 130.7 (Ar-$\underline{C}$), 128.7 ($\underline{C}$(5)H and $\underline{C}$(6)H), 123.9 ($\underline{C}$(3)H and $\underline{C}$(8)H), 52.9 (O$\underline{C}H_3$); *m/z* (+ES) 297 ($[M+H]^+$, 100 %), 319 ($[M+Na]^+$, 30 %).

1,10-phenanthroline-2,9-dicarboxamide (20)



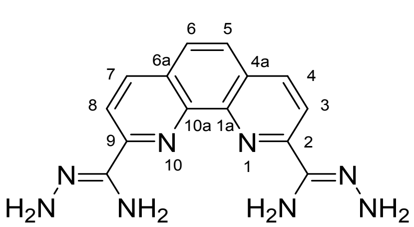
A suspension of bis-ester **16** (0.80 g, 2.7 mmol) and NH_4Cl (0.060 g) in concentrated NH_4OH (22 mL) was stirred at ambient temperature for 72 h. The precipitate was filtered, washed with H_2O (40 mL) and Et_2O (60 mL) and dried *in vacuo* to yield amide **20** (0.55 g, 76 %) as a pale yellow solid. m.p. >300 °C [Lit.[2] m.p. >300 °C]; ν_{max} / cm^{-1} 3141br (N-H), 3283br (N-H), 1692s (C=O), 1518m (C=C); δ_H (500 MHz; DMSO-d_6) 8.96 (2H, br s, N$\underline{H_2}$), 8.70 (2H, d, *J* 8.4, C(4)$\underline{H}$ and C(7)$\underline{H}$), 8.45 (2H, d, *J* 8.4, C(3)$\underline{H}$ and C(8)$\underline{H}$), 8.16 (2H, s, C(5)$\underline{H}$ and C(6)$\underline{H}$), 7.86 (2H, br s, N$\underline{H_2}$); δ_C (125 MHz; DMSO-d_6) 166.2 (C=O), 150.1 (Ar-$\underline{C}$), 144.0 (Ar-$\underline{C}$), 138.1 ($\underline{C}$(4)H and $\underline{C}$(7)H), 130.3 (Ar-$\underline{C}$), 128.0 ($\underline{C}$(5)H and $\underline{C}$(6)H), 121.2 ($\underline{C}$(3)H and $\underline{C}$(8)H); *m/z* (+ES) 289 ($[M+Na]^+$, 52 %).

1,10-phenanthroline-2,9-dicarbonitrile (24)



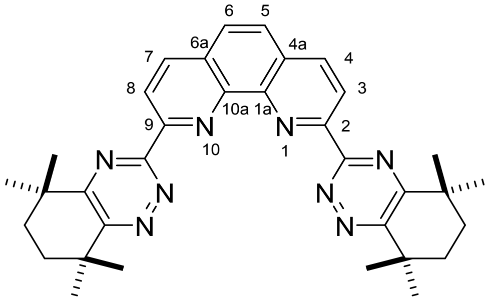
To DMF (16 mL) under a N_2 atmosphere was added oxalyl chloride (0.50 mL, 0.74 g, 5.83 mmol) at 0 ^{0}C with stirring. A white precipitate formed immediately which was accompanied by gas evolution. Once the evolution of gas had stopped, a suspension of amide **20** (0.55 g, 2.06 mmol) in DMF (12 mL) was added. The resulting tan mixture was left to stir for 6 h at 0 ^{0}C. Pyridine (0.75 mL, 0.74 g, 9.27 mmol) was added and the mixture left to stir for a further 30 min before being neutralised with a sat. solution of aqueous K_2CO_3 (20 mL), forming a precipitate. Precipitation was further encouraged through the addition of H_2O (30 mL). The precipitate was filtered, washed with H_2O (3 x 20 mL) and Et_2O (3 x 20 mL). The tan solid was dried *in vacuo* over silica to yield **24** as a tan powder (0.25 g, 54 %). m.p. >300 °C [Lit.[2] m.p. >300 °C]; ν_{max} / cm^{-1} 3079w (C-H), 3056w (C-H), 2237m (C≡N), 1616m (C=C), 1492m (C=C); δ_H (500 MHz; DMSO-d$_6$) 8.85 (2H, d, *J* 8.2, C(3)$\underline{H}$ and C(8)$\underline{H}$), 8.43 (2H, d, *J* 8.2, C(4)$\underline{H}$ and C(7)$\underline{H}$), 8.28 (2H, s, C(5)$\underline{H}$ and C(6)$\underline{H}$); δ_C (125 MHz; DMSO-d$_6$) 144.7 (Ar-$\underline{C}$), 138.2 ($\underline{C}$(4)H and $\underline{C}$(7)H), 132.7 (Ar-$\underline{C}$), 130.2 (Ar-$\underline{C}$), 128.7 ($\underline{C}$(5)H and $\underline{C}$(6)H), 127.0 ($\underline{C}$(3)H and $\underline{C}$(8)H), 117.1 ($\underline{C}$≡N); *m/z* (+APCI) 231 ([M+H]$^+$, 65 %).

(2Z,9Z)-1,10-phenanthroline-2,9-bis(carbohydrazonamide) (28)



A suspension of **24** (0.25 g, 1.09 mmol) in EtOH (11 mL) was treated with hydrazine hydrate (8 mL, 50-60 %). The suspension was left to stir for 72 h at ambient temperature. H_2O (20 mL) was then added and the resulting precipitate was filtered and washed with H_2O (2 x 15 mL) and Et_2O (2 x 30 mL). The precipitate was dried *in vacuo* to yield compound **28** as a yellow powder (0.25 g, 78 %). m.p. >300 °C [Lit.[3] m.p. >300 °C]; ν_{max} / cm^{-1} 3391br (N-H), 3310br (N-H), 1641m (N-H), 1494m (C=C); δ_H (400 MHz; DMSO-d_6) 8.38 (2H, d, *J* 8.6, C(4)$\underline{H}$ and C(7)$\underline{H}$), 8.28 (2H, d, *J* 8.6, C(3)$\underline{H}$ and C(8)$\underline{H}$), 7.95 (2H, s, C(5)$\underline{H}$ and C(6)$\underline{H}$), 6.13 (4H, br s, 2 x $N\underline{H}_2$), 5.62 (4H, br s, 2 x NH_2); δ_C (125 MHz; DMSO) 151.3 ($\underline{C}$=NNH_2), 143.5 (Ar-$\underline{C}$), 143.3 (Ar-$\underline{C}$), 136.1 ($\underline{C}$(3)H and $\underline{C}$(8)H), 128.2 (Ar-$\underline{C}$), 126.1 ($\underline{C}$(5)H and $\underline{C}$(6)H), 119.0 ($\underline{C}$(4)H and $\underline{C}$(7)H); *m/z* (+ES) 295 ($[M+H]^+$, 100 %), 317 ($[M+Na]^+$, 53 %).

2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[e][1,2,4]triazin-3-yl)-1,10-phenanthroline (3)

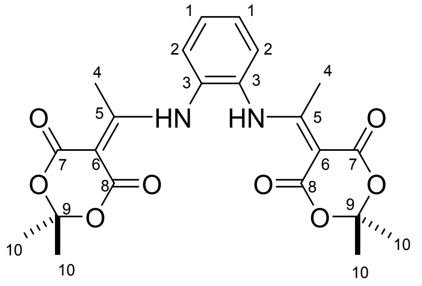


A stirred suspension of **28**(0.15 g, 0.51 mmol) and 3,3,6,6-tetramethylcyclohexane-1,2-dione (0.19 g, 1.11 mmol) in EtOH (6.5 mL) was heated at reflux for 72 h. After this time, the yellow suspension was allowed to cool to ambient temperature and taken to dryness *in vacuo*. The resulting yellow solid was triturated with cold Et_2O (3 x 10 mL) and MeOH (3 x 10 mL) to give **3** (0.18 g, 63 %) as a bright yellow solid. m.p. 246-247 °C [Lit.[3] m.p. 244-246 °C]; ν_{max} / cm^{-1} 3335br, 2956m, 2931m, 2862m, 1645m, 1620m, 1509m; δ_H (400 MHz; $CDCl_3$) 8.91 (2H, d, *J* 8.3, C(3)$\underline{H}$ and C(8)$\underline{H}$), 8.49 (2H, d, *J* 8.3, C(4)$\underline{H}$ and C(7)$\underline{H}$), 7.96 (2H, s, C(5)$\underline{H}$ and C(6)$\underline{H}$), 1.90 (8H, s, 4 x $C\underline{H}_2$), 1.59 (12H, s, 4 x $C\underline{H}_3$), 1.55 (12H, s, 4 x $C\underline{H}_3$; δ_C

(100 MHz; $CDCl_3$) 165.5 (Ar-C), 163.6 (Ar-C), 161.7 (Ar-C), 154.1 (Ar-C), 146.7 (Ar-C), 137.7 (C(4)H and C(7)H), 130.1 (Ar-C), 127.9 (C(5)H and C(6)H), 123.8 (C(3)H and C(8)H), 37.8 (quat C), 36.9 (quat C), 34.0 (CH_2), 30.1 (CH_3), 29.6 (CH_3); *m/z* (+ES) 559 ($[M+H]^+$, 100 %).

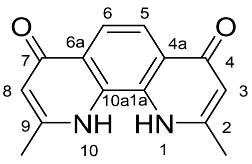
1.2 Synthesis of 4,7-dichloro-CyMe$_4$-BTPhen (33)

5,5'-((1,2-phenylenebis(azanediyl))bis(ethan-1-yl-1-ylidene))bis(2,2-dimethyl-1,3-dioxane-4,6-dione) (7a)



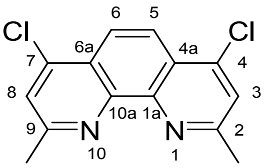
A stirred solution of trimethyl orthoacetate (500 mL, 472.00g, 3.93 mol) and Meldrum's acid (20.00 g, 138.76 mmol) was heated at a gentle reflux for 15 min. The resulting yellow solution was cooled to 40 ^{0}C and *o*-phenylenediamine (6.90 g, 63.81 mmol) added portionwise. The resulting suspension was heated at reflux for 2 h and then left to stir at ambient temperature for 17 h. The white precipitate was collected by filtration, washed with ice-cold Et_2O (4 x 100 mL) and dried *in vacuo* to yield the desired compound as a flaky white solid (18.40 g, 65 %). M.p. 189-190 °C [Lit.[4] m.p. 187-188 °C]; ν_{max} / cm^{-1} 2990w, 2943w, 1711s, 1667s, 1605s, 1542m, 1500m; δ_H (400 MHz; $CDCl_3$) 12.81 (2H, s, 2 x NH), 7.52 (2H, dd, *J* 5.8, 3.6, 2 x Ar-H), 7.37 (2H, dd, *J* 5.8, 3.6, 2 x Ar-H), 2.55 (6H, s, 2 x CH_3), 1.73 (12H, s, 4 x CH_3); δ_C (100 MHz; $CDCl_3$) 173.1 (C(5), C(7) or C(8)), 167.6 (C(5), C(7) or C(8)), 162.5 (C(5), C(7) or C(8)), 132.4 (C(3)), 129.3 (C(2)H or C(1)H), 128.0 (C(2)H or C(1)H), 103.3 (C(9), acetal), 87.4 (C(6)), 26.6 (C(10)H_3), 19.6 (C(4)H_3); *m/z* (-ES) 443 ($[M-H]^-$, 50 %).

2,9-dimethyl-1,10-dihydro-1,10-phenanthroline-4,7-dione (7b)



Diphenyl ether (500 mL) at 240 °C was treated portion wise with solid **7a** (16.50 g, 37.16 mmol) giving rise to vigorous gas evolution. The resulting orange solution was heated at reflux for 40 min, cooled to 70 °C and filtered. The brown precipitate was washed with acetone (2 x 90 mL), hexane (2 x 90 mL) and Et_2O (2 x 90 mL) to yield the desired **7b** as a light-brown powder (8.46 g, 95 %). M.p. >300 °C [Lit.[4] m.p. >300 °C]; ν_{max} / cm^{-1} 3362w, 3963m, 1680m, 1596s; δ_H (400 MHz; NaOD in D_2O) 7.32 (2H, s, C(5)$\underline{H}$ and C(6)$\underline{H}$), 5.98 (2H, s, C(3)$\underline{H}$ and C(8)$\underline{H}$), 1.94 (6H, s, 2 x C$\underline{H}_3$); δ_C (125 MHz; NaOD in D_2O) 172.1 ($\underline{C}$(2) and $\underline{C}$(9)), 159.2 ($\underline{C}$(1a) and $\underline{C}$(10a)), 145.7 ($\underline{C}$(4) and $\underline{C}$(7)), 122.9 ($\underline{C}$(4a) and $\underline{C}$(6a)), 116.6 ($\underline{C}$(3)H and $\underline{C}$(8)H), 109.4 ($\underline{C}$(5)H and $\underline{C}$(6)H), 23.9 ($\underline{C}H_3$); *m/z* (MALDI-α-CHCA) 241 ($[M+H]^+$, 100 %).

4,7-dichloro-2,9-dimethyl-1,10-phenanthroline (8)

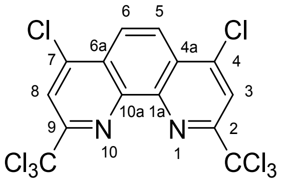


Warning: Extreme caution must be taken whilst quenching phosphorus oxychloride.

A stirred solution of 2,9-dimethyl-1,10-dihydro-1,10-phenanthroline-4,7-dione (**7b)** (0.80 g, 2.89 mmol) in phosphorus oxychloride (23.4 mL, 38.49 g, 0.25 mol) under an atmosphere of N_2 was heated at 90°C for 3.5 h. The hot solution was carefully added to a vigorously stirred mixed of H_2O (28 mL) and ice (66 g) and left to stir for 15 min. $CHCl_3$ (20 mL) was added and the resulting two phase mixture was adjusted to pH 14 through the addition of aqueous

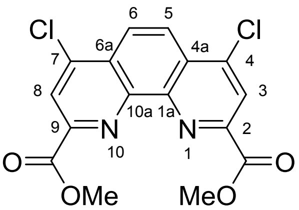
NaOH (42.5 wt %, 43 mL). The organic layer was isolated and the aqueous phase washed a further four times with $CHCl_3$ (4 x 20 mL). The combined organic extracts were washed with NaOH (42.5 wt %, 20 mL), dried over $MgSO_4$ and concentrated *in vacuo* to afford **8** as a tan powder (0.76 g, 98 %). M.p. 198-200 °C [Lit.[4] m.p. 202 °C]; ν_{max} / cm^{-1} 2963w, 1637w, 1572m; δ_H (400 MHz; $CDCl_3$) 8.28 (2H, s, Ar-H), 7.66 (2H, s, Ar-H), 2.97 (6H, s, 2 x CH_3); δ_C (100 MHz; $CDCl_3$) 159.9 (C(4) and (C(7)), 146.0 (C(2) and C(9), C(4a) and C(6a) or C(1a) and C(10a)), 142.8 (C(2) and C(9), C(4a) and C(6a) or C(1a) and C(10a)), 125.0 (C(2) and C(9), C(4a) and C(6a) or C(1a) and C(10a)), 124.2 (C(3)H and C(8)H) or (C(5)H and C(6)H), 122.2 (C(3)H and C(8)H) or (C(5)H and C(6)H), 25.8 (2 x CH_3); *m/z* (+ES) 277 ([M{$^{35}Cl_2$}+H]$^+$, 100 %), 279 ([M{$^{35}Cl^{37}Cl$}+H]$^+$, 63 %), 281 ([M{$^{37}Cl_2$}+H]$^+$, 11 %).

4,7-dichloro-2,9-bis(trichloromethyl)-1,10-phenanthroline (13)



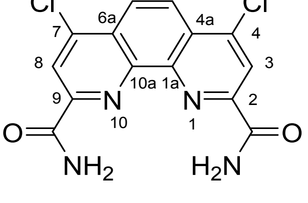
Compound **13** (6.30 g, 93 %) was prepared using the procedure described for compound **12**. M.p. 174-176 °C [Lit.[4] m.p. 174-175 °C]; ν_{max} / cm^{-1} 1607m, 1568m, 1471m; δ_H (400 MHz; $CDCl_3$) 8.49 (2H, s, C(3)H and C(8)H or C(5)H and C(6)H), 8.43 (2H, s, C(3)H and C(8)H or C(5)H and C(6)H); δ_C (100 MHz; $CDCl_3$) 158.3 (CCl_3), 144.6 (C(5)H and C(6)H or C(3)H and C(8)H), 144.1 (C(5)H and C(6)H or C(3)H and C(8)H), 127.5 (Ar-C), 124.5 (Ar-C), 121.2 (Ar-C), 97.1 (Ar-C); *m/z* (+ES) 503 ([M{$^{35}Cl_8$}+Na]$^+$, 33 %), 505 ([M{$^{35}Cl_7{}^{37}Cl$} + Na]$^+$, 100 %), 507 ([M{$^{35}Cl_6{}^{37}Cl_2$}+Na]$^+$, 100 %), 509 ([M{$^{35}Cl_5{}^{37}Cl_3$}+Na]$^+$, 52 %).

Dimethyl 4,7-dichloro-1,10-phenanthroline-2,9-dicarboxylate (17)



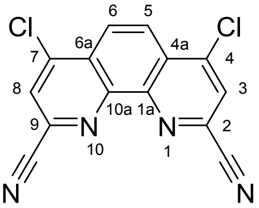
A stirred suspension of **13** (0.50 g, 1.04 mmol) in H_2SO_4 (95 %, 0.62 mL) was heated at 95 °C for 2 h. The resulting solution was cooled to ambient temperature and MeOH (0.55 mL) added dropwise. The mixture was heated at reflux for 1 h, allowed to cool and neutralized through the addition of a sat. solution of $NaHCO_3$ (15 mL). The precipitate was collected by filtration, washed with H_2O (3 x 15 mL) and Et_2O (3 x 15 mL) and dried *in vacuo* to yield **17** (0.25 g, 66 %) as a light grey solid. M.p. 298-302 °C (decomposed); ν_{max} / cm^{-1} 1719s, 1531m; δ_H (400 MHz; CD_2Cl_2) 8.56 (2H, s, C(3)$\underline{H}$ and C(8)$\underline{H}$ or C(5)$\underline{H}$ and C(6)$\underline{H}$), 8.50 (2H, s, C(3)$\underline{H}$ and C(8)$\underline{H}$ or C(5)$\underline{H}$ and C(6)$\underline{H}$), 4.12 (6H, s, 2 x OC$\underline{H}_3$); δ_C (100 MHz; CD_2Cl_2) 165.4 ($\underline{C}$=O), 149.0 (Ar-$\underline{C}$), 147.0 (Ar-$\underline{C}$), 144.9 (Ar-$\underline{C}$), 129.4 (Ar-$\underline{C}$), 125.6 ($\underline{C}$(5)H and $\underline{C}$(6)H or $\underline{C}$(3)H and $\underline{C}$(8)H), 125.2 ($\underline{C}$(5)H and $\underline{C}$(6)H or $\underline{C}$(3)H and $\underline{C}$(8)H), 53.5 (O$\underline{C}H_3$); *m/z* (+ES) 387 ([M{$^{35}Cl_2$}+Na]$^+$, 100 %), 389 ([M{$^{35}Cl^{37}Cl$}+Na]$^+$, 70 %), 391 ([M{$^{37}Cl_2$} + Na]$^+$ 15 %); HRMS (+ES) calculated for $C_{16}H_{10}O_4N_2{}^{35}Cl_2Na$ ([M+Na]$^+$): 386.9910, found: 386.9914.

4,7-dichloro-1,10-phenanthroline-2,9-dicarboxamide (21)



A suspension of bis-ester **17** (6.00 g, 16.50 mmol) and NH_4Cl (0.42 g) in concentrated NH_4OH (133.8 mL) was stirred at ambient temperature for 48 h. The resulting precipitate was collected by filtration, washed with H_2O (200 mL) and Et_2O (200 mL) and dried *in vacuo* to yield bis-amide **21** (4.70 g, 85 %) as a light brown solid. M.p. 315-318 °C (decomposed); ν_{max} / cm^{-1} 3152br, 1680s, 1533m; δ_H (500 MHz; DMSO-d_6) 8.95 (2H, br s, N$\underline{H}_2$), 8.56 (2H, s, C(3)$\underline{H}$ and C(8)$\underline{H}$ or C(5)$\underline{H}$ and C(6)$\underline{H}$), 8.53 (2H, s, C(3)$\underline{H}$ and C(8)$\underline{H}$ or C(5)$\underline{H}$ and C(6)$\underline{H}$), 7.98 (2H, br s, N$\underline{H}_2$); δ_C (125 MHz; DMSO-d_6) 165.7 ($\underline{C}$ONH$_2$), 150.8 (Ar-$\underline{C}$), 145.0 (Ar-$\underline{C}$), 143.2 (Ar-$\underline{C}$), 127.6 (Ar-$\underline{C}$), 124.5 ($\underline{C}$(5)H and $\underline{C}$(6)H or $\underline{C}$(3)H and $\underline{C}$(8)H), 121.7 ($\underline{C}$(5)H and $\underline{C}$(6)H or $\underline{C}$(3)H and $\underline{C}$(8)H); *m/z* (MALDI-dithranol) 357 ([M{$^{35}Cl_2$} + Na]$^+$, 100 %), 359 ([M{$^{35}Cl^{37}Cl$} + Na]$^+$, 65 %), 361 ([M{$^{37}Cl_2$}+Na]$^+$, 13 %); HRMS (+ES) calculated for $C_{14}H_9O_2N_4{}^{35}Cl_2Na$ ([M+H]$^+$): 335.0103, found: 335.0131.

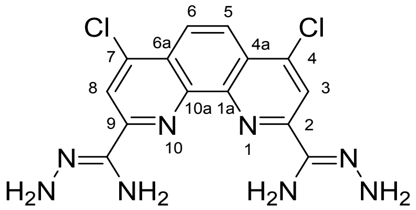
4,7-dichloro-1,10-phenanthroline-2,9-dicarbonitrile (25)



To DMF (96.0 mL) under an N_2 atmosphere was added oxalyl chloride (2.6 mL, 3.84 g, 30.00 mmol) at 0 °C with stirring. A white precipitate formed immediately which was accompanied by gas evolution. Once gas evolution of gas had ceased, a suspension of bis-amide **21** (4.00 g, 12.00 mmol) in DMF (68.8 mL) was added. The resulting tan mixture was left to stir for 6 h at 0 ^{0}C. Pyridine (4.3 mL, 4.24 g, 35.68 mmol) was added and the mixture left to stir for a further 30 min before being neutralised with a sat. solution of aqueous K_2CO_3 (240 mL), forming a precipitate. Precipitation was further encouraged through the addition of H_2O (300 mL). The precipitate was collected by filtration, washed with H_2O (3 x 60 mL) and Et_2O (3 x 250 mL). The solid was dried *in vacuo* over silica to yield **25** as a fine tan powder (2.5 g, 72 %). M.p. 280-284 °C (decomposed); ν_{max} / cm^{-1} 3079m, 3038m, 2237m, 1608s, 1560s, 1528s, 1467s; δ_H (500 MHz; DMSO-d_6) 8.81 (2H, s, C(3)$\underline{H}$ and C(8)$\underline{H}$ or C(5)$\underline{H}$ and

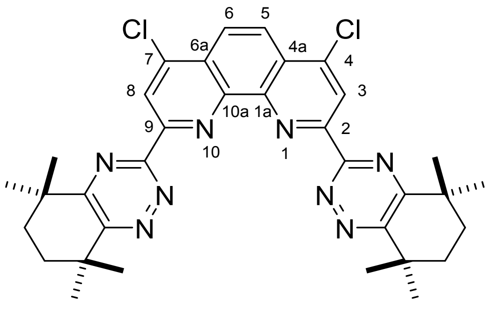
C(6)H), 8.58 (2H, s, C(3)H and C(8)H or C(5)H and C(6)H); δ_C (125 MHz; DMSO-d_6) 145.5 (Ar-C), 143.6 (Ar-C), 133.4 (Ar-C), 128.4 (Ar-C), 128.0 (C(5)H and C(6)H or C(3)H and C(8)H), 125.8 (C(5)H and C(6)H or C(3)H and C(8)H), 116.5 (C≡N); *m/z* (+ES) 299 ([M+H]$^+$, 8 %); HRMS (+ES) calculated for $C_{14}H_5N_4{}^{35}Cl_2$ ([M+H]$^+$): 298.9890, found: 298.9886.

(2*Z*,9*Z*)-4,7-dichloro-1,10-phenanthroline-2,9-bis(carbohydrazonamide) (29)



A suspension of **25** (0.30 g, 1.00 mmol) in EtOH (7.5 mL) was treated with hydrazine hydrate (7.5 mL, 50-60 %). The suspension was left to stir for 72 h at ambient temperature. H_2O (20 mL) was then added and the resulting precipitate was collected by filtration and washed with H_2O (2 x 10 mL) and Et_2O (2 x 50 mL). The precipitate was dried *in vacuo* to yield compound **29** as an orange solid (0.30 g, 84 %). M.p. 222-225 °C (decomposed); ν_{max} / cm^{-1} 3393br, 3304br, 1605m, 1567m, 1525m; δ_H (500 MHz; DMSO-d_6) 8.39 (2H, s, C(3)H and C(8)H or C(5)H and C(6)H), 8.30 (2H, s, C(3)H and C(8)H or C(5)H and C(6)H), 6.12 (4H, br s, 2 x NH$_2$), 5.84 (4H, br s, 2 x NH$_2$); δ_C (125 MHz; DMSO) 152.0 (C=NNH$_2$), 144.6 (Ar-C), 142.0 (Ar-C), 140.8 (Ar-C), 125.6 (Ar-C), 122.4 (C(5)H and C(6)H or C(3)H and C(8)H), 119.4 (C(5)H and C(6)H or C(3)H and C(8)H); *m/z* (+ES) 363 ([M{$^{35}Cl_2$}+H]$^+$, 100 %), 365 ([M{$^{35}Cl^{37}Cl$}+H]$^+$, 78 %), 367 ([M{$^{37}Cl_2$}+H]$^+$, 78 %); HRMS (+ES) calculated for $C_{14}H_{12}N_8{}^{35}Cl_2Na$ ([M+Na]$^+$): 385.0445, found: 385.0454.

4,7-dichloro-2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[e][1,2,4]triazin-3-yl)-1,10-phenanthroline (33)



Method 1:

A stirred suspension of **29** (0.50 g, 1.38 mmol) and 3,3,6,6-tetramethylcyclohexane-1,2-dione (**32**) (0.51 g, 3.04 mmol) in THF (27 mL) was treated with Et$_3$N (2.3 mL, 16.25 mmol). The resulting suspension was heated at reflux for 3.5 d. The suspension was allowed to cool to ambient temperature and taken to dryness *in vacuo* to yield the crude product as an orange solid. This material was purified by flash silica chromatography, eluting with a DCM: MeOH (0-5 vol%) gradient, to give **33** as a yellow solid (0.005 g, 0.6 %).

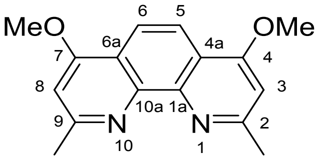
Method 2:

A stirred suspension of **29** (0.50 g, 1.38 mmol) and 3,3,6,6-tetramethylcyclohexane-1,2-dione (**32**) (0.51 g, 3.04 mmol) in EtOH (9.8 mL) was heated at reflux for 20 h. The resulting suspension was allowed to cool to ambient temperature and taken to dryness *in vacuo*. The dark brown solid was triturated with cold hexane (3 x 250 mL). The yellow hexane solution was then taken to dryness and the residue washed with EtOH (1 x 50 mL), to give **33** (0.10 g, 11 %) as a yellow powder. M.p. 190-193 °C; ν_{max} / cm^{-1} 3544w, 3480w, 2958m, 1644m, 1514s, 1480w; δ_H (500 MHz; CDCl$_3$) 8.97 (2H, s, C(3)$\underline{H}$ and C(8)$\underline{H}$ or C(5)$\underline{H}$ and C(6)$\underline{H}$), 8.50 (2H, s, C(3)$\underline{H}$ and C(8)$\underline{H}$ or C(5)$\underline{H}$ and C(6)$\underline{H}$), 1.91 (8H, s, 4 x C$\underline{H}_2$), 1.56 (12H, s, 4 x C$\underline{H}_3$), 1.55 (12H, s, 4 x C$\underline{H}_3$); δ_C (125 MHz; CDCl$_3$) 165.1 (Ar-$\underline{C}$), 163.6 (Ar-$\underline{C}$), 160.5 (Ar-$\underline{C}$), 154.3 (Ar-$\underline{C}$), 147.3 (Ar-$\underline{C}$), 143.9 (Ar-$\underline{C}$), 127.7 (Ar-$\underline{C}$), 124.2 ($\underline{C}$(5)H and $\underline{C}$(6)H or

C(3)H and C(8)H), 124.0 (C(5)H and C(6)H or C(3)H and C(8)H), 37.5 (quat C), 36.7 (quat C), 33.5 (CH_2), 29.8 (CH_3), 29.3 (CH_3); *m/z* (+ES) 649 ([M{$^{35}Cl_2$} + Na]$^+$, 100 %), 651 ([M{$^{35}Cl^{37}Cl$}+Na]$^+$, 60 %), 653 ([M{$^{37}Cl_2$}+ Na]$^+$, 9 %); HRMS (+ES) calculated for $C_{34}H_{37}N_8{}^{35}Cl_2Na$ ([M+Na]$^+$): 627.2524, found: 627.2518.

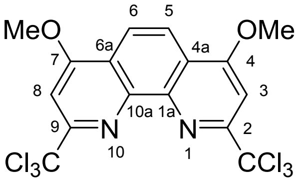
1.3 Synthesis of 4,7-dimethoxy-CyMe$_4$-BTPhen (34)

4,7-dimethoxy-2,9-dimethyl-1,10-phenanthroline (9)



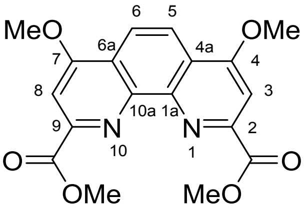
Anhydrous MeOH (60 mL) was purged with N_2 for 15 minutes before being treated with small aliquots of sodium metal (0.46 g, 20 mmol). The resulting suspension was left to stir at ambient temperature until complete dissolution was achieved. Compound **8** (1.00 g, 3.62 mmol) was added and the resulting suspension was heated under reflux for 72 h. Concentration of the yellow solution *in vacuo* to ~10 mL, followed by the addition of H_2O (100 mL) resulted in the formation of a light brown precipitate. The suspension was refrigerated overnight, filtered and the residue washed with H_2O (3 x 50 mL) and Et_2O (3 x 30 mL), to obtain target **9** as a white solid (0.93 g, 96 %). M.p. 209-211 °C [Lit.[5] m.p. 209-210 °C]; ν_{max} / cm^{-1} 1609m, 1594m; δ_H (400 MHz; $CDCl_3$) 8.09 (2H, s, C(5)H and C(6)H), 6.87 (2H, s, C(3)H and C(8)H), 4.08 (6H, s, 2 x CH_3), 2.90 (6H, s, 2 x OCH_3); δ_C (100 MHz; $CDCl_3$) 162.3 (Ar-C), 160.2 (Ar-C), 145.9 (Ar-C), 119.4 (Ar-C), 117.9 (C(5)H and C(6)H), 102.7 (C(3)H and C(8)H), 55.6 (CH_3), 26.5 (OCH_3); *m/z* (+ES) 269 ([M+H]$^+$, 100 %).

4,7-dichloro-2,9-bis(trichloromethyl)-1,10-phenanthroline (14)



Compound **14** was prepared using the procedure described for compound **12**. M.p. 222-225 °C; ν_{max} / cm^{-1} 1586m, 1338m; δ_H (500 MHz; $CDCl_3$) 8.28 (2H, s, C(5)$\underline{H}$ and C(6)$\underline{H}$), 7.62 (2H, s, C(3)$\underline{H}$ and C(8)$\underline{H}$), 4.20 (6H, s, 2 x $OC\underline{H}_3$); δ_C (100 MHz; $CDCl_3$) 163.7 ($\underline{C}Cl_3$), 159.0 (Ar-$\underline{C}$), 143.8 (Ar-$\underline{C}$), 121.9 (Ar-$\underline{C}$), 120.6 ($\underline{C}$(5)H and $\underline{C}$(6)H), 99.7 ($\underline{C}$(3)H and $\underline{C}$(8)H), 98.6 (Ar-$\underline{C}$), 56.4 ($O\underline{C}H_3$); *m/z* (+ES) 473 ($[M\{^{35}Cl_6\} + H]^+$, 38 %), 475 ($[M\{^{35}Cl_5{}^{37}Cl\} + H]^+$, 100 %), 477 ($[M\{^{35}Cl_4{}^{37}Cl_2\} + H]^+$, 96 %), 479 ($[M\{^{35}Cl_3{}^{37}Cl_3\} + H]^+$, 30 %); HRMS (+ES) calculated for $C_{16}H_{10}N_2{}^{35}Cl_6O_2Na$ ($[M+Na]^+$): 494.8771, found: 494.8772.

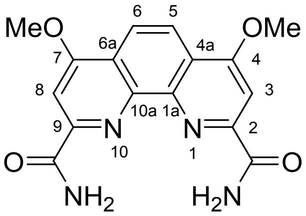
Dimethyl 4,7-dimethoxy-1,10-phenanthroline-2,9-dicarboxylate (18)



A stirred suspension of **14** (0.10 g, 0.21 mmol) in H_2SO_4 (95 %, 0.5 mL) was heated at 115 °C for 48 h. The resulting solution was cooled to ambient temperature and MeOH (0.55 mL) added dropwise. The mixture was heated at reflux for 2 h, allowed to cool and neutralized through the addition of a sat. solution of $NaHCO_3$ (10 mL). The resulting precipitate was collected by filtration, washed with H_2O (3 x 10 mL) and Et_2O (3 x 10 mL) and dried *in vacuo* to yield **18** (0.06 g, 74 %) as a pale yellow solid. M.p. 289-291 °C; ν_{max} / cm^{-1} 1745s, 1581m; δ_H (400 MHz; DMSO) 8.27 (2H, s, C(3)$\underline{H}$ and C(8)$\underline{H}$ or C(5)$\underline{H}$ and C(6)$\underline{H}$), 7.85 (2H, s, C(3)$\underline{H}$ and C(8)$\underline{H}$ or C(5)$\underline{H}$ and C(6)$\underline{H}$), 4.19 (6H, s, 2 x $OC\underline{H}_3$), 4.01 (6H, s, 2 x

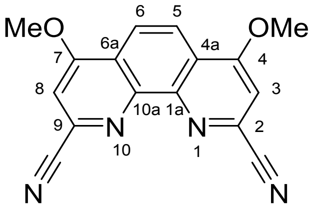
COOC$\underline{H}_3$); δ_C (125 MHz; DMSO) 165.6 ($\underline{C}$=O), 162.9 ($\underline{C}$-OCH$_3$), 148.9 (Ar-$\underline{C}$), 145.6 (Ar-$\underline{C}$), 122.0 (Ar-$\underline{C}$), 120.7 ($\underline{C}$(5)H and $\underline{C}$(6)H or $\underline{C}$(3)H and $\underline{C}$(8)H), 103.9 ($\underline{C}$(5)H and $\underline{C}$(6)H or $\underline{C}$(3)H and $\underline{C}$(8)H), 56.8 (O$\underline{C}$H$_3$), 52.8 (CO$_2\underline{C}$H3); *m/z* (+ES) 379 ([M+Na]$^+$, 60 %), 380 ([M+Na+H]$^+$, 50 %); HRMS (+ES) calculated for $C_{18}H_{16}O_6N_2Na$ ([M+Na]$^+$): 379.0906, found: 379.0905.

4,7-dichloro-1,10-phenanthroline-2,9-dicarboxamide (22)



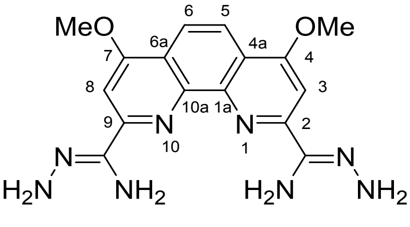
A suspension of bis-ester **18** (0.70 g, 2.0 mmol) and NH$_4$Cl (50 mg) in concentrated NH$_4$OH (16 mL) was stirred at ambient temperature for 72 h. The resulting precipitate was collected by filtration, washed with H$_2$O (30 mL) and Et$_2$O (30 mL) and dried *in vacuo* to yield bis-amide **22** (0.53 g, 81 %) as a dark green solid. M.p. >300 °C; ν_{max} / cm^{-1} 3207br, 1673s, 1555m, 1506m; δ_H (500 MHz; DMSO-d$_6$) 8.88 (2H, br s, N$\underline{H}_2$), 8.25 (2H, s, C(3)$\underline{H}$ and C(8)$\underline{H}$ or C(5)$\underline{H}$ and C(6)$\underline{H}$), 7.94 (2H, s, C(3)$\underline{H}$ and C(8)$\underline{H}$ or C(5)$\underline{H}$ and C(6)$\underline{H}$), 7.82 (2H, br s, N$\underline{H}_2$), 4.19 (6H, s, 2 x OC$\underline{H}_3$); δ_C (125 MHz; DMSO-d$_6$) 166.1 ($\underline{C}$ONH$_2$), 163.0 (Ar-$\underline{C}$), 151.7 (Ar-$\underline{C}$), 144.8 (Ar-$\underline{C}$), 121.6 ($\underline{C}$(5)H and $\underline{C}$(6)H or $\underline{C}$(3)H and $\underline{C}$(8)H), 120.1 ($\underline{C}$(5)H and $\underline{C}$(6)H or $\underline{C}$(3)H and $\underline{C}$(8)H), 101.12 (Ar-$\underline{C}$), 56.6 ($\underline{C}$OCH$_3$); *m/z* (-ES) 326 ([M]$^-$, 69 %); HRMS (+ES) calculated for $C_{16}H_{15}O_4N_4$ ([M+H]$^+$): 327.1093, found: 327.1099.

4,7-dimethoxy-1,10-phenanthroline-2,9-dicarbonitrile (26)



To DMF (7 mL) under an atmosphere of N_2 was added oxalyl chloride (0.5 mL, 0.72 g, 5.68 mmol) at 0 °C with stirring. A white precipitate formed immediately which was accompanied by gas evolution. Once the gas evolution had ceased, a suspension of bis-amide **22** (0.50 g, 1.72 mmol) in DMF (12 mL) was added. The resulting tan coloured mixture was left to stir for 6 h at 0 ^{0}C. Pyridine (0.5 mL, 0.49 g, 4.13 mmol) was added and the mixture left to stir for a further 30 min before being neutralised with a sat. solution of aqueous K_2CO_3 (15 mL), resulting in formation of a precipitate. Precipitation was further encouraged through the addition of H_2O (20 mL). The precipitate collected by filtration, washed with H_2O (3 x 15 mL) and Et_2O (3 x 15 mL). The resulting tan solid was dried *in vacuo* to yield **26** as an off white solid (0.22 g, 50 %). M.p. 294-296 °C (decomposed); ν_{max} / cm^{-1} 3420m, 2248w, 1614m, 1577m, 1556m; δ_H (500 MHz; DMSO-d$_6$) 8.27 (2H, s, C(3)$\underline{H}$ and C(8)$\underline{H}$ or C(5)$\underline{H}$ and C(6)$\underline{H}$), 8.01 (2H, s, C(3)$\underline{H}$ and C(8)$\underline{H}$ or C(5)$\underline{H}$ and C(6)$\underline{H}$), 4.19 (6H, s, 2 x OC$\underline{H}_3$); δ_C (125 MHz; DMSO-d$_6$) 162.9 ($\underline{C}$-OCH$_3$), 145.5 (Ar-$\underline{C}$), 134.1 (Ar-$\underline{C}$), 122.2 (Ar-$\underline{C}$), 121.4 ($\underline{C}$(5)H and $\underline{C}$(6)H or $\underline{C}$(3)H and $\underline{C}$(8)H), 117.8 ($\underline{C}$≡N), 108.6 ($\underline{C}$(5)H and $\underline{C}$(6)H or $\underline{C}$(3)H and $\underline{C}$(8)H), 57.6 (O$\underline{C}$H$_3$); *m/z* (+ES) 291 ([M+H]$^+$, 100 %); HRMS (+ES) calculated for $C_{16}H_{11}N_4O_2$ ([M+H]$^+$): 291.0882, found: 291.0894.

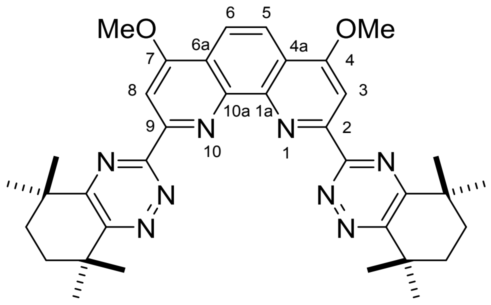
4,7-dimethoxy-1,10-phenanthroline-2,9-dicarbonitrile (30)



A suspension of **26** (0.22 g, 0.76 mmol) in EtOH (5.5 mL) was treated with hydrazine hydrate (5.5 mL, 50-60 %). The suspension was left to stir for 72 h at ambient temperature, before being concentrated *in vacuo*. The yellow residue was washed with H_2O (2 x 10 mL), Et_2O (2 x 50 mL) and dried *in vacuo* to yield compound **30** as a pale yellow solid (0.15 g, 54 %).

M.p. >300 °C; ν_{max} / cm^{-1} 3317br, 3176br, 1613m, 1584m, 1553m; δ_H (500 MHz; DMSO-d_6) 8.09 (2H, s, C(3)$\underline{H}$ and C(8)$\underline{H}$ or C(5)$\underline{H}$ and C(6)$\underline{H}$), 7.76 (2H, s, C(3)$\underline{H}$ and C(8)$\underline{H}$ or C(5)$\underline{H}$ and C(6)$\underline{H}$), 6.09 (4H, br s, 2 x N$\underline{H}_2$), 5.58 (4H, br s, 2 x N$\underline{H}_2$), 4.09 (6H, s, 2 x OC$\underline{H}_3$); δ_C (125 MHz; DMSO) 161.3 ($\underline{C}$-OCH_3), 152.7 ($\underline{C}$=NNH_2), 144.3 (Ar-$\underline{C}$), 143.4 (Ar-$\underline{C}$), 120.5 (Ar-$\underline{C}$), 118.5 ($\underline{C}$(5)H and $\underline{C}$(6)H), 98.1 ($\underline{C}$(3)H and $\underline{C}$(8)H), 56.1 (O$\underline{C}H_3$); *m/z* (+ES) 355 ($[M+H]^+$, 27 %), 377 ($[M+Na]^+$, 30 %); HRMS (+ES) calculated for $C_{16}H_{18}N_8O_2Na$ ($[M+Na]^+$): 377.1450, found: 377.1453.

4,7-dimethoxy-2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[e][1,2,4]triazin-3-yl)-1,10-phenanthroline (34)

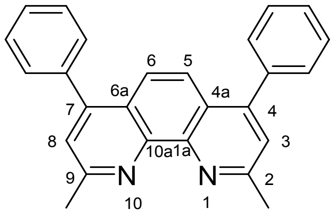


A stirred suspension of **30** (0.22 g, 0.62 mmol) and 3,3,6,6-tetramethylcyclohexane-1,2-dione (**32**) (0.24 g, 1.36 mmol) in EtOH (4.8 mL) was heated at reflux for 3 h. The resulting solution was allowed to cool to ambient temperature and taken to dryness *in vacuo*. The dark brown solid was triturated with cold Et_2O (3 x 20 mL) and the ethereal washings were then taken to dryness *in vacuo.* Trituration with hexane (3 x 30 mL) provided **34** as an orange powder (0.13 g, 34 %). M.p. 248-251 °C; ν_{max} / cm^{-1} 3302br, 3210br, 1616s, 1584s, 1485m, 1390m, 1372m; δ_H (400 MHz; $CDCl_3$) 8.41 (2H, s, C(3)$\underline{H}$ and C(8)$\underline{H}$ or C(5)$\underline{H}$ and C(6)$\underline{H}$), 8.32 (2H, s, C(3)$\underline{H}$ and C(8)$\underline{H}$ or C(5)$\underline{H}$ and C(6)$\underline{H}$), 4.23 (6H, s, 2 x OC$\underline{H}_3$), 1.90 (8H, s, 4 x C$\underline{H}_2$), 1.60 (12H, s, 4 x C$\underline{H}_3$), 1.54 (12H, s, 4 x C$\underline{H}_3$); δ_C (100 MHz; $CDCl_3$) 165.4 (Ar-$\underline{C}$), 163.2 (Ar-$\underline{C}$), 163.0 (Ar-$\underline{C}$), 161.6 (Ar-$\underline{C}$), 154.9 (Ar-$\underline{C}$), 147.1 (Ar-$\underline{C}$), 122.2 (Ar-$\underline{C}$), 120.1 ($\underline{C}$(5)H and $\underline{C}$(6)H or $\underline{C}$(3)H and $\underline{C}$(8)H), 103.3 ($\underline{C}$(5)H and $\underline{C}$(6)H or $\underline{C}$(3)H and $\underline{C}$(8)H), 56.2

(OC̲H$_3$), 37.6 (quat C̲), 36.6 (quat C̲), 33.7 (C̲H$_2$), 29.9 (C̲H$_3$), 29.4 (C̲H$_3$); *m/z* (+APCI) 619 ([M+H]$^+$, 100 %), 620 ([M+2H]$^+$, 32 %); HRMS (+APCI) calculated for $C_{36}H_{42}N_8O_2$ ([M+H]$^+$): 619.3509, found: 619.3503.

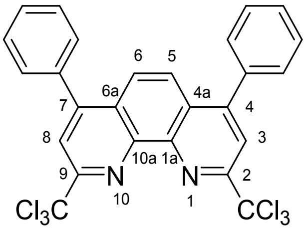
1.4 Synthesis of 4,7-diphenyl-CyMe$_4$-BTPhen (35)

2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (10)



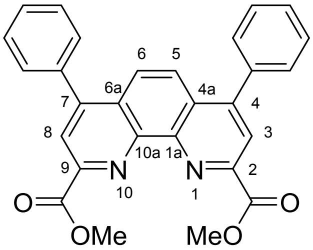
A thoroughly degassed suspension of **8** (1.00 g, 3.60 mmol), K_2CO_3 (1.50 g, 10.90 mmol), phenylboronic acid (1.33 g, 10.90 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.21 g, 0.20 mmol, 5 mol %) in THF : H_2O (5:1), (20 mL) was heated at reflux for 24 h. The resulting suspension was cooled to ambient temperature, taken to dryness *in vacuo* and the residue was dissolved in $CHCl_3$ (20 mL). The organic extract was washed with H_2O (1 x 20 mL), aqueous 1M NaOH (2 x 20 mL), brine (1 x 20 mL) and dried over $MgSO_4$. Filtration of the organic extracts through a pad of silica, followed by removal of the solvent, gave rise to **10** as a crystalline white solid (1.28 g, 98 %). M.p. 279-280 °C [Lit.[6] m.p. 281-282 °C]; ν_{max} / cm^{-1} 3055w, 3037s, 1544m; δ_H (500 MHz; $CDCl_3$) 7.76 (2H, s, C(3)H̲ and C(8)H̲ or C(5)H̲ and C(6)H̲), 7.53 (10H, m, Ar-H̲), 7.46 (2H, s, C(3)H̲ and C(8)H̲ or C(5)H̲ and C(6)H̲)), 3.01 (6H, s, 2 x CH̲$_3$); δ_C (125 MHz; $CDCl_3$) 158.7 (Ar-C̲), 148.4 (Ar-C̲), 145.9 (Ar-C̲), 138.2 (Ar-C̲), 129.6 (C̲(3) and C̲(8) or C̲(5) and C̲(6)), 128.5 (C̲(3) and C̲(8) or C̲(5) and C̲(6)), 128.3 (Ar-C̲H), 124.6 (Ar-C̲), 123.9 (Ar-C̲H), 122.9 (Ar-C̲H), 26.0 (C̲H$_3$); *m/z* (+ES) 361 ([M+H]$^+$, 100 %), 362 ([M+2H]$^+$, 40 %).

4,7-dichloro-2,9-bis(trichloromethyl)-1,10-phenanthroline (15)



Compound **15** (1.50 g, 80 %) was prepared using the procedure described for compound **12**. M.p. 292-294 °C [Lit.[7] m.p. 286-289 °C]; ν_{max} / cm^{-1} 1592m, 1546m, 1428m; δ_H (400 MHz; CDCl$_3$) 8.28 (2H, s, C(5)$\underline{H}$ and C(6)$\underline{H}$), 8.01 (2H, s, C(3)$\underline{H}$ and C(8)$\underline{H}$), 7.58 (10H, m, Ar-$\underline{H}$); δ_C (100 MHz; CDCl$_3$) 157.5 ($\underline{C}$Cl$_3$), 151.0 (Ar-$\underline{C}$), 144.0 (Ar-$\underline{C}$), 136.9 (Ar-$\underline{C}$), 129.7 ($\underline{C}$(5)H and $\underline{C}$(6)H or ($\underline{C}$(3)H and $\underline{C}$(8)H), 129.1 (Ar-$\underline{C}$H), 128.9 ($\underline{C}$(5)H and $\underline{C}$(6)H or ($\underline{C}$(3)H and $\underline{C}$(8)H), 127.2 (Ar-$\underline{C}$), 125.3 (Ar-$\underline{C}$H), 120.6 (Ar-$\underline{C}$H), 98.3 (Ar-$\underline{C}$H); *m/z* (+ES) 565 ([M{^{35}Cl$_6$}+H]$^+$, 80 %), 566 ([M{^{35}Cl$_5$^{37}Cl}+H]$^+$, 15 %), 567 ([M{^{35}Cl$_4$^{37}Cl$_2$}+H]$^+$, 100 %), 568 ([M{^{35}Cl$_3$^{37}Cl$_3$}+H]$^+$, 30 %).

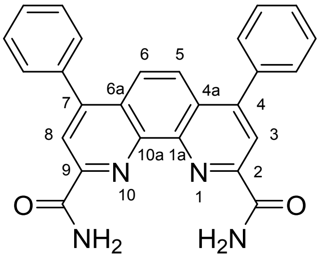
Dimethyl 4,7-diphenyl-1,10-phenanthroline-2,9-dicarboxylate (19)



A stirred suspension of **15** (1.30 g, 2.31 mmol) in H$_2$SO$_4$ (95 %, 2.5 mL) was heated at 95°C for 2 h. The resulting solution was cooled to ambient temperature and MeOH (2.2 mL) added dropwise. The mixture was heated at reflux for 1 h, allowed to cool and neutralized through the addition of a sat. solution of NaHCO$_3$ (20 mL). The precipitate was collected by filtration, washed with H$_2$O (3 x 15 mL) and Et$_2$O (3 x 20 mL) and dried *in vacuo* to yield **19** (0.78 g, 76 %) as a light brown solid. M.p. 192-195 °C; ν_{max} / cm^{-1} 3447br, 3951w, 1725s, 1617w; δ_H

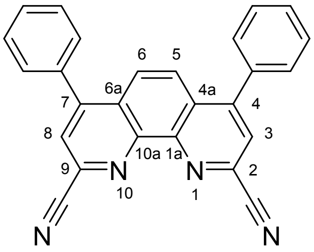
(500 MHz; DMSO) 8.29 (2H, s, C(3)<u>H</u> and C(8)<u>H</u> or C(5)<u>H</u> and C(6)<u>H</u>), 8.03 (2H, s, C(3)<u>H</u> and C(8)<u>H</u> or C(5)<u>H</u> and C(6)<u>H</u>), 7.64 (10H, m, Ar-<u>H</u>), 4.05 (6H, s, 2 x COOC<u>H</u>$_3$); δ_C (125 MHz; DMSO) 165.4 (<u>C</u>=O), 149.6 (Ar-<u>C</u>), 147.1 (Ar-<u>C</u>), 145.9 (Ar-<u>C</u>), 136.5 (Ar-<u>C</u>), 129.8 (<u>C</u>(5)H and <u>C</u>(6)H or <u>C</u>(3)H and <u>C</u>(8)H), 129.3 (Ar-<u>C</u>H), 129.1 (<u>C</u>(5)H and <u>C</u>(6)H or <u>C</u>(3)H and <u>C</u>(8)H), 127.9 (Ar-<u>C</u>), 126.0 (Ar-<u>C</u>H), 124.0 (Ar-<u>C</u>H), 53.0 (CO$_2$<u>C</u>H$_3$); *m/z* (+ES) 449 ([M+H]$^+$, 80 %), 471 ([M+Na]$^+$, 73 %), 487 ([M+K]$^+$, 82 %); HRMS (+ES) calculated for $C_{28}H_{20}O_4N_2Na$ ([M+Na]$^+$): 471.1320, found: 471.1321.

4,7-diphenyl-1,10-phenanthroline-2,9-dicarboxamide (23)



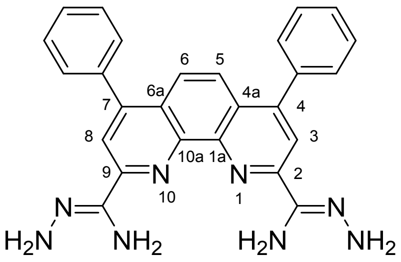
A suspension of bis-ester **19** (0.20 g, 0.45 mmol) and NH_4Cl (14 mg) in concentrated NH_4OH (4.5 mL) was stirred at ambient temperature for 72 h. The resulting precipitate was collected by filtration, washed with H_2O (15 mL) and Et_2O (2 x 30 mL) and dried *in vacuo* to yield bis-amide **23** (0.13 g, 67 %) as a green solid. M.p. 215-217 °C; ν_{max} / cm^{-1} 3210br, 1677s, 1589m; δ_H (500 MHz; DMSO-d$_6$) 9.08 (2H, br s, N<u>H</u>$_2$), 8.33 (2H, s, C(3)<u>H</u> and C(8)<u>H</u> or C(5)<u>H</u> and C(6)<u>H</u>), 7.99 (2H, s, C(3)<u>H</u> and C(8)<u>H</u> or C(5)<u>H</u> and C(6)<u>H</u>), 7.64 (10H, m, Ar-<u>H</u>), 7.60 (2H, br s, N<u>H</u>$_2$); δ_C (125 MHz; DMSO-d$_6$) 166.1 (<u>C</u>ONH$_2$), 149.8 (Ar-<u>C</u>), 149.3 (Ar-<u>C</u>), 145.1 (Ar-<u>C</u>), 137.1 (Ar-<u>C</u>), 129.7 (<u>C</u>(5)H and <u>C</u>(6)H or <u>C</u>(3)H and <u>C</u>(8)H), 129.6 (Ar-<u>C</u>H), 129.0 (<u>C</u>(5)H and <u>C</u>(6)H or <u>C</u>(3)H and <u>C</u>(8)H), 127.4 (Ar-<u>C</u>), 125.3 (Ar-<u>C</u>H), 121.4 (Ar-<u>C</u>H); *m/z* (+ES) 419 ([M+H]$^+$, 8 %), 441 ([M+Na]$^+$, 20 %); HRMS (+ES) calculated for $C_{26}H_{18}O_2N_4Na$ ([M+Na]$^+$): 441.1327, found: 441.1342.

4,7-diphenyl-1,10-phenanthroline-2,9-dicarbonitrile (27)



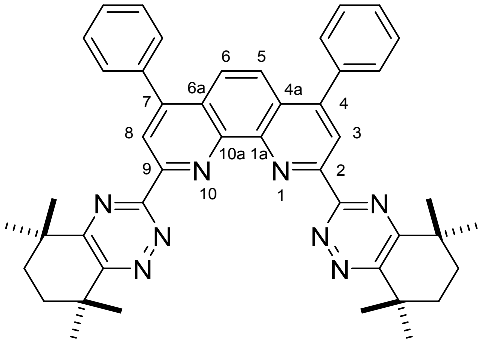
To DMF (2.4 mL) under an atmosphere of N_2 was added oxalyl chloride (0.04 mL, 0.07 g, 0.60 mmol) at 0 °C with stirring. A white precipitate formed immediately which was accompanied by gas evolution. Once the gas evolution had ceased, a suspension of bis-amide **23** (0.10 g, 0.24 mmol) in DMF (1.4 mL) was added. The resulting mixture was left to stir for 6 h at 0 °C. Pyridine (0.1 mL, 0.09 g, 1.07 mmol) was added and the mixture left to stir for a further 30 min before being neutralised with a sat. solution of aqueous K_2CO_3 (5 mL), resulting in formation of a precipitate. Precipitation was further encouraged through the addition of H_2O (10 mL). The precipitate was collected by filtration, washed with H_2O (3 x 10 mL) and Et_2O (3 x 10 mL) and dried *in vacuo* to yield **27** as a tan brown solid (0.06 g, 69 %). M.p. 224 °C (decomposed); ν_{max} / cm^{-1} 2238w, 1757m, 1483m; δ_H (500 MHz; DMSO-d_6) 8.43 (2H, s, C(3)$\underline{H}$ and C(8)$\underline{H}$ or C(5)$\underline{H}$ and C(6)$\underline{H}$), 8.06 (2H, s, C(3)$\underline{H}$ and C(8)$\underline{H}$ or C(5)$\underline{H}$ and C(6)$\underline{H}$), 7.64 (10H, m, Ar-$\underline{H}$); δ_C (125 MHz; DMSO-d_6) 149.9 (Ar-$\underline{C}$), 145.8 (Ar-$\underline{C}$), 135.4 (Ar-$\underline{C}$), 132.8 (Ar-$\underline{C}$), 129.9 ($\underline{C}$(5)H and $\underline{C}$(6)H or $\underline{C}$(3)H and $\underline{C}$(8)H), 129.6 (Ar-$\underline{C}$H), 129.0 ($\underline{C}$(5)H and $\underline{C}$(6)H or $\underline{C}$(3)H and $\underline{C}$(8)H), 127.9 (Ar-$\underline{C}$H), 127.8 (Ar-$\underline{C}$), 126.7 (Ar-$\underline{C}$H), 117.7 ($\underline{C}$≡N); *m/z* (+ES) 383 ($[M+H]^+$, 52 %), 405 ($[M+Na]^+$, 60%); HRMS (+ES) calculated for $C_{26}H_{15}N_4$ ($[M+H]^+$): 383.1297, found: 383.1297.

(2Z,9Z)-4,7-diphenyl-1,10-phenanthroline-2,9-bis(carbohydrazonamide) (31)



A suspension of **27** (0.20 g, 0.52 mmol) in EtOH (5 mL) was treated with hydrazine hydrate (5 mL, 50-60 %). The suspension was left to stir for 72 h at ambient temperature, before being concentrated *in vacuo*. The yellow precipitate was washed with H_2O (2 x 10 mL), Et_2O (2 x 50 mL) and dried *in vacuo* to yield compound **31** as a bright yellow solid (0.18 g, 77 %). M.p. >300 °C ; ν_{max} / cm^{-1} 3306br, 3171br, 1609m, 1558m, 1540m; δ_H (500 MHz; DMSO-d_6) 8.20 (2H, s, C(3)$\underline{H}$ and C(8)$\underline{H}$ or C(5)$\underline{H}$ and C(6)$\underline{H}$), 7.80 (2H, s, C(3)$\underline{H}$ and C(8)$\underline{H}$ or C(5)$\underline{H}$ and C(6)$\underline{H}$), 7.59 (10H, m, Ar-$\underline{H}$), 6.18 (4H, br s, 2 x N$\underline{H}_2$), 5.67 (4H, br s, 2 x N$\underline{H}_2$); δ_C (125 MHz; DMSO) 151.1 (2 x $\underline{C}$=NNH_2), 148.2 (Ar-$\underline{C}$), 144.9 (Ar-$\underline{C}$), 144.7 (Ar-$\underline{C}$), 137.9 (Ar-$\underline{C}$), 129.9 ($\underline{C}$(5)H and $\underline{C}$(6)H or $\underline{C}$(3)H and $\underline{C}$(8)H), 129.4 ($\underline{C}$(5)H and $\underline{C}$(6)H or $\underline{C}$(3)H and $\underline{C}$(8)H), 129.3 (Ar-$\underline{C}$H), 126.2 (Ar-$\underline{C}$), 124.0 (Ar-$\underline{C}$H), 119.9 (Ar-$\underline{C}$H).; *m/z* (+ES) 447 ($[M+H]^+$, 70 %), 469 ($[M+Na]^+$, 32 %); HRMS (+ES) calculated for $C_{26}H_{22}N_8Na$ ($[M+Na]^+$): 469.1865, found: 469.1868.

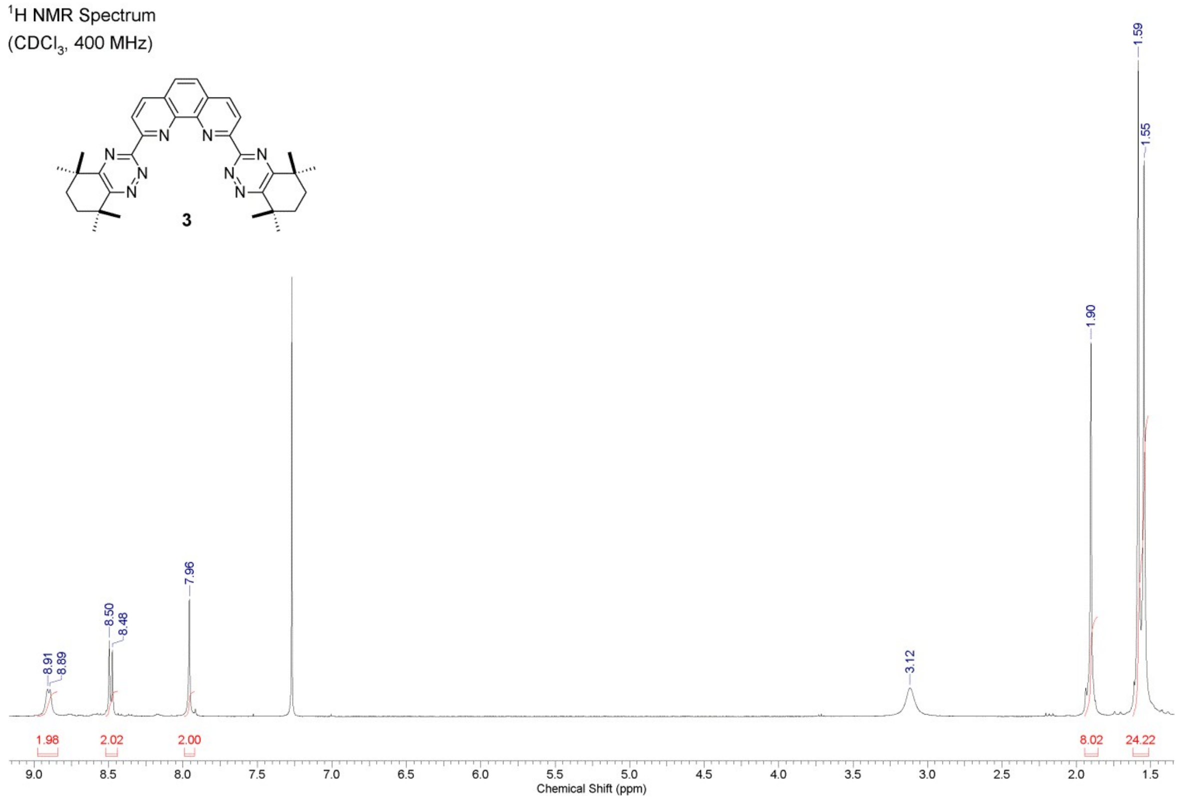
4,7-diphenyl-2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[e][1,2,4]triazin-3-yl)-1,10-phenanthroline (35)

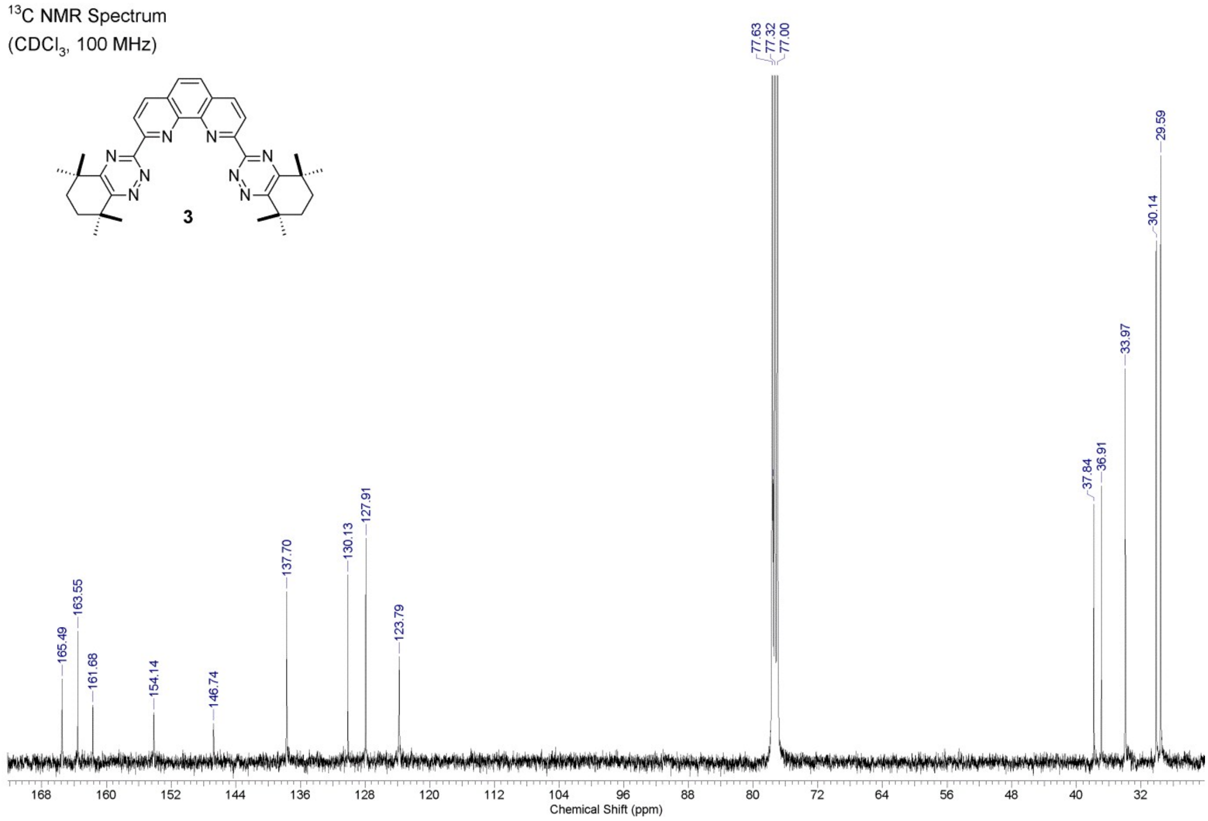


A stirred suspension of **31** (0.20 g, 0.45 mmol) and 3,3,6,6-tetramethylcyclohexane-1,2-dione (**32**) (0.17 g, 0.99 mmol) in EtOH (4.5 mL) was heated at reflux for 4 h. After which, the brown suspension was allowed to cool to ambient temperature and taken to dryness *in vacuo*. The brown solid was triturated with cold Et_2O (3 x 20 mL) to obtain the desired compound **35** (0.12 g, 38 %) as a beige powder. M.p. 263-265 °C; ν_{max} / cm^{-1} 3388br, 2954s, 1614m, 1482s; δ_H (500 MHz; $CDCl_3$ + 0.5 v% CF_3COOD) 9.10 (2H, s, C(3)$\underline{\text{H}}$ and C(8)$\underline{\text{H}}$ or C(5)$\underline{\text{H}}$ and C(6)$\underline{\text{H}}$), 8.41 (2H, s, C(3)$\underline{\text{H}}$ and C(8)$\underline{\text{H}}$ or C(5)$\underline{\text{H}}$ and C(6)$\underline{\text{H}}$), 7.73 (10H, m, Ar-$\underline{\text{H}}$), 2.05 (8H, s, 4 x C$\underline{\text{H}}_2$), 1.61 (12H, s, 4 x C$\underline{\text{H}}_3$), 1.60 (12H, s, 4 x C$\underline{\text{H}}_3$); δ_C (125 MHz; $CDCl_3$) 163.3 (Ar-$\underline{\text{C}}$), 162.7 (Ar-$\underline{\text{C}}$), 160.0 (Ar-$\underline{\text{C}}$), 151.6 (Ar-$\underline{\text{C}}$), 149.8 (Ar-$\underline{\text{C}}$), 147.7 (Ar-$\underline{\text{C}}$), 129.7 (Ar-$\underline{\text{C}}$), 129.6 ($\underline{\text{C}}$(5)H and $\underline{\text{C}}$(6)H or $\underline{\text{C}}$(3)H and $\underline{\text{C}}$(8)H), 129.0 ($\underline{\text{C}}$(5)H and $\underline{\text{C}}$(6)H or $\underline{\text{C}}$(3)H and $\underline{\text{C}}$(8)H), 128.8 (Ar-$\underline{\text{C}}$H), 127.7 (Ar-$\underline{\text{C}}$), 125.3 (Ar-$\underline{\text{C}}$H), 122.3 (Ar-$\underline{\text{C}}$H), 36.9 (quat $\underline{\text{C}}$), 35.8 (quat $\underline{\text{C}}$), 33.1 ($\underline{\text{C}}H_2$), 32.9 ($\underline{\text{C}}H_2$), 29.0 ($\underline{\text{C}}H_3$), 28.7($\underline{\text{C}}H_3$); *m/z* (+ES) 711 ($[M+H]^+$, 100 %), 712 ($[M+2H]^+$, 50 %); HRMS (+APCI) calculated for $C_{46}H_{47}N_8$ ($[M+H]^+$): 711.3924, found: 711.3947.

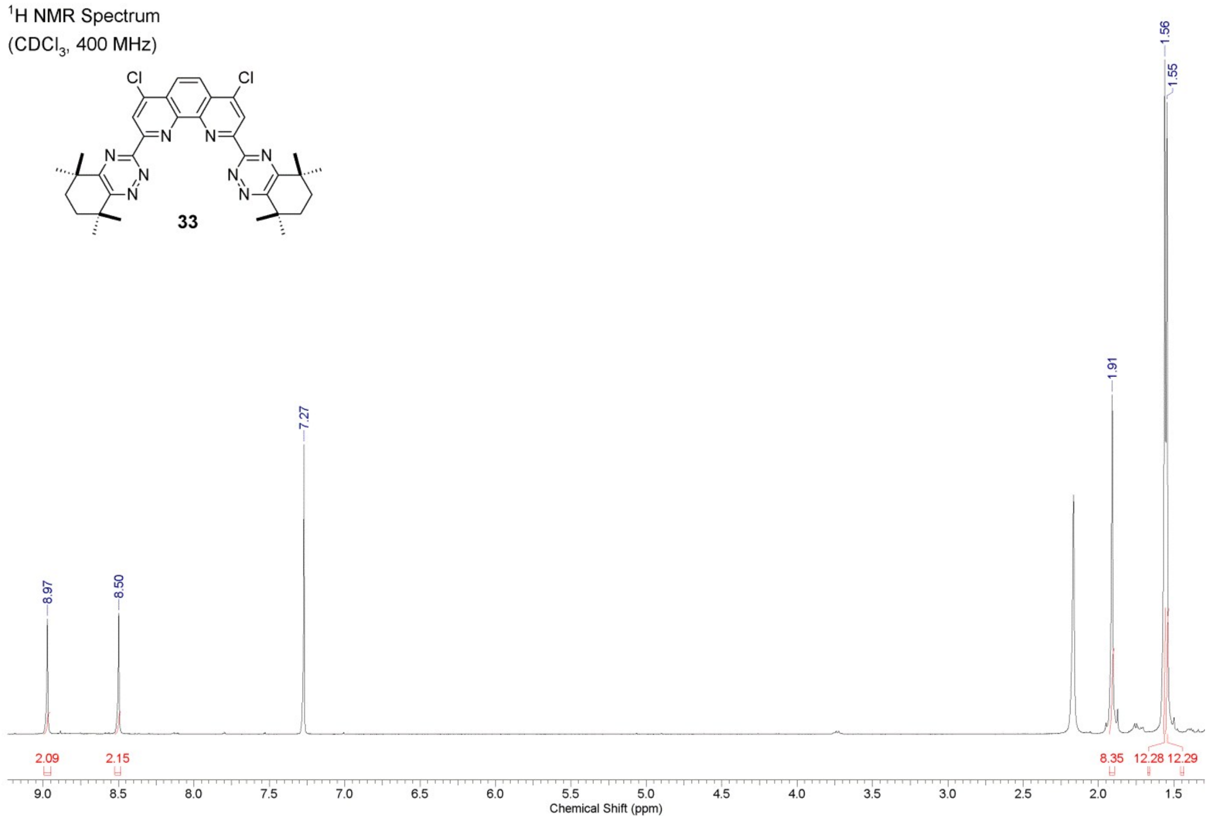
1.5 Key ^{1}H and ^{13}C NMR Spectra

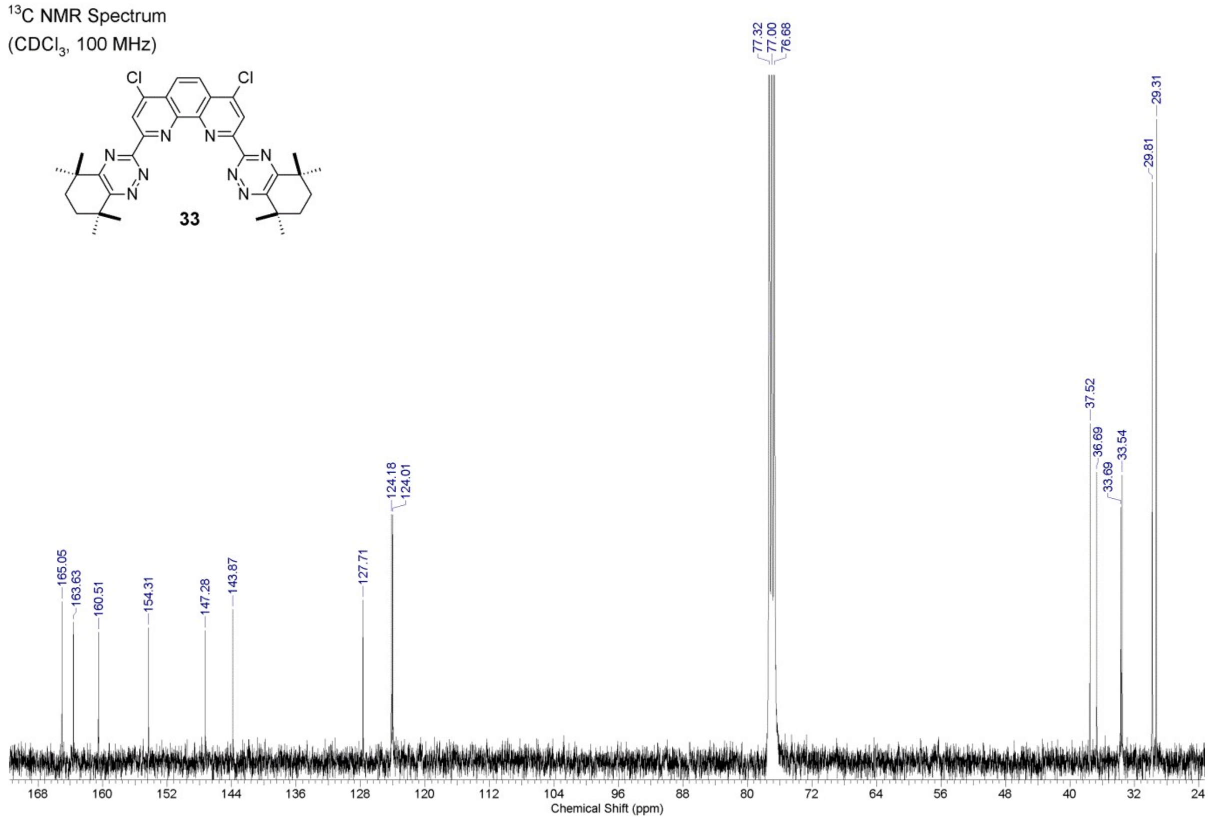
Compound 3



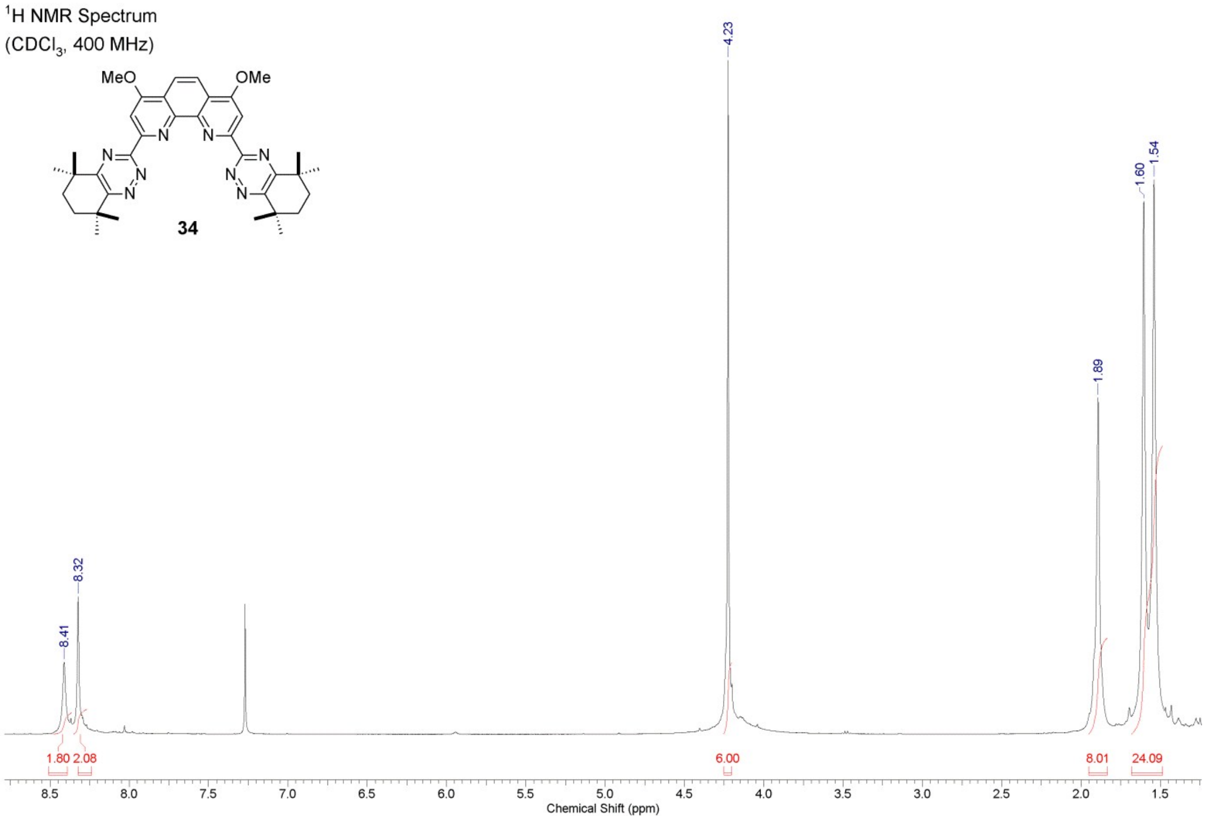


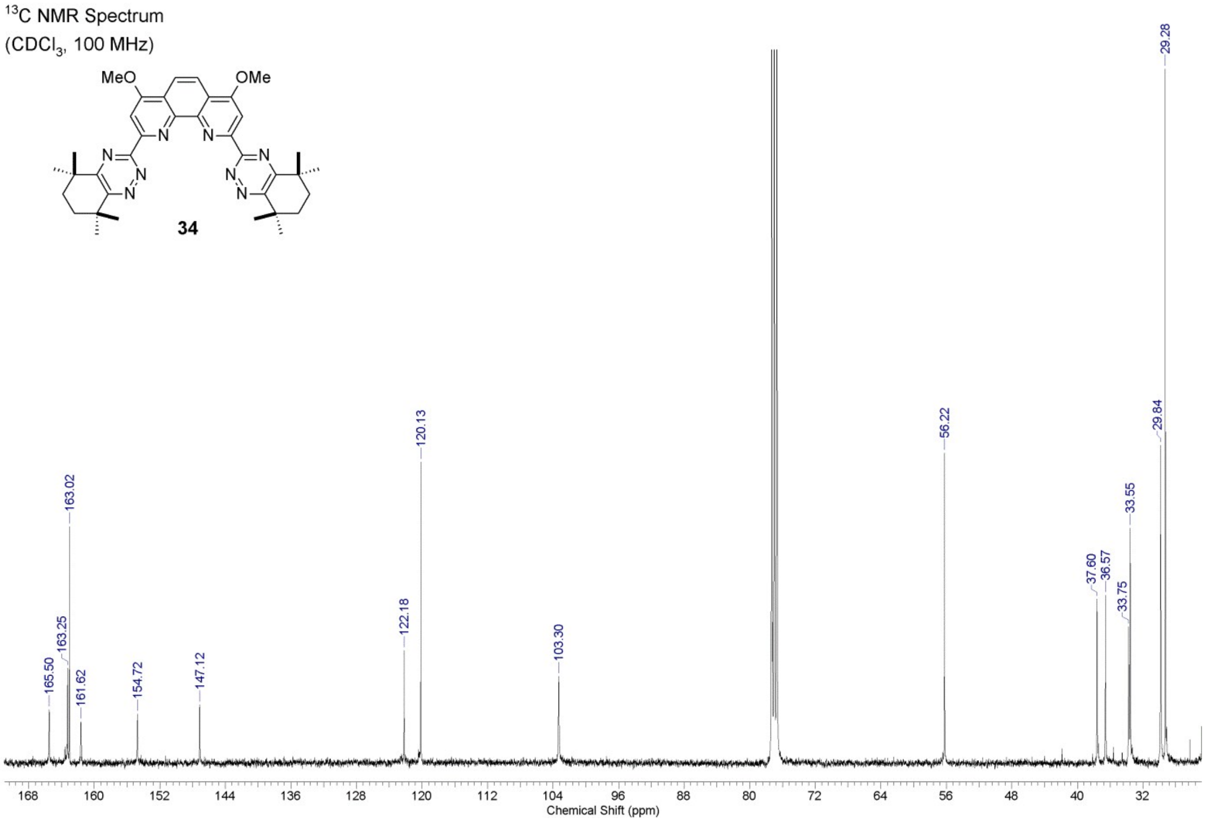
Compound 33


^{1}H NMR Spectrum
($CDCl_3$, 400 MHz)
Cl
Cl
N
N
N
N
N
N
N
N
33
8.97
8.50
7.27
1.91
1.56
1.55
2.09
2.15
8.35
12.28
12.29
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
Chemical Shift (ppm)

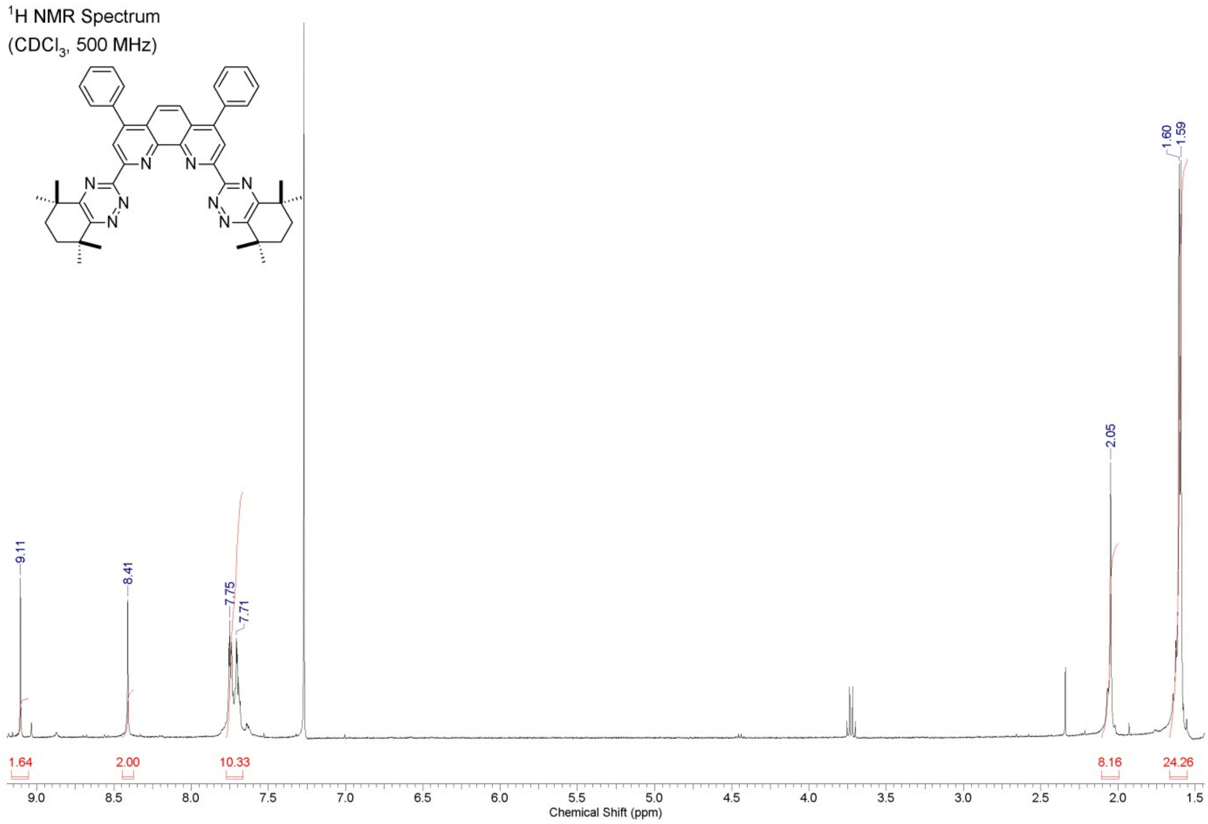

^{13}C NMR Spectrum
($CDCl_3$, 100 MHz)
Cl
Cl
N
N
N
N
N
N
N
N
33
165.05
163.63
160.51
154.31
147.28
143.87
127.71
124.18
124.01
77.32
77.00
76.68
37.52
36.69
33.69
33.54
29.81
29.31
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
Chemical Shift (ppm)

Compound 34



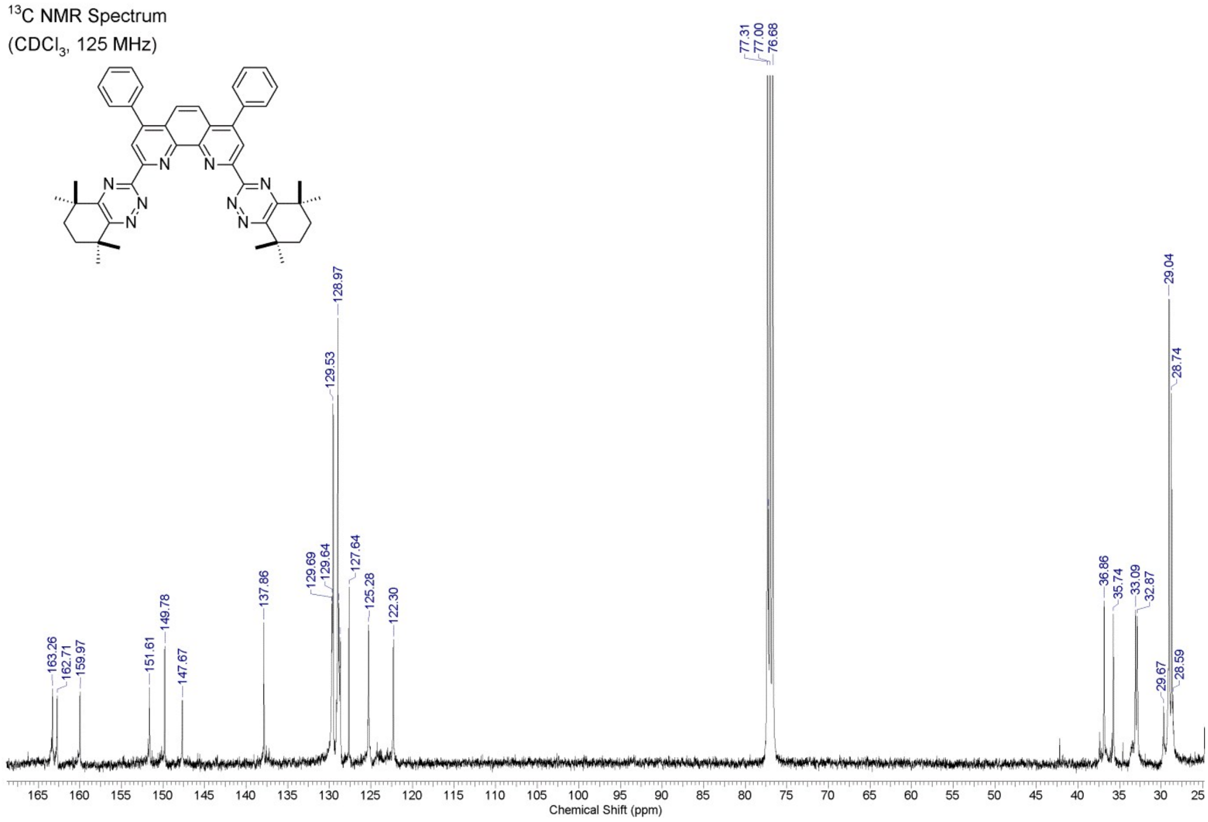


Compound 35



^{1}H NMR Spectrum

($CDCl_3$, 500 MHz)



^{13}C NMR Spectrum

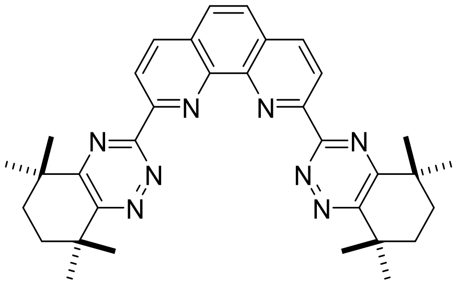
($CDCl_3$, 125 MHz)

2. Solvent Extraction Studies

2.1 General Procedure for Extraction Kinetic Studies

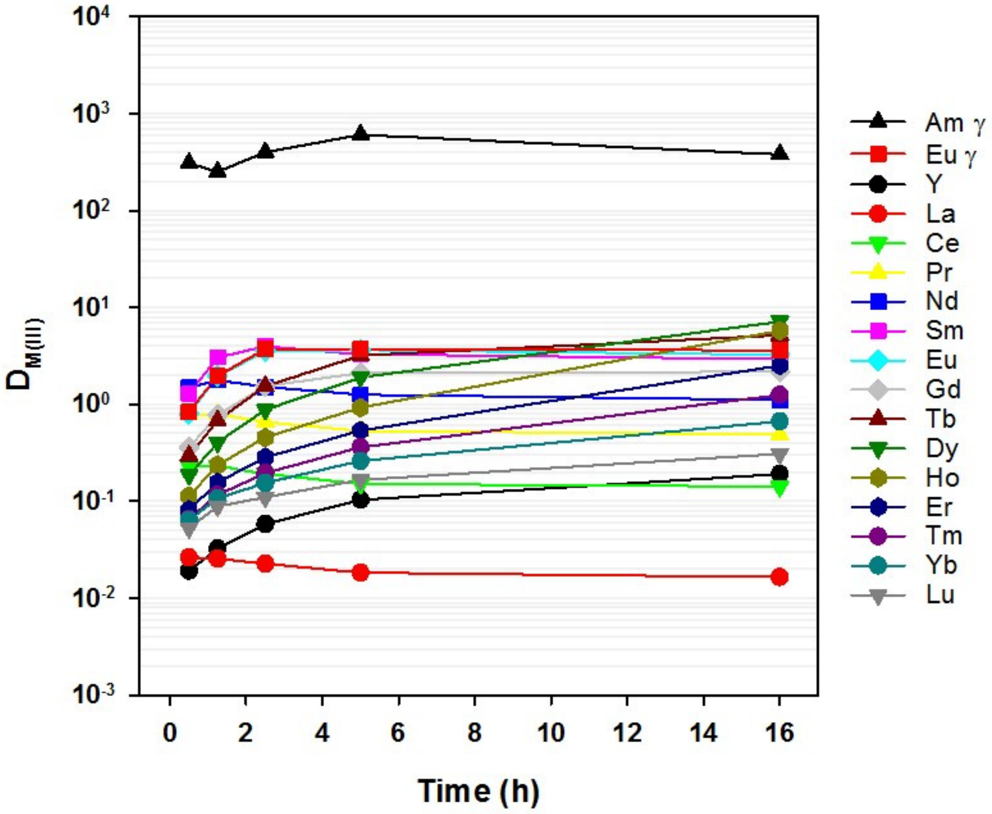
A 500 µL aliquot of **3** (10 mM), **33** (10 mM), **34** (10 mM) or **35** (4.5 mM) in 1-octanol was contacted with a 500 µL aliquot of 0.1M HNO_3 in a 2 mL glass vial. The aqueous phase was spiked with $^{241}Am^{3+}$, $^{152}Eu^{3+}$ (1 kBq/mL), Y^{3+} (10 mg/L) and all of the lanthanides (La^{3+}-Lu^{3+} excluding Pm^{3+} 10 mg/L each). The resulting biphasic system was shaken at T=20 °C on an orbital shaker at 2500/min for varying contact times. The phases were centrifugally separated and 300 µL of each phase was analysed using a Packard Cobra Auto Gamma 5003 spectrometer. Back-extraction of all the cationic metal species was achieved by shaking the organic phase (300 µL) with an aqueous 0.5 M glycolate solution (3 mL, pH = 4) for 2 hours. The aqueous phases (300 µL) were also diluted with aqueous glycolate (2.70 mL). A 100 µL aliquot of the glycolate solution was diluted with 2 % ultrapure aqueous HNO_3 (4.9 mL) and analysed using a Perkin-Elmer Elan 6100, ICP-mass spectrometer. Each experiment was run in duplicate and the displayed values are an average of the two experiments.

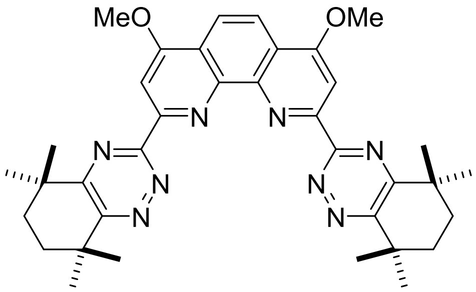
2.2 Kinetic Results



10 mM BTPhen (3) in 1-octanol

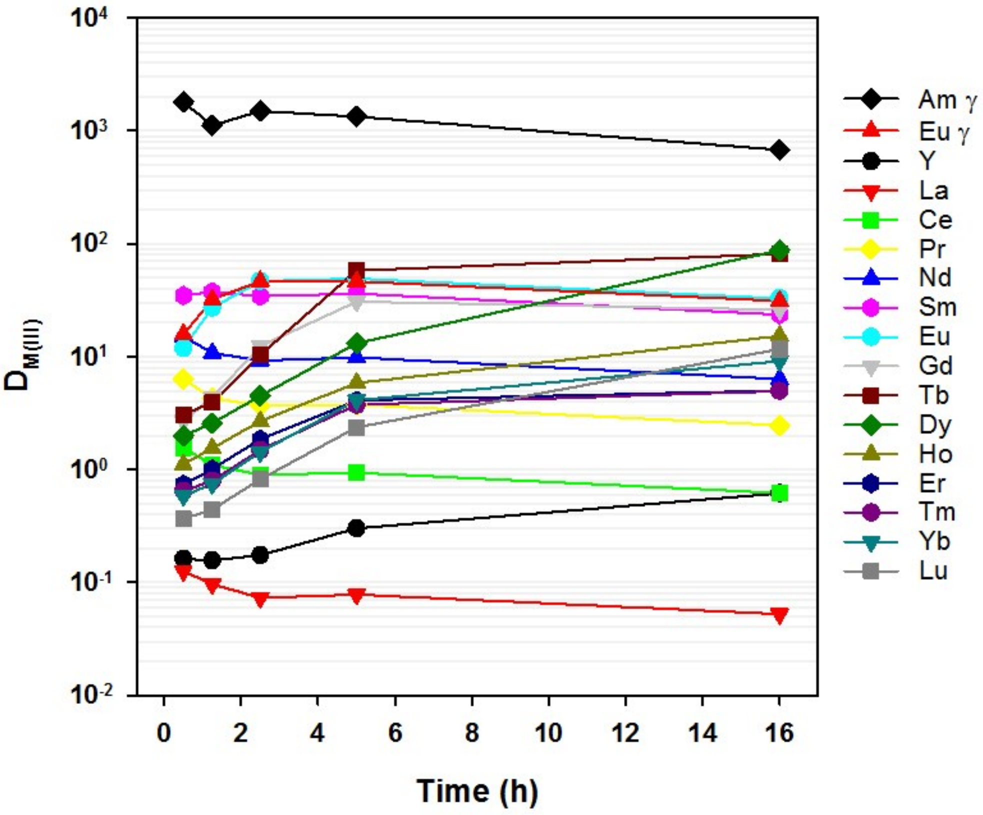
^{241}Am(III) + ^{152}Eu(III) + Ln(III) + Y(III) in 0.1M HNO_3

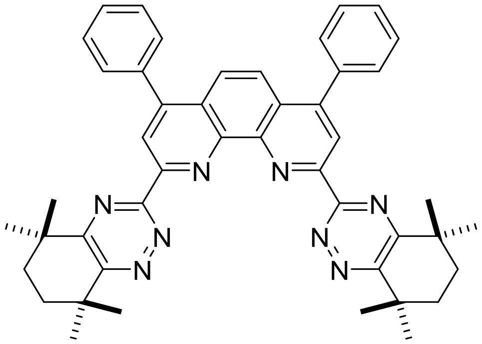




10 mM 4,7-MeO-BTPhen (34) in 1-octanol

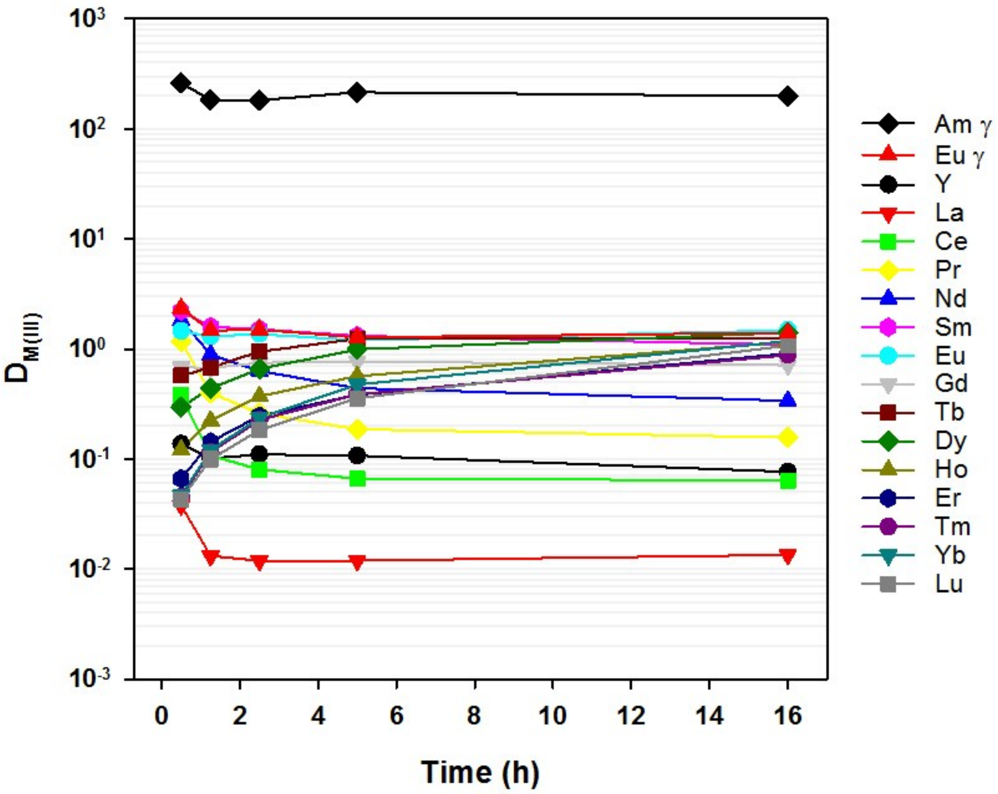
^{241}Am(III) + ^{152}Eu(III) + Ln(III) + Y(III) in 0.1M HNO$_3$

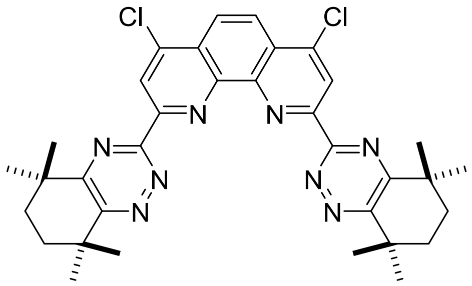




4.5 mM 4,7-Phenyl-BTPhen (35) in 1-octanol

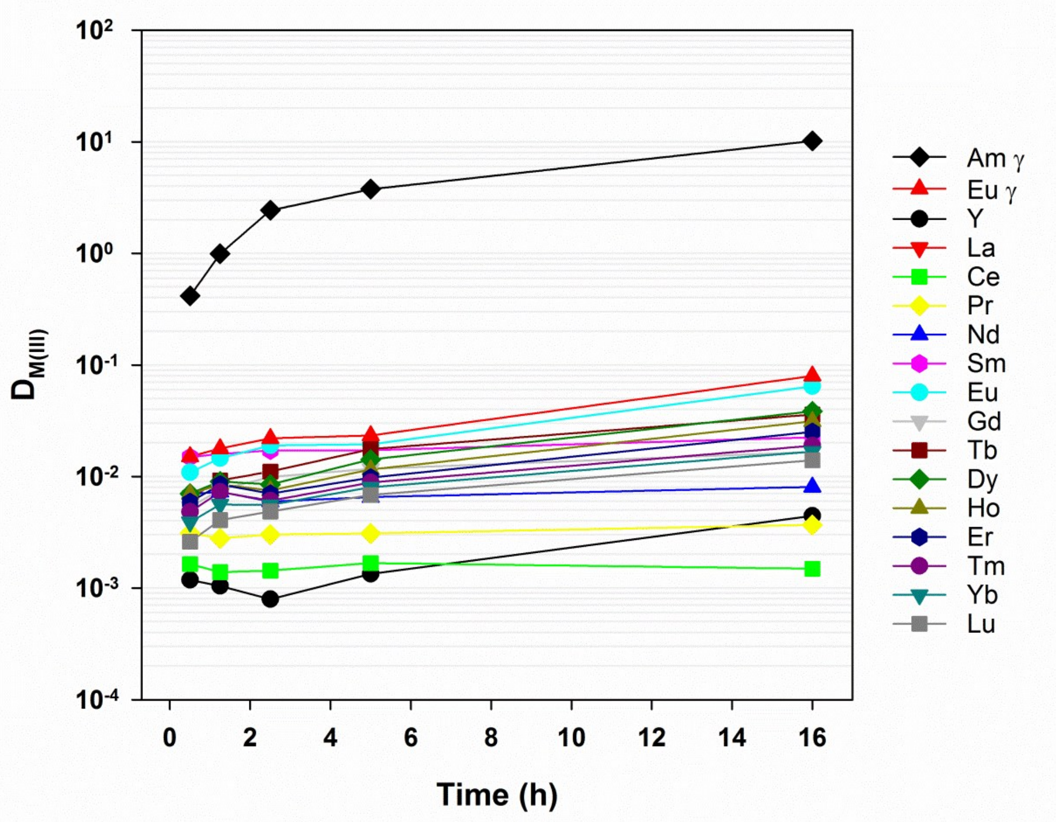
^{241}Am(III) + ^{152}Eu(III) + Ln(III) + Y(III) in 0.1M HNO_3





10 mM 4,7-Cl-BTPhen (33) in 1-octanol

^{241}Am(III) + ^{152}Eu(III) + Ln(III) + Y(III) in 0.1M HNO_3



2.3 General Procedure for Acid Dependence Studies

A 500 µL aliquot of **3** (10 mM), **33** (10 mM), **34** (10 mM) or **35** (4.5 mM) in 1-octanol was contacted with a 500 µL aliquot of 0.1M – 3M HNO_3 in a 2 mL glass vial. The aqueous phase was spiked with $^{241}Am^{3+}$, $^{152}Eu^{3+}$ (1 kBq/mL), Y^{3+} (10 mg/L) and all of the lanthanides (La^{3+}-Lu^{3+} excluding Pm^{3+} 10 mg/L each). The resulting biphasic system was shaken at T=20 °C on an orbital shaker at 2500/min for 20 hours.[+] The phases were centrifugally separated and 300 µL of each phase was analysed using a Packard Cobra Auto Gamma 5003 spectrometer. Back-extraction of all the cationic metal species was achieved by shaking the organic phase (300 µL) with an aqueous 0.5 M glycolate solution (3 mL, pH = 4) for 2 hours. The aqueous phases (300 µL) were also diluted with aqueous glycolate (2.70 mL). A 100 µL aliquot of the glycolate solution was diluted with 2 % ultrapure aqueous HNO_3 (4.9 mL) and analysed using a Perkin-Elmer Elan 6100, ICP-mass spectrometer. Each experiment was run in duplicate and the displayed values are an average of the two experiments.

2.4 General Procedure for Ligand Dependence Studies

A 500 µL aliquot of **3**, **33**, **34** or **35** in 1-octanol (45 µM – 10 mM) was contacted with a 500 µL aliquot of 0.1M HNO_3 in a 2 mL glass vial. The aqueous phase was spiked with $^{241}Am^{3+}$, $^{152}Eu^{3+}$ (1 kBq/mL), Y^{3+} (10 mg/L) and all of the lanthanides (La^{3+}-Lu^{3+} excluding Pm^{3+} 10 mg/L each). The resulting biphasic system was shaken at T=20 °C on an orbital shaker at 2500/min for 20 hours.[+] The phases were centrifugally separated and 300 µL of each phase was analysed using a Packard Cobra Auto Gamma 5003 spectrometer. Back-extraction of all the cationic metal species was achieved by shaking the organic phase (300 µL) with an aqueous 0.5 M glycolate solution (3 mL, pH = 4) for 2 hours. The aqueous phases (300 µL) were also diluted with aqueous glycolate (2.70 mL). A further 100 µL aliquot of the glycolate solution was diluted with 2 % ultrapure aqueous HNO_3 (4.9 mL) and analysed using a Perkin-Elmer Elan 6100, ICP-mass spectrometer.[+] Each experiment was run in duplicate and the displayed values are an average of the two experiments.

[+] Samples were shaken for 20 h, to ensure equilibrium was reached in all systems.

3. Ligand Basicity Studies

Due to the limited availability of compounds **33-34** (<5 mg) and their limited solubility in binary and ternary water containing solvent systems, the ligand basicity studies were implemented in deuterated methanol. For the purposes of this study, the relative pKa values of ligands **3** and **33- 34** were deemed sufficient to quantify the effects of 4,7-functionalisation on ligand basicity. Prior to implementing the devised procedure to compounds **3** and **32-33**, the methodology was validated using commercially available neocuproine. During this validation, the pKa value of neocuproine was determined in both MeOD: D_2O (v:v) and neat MeOD, with a difference of 0.6 pKa units being recorded between the two systems. This confirms that the observed pKa values fall within reasonable range of the absolute pKa values. The use of a pH meter to provide an approximation of the pD was deemed appropriate following this validation. The measured pD values were uncorrected in this instance due to the non-aqueous solvent composition.[8]

3.1 General Procedure for Ligand Basicity Measurements

Sample Preparation

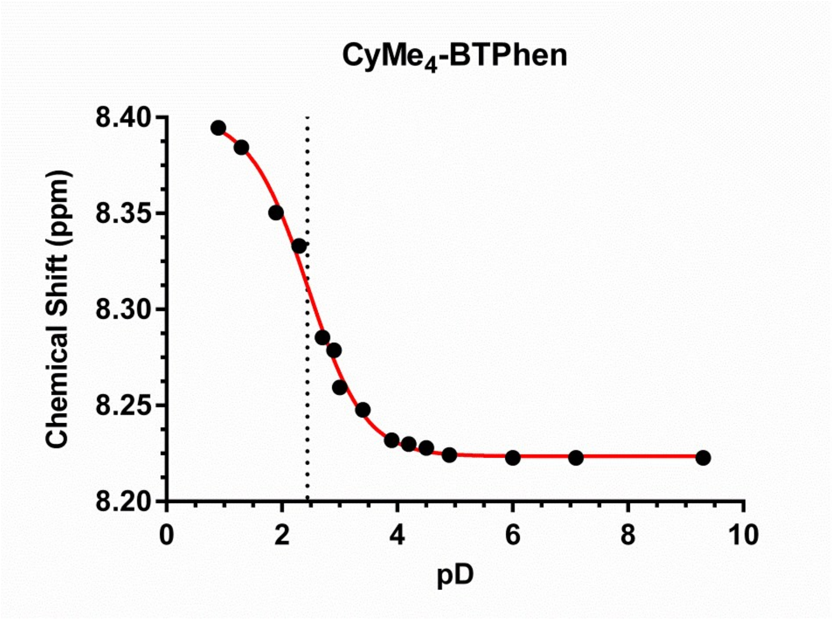
Stock solution of ligands **3** and **33-34** in deuterated methanol (0.2 mM) were prepared. The solutions were aliquoted into 1 mL samples and the pD of each was adjusted through the addition of aqueous solutions of NaOD and DCl (0.1, 0.5 and 4 M). pD values were recorded using a Hamilton® Spintode pH probe in combination with a Mettler Toledo Seven Compact pH meter. Prior to potentiometric titration, the pH apparatus was calibrated using pH 4.00 ± 0.01, 7.00 ± 0.01 and 10.00 ± 0.01 buffer solutions. In the range of the predicted pKa values, smaller pD intervals were utilised. Once titrated, all samples were transferred to 5 mm NMR tubes.

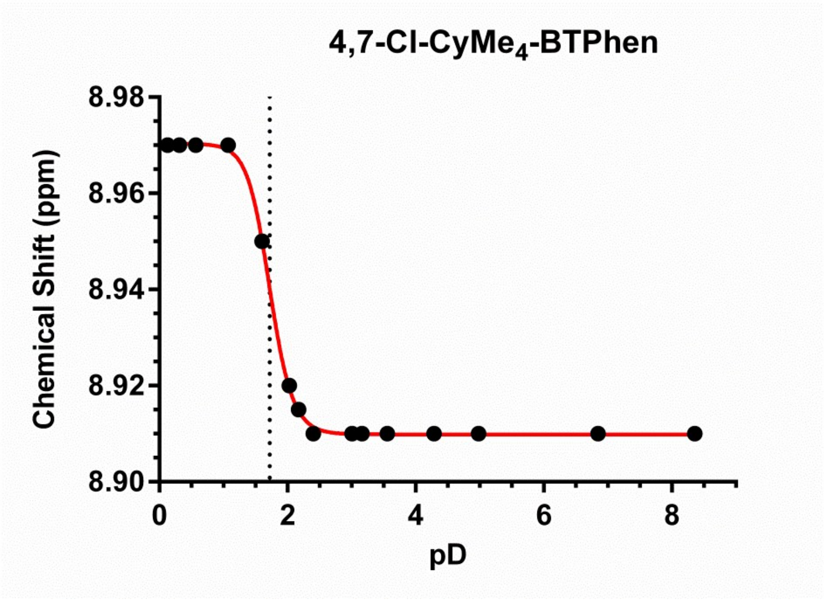
^{1}H NMR Experiments

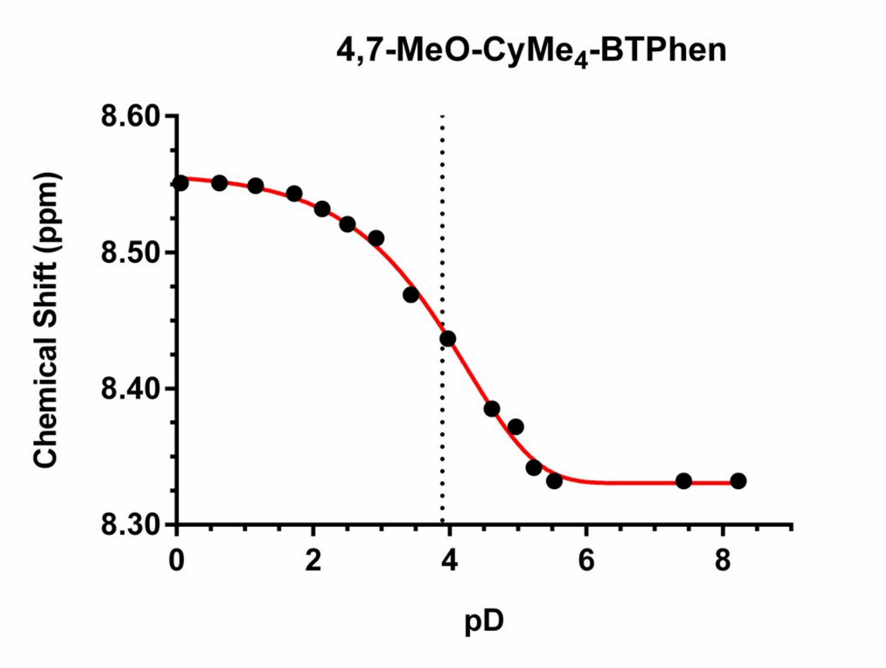
NMR experiments were implemented on a Bruker Avance III 500 MHz spectrometer with Prodigy smart probe. The temperature of the sample was regulated at 298 K. ^{1}H NMR spectra were recorded using WATERGATE to suppress residual OH signals (Bruker pulse sequence *zgesgp*), excitation sculpting used 2 ms rectangular pulses and two pairs of 1 ms half-sine gradients with amplitudes of 0.16 T m^{-1} and 0.06 T m^{-1} respectively. The gradient recovery delay was 0.2 ms. 64 transients were collected for each sample with 65536 complex points per transient with an acquisition time of 3.17 s and an inter-scan delay of 2.4 s. Spectra were processed using 0.3 Hz Lorentzian weighting, were zero-filled once and referenced to the residual methanolic solvent signal at 3.31 ppm.

3.2 Inflection Point Analysis

Plotting the recorded chemical shifts (δ) of the aromatic reporter protons *vs* pD yielded a series of Sigmoidal curves. Non-linear curve fitting of the Sigmoidal plots was implemented using Graphpad Prism® 6. pKa values were recorded as the inflection point of the resulting curves. The plots obtained for compounds **3, 33** and **34** are provided below:

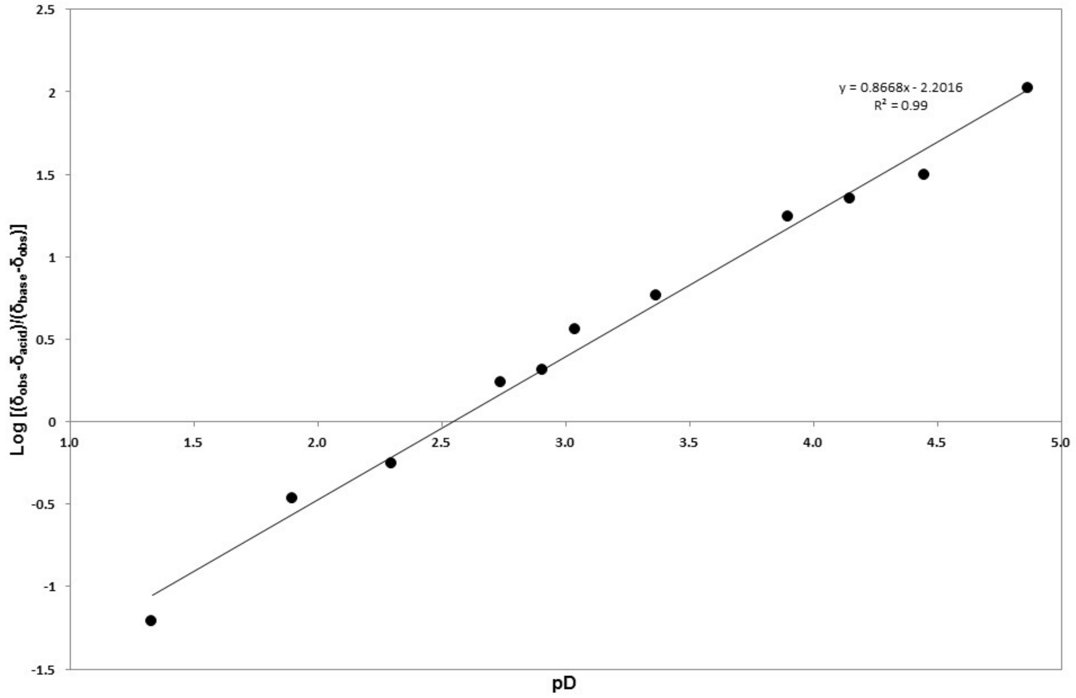




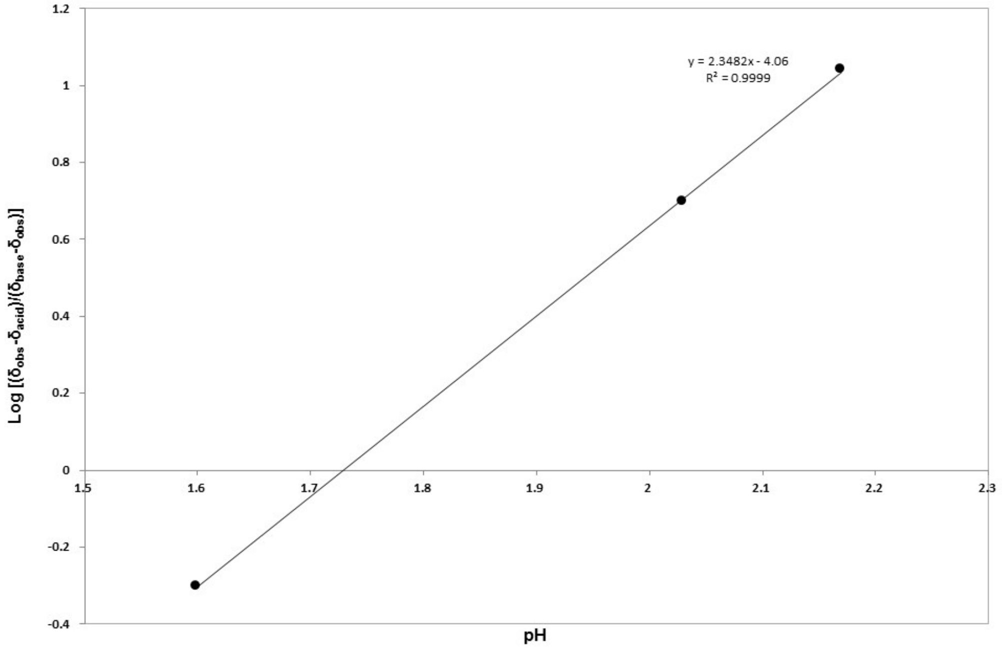

4,7-MeO-CyMe4-BTPhen
Chemical Shift (ppm)
8.60
8.50
8.40
8.30
0
2
4
6
8
pD

3.3 Henderson-Hasselbalch (H-H) Analysis

CyMe$_4$-BTPhen (3)



4,7-Cl-CyMe$_4$-BTPhen (33)



4. Time Resolved Laser Fluorescence Spectroscopy (TRLFS)

TRLFS Setup

The TRLFS setup consisted of a Nd:YAG laser (Continuum Surelite Laser, 10 Hz) pumping a dye laser system (NARROWscan D-R Dye Laser). For the excitation of Cm(III) a wavelength of 396.6 nm was used. Spectral decomposition was performed by a spectrograph (Shamrock 303i) with 1199 lines mm^{-1} grating. The spectra were recorded by an ICCD camera (iStar Gen III, ANDOR). Using the integrated delay controller a delay of 1 µs between excitation and measurement was used to discriminate scattering light and short lived fluorescence of organic compounds.

TRLFS Sample Preparation

TRLFS samples were prepared analogously to Bremer *et al.* by dissolving 4.7 µl of Cm(III) stock solution ($2.12 \cdot 10^{-5}$ M in 16.7 mM $HClO_4$) in 988 µl EtOH, 7.5 µl conc. $HClO_4$.[9] Ethanol was used due to the higher solubility of **33** and **34** in comparison to MeOH which was used by Bremer *et al.*

Ligand solutions were prepared using a solvent consisting of 988 µl EtOH, 7.5 µl conc. $HClO_4$ and 4.7 µl water. 3.13 mg **33** were dissolved in 3 ml of the solvent to obtain a stock solution containing 1.67 mM of **33**. Using a dilution (1:10) of the stock solution the ligand concentration in the TRLFS sample was adjusted to 3.3×10^{-7} M. Solutions containing **34** were prepared by dissolving 6.18 mg of ligand in 1 ml of solvent resulting in a concentration of 10 mM and subsequent dilution to 10^{-4} M. This diluted solution was used to prepare the TRLFS sample of **33** with a concentration of 2×10^{-7} M.

REFERENCES

(1) Vreelandl, T.; Newkome, G.; Kiefer, G.; Puckett, W. . *J. Am. Chem. Soc.* **1983**, No. 7, 5112.

(2) Mäkelä, M.; Zhang, L.; Zetterberg, K.; Hansson, S. *Synth. Commun.* **1992**, *22* (March 2015), 2811.

(3) Lewis, F. W.; Harwood, L. M.; Hudson, M. J.; Drew, M. G. B.; Desreux, J. F.; Bouslimani, N.; Modolo, G.; Wilden, A.; Sypula, M.; Vu, T.; Simonin, J. *J. Am. Chem. Soc.* **2011**, *133*, 13093.

(4) Larsen, A. F.; Ulven, T. *Org. Lett.* **2011**, *13* (13), 21.

(5) Altman, R. A.; Buchwald, S. L. *Org. L* **2006**, *8* (13), 2779.

(6) Society, A. C. *Reagent Chemicals: Specifications and Procedures : American Chemical Society Specifications, Official from January 1, 2006*; Oxford University Press, 2006.

(7) Evangelista, R. A.; Pollak, A. 1,10-phenanthroline-2,9-dicarboxylic acid-derivatives and their use in fluorescent immunoassay. EP0171978, February 19, 1986.

(8) Popov, K.; Rönkkömäki, H.; Lajunen, L. H. J. *Pure Appl. Chem.* **2006**, *78* (3), 663.

(9) Bremer, A.; Whittaker, D. M.; Sharrad, C.; Geist, A.; Panak, P. J. *Dalton Trans.* **2013**, *43* (6), 2684.