Electronic Supplementary Material (ESI) for Dalton Transactions.

Synthesis of functionalized BTPhen derivatives - effects on solubility and americium extraction

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Supplementary Information

Complex Matrix $SF_{Am/Eu}$ calculated results (by gamma spectroscopy)

Results calculated from D_{Am}/D_{Eu} data as shown by Lewis *et al* in reference 17 in the manuscript

Ligand	$SF_{Am/Eu}$
$CyMe_4BTPhen$	350
4,4-F_2-benzil-BTPhen **18**	32
4,4-Cl_2-benzil-BTPhen **15**	90
4,4-Br_2-benzil-BTPhen **19**	153
3,3-$(MeO)_2$-benzil-BTPhen **16**	75
4,4-$(MeO)_2$-Benzil-BTPhen **17**	252
4,4-Me_2-benzil-BTPhen **20**	95

Table 1. $SF_{Am/Eu}$ from separation of complex matrix using benzil-BTPhen ligands

Complex Nuclear Matrix Separations with Benzil-BTPhens

The most promising benzil-BTPhens (omitting benzil-BTPhen and 2,2-Cl_2-benzil-BTPhen) were screened for Am extraction from more complex matrices containing competing ions expected to be encountered in reprocessing. A solution was generated containing all lanthanides (except Pm) and Sr, Y, Cs, Ba as fission products, and extraction was carried out using each of the ligands in the same procedure as above. The $SF_{Am/Eu}$ results were comparable to those obtained in the Am/Eu separations above for all ligands (see Supplementary Information). Recovery of the matrix elements was determined post-extraction by ICP-MS (Table 7).

Although recoveries for the matrix elements were typically high, the data shows most ligands are co-extracting one or more elements. 4,4-$(MeO)_2$-Benzil-BTPhen, which has the best separation factor for Am/Eu, co-extracts ~10-15% of all matrix elements and therefore would not be a viable ligand for selective Am extraction, as high decontamination factor (>1000) could not be achieved. The 4,4-Cl_2, 4,4-Br_2 and 4,4-Me_2-benzil-BTPhens also show co-extraction of the lanthanide ions (~10%). 3,3-$(MeO)_2$-benzil-BTPhen shows high recoveries of the matrix elements (>93% in all cases) but the lack of Am selectivity is still a concern. 4,4-F_2-benzil-BTPhen showed the lowest co-extraction of matrix elements, but this may reflect slow extraction kinetics, so that the longer experiments which would be required for high Am recovery might also be expected to result in more co-extraction.

Table 2: Percentage recovery for matrix elements from separation of complex matrix using benzil-BTPhen, determined by ICP-MS mean ± 1 σ, n = 3).

Ligand	^{88}Sr	^{89}Y	^{133}Cs	^{137}Ba	^{139}La	^{140}Ce
4,4-F_2-benzil-BTPhen **18**	96.7 ± 1.1	95.6 ± 0.5	99.9 ± 1.0	99.9 ± 0.7	98.2 ± 0.5	97.6 ± 0.7
4,4-Me_2-benzil-BTPhen **20**	91.6 ± 1.3	95.6 ± 0.8	95.5 ± 1.0	94.8 ± 0.8	93.5 ± 0.7	93.0 ± 0.8
4,4-$(MeO)_2$-Benzil-BTPhen **17**	86.2 ± 1.5	95.6 ± 0.9	89.9 ± 0.9	88.9 ± 0.8	87.7 ± 0.9	87.7 ± 0.7
4,4-Br_2-benzil-BTPhen **19**	88.8 ± 1.7	95.6 ± 0.9	92.5 ± 1.2	91.8 ± 0.8	90.4 ± 0.9	90.3 ± 0.7
4,4-Cl_2-benzil-BTPhen **15**	91.8 ± 1.6	95.6 ± 0.7	95.4 ± 1.1	95.0 ± 0.8	93.5 ± 0.7	93.0 ± 0.6
3,3-$(MeO)_2$-benzil-BTPhen **16**	94.6 ± 1.3	95.5 ± 1.4	98.3 ± 1.2	98.3 ± 0.8	96.6 ± 0.7	95.9 ± 0.6

Ligand	^{141}Pr	^{146}Nd	^{147}Sm	^{157}Gd	^{159}Tb	^{163}Dy
4,4-F_2-benzil-BTPhen **18**	99.5 ± 0.7	99.1 ± 0.8	98.6 ± 0.9	97.8 ± 0.9	98.1 ± 0.9	97.2 ± 1.2
4,4-Me_2-benzil-BTPhen **20**	94.5 ± 0.8	88.2 ± 0.9	94.0 ± 0.7	93.1 ± 0.9	93.0 ± 0.9	92.2 ± 1.1
4,4-$(MeO)_2$-Benzil-BTPhen **17**	89.2 ± 0.9	86..4 ± 0.8	88.6 ± 0.8	87.5 ± 0.9	87.6 ± 0.9	86.7 ± 1.0
4,4-Br_2-benzil-BTPhen **19**	91.9 ± 1.0	85.0 ± 1.0	90.7 ± 0.7	90.6 ± 0.8	90.3 ± 0.8	89.5 ± 1.0
4,4-Cl_2-benzil-BTPhen **15**	95.1 ± 0.9	98.8 ± 0.9	93.7 ± 0.9	93.5 ± 0.9	93.7 ± 0.9	92.6 ± 1.0
3,3-$(MeO)_2$-benzil-BTPhen **16**	97.8 ± 0.7	95.5 ± 0.9	96.6 ± 0.6	96.6 ± 0.9	96.5 ± 0.9	95.6 ± 1.1

Ligand	^{165}Ho	^{166}Er	^{169}Tm	^{172}Yb	^{175}Lu
4,4-F_2-benzil-BTPhen **18**	98.4 ± 0.8	97.9 ± 0.9	95.5 ± 0.8	94.7 ± 1.0	97.2 ± 0.9
4,4-Me_2-benzil-BTPhen **20**	93.6 ± 0.8	92.7 ± 0.9	90.5 ± 0.9	90.1 ± 0.9	92.6 ± 0.8
4,4-$(MeO)_2$-Benzil-BTPhen **17**	88.0 ± 0.8	86.9 ± 0.8	84.7 ± 0.8	84.7 ± 0.9	86.7 ± 0.8
4,4-Br_2-benzil-BTPhen **19**	90.7 ± 0.6	89.7 ± 0.8	87.3 ± 0.7	87.4 ± 0.9	89.3 ± 0.7
4,4-Cl_2-benzil-BTPhen **15**	93.6 ± 0.7	92.8 ± 0.8	90.2 ± 0.6	90.5 ± 0.8	92.6 ± 0.8
3,3-$(MeO)_2$-benzil-BTPhen **16**	96.6 ± 0.8	96.1 ± 0.8	93.2 ± 0.8	93.5 ± 0.9	95.9 ± 0.8

BTPhen ligand Am (III) extraction versus time

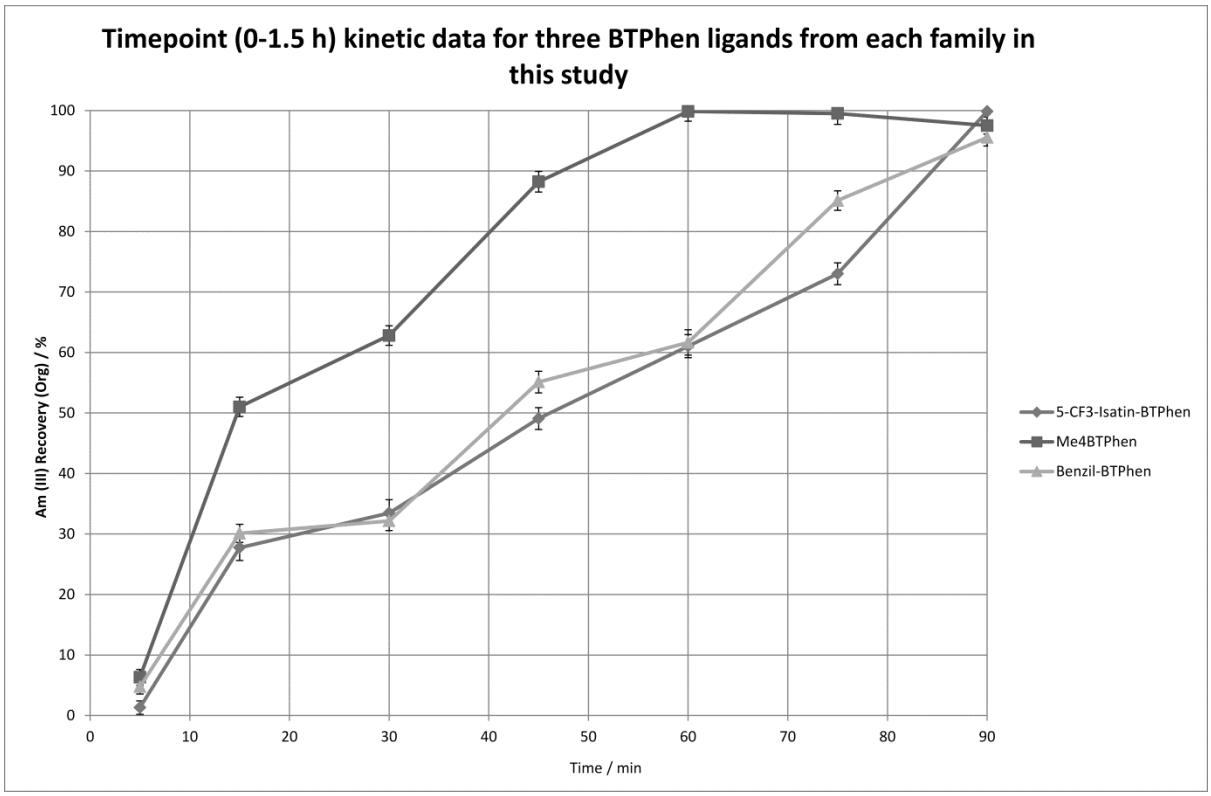

Figure 1. Extraction recovery (Am III) versus time for three BTPhen ligands from this study determined by gamma spectroscopy.

A ligand from each family was taken and Am (III) extraction as a function of time (5-90 min) in 3 M HNO_3 was determined using gamma spectroscopy. The three ligands (Me_4BTPhen, 5-CF_3-Isatin-BTPhen and Benzil-BTPhen) were shown to almost quantitatively extract Am (III) from solution within 1.5 h and the results show that Me_4BTPhen has the fastest kinetics with the isatin and benzil BTPhens showing markedly similar kinetic profiles. Again, the Eu (III) co-extraction is the factor that reduces observed separation factors. The results also show that 1.5 h is suitable for equilibrium studies between the three ligand families The effect on the kinetics is an indicator that design of these ligands could potentially improve this problem in future extractants. Furthermore it appears the lower molecular weight/smaller ligands appear to have faster kinetics overall which could influence the design of future extractants.

BTPhen ligand experimental data

2,9-bis(9H-[1,2,4]triazino[6,5-b]indol-3-yl)-1,10-phenanthroline (2)

Bright orange solid (200 mg, 56 %); m.p.= 192 °C; R_f = 0.70 (92:8 DCM: MeOH); IR (ν_{max} / cm^{-1}): 3441 (N-H), 2888, 2815 (C-H Ar), 1614 (C=N), 1330 (C-N); MS (ES^+) found *m/z* 597.4 $[M+H+DMSO]^+$, HRMS found *m/z* 517.1604 $[M+H]^+$ requires 517.1632; δ_H (400 MHz, DMSO-d_6) 11.05 (2 H, s, N*H*), 8.81 (2 H, d, *J* = 7.8 Hz, Ar*H*), 8.49 (2 H, d, *J* = 7.3 Hz, Ar*H*), 8.24 (2 H, d, J = 7.2 Hz, Ar*H*), 7.95 (2 H, s, Ar*H*), 7.59 (2 H, t, *J* = 7.8 Hz, Ar*H*), 7.51 (2 H, d, *J* = 8.1 Hz, Ar*H*), 7.07 (2 H, t, *J* = 7.9 Hz, Ar*H*) ppm; δ_C (101 MHz, DMSO-d_6) 184.7, 159.8, 151.2, 146.5, 142.3, 138.8, 138.4, 130.7, 125.2, 124.9, 123.2, 118.3, 112.7 ppm.

2,9-bis(8-fluoro-9H-[1,2,4]triazino[6,5-b]indol-3-yl)-1,10-phenanthroline (3)

Red/orange solid (120 mg, 31 %); m.p.= 179 °C; R_f = 0.60 (92:8 DCM: MeOH); IR (ν_{max} / cm^{-1}): 3444 (N-H), 3093, 3061 (C-H Ar), 1637 (C=N), 1325 (C-N), 1206 (C-F); MS (ES^+) found *m/z* 386.5 [M/2 + halo exchange]$^+$, HRMS found *m/z* 553.1065 $[M+H]^+$ requires 553.1044; δ_H (400 MHz, DMSO-d_6) 11.57 (2 H, s, N*H*), 8.35 (2 H, d, *J* = 7.3 Hz, Ar*H*), 8.29 (2 H, d, *J* = 7.1 Hz, Ar*H*), 8.26 (2 H, s, Ar*H*), 7.80 (2 H, d, *J* = 7.3 Hz, Ar*H*), 7.58–7.50 (2 H, m, Ar*H*), 7.38 (2 H, d, *J* = 7.3 Hz, Ar*H*) ppm. δ_C (101 MHz, DMSO-d_6) 183.7, 159.7, 154.9, 152.8, 148.9, 146.5, 137.9, 137.8, 125.3, 125.1, 123.8, 121.1, 118.7 ppm.

2,9-bis(8-chloro-9H-[1,2,4]triazino[6,5-b]indol-3-yl)-1,10-phenanthroline (4)

Red solid (90 mg, 21 %); m.p.= 184 °C; R_f = 0.85 (92:8 DCM: MeOH); IR (ν_{max} / cm^{-1}): 3475 (N-H), 3169, 3075 (C-H Ar), 1611 (C=N), 1317 (C-N), 775 (C-Cl); MS (ES^-) found *m/z* 604.7 $[M + Na – 2H]^+$, HRMS found *m/z* 585.0852 $[M+H]^+$ requires 585.0853; δ_H (400 MHz, DMSO-d_6) 11.47 (2 H, s, N*H*), 8.41 (2 H. d, *J* = 8.3 Hz, Ar*H*), 8.26 (2 H, d, *J* = 8.3 Hz, Ar*H*), 8.08 (2 H, s, Ar*H*), 7.67 (2 H, dd, *J* = 8.2 Hz, Ar*H*), 7.49 (2 H, d, *J* = 7.3 Hz, Ar*H*), 7.10 (2 H, t, J = 7.4 Hz, Ar*H*) ppm. δ_C (101 MHz, DMSO-d_6) 183.9, 166.9, 160.1, 148.2, 142.7, 141.5, 137.9, 132.2, 124.2, 123.6, 120.4, 119.4, 116.6 ppm.

2,9-bis(8-bromo-9H-[1,2,4]triazino[6,5-b]indol-3-yl)-1,10-phenanthroline (5)

Orange solid (240 mg, 52 %); m.p.= 177 °C; R_f = 0.79 (92:8 DCM: MeOH); IR (ν_{max} / cm^{-1}): 3455 (N-H), 3176, 3104 (C-H Ar), 1609 (C=N), 1314 (C-N), 686 (C-Br); HRMS Accurate found *m/z* 687.6647 $[M+NH_4]^+$ requires 687.6682; δ_H (400 MHz, DMSO-d_6) 11.30 (2H, s, N*H*), 8.52 (2 H, d, *J* = 8.0 Hz, Ar*H*), 8.08 (2 H, s, Ar*H*), 7.66–7.55 (4 H, m, Ar*H*), 7.52 (2 H, dd, *J* = 7.3 Hz Ar*H*), 7.03 (2H, t, *J* = 8.1 Hz, Ar*H*) ppm δ_C (101 MHz, DMSO-d_6) 184.1, 160.2, 149.9, 140.8, 137.2, 134.2, 124.6, 124.0, 120.6, 116.0, 105.1, 45.9, 9.0 ppm.

2,9-bis(6-fluoro-9H-[1,2,4]triazino[6,5-b]indol-3-yl)-1,10-phenanthroline (6)

Orange solid (160 mg, 43 %); m.p.= 244 °C; IR (ν_{max} / cm^{-1}): 3308 (N-H), 3078, 2861 (C-H Ar), 1621 (C=C), 1142 (C-F); HRMS found *m/z* 553.1404 $[M+H]^+$ requires 553.1449; δ_H (400 MHz, DMSO-d_6) 11.08 (2 H, s, N*H*), 8.85–8.81 (2 H, m, Ar*H*), 8.79–8.75 (2 H, m, Ar*H*), 8.24 (2 H, s, Ar*H*) 7.49–7.37 (4 H, m, Ar*H*), 6.95–6.90 (2 H, d, J = 8.3 Hz, Ar*H*) ppm. δ_C (101 MHz, DMSO-d_6) 184.4, 159.9, 159.7, 157.4, 153.6, 147.4, 137.1, 125.1, 124.8, 119.0, 113.9, 111.9, 111.7, 109.9 ppm.

2,9-bis(6-chloro-9H-[1,2,4]triazino[6,5-b]indol-3-yl)-1,10-phenanthroline (7)

Orange solid (130 mg, 33 %); m.p.= 217 °C; R_f = 0.73 (92:8 DCM: MeOH); IR (ν_{max} / cm^{-1}): 3440 (N-H), 3091, 3065, 2986 (C-H Ar), 1615 (C=C), 1167 (C-N), 705 (C-Cl); HRMS *m/z* found 585.0803 $[M+H]^+$ requires 585.0858; δ_H (400 MHz, DMSO-d_6) 11.11 (2 H, s, N*H*), 8.85 (2 H, d, *J* = 8.6 Hz, Ar*H*), 8.72 (2 H, d, *J* = 8.3 Hz, Ar*H*), 8.24 (2 H, s, Ar*H*), 7.62 (2 H, d, *J* = 8.6 Hz, Ar*H*), 7.56 (2 H, s, Ar*H*), 6.93 (2 H, d, *J* = 8.3 Hz, Ar*H*) ppm. δ_C (101 MHz, DMSO-d_6) 183.8, 159.6, 159.3, 149.7, 145.7, 137.7, 131.9, 127.2, 124.6, 119.6, 119.4, 114.3, 111.55 ppm.

2,9-bis(6-bromo-9H-[1,2,4]triazino[6,5-b]indol-3-yl)-1,10-phenanthroline (8)

Red solid (121 mg, 26 %); m.p.= 190 °C**;** R_f = 0.63 (92:8 DCM: MeOH); IR (ν_{max} / cm^{-1}): 3435 (N-H), 3286, 3154, 2918 (C-H Ar), 1616 (C=C), 1140 (C-N), 609 (C-Br); HRMS found *m/z* 775.2536 $[M+Na+DMSO]^+$ requires 775.2510; δ_H (400 MHz, DMSO-d_6) 10.94 (2 H, s, N*H*), 8.79 (2 H, d, *J* = 5.8 Hz, Ar*H*), 8.74–8.70 (2 H, m Ar*H*), 8.64 (2 H, s, Ar*H*), 8.29 (2 H, s, Ar*H*), 7.40 (2 H, d, *J* = 7.8 Hz, Ar*H*), 7.18 (2 H, d, *J* = 7.8 Hz) ppm. δ_C (101 MHz, DMSO-d_6) 185.1, 166.2, 163.3, 159.9, 149.0, 141.9, 139.2, 138.3, 132.5, 128.4, 125.3, 118.2, 112.5 ppm.

2,9-bis(6-iodo-9H-[1,2,4]triazino[6,5-b]indol-3-yl)-1,10-phenanthroline (9)

Purple solid (180 mg, 34 %); m.p.= 155-157 °C; R_f= 0.64 (92:8 DCM: MeOH); IR (ν_{max} / cm^{-1}): 3455 (N-H), 3224, 3093 (C-H Ar), 1602 (C=N), 1382 (C-N), 595 (C-I); HRMS found *m/z* 768.5368 $[M+H]^+$ requires 768.5313; δ_H (400 MHz, DMSO-d_6) 11.21 (2 H, s, N*H*), 7.91–7.76 (8 H, m, Ar*H*), 6.76 (2 H, d, *J* = 8.6 Hz, Ar*H*), 5.76 (2 H, s, Ar*H*) ppm. δ_C (101 MHz, DMSO-d_6) 183.5, 159.2, 151.6, 150.4, 146.2, 137.1, 132.9, 125.3, 120.4, 115.1, 112.3, 96.6, 85.9 (I-*C*) ppm.

2,9-bis(6-nitro-9H-[1,2,4]triazino[6,5-b]indol-3-yl)-1,10-phenanthroline (10)

Brown solid (50 mg, 11 %); R_f = 0.75 (92:8 DCM: MeOH); IR (ν_{max} / cm^{-1}): 1547 (N-O), 1363 (N-O); HRMS found *m/z* 607.9985 $[M+H]^+$ requires 607.9939; δ_H (400 MHz, MeOH-d_4) 8.39–8.32 (2 H, m, Ar*H*), 8.17 (1 H, dd, *J* = 9.46, Ar*H*), 8.14–8.04 (1 H, m, Ar*H*), 7.64–7.53 (1 H, m, Ar*H*), 7.42 (1 H, d, *J* = 8.07 Hz), 7.38–7.28 (1 H, m, Ar*H*), 7.17–7.04 (1 H, m, Ar*H*) 7.00–6.88 (2 H, m, Ar*H*) 6.80 (1 H, d, *J* = 9.33 Hz, Ar*H*) 6.72–6.65 (1 H, m,

Ar*H*) ppm. δ_C (101 MHz, MeOH-d_4) 139.8, 138.3, 134.3, 130.0, 129.7, 129.1, 128.2, 126.3, 124.7, 123.1, 122.2, 117.3, 116.3 ppm.

2,9-bis(6-methyl-9H-[1,2,4]triazino[6,5-b]indol-3-yl)-1,10-phenanthroline (11)

Orange solid (150 mg, 41 %); m.p.= 237 ^oC; IR (ν_{max} / cm^{-1}): 3432 (N-H), 3195, 2995 (C-H Ar), 1611 (C=C); MS (ES^+) found *m/z* 545.6 $[M+H]^+$, HRMS found *m/z* 545.1970 $[M+H]^+$ requires 545.1951; δ_H (400 MHz, DMSO-d_6) 11.11 (2 H, s N*H*), 9.11–8.10 (4 H, m, Ar*H*), 8.04–6.47 (8 H, m, Ar*H*), 3.42 (6 H, s, 2 x CH_3) ppm. δ_C (101 MHz, DMSO-d_6) 159.1, 155.8, 150.0, 140.6, 140.5, 136.2, 135.5, 127.7, 127.6, 127.4, 127.4, 120.1, 116.7, 114.7, 24.8 ppm.

2,9-bis(6-(trifluoromethoxy)-9H-[1,2,4]triazino[6,5-b]indol-3-yl)-1,10-phenanthroline (12)

Bright red solid (210 mg, 45 %); R_f = 0.61 (92:8 DCM: MeOH); IR (ν_{max} / cm^{-1}): 3404 (N-H), 1656 (N-H), 1255 (C-O), 997 (C-F); MS (ES^+) found *m/z* 721.3 $[M+H+K]^+$, HRMS found *m/z* 687.3612 $[M + 3H]^+$ requires 687.3611; δ_H (400 MHz, DMSO-d_6) 11.29 (2 H, s, N*H*), 7.59 (2 H, d, *J* = 8.3 Hz, Ar*H*), 7.52 (2 H, s, Ar*H*), 7.45 (2 H, s, Ar*H*), 7.40 (2 H, m, Ar*H*), 7.02 (2 H, d *J* = 8.3 Hz, Ar*H*), 6.81 (2 H, d, *J* = 8.1 Hz, Ar*H*) ppm. δ_C (101 MHz, DMSO-d_6) 183.9, 159.9, 151.2, 150.0, 143.8, 136.8, 131.4, 128.0, 125.9, 124.4, 121.8, 119.1, 118.2, 113.9 ppm; δ_F (400 MHz, DMSO-d_6) -57.6 (3 F, s, CF_3) ppm.

2,9-bis(5,8-dichloro-9H-[1,2,4]triazino[6,5-b]indol-3-yl)-1,10-phenanthroline (13)

Orange solid (210 mg, 48 %); m.p.= 232 ^oC; R_f = 0.67 (92:8 DCM: MeOH); IR (ν_{max} / cm^{-1}): 3449 (N-H), 1665 (N-H), 1606 (C=N), 1164 (C-N), 655 (C-Cl), 622 (C-Cl), 595 (C-Cl); MS (ES^-) found *m/z* 689.2 $[M-H+Cl]^+$, HRMS found *m/z* 663.4526 $[M-H+Cl]^+$ requires 663.4546; δ_H (400 MHz, DMSO-d_6) 11.37 (2 H, s, N*H*), 7.65 (2 H, d, *J* = 8.6 Hz, Ar*H*), 7.26 (2 H, d, *J* = 8.3 Hz, Ar*H*), 7.82 (2 H, d, *J* = 8.8 Hz, Ar*H*), 7.09 (2 H, d, *J* = 8.6 Hz, Ar*H*), 6.39 (2 H, s, Ar*H*) ppm. δ_C (101 MHz, DMSO-d_6) 183.7, 180.8, 159.4, 149.5, 144.9, 138.2, 131.2, 129.9, 124.8, 117.1, 115.3, 113.9, 55.4 ppm.

2,9-bis(5,6-diphenyl-1,2,4-triazin-3-yl)-1,10-phenanthroline (14)

Yellow solid (100 mg, 23 %); m.p.= 182 ^oC; R_f 0.50 (92:8 DCM: MeOH); IR (ν_{max} / cm^{-1}): 3057, 2927 (C-H Ar), 1618 (C=N), 1551 (C=C);MS (ES^+) found *m/z* 662.8 $[M+(K^+$ to $NH_4^+)]^+$, HRMS found *m/z* 643.5410 $[M+H]^+$ requires 643.5421; δ_H (400 MHz, DMSO-d_6) 9.01–8.63 (2 H, m, Ar*H*), 8.53 (2 H, s, Ar*H*), 8.30–8.05 (2 H, m, Ar*H*), 7.97–7.92 (8 H, m, Ar*H*), 7.78–7.58 (8 H, m, Ar*H*), 7.58–7.26 (4 H, m, Ar*H*) ppm. δ_C (101 MHz, DMSO-d_6) 178.7, 167.8, 161.0, 145.2, 133.1, 130.3, 129.9, 129.1, 128.8, 128.5, 126.4, 119.4 ppm.

2,9-bis(5,6-bis(4-chlorophenyl)-1,2,4-triazin-3-yl)-1,10-phenanthroline (15)

Yellow solid (100 mg, 18 %); m.p.= 239-242 ^{o}C; R_f = 0.90 (92:8 DCM: MeOH); IR (ν_{max} / cm^{-1}): 3058, 2927 (C-H Ar), 1505 (C=C), 648, 639, 619, 608 (C-Cl); HRMS found *m/z* 779.0768; δ_H (400 MHz, DMSO-d_6) 7.91–7.70 (11 H, m, Ar*H*), 7.40–7.28 (11 H, m, Ar*H*) ppm; δ_C (101 MHz, DMSO-d_6) 188.0, 162.9, 161.5, 159.6, 157.4, 153.1, 131.6, 131.5, 128.5, 115.4, 115.1 ppm.

2,9-bis(5-(3-methoxyphenyl)-6-(m-tolyl)-1,2,4-triazin-3-yl)-1,10-phenanthroline (16)

Yellow solid (130 mg, 25 %); m.p.= 192 ^{o}C; IR (ν_{max} / cm^{-1}): 3076, 3011, 2966 (C-H Ar), 1666 (C=C), 1303 (C-N), 1031 (C-O); MS (ES^{-}) found *m/z* 778.5, HRMS found *m/z* 763.2797 [M+H]$^{+}$ requires 763.2781; δ_H (400 MHz, DMSO-d_6) 8.51 (2 H, d, *J* = 8.6 Hz, Ar*H*), 8.28–8.19 (2 H, m, Ar*H*), 7.99 (2 H, s, Ar*H*), 7.80 (8 H, d, *J* = 8.1 Hz, Ar*H*), 7.44 (8 H, d, *J* = 7.8 Hz, Ar*H*), 2.42 (12 H, s, 4 x *CH*$_3$O); δ_C (101 MHz, DMSO-d_6) 195.1, 169.9, 146.9, 135.6, 130.5, 130.1, 126.6, 118.3, 109.1, 87.7, 86.0, 79.1, 21.9 ppm.

2,9-bis(5,6-bis(4-methoxyphenyl)-1,2,4-triazin-3-yl)-1,10-phenanthroline (17)

Yellow solid (85 mg, 16 %); m.p.= 166-168 ^{o}C; R_f = 0.50 (92:8 DCM: MeOH); IR (ν_{max} / cm^{-1}): 3069, 2934 (C-H Ar), 2839 (C-H), 1603 (C=C), 1017 (C-O); HRMS found *m/z* 763.2775 [M+H]$^{+}$ requires 763.2781; δ_H (400 MHz, DMSO-d_6) 10.22 (2 H, s, Ar*H*), 8.92 (8 H, d, *J* = 3.8 Hz, Ar*H*), 8.37 (8 H, d, *J* = 2.0 Hz, Ar*H*) 8.28 (2 H, d, *J* = 9.1 Hz, Ar*H*), 8.10 (2 H, d, *J* = 9.1 Hz, Ar*H*), 7.91 (d, *J*=9.1 Hz, 1 H, Ar*H*), 7.86 (2 H, s, Ar*H*), 3.88 (12 H, s, 4 x *CH*$_3$O) ppm; δ_C (101 MHz, DMSO-d_6) 149.9, 145.4, 144.1, 134.6, 129.9, 124.2, 119.9, 108.8, 101.8, 99.8, 92.8, 91.8, 72.6 ppm.

2,9-bis(5,6-bis(4-fluorophenyl)-1,2,4-triazin-3-yl)-1,10-phenanthroline (18)

Yellow solid (95 mg, 20 %); m.p.= 246 ^{o}C; IR (ν_{max} / cm^{-1}): 3074 (C-H Ar), 1598 (C=C), 1274 (C-N), 1155 (C-F); MS (ES^{+}) found *m/z* 715 [M+H]$^{+}$, HRMS found 715.1961 [M+H]$^{+}$ requires 715.1981; δ_H (400 MHz, DMSO-d_6) 8.11–8.00 (11 H, m, Ar*H*), 7.54–7.41 (11 H, m, Ar*H*) ppm; δ_C (101 MHz, DMSO-d_6) 193.0, 167.9, 165.5, 158.6, 158.0, 154.5, 133.6, 133.5, 129.5, 117.4, 117.1 ppm.

2,9-bis(5,6-bis(4-bromophenyl)-1,2,4-triazin-3-yl)-1,10-phenanthroline (19)

Yellow solid (204 mg, 30 %); m.p.= 193-194 ^{o}C; R_f = 0.68 (92:8 DCM: MeOH); IR (ν_{max} / cm^{-1}): 1587 (C=C), 575, 562, 558, 552 (C-Br); HRMS found *m/z* 959.8737; δ_H (400 MHz, DMSO-d_6) 8.81–8.53 (8 H, d, *J* = 9.2 Hz, Ar*H*), 8.15 (2 H, s, Ar*H*), 7.86 (2 H, d, *J* = 6.8 Hz,

Ar*H*), 7.55 (2 H, s, Ar*H*), 6.97 (8 H, s, Ar*H*) ppm. δ_C (101 MHz, DMSO-d_6) 155.0, 151.3, 143.2, 139.1, 133.9, 133.1, 132.1, 131.5, 131.3, 130.5, 128.5, 125.3 ppm.

2,9-bis(5,6-di-p-tolyl-1,2,4-triazin-3-yl)-1,10-phenanthroline (20)

Yellow solid (132 mg, 28 %); m.p.= 109 ^oC; IR (ν_{max} / cm^{-1}): 3063, 3048, 2976 (C-H Ar), 1659 (C=C), 1329 (C-N); HRMS found *m/z* 699.2965 $[M+H]^+$ requires 699.2984; δ_H (400 MHz, DMSO-d_6) 8.56 (2 H, d, *J* = 8.3 Hz, Ar*H*), 8.35 (2 H, d, *J* = 7.1 Hz, Ar*H*), 8.29 (2 H, s, Ar*H*), 7.47–7.35 (16 H, m, Ar*H*), 3.38 (12 H, s, CH_3) ppm; δ_C (101 MHz, DMSO-d_6) 194.9, 160.3, 142.5, 141.3, 133.9, 131.2, 123.4, 122.4, 116.5, 113.1, 105.6, 101.9, 55.9 ppm.

4,4',4'',4'''-((1,10-phenanthroline-2,9-diyl)bis(1,2,4-triazine-3,5,6-triyl))tetrakis(N,N-dimethylaniline) (21)

Green solid (80 mg, 14 %); m.p.= 239 ^oC; IR (ν_{max} / cm^{-1}): 3011, 2917, 2829 (C-H Ar), 1581 (C=C), 1155, 1132 (C-N);MS (ES^+) found *m/z* 833.8 $[M+H/H_2O]^+$, HRMS found *m/z* 883.2365 $[M+MeOH+2H]^+$ require 883.2346; δ_H (400 MHz, DMSO-d_6) 8.41–8.37 (2 H, m, Ar*H*), 8.30 (2 H, d, *J* = 8.6 Hz, Ar*H*), 7.95 (2 H, s, Ar*H*), 7.65 (8 H, d, *J* = 9.1 Hz, Ar*H*), 6.76 (8 H, d, *J* = 9.3 Hz, Ar*H*), 3.04 (24 H, s, 8 x CH_2) ppm; δ_C (101 MHz, DMSO-d_6) 193.9, 154.7, 144.2, 143.9, 136.6, 131.9, 128.7, 126.6, 120.8, 119.5, 111.6 ppm.

2,9-bis(5,6-bis(2-chlorophenyl)-1,2,4-triazin-3-yl)-1,10-phenanthroline (22)

Yellow solid (104 mg, 19 %); m.p.= 222-232 ^oC; R_f = 0.90 (92:8 DCM: MeOH); IR (ν_{max} / cm^{-1}): 3058, 2927 (C-H Ar), 1505 (C=C), 648, 639, 620, 611 (C-Cl); HRMS found *m/z* 779.1088 $[M+H]^+$ requires 779.1035; δ_H (400 MHz, DMSO-d_6) 8.56 (2 H, d, *J*=8.6 Hz, Ar*H*), 8.15 (2 H, d, *J*=8.3 Hz, Ar*H*), 8.08 (2 H, s, Ar*H*), 7.73 (8 H, d, *J*=7.3 Hz, Ar*H*), 7.66–7.38 (8 H, m, Ar*H*) ppm; δ_C (101 MHz, DMSO-d_6) 193.4, 158.6, 149.0, 141.0, 132.6, 131.7, 130.1, 129.5, 127.3, 127.1, 118.7 ppm

2,9-bis(9H-indeno[1,2-e][1,2,4]triazin-3-yl)-1,10-phenanthroline (23)

Black solid (190 mg, 53 %); m.p.= 192 ^oC; R_f = 0.69 (92:8 DCM: MeOH); IR (ν_{max} / cm^{-1}): 3069, 2929 (C-H Ar), 1602 (C=C);MS (ES^-) found *m/z* 639.6 [M+I to H exchange]$^-$, HRMS found *m/z* 529.1647 $[M+NH_4]^+$ requires 529.1652; δ_H (400 MHz,$CDCl_3$) 8.24 (2 H, d, *J* = 8.4 Hz, Ar*H*), 8.04 (2 H, d, *J* = 8.1 Hz, Ar*H*), 7.92 (2 H, s, Ar*H*), 7.76–7.58 (6 H, m, Ar*H*), 3.42 (4 H, s, 2 x CH_2) ppm; δ_C (101 MHz, $CDCl_3$) 198.9, 171.6, 157.3, 153.9, 150.5, 150.4, 143.5, 136.6, 135.6, 134.4, 133.6, 125.2 ppm.

2,9-bis(6-ethyl-5-methyl-1,2,4-triazin-3-yl)-1,10-phenanthroline (24)

Brown oil (60 mg, 21 %); m.p.= 159 ^{o}C; R_f = 0.56 (92:8 DCM: MeOH); IR (ν_{max} / cm^{-1}): 2971, 2923 (C-H Ar), 2850 (C-H), 1619 (C=C);MS (ES$^+$) found *m/z* 559.7 [M+NaCl$_2$/CO$_2$]$^+$, HRMS found 423.2035; δ_H (400 MHz, MeOD-*d*$_4$, mixture of regioisomers) 8.99–7.55 (6 H, m, Ar*H*), 1.28–1.05 (6 H, m, 2 x C*H*$_3$), 1.05–0.99 (6 H, m, 2 x C*H*$_3$), 0.84–0.70 (4 H, m, 2 x C*H*$_2$) ppm; δ_C (101 MHz, MeOD-*d*$_4$) 136.8, 121.3, 117.6, 40.0, 31.7, 29.4, 22.3, 20.3, 13.3, 13.1, 12.8, 11.8, 7.8 ppm.

2,9-bis(5-methyl-6-propyl-1,2,4-triazin-3-yl)-1,10-phenanthroline (25)

Dark brown oil (190 mg, 58 %); R_f = 0.77 (92:8 DCM: MeOH); IR (ν_{max} / cm^{-1}): 2975, 2937 (C-H Ar), 2878 (C-H), 1619 (C=C); MS (ES$^+$) found *m/z* 243.2 [M/2+NH$_4$]$^+$, HRMS found *m/z* 451.2448 [M+H]$^+$ requires 451.2410; δ_H (400 MHz, DMSO-*d*$_6$, mixture of regioisomers) 8.80 (2 H, d, *J* = 8.3 Hz, Ar*H*), 8.65 (2 H, d, *J* = 8.3 Hz, Ar*H*), 7.96 (2 H, s, Ar*H*), 4.26 (4 H, t, *J* = 6.9 Hz, 2 x C*H*$_2$), 3.17 (6 H, s, 2 x C*H*$_3$), 2.29–2.17 (4H, m, 2 x C*H*$_2$), 0.99 (6 H, t, *J* = 6.9 Hz, 2 x C*H*$_3$) ppm; δ_C (101 MHz, DMSO-*d*$_6$) 175.7, 144.9, 112.4, 89.4, 85.6, 27.4, 26.7, 22.9, 19.3, 12.8, 9.6 ppm.

2,9-bis(5,6-diethyl-1,2,4-triazin-3-yl)-1,10-phenanthroline (26)

Dark brown oil (150 mg, 49 %); R_f = 0.50 (92:8 DCM: MeOH); IR (ν_{max} / cm^{-1}): 2962, 2934 (C-H Ar), 2873 (C-H), 1618 (C=C); MS (ES$^+$) found *m/z* 249.5 [M/2+H+Na]$^+$, HRMS found *m/z* 451.2348 [M+H]$^+$ requires 451.2345; δ_H (400 MHz, DMSO-*d*$_6$) 8.22 (2 H, d, *J* = 8.8 Hz, Ar*H*), 8.19 (2 H, d, *J* = 8.8 Hz, Ar*H*), 7.99 (2 H, s, Ar*H*), 2.26–2.15 (8 H, m, 4 x C*H*$_2$), 1.09 (12 H, t, *J* = 7.1 Hz, 4 x C*H*$_3$) ppm; δ_C (101 MHz, DMSO-*d*$_6$) 174.8, 172.5, 169.0, 42.6, 36.0, 21.7, 21.5, 18.4, 14.6, 13.9, 13.6 ppm.

Gaussian DFT calculations

Benzil-BTPhen

Staggered benzil-rings in [ML]$^{3+}$ complexes

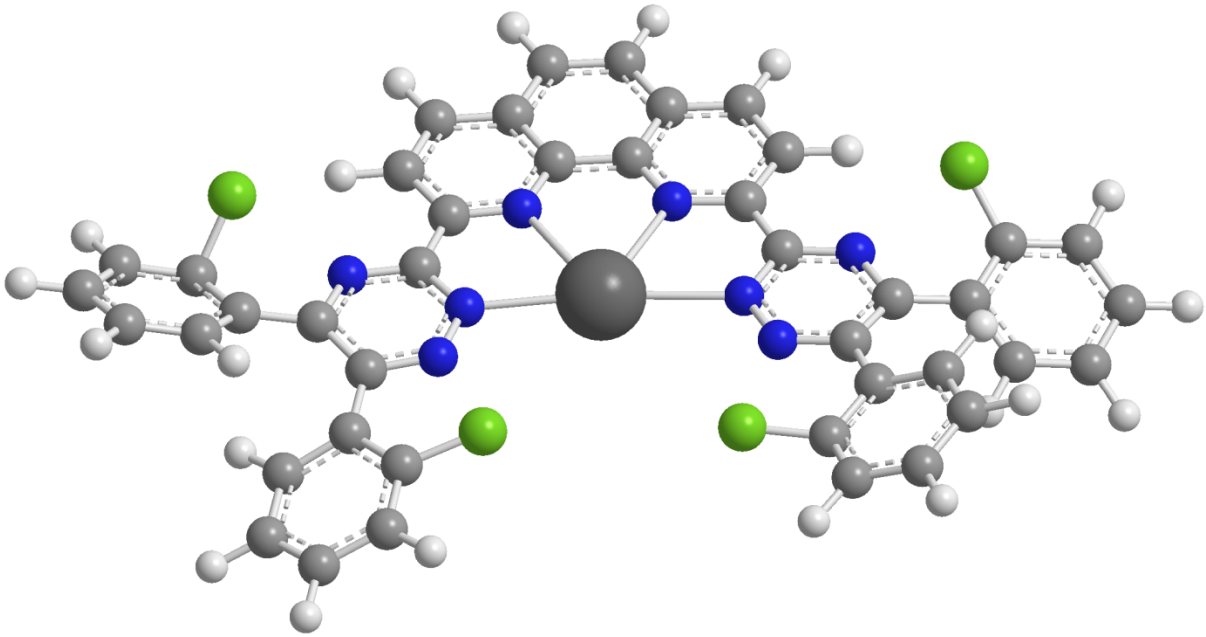

Figure 1: example minima structure with 2,2-Cl_2-benzil-BTPhen

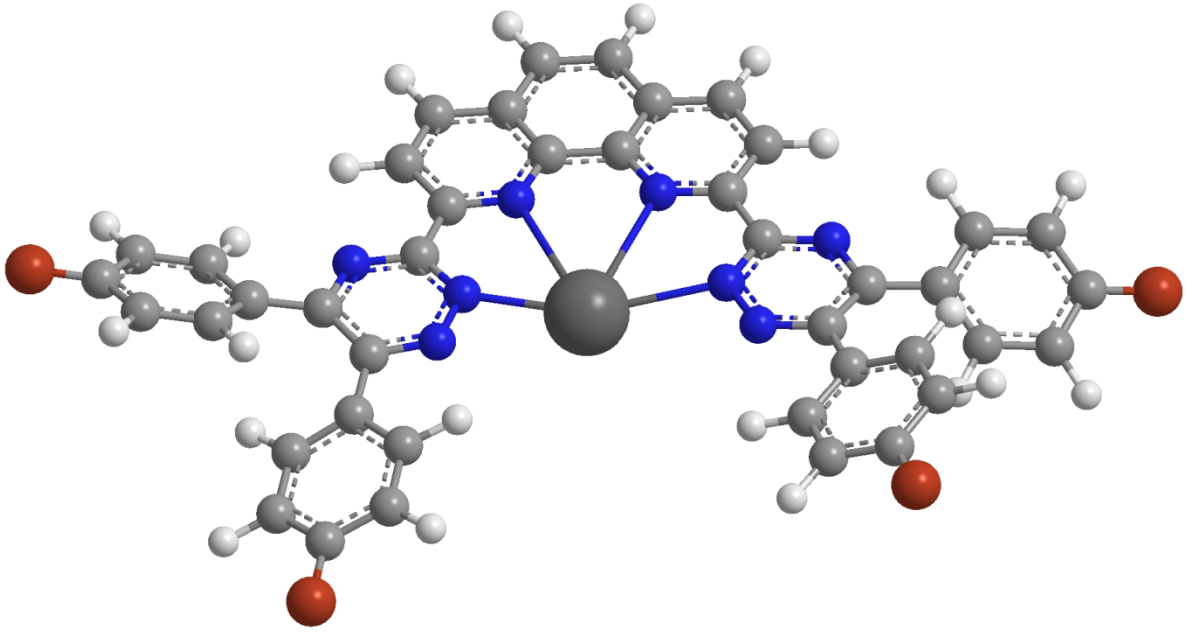

Figure 2: example minima structure with 4,4-Br_2-benzil-BTPhen

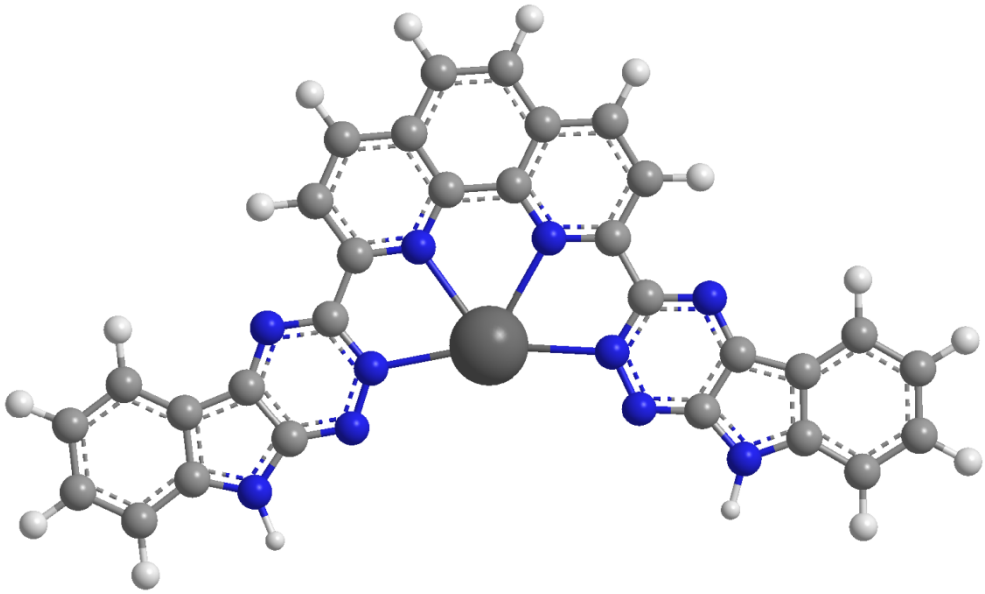

Figure 3: example minima structure with isatin-BTPhen