

ELECTRONIC SUPPLEMENTARY INFORMATION

for the paper entitled

Hydrophilic Sulfonated Bis-1,2,4-Triazine Ligands Are Highly Effective Reagents for Separating Actinides(III) from Lanthanides(III) via Selective Formation of Aqueous Actinide Complexes

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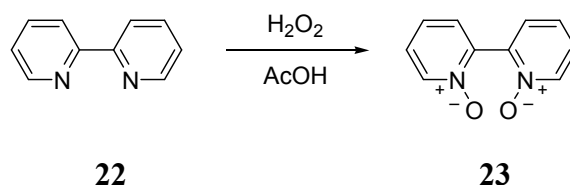
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1: Experimental Procedures

General procedures

Melting points were obtained on a Stuart SMP10 instrument. IR spectra were recorded as Nujol® mulls (N) on a Perkin Elmer RX1 FT-IR instrument. ^1H , $^{13}\text{C}\{-^1\text{H}\}$ and ^{13}C NMR spectra were recorded using either a Bruker AMX400 or an Avance DFX400 instrument. Chemical shifts are reported in parts per million downfield from tetramethylsilane. Assignments were verified with $^1\text{H}\text{-}^1\text{H}$ and $^1\text{H}\text{-}^{13}\text{C}$ COSY experiments as appropriate. Mass spectra were obtained under electrospray conditions on a Thermo Scientific LTQ Orbitrap XL instrument. Elemental microanalyses were carried out by Medac Ltd., Brunel Science Centre, Surrey (UK). Solvent extraction studies were performed at the Karlsruher Institut für Technologie (Germany) and at the Czech Technical University in Prague (Czech Republic). All organic reagents were obtained from either Acros or Aldrich, while inorganic reagents were obtained from either BDH or Aldrich and used as received.

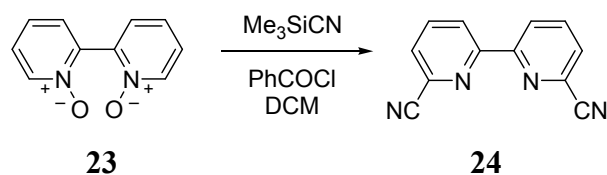
2,2'-Bipyridine-1,1'-dioxide **23**¹⁻¹¹



2,2'-Bipyridine **22** (24.0 g, 153.668 mmol) was dissolved in acetic acid (150 mL) and hydrogen peroxide (60 mL, 30 %, 537.840 mmol, 3.5 eq) was added dropwise at such a rate that the temperature did not exceed 70–80 °C. After the addition was complete, the solution was stirred at 75 °C for 8 h, and was then allowed to cool to room temperature and stirring was continued overnight. The solution was diluted with acetone (2000 mL) and the precipitated solid was filtered and washed

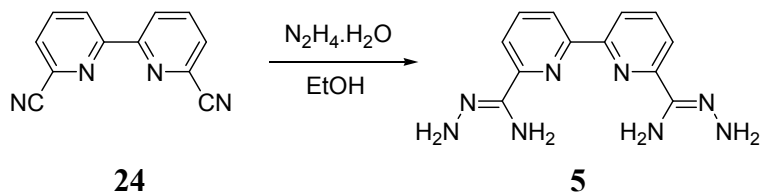
with acetone (200 mL). The solid was dried at 70 °C for 2 h to afford the title compound **23** as a white solid (27.05 g, 93 %). ¹H NMR (400.1 MHz, D₂O) δ: 7.64–7.68 (m, 4H, 4 × ArH), 7.73–7.78 (m, 2H, 2 × ArH), 8.36–8.39 (m, 2H, 2 × ArH) ppm; ¹³C NMR (100.6 MHz, D₂O) δ: 128.4 (2 × ArC), 128.8 (2 × ArC), 131.5 (2 × ArC), 139.7 (2 × ArC), 141.8 (2 × quat) ppm.

2,2'-Bipyridine-6,6'-dicarbonitrile **24**^{7,11-13}



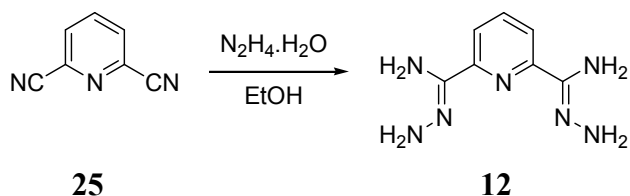
The starting material **23** (26.25 g, 139.494 mmol) was dissolved in DCM (500 mL) and trimethylsilyl cyanide (52.35 mL, 418.482 mmol, 3 eq) was added. Benzoyl chloride (48.57 mL, 418.482 mmol, 3 eq) was added slowly dropwise via an addition funnell at such a rate as to maintain a gentle reflux. The solution was stirred at room temperature for 3 days, and then heated under reflux for 24 h. The solution was allowed to cool to room temperature, 10 % aq. potassium carbonate solution (100 mL) was added and the phases were vigorously stirred for 10 min. The insoluble solid was filtered and washed with water (100 mL) and ether (50 mL) and allowed to dry in air to afford the title compound **24** as a white solid (14.07 g). The phases of the filtrate were mixed and separated and the aqueous phase was extracted with DCM (50 mL). The combined organic phases were dried and evaporated and the resulting residue was triturated with MeOH (100 mL). The insoluble solid was filtered and washed with MeOH (100 mL) and ether (30 mL) and was allowed to dry in air to yield an additional 3.05 g of product **24**. Total yield 17.12 g (60 %). ¹H NMR (400.1 MHz, CDCl₃, Me₄Si) δ: 7.78 (dd, *J* = 7.6 and 1.0, 2H, 5-H and 5'-H), 8.02 (dd, *J* = 7.6 and 8.1, 2H, 4-H and 4'-H), 8.72 (dd, *J* = 8.1 and 1.0, 2H, 3-H and 3'-H) ppm; ¹³C NMR (100.6 MHz, CDCl₃, Me₄Si) δ: 117.1 (2 × quat), 124.7 (2 × ArC), 129.1 (2 × ArC), 133.4 (2 × quat), 138.5 (2 × ArC), 155.6 (2 × quat) ppm.

2,2'-Bipyridine-6,6'-dicarbohydrazonamide **5**^{14,15}



The starting material **24** (17.12 g, 83.106 mmol) was suspended in EtOH (400 mL) and hydrazine hydrate (230 mL, 64 %) was added. The mixture was stirred at room temperature for 14 days. The mixture was diluted with water (2500 mL) and the insoluble solid was filtered and washed with water (400 mL) and EtOH (200 mL). The solid was allowed to dry in air to afford the title compound **5** as a pale yellow solid (22.43 g, 99 %). ^1H NMR (400.1 MHz, $\text{DMSO}-d_6$) δ : 5.42 (br s, 4H, $2 \times \text{NH}_2$), 5.95 (br s, 4H, $2 \times \text{NH}_2$), 7.89 (t, $J = 7.7$, 2H, 4-H and 4'-H), 7.97 (dd, $J = 7.7$ and 1.0, 2H, 5-H and 5'-H), 8.61 (dd, $J = 7.7$ and 1.0, 2H, 3-H and 3'-H) ppm; ^{13}C NMR not visible.

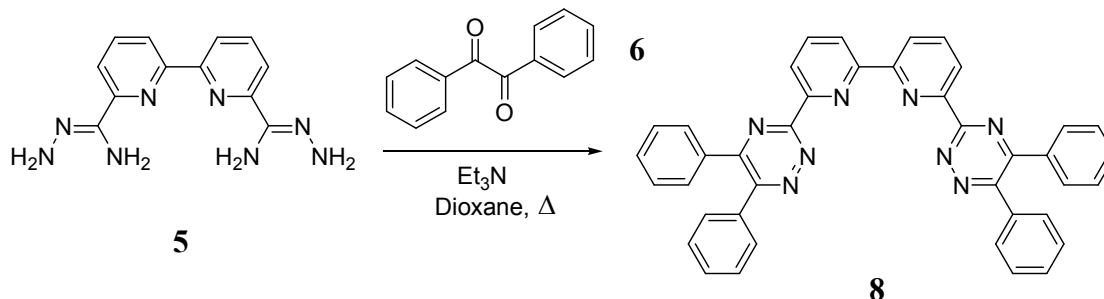
Pyridine-2,6-dicarbohydrazonamide **12**¹⁶



The starting material **25** (5.28 g, 40.892 mmol) was suspended in EtOH (100 mL) and hydrazine hydrate (100 mL, 64 %) was added. The mixture was stirred at room temperature for 14 days. The mixture was diluted with water (300 mL) and the insoluble solid was filtered and washed with water (400 mL). The solid was allowed to dry in air to afford the title compound **12** as a white solid (5.26 g, 67 %). ^1H NMR (400.1 MHz, $\text{DMSO}-d_6$) δ : 5.25 (br s, 4H, $2 \times \text{NH}_2$), 6.05 (br s, 4H, $2 \times \text{NH}_2$), 7.66 (app dd, $J = 8.3$ and 7.3, 1H, 4-H), 7.81 (d, $J = 7.6$, 2H, 3-H and 5-H) ppm; ^{13}C NMR (100.6

MHz, DMSO-*d*₆) δ: 117.9 (C-3 and C-5), 135.9 (C-4), 143.5 (C-2 and C-6), 150.2 (2 × C=NNH₂) ppm.

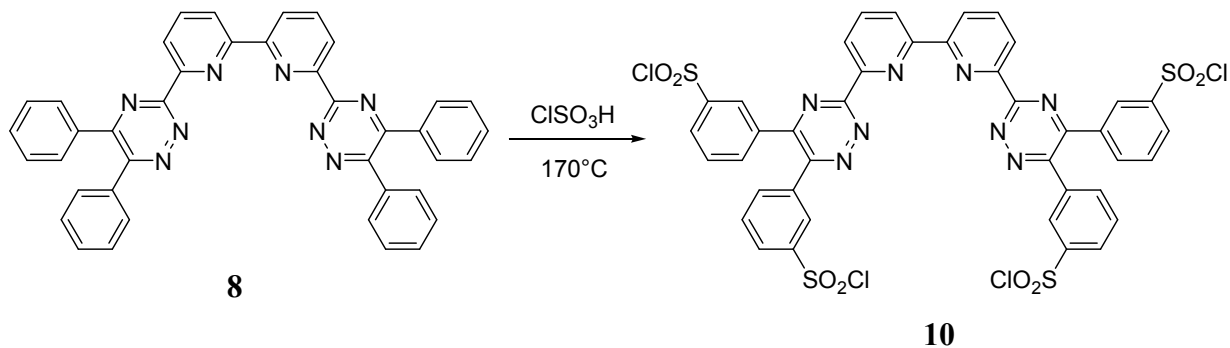
6,6'-Bis(5,6-diphenyl-1,2,4-triazin-3-yl)-2,2'-bipyridine **8**



The starting material **5** (0.90 g, 3.333 mmol) was suspended in 1,4-dioxane (140 mL) and benzil **6** (1.54 g, 7.333 mmol, 2.2 eq) was added. Triethylamine (18 mL) was added and the mixture was heated under reflux for 3 days. The mixture was allowed to cool to room temperature and the insoluble solid was filtered and washed with DCM (40 mL). The solid was allowed to dry in air to afford the title compound **8** as a yellow solid (1.49 g, 72 %). Mp above 300 °C (from dioxane); Found: C, 77.26; H, 4.40; N, 18.47 %; $\text{C}_{40}\text{H}_{26}\text{N}_8$ requires C, 77.65; H, 4.24; N, 18.10 %; IR ν_{max} (N) 3051, 1600, 1576, 1562, 1507, 1484, 1443, 1400, 1374, 1261, 1214, 1183, 1131, 1091, 1076, 1050, 1024, 1003, 987, 921, 870, 837, 809, 771, 743, 726, 698, 648, 637, 594 cm^{-1} ; ^1H NMR (400.1 MHz, CDCl_3 , Me_4Si) δ: 7.40–7.52 (m, 12H, 8 × *m*-ArH and 4 × *p*-ArH), 7.68–7.71 (m, 4H, 4 × *o*-ArH), 7.76–7.78 (m, 4H, 4 × *o*-ArH), 8.14 (t, $J = 7.8$, 2H, 4-H and 4'-H), 8.76 (dd, $J = 7.8$ and 0.9, 2H, 3-H and 3'-H), 9.03 (dd, $J = 7.8$ and 0.9, 2H, 5-H and 5'-H) ppm; ^{13}C NMR (100.6 MHz, CDCl_3 , Me_4Si) δ: 123.4 (C-5 and C-5'), 124.5 (C-3 and C-3'), 128.6 (4 × *m*-ArC), 128.6 (4 × *o*-ArC), 129.5 (4 × *m*-ArC), 129.8 (2 × *p*-ArC), 130.0 (4 × *o*-ArC), 130.8 (2 × *p*-ArC), 135.3 (2 × quat), 135.7 (2 × quat),

138.1 (C-4 and C-4'), 156.0 (2 × quat), 156.2 (2 × quat), 156.3 (2 × quat), 160.9 (2 × quat), 165.4 (2 × quat) ppm; HRMS (CI) m/z 619.2311: calculated for $[C_{40}H_{26}N_8 + H]^+$ 619.2358.

3,3',3'',3'''-[3-(2,2'-Bipyridine-6,6'-diyl)-1,2,4-triazine-5,5,6,6-tetrayl]tetrabenzenesulfonyl chloride **10**

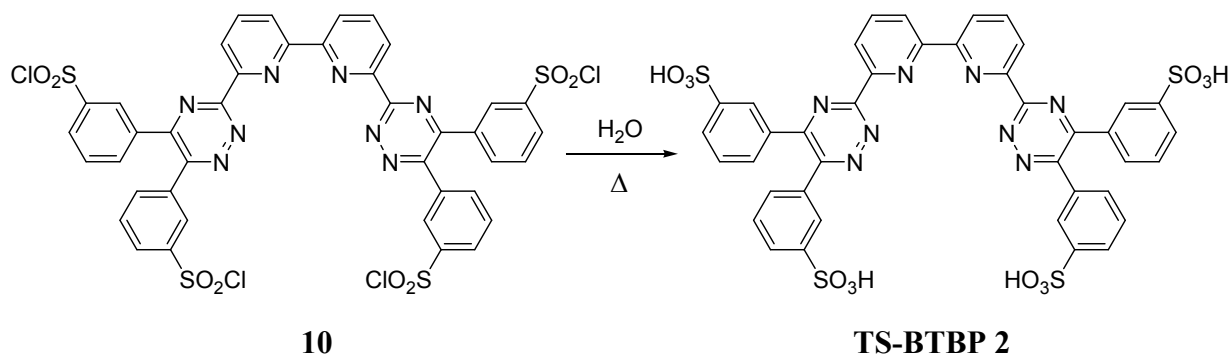


The starting material **8** (1.61 g, 2.605 mmol) was placed in a round bottomed flask and chlorosulfonic acid (15 mL) was added. The solution was stirred at 170 °C for 5 h. The solution was allowed to cool to room temperature and then carefully poured onto ice (ca. 150 mL). The precipitated solid was filtered and washed with water (100 mL) and allowed to dry in air to afford the title compound **10** as a yellow/green solid (2.58 g, 98 %). Mp above 300 °C (from H₂O); Found: C, 47.12; H, 2.32; N, 10.85; S, 12.49 %; C₄₀H₂₂N₈O₈S₄Cl₄ requires C, 47.44; H, 2.19; N, 11.06; S, 12.67 %; IR ν_{\max} (N) 3095, 1620, 1596, 1575, 1540, 1527, 1476, 1420, 1365, 1302, 1215 (SO₂), 1160 (SO₂), 1116 (SO₂), 1027 (SO₂), 993, 899, 851, 797, 738, 677, 609 cm⁻¹; ¹H NMR (400.1 MHz, DMSO-*d*₆) δ : 7.27–7.37 (m, 8H, 8 × ArH), 7.61–7.75 (m, 4H, 4 × ArH), 8.23 (t, J = 1.6, 2H, 2 × ArSO₂Cl 2-H), 8.33–8.40 (m, 4H, 4-H, 4'-H and 2 × ArSO₂Cl 2-H), 8.65 (app d, J = 7.6, 2H, 3-H and 3'-H), 8.87 (app d, J = 7.6, 2H, 5-H and 5'-H) ppm; ¹³C NMR (100.6 MHz, DMSO-*d*₆) δ : 122.6 (C-5 and C-5'), 124.6 (C-3 and C-3'), 125.7 (2 × ArC), 126.3 (2 × ArSO₂Cl C-2), 126.8 (2 × ArC), 127.0 (2 × ArC), 127.7 (2 × ArC), 127.8 (2 × ArC), 129.8 (2 × ArC), 129.9 (2 × ArC), 134.8 (2 ×

ArSO₂Cl C-3), 135.0 (2 × ArSO₂Cl C-3), 139.0 (C-4 and C-4'), 148.8 (2 × quat), 152.3 (2 × quat), 153.0 (2 × quat), 155.2 (2 × ArSO₂Cl C-1), 156.2 (2 × ArSO₂Cl C-1), 157.7 (2 × quat), 160.2 (2 × quat) ppm; HRMS (CI, DMSO) *m/z* 939.0648 (as tetrasulfonic acid): calculated for [C₄₀H₂₆N₈O₁₂S₄ + H]⁺ 939.0631.

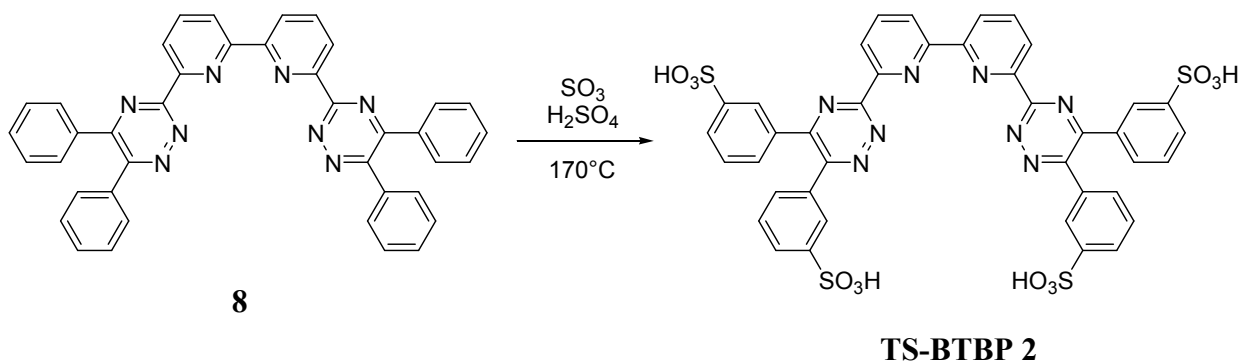
3,3',3'',3'''-[3-(2,2'-Bipyridine-6,6'-diyl)-1,2,4-triazine-5,5,6,6-tetrayl]tetrabenzenesulfonic acid TS-BTBP 2

Method A:



The starting material **10** (1.00 g, 0.990 mmol) was placed in a round bottomed flask and water (120 mL) was added. The mixture was heated under reflux for 2 days. The resulting solution was allowed to cool to room temperature and was then evaporated to afford the title compound **TS-BTBP 2** as a green solid (0.90 g, 97 %).

Method B:

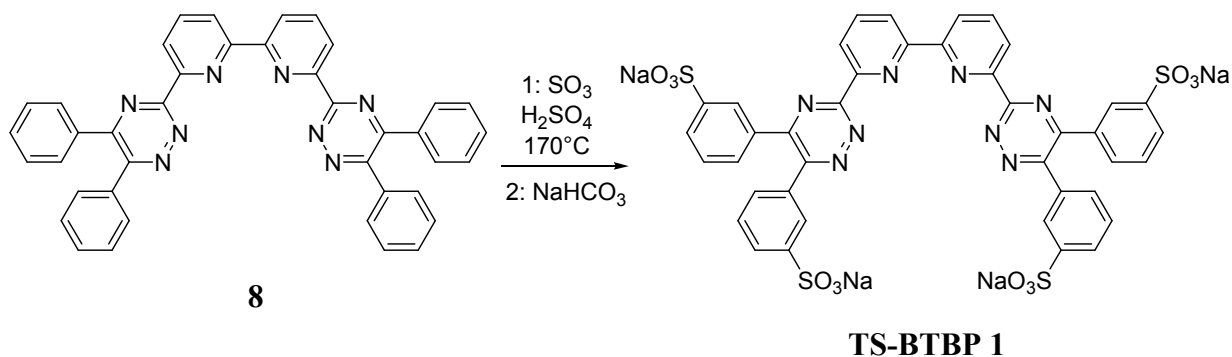


The starting material **8** (0.10 g, 0.161 mmol) was placed in a round bottomed flask and oleum (4 mL, 20 % SO₃ in H₂SO₄) was added. The solution was stirred at 170 °C for 3 h. The solution was allowed to cool to room temperature and acetone (150 mL) was added. The precipitated solid was filtered through a glass fiber filter paper, washed with acetone (50 mL) and was allowed to dry in air to afford a solid which was dried at 70 °C for 30 min to afford the title compound **TS-BTBP 2** as a green solid (0.15 g, 98 %). Mp above 300 °C (from H₂O); Found: C, 50.88; H, 3.16; N, 11.67; S, 13.42 %; C₄₀H₂₆N₈O₁₂S₄ requires C, 51.17; H, 2.79; N, 11.93; S, 13.66 %; IR ν_{\max} (N) 3173, 3089, 1693, 1620, 1574, 1526, 1476, 1420, 1363, 1301, 1231 (SO₂), 1141 (SO₂), 1104 (SO₂), 1022 (SO₂), 991, 898, 797, 738, 676, 644, 607 cm⁻¹; ¹H NMR (400.1 MHz, D₂O) δ : 7.12–7.20 (m, 2H, 2 \times ArH), 7.23–7.36 (m, 4H, 4 \times ArH), 7.39–7.45 (m, 2H, 4-H and 4'-H), 7.58 (app d, J = 7.5, 2H, 3-H and 3'-H), 7.70–7.78 (m, 4H, 4 \times ArH), 7.84 (d, J = 7.5, 2H, 5-H and 5'-H) ppm; ¹³C NMR (100.6 MHz, D₂O) δ : 125.0 (2 \times quat), 125.7 (2 \times ArC), 126.1 (C-3 and C-3'), 126.5 (2 \times ArC), 127.1 (C-5 and C-5'), 127.5 (2 \times quat), 127.7 (2 \times ArC), 128.7 (2 \times ArC), 129.4 (2 \times ArC), 129.7 (2 \times ArC), 132.1 (2 \times ArC), 132.3 (2 \times ArC), 133.1 (2 \times quat), 133.6 (2 \times quat), 140.2 (C-4 and C-4'), 143.3 (2 \times quat), 143.5 (2 \times quat), 156.3 (2 \times quat), 156.5 (2 \times quat), 157.1 (2 \times quat) ppm; ¹H NMR (400.1 MHz, DMSO-*d*₆) δ : 7.30–7.38 (m, 6H, 2 \times ArSO₃H 5-H and 4 \times ArSO₃H 4-H), 7.62–7.77 (m, 6H, 2 \times ArSO₃H 5-H and 4 \times ArSO₃H 6-H), 8.23 (t, J = 1.5, 2H, 2 \times ArSO₃H 2-H), 8.34–8.38 (m, 4H, 4-H, 4'-H and 2 \times ArSO₃H 2-H), 8.66 (dd, J = 7.8 and 0.8, 2H, 3-H and 3'-H), 8.87 (dd, J = 7.8 and 0.8, 2H, 5-H and 5'-H) ppm; ¹³C NMR (100.6 MHz, DMSO-*d*₆) δ : 122.6 (C-5 and C-5'), 124.6 (C-3 and C-3'), 126.3 (2 \times ArSO₃H C-6), 127.0 (2 \times ArSO₃H C-2), 127.6 (2 \times ArSO₃H C-2), 127.7 (2 \times ArSO₃H C-5), 127.9 (2 \times ArSO₃H C-5), 129.0 (2 \times ArSO₃H C-6), 129.8 (2 \times ArSO₃H C-4), 129.9 (2 \times ArSO₃H C-4), 134.8 (2 \times ArSO₃H C-3), 135.0 (2 \times ArSO₃H C-3), 139.0 (C-4 and C-4'), 148.6 (2 \times quat), 148.7 (2 \times quat), 152.2 (2 \times quat), 155.2 (2 \times ArSO₃H C-1), 155.7 (2 \times ArSO₃H C-1), 156.2 (2

× quat), 160.2 (2 × quat) ppm; HRMS (CI, H₂O) *m/z* 939.0638: calculated for [C₄₀H₂₆N₈O₁₂S₄ + H]⁺ 939.0631.

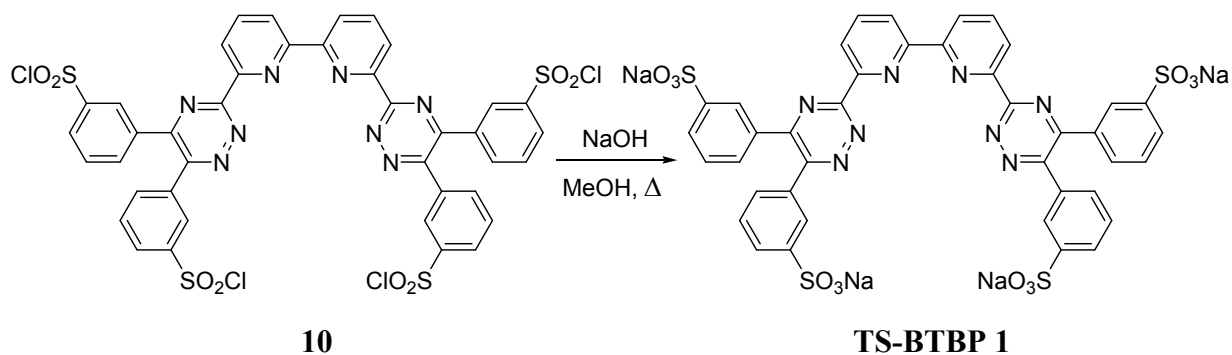
Tetrasodium 3,3',3'',3'''-[3-(2,2'-bipyridine-6,6'-diyl)-1,2,4-triazine-5,5,6,6-tetrayl]tetrabenzenesulfonate TS-BTBP 1

Method A:



The starting material **8** (0.10 g, 0.161 mmol) was placed in a round bottomed flask and oleum (4 mL, 20 % SO₃ in H₂SO₄) was added. The solution was stirred at 170 °C for 3 h. The solution was allowed to cool to room temperature and carefully poured onto ice (ca. 100 mL). Solid sodium hydrogen carbonate was added to the resulting solution until the evolution of CO₂ had ceased, and the insoluble solids were filtered. The filtrate was evaporated to yield a light yellow solid that was triturated with hot MeOH (20 mL). The insoluble solids were filtered and washed with MeOH (20 mL) and the filtrate was evaporated to afford the title compound **TS-BTBP 1** as a light green solid (0.16 g, 96 %).

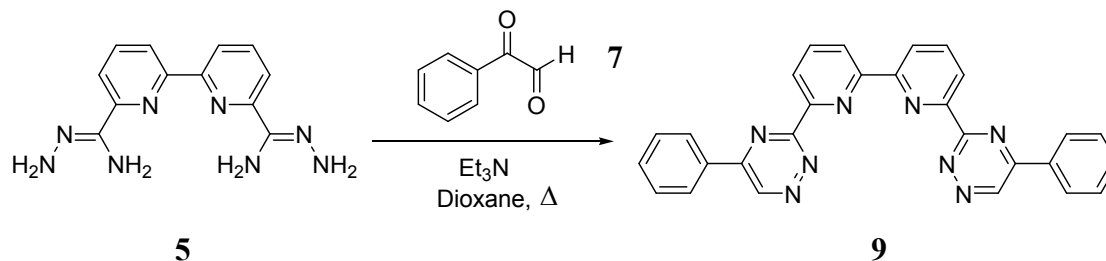
Method B:



The starting material **10** (0.60 g, 0.594 mmol) was suspended in MeOH (60 mL) and a solution of finely powdered NaOH (0.142 g, 3.564 mmol, 6 eq) in MeOH (15 mL) was added. The mixture was heated under reflux for 4 h. The solution was allowed to cool to room temperature and was filtered. Excess NaOH in the filtrate was neutralized by the dropwise addition of HCl (ca. 1–2 mL, 2 M) until the pH was neutral. The filtrate was then diluted with acetone (600 mL) and the precipitated solid was filtered and washed with MeOH (5 mL) and acetone (20 mL). The solid was dried at 70 °C for 30 min to afford the title compound **TS-BTBP 1** as a green solid (0.40 g, 66 %). Mp above 300 °C (from MeOH); Found: C, 46.38; H, 2.45; N, 10.77; S, 12.62 %; C₄₀H₂₂N₈O₁₂S₄Na₄ requires C, 46.79; H, 2.16; N, 10.91; S, 12.49 %; IR ν_{\max} (N) 3066, 1639, 1591, 1542, 1502, 1418, 1377, 1314, 1183 (SO₂), 1122 (SO₂), 1097, 1035 (SO₂), 995, 907, 800, 745, 687, 614 cm⁻¹; ¹H NMR (400.1 MHz, D₂O) δ : 6.75–6.90 (m, 2H, 2 \times ArH), 7.23–7.40 (m, 6H, 6 \times ArH), 7.43 (t, J = 7.6, 2H, 4-H and 4'-H), 7.62–7.72 (m, 2H, 2 \times ArH), 7.75 (app d, J = 7.6, 2H, 3-H and 3'-H), 7.84 (app d, J = 7.6, 2H, 5-H and 5'-H), 7.93–8.15 (m, 4H, 4 \times ArH), 8.23–8.36 (m, 2H, 2 \times ArH) ppm; ¹³C NMR (100.6 MHz, D₂O) δ : 125.1 (2 \times ArC), 125.2 (2 \times ArC), 125.9 (2 \times ArC), 126.0 (C-3 and C-3'), 127.1 (C-5 and C-5'), 128.1 (2 \times ArC), 128.9 (2 \times ArC), 129.5 (2 \times ArC), 129.7 (2 \times ArC), 132.0 (2 \times ArC), 132.7 (2 \times quat), 133.2 (2 \times quat), 134.2 (2 \times quat), 139.7 (C-4 and C-4'), 143.3 (2 \times quat), 151.1 (2 \times quat), 155.8 (2 \times quat), 156.6 (2 \times quat), 157.6 (2 \times quat), 160.8 (2 \times quat) ppm; ¹H NMR (400.1 MHz, DMSO-*d*₆) δ : 7.29–7.38 (m, 6H, 2 \times ArSO₃Na 5-H and 4 \times ArSO₃Na 4-H), 7.63–7.78 (m, 6H,

2 × ArSO₃Na 5-H and 4 × ArSO₃Na 6-H), 8.26 (app s, 2H, 2 × ArSO₃Na 2-H), 8.35–8.39 (m, 4H, 4-H, 4'-H and 2 × ArSO₃Na 2-H), 8.67 (app d, *J* = 7.8, 2H, 3-H and 3'-H), 8.86 (app d, *J* = 7.8, 2H, 5-H and 5'-H) ppm; ¹³C NMR (100.6 MHz, DMSO-*d*₆) δ: 122.8 (C-5 and C-5'), 124.6 (C-3 and C-3'), 126.3 (2 × ArSO₃Na C-6), 127.0 (2 × ArSO₃Na C-2), 127.6 (2 × ArSO₃Na C-2), 127.7 (2 × ArSO₃Na C-5), 127.9 (2 × ArSO₃Na C-5), 129.0 (2 × ArSO₃Na C-6), 129.7 (2 × ArSO₃Na C-4), 129.9 (2 × ArSO₃Na C-4), 134.7 (2 × ArSO₃Na C-3), 134.9 (2 × ArSO₃Na C-3), 139.1 (C-4 and C-4'), 148.7 (2 × quat), 148.8 (2 × quat), 152.3 (2 × quat), 155.2 (2 × ArSO₃Na C-1), 155.6 (2 × ArSO₃Na C-1), 156.2 (2 × quat), 160.1 (2 × quat) ppm; HRMS (CI, H₂O) *m/z* 939.0679 (as tetrasulfonic acid): calculated for [C₄₀H₂₆N₈O₁₂S₄ + H]⁺ 939.0631.

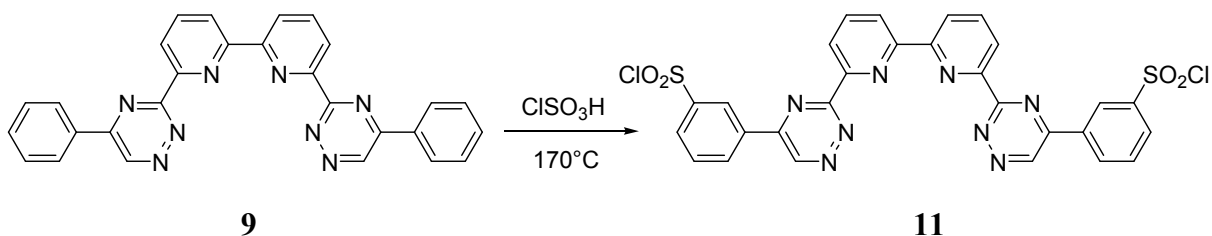
6,6'-Bis(5-phenyl-1,2,4-triazin-3-yl)-2,2'-bipyridine **9**



The starting material **5** (1.00 g, 3.703 mmol) was suspended in 1,4-dioxane (100 mL) and phenylglyoxal **7** (1.24 g, 8.148 mmol, 2.2 eq) was added. Triethylamine (16 mL) was added and the mixture was heated under reflux for 3 days. The mixture was allowed to cool to room temperature and the insoluble solid was filtered and washed with DCM (20 mL). The solid was allowed to dry in air to afford the title compound **9** as a yellow solid (1.53 g, 89 %). Mp above 300 °C (from 1,4-dioxane); Found: C, 71.78; H, 3.81; N, 23.67 %; C₂₈H₁₈N₈ requires C, 72.09; H, 3.89; N, 24.01 %; IR ν_{\max} (N) 3092, 3057, 1601, 1577, 1560, 1538, 1505, 1436, 1419, 1357, 1337, 1319, 1269, 1187, 1157, 1123, 1082, 1046, 1027, 992, 980, 927, 900, 872, 830, 796, 762, 747, 682, 669, 662, 636 cm⁻¹;

^1H NMR (400.1 MHz, CDCl_3 , Me_4Si) δ : 7.63–7.67 (m, 6H, $4 \times m\text{-ArH}$ and $2 \times p\text{-ArH}$), 8.16 (t, $J = 7.8$, 2H, 4-H and 4'-H), 8.37–8.40 (m, 4H, $4 \times o\text{-ArH}$), 8.74 (dd, $J = 7.8$ and 0.9, 2H, 3-H and 3'-H), 9.04 (dd, $J = 7.8$ and 0.9, 2H, 5-H and 5'-H), 9.78 (s, 2H, $2 \times \text{HC}=\text{N}$) ppm; ^{13}C NMR not visible; HRMS (CI) m/z 489.1544: calculated for $[\text{C}_{28}\text{H}_{18}\text{N}_8 + \text{Na}]^+$ 489.1547.

3,3'-[3-(2,2'-Bipyridine-6,6'-diyl)-1,2,4-triazine-5,5'-diyl]dibenzenesulfonyl chloride **11**

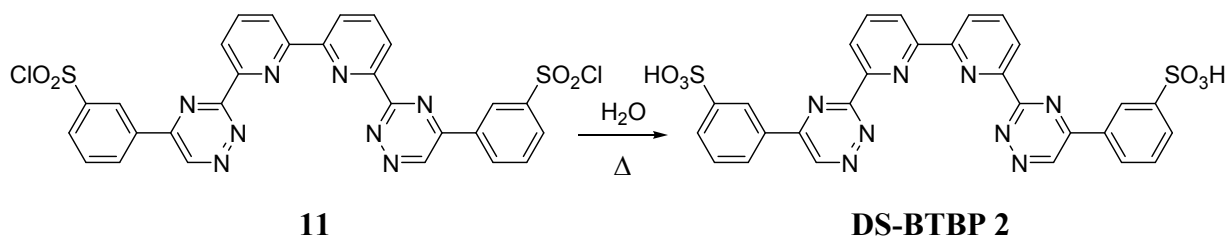


The starting material **9** (0.50 g, 1.072 mmol) was placed in a round bottomed flask and chlorosulfonic acid (6 mL) was added. The solution was stirred at 170 °C for 3 h. The solution was allowed to cool to room temperature and then carefully poured onto ice (ca. 50 mL). The precipitated solid was filtered and washed with water (25 mL) and allowed to dry in air to afford the title compound **11** as a yellow/green solid (0.66 g, 93 %). Mp above 300 °C (from H_2O); Found: C, 50.32; H, 2.71; N, 16.54; S, 9.38 %; $\text{C}_{28}\text{H}_{16}\text{N}_8\text{O}_4\text{S}_2\text{Cl}_2$ requires C, 50.69; H, 2.43; N, 16.88; S, 9.67 %; IR ν_{max} (N) 3178, 3088, 1623, 1585, 1542, 1507, 1474, 1441, 1373, 1321, 1290, 1272, 1163 (SO_2), 1120 (SO_2), 1051, 1031 (SO_2), 991, 911, 861, 821, 780, 767, 738, 700, 686, 662, 652, 606 cm^{-1} ; ^1H NMR (400.1 MHz, $\text{DMSO}-d_6$) δ : 7.68 (t, $J = 7.7$, 2H, $2 \times \text{ArSO}_2\text{Cl}$ 5-H), 7.94 (dt, $J = 7.8$ and 1.2, 2H, $2 \times \text{ArSO}_2\text{Cl}$ 4-H), 8.36 (t, $J = 7.8$, 2H, 4-H and 4'-H), 8.50 (dt, $J = 7.8$ and 1.2, 2H, $2 \times \text{ArSO}_2\text{Cl}$ 6-H), 8.67 (dd, $J = 7.8$ and 0.8, 2H, 3-H and 3'-H), 8.75 (t, $J = 1.2$, 2H, $2 \times \text{ArSO}_2\text{Cl}$ 2-H), 8.89 (dd, $J = 7.8$ and 0.8, 2H, 5-H and 5'-H), 10.20 (s, 2H, $2 \times \text{HC}=\text{N}$) ppm; ^{13}C NMR (100.6 MHz, $\text{DMSO}-d_6$) δ : 122.7 (C-5 and C-5'), 124.6 (C-3 and C-3'), 124.9 ($2 \times \text{ArSO}_2\text{Cl}$ C-2), 128.2 ($2 \times \text{ArSO}_2\text{Cl}$ C-6), 129.0 ($2 \times \text{ArSO}_2\text{Cl}$ C-5), 129.8 ($2 \times \text{ArSO}_2\text{Cl}$ C-4), 132.8 ($2 \times \text{ArSO}_2\text{Cl}$ C-3), 139.0

(C-4 and C-4'), 146.0 (2 × HC=N), 149.4 (2 × quat), 152.4 (2 × quat), 154.8 (2 × quat), 155.1 (2 × ArSO₂Cl C-1), 161.9 (2 × quat) ppm; HRMS (CI) *m/z* 627.0858 (as disulfonic acid): calculated for [C₂₈H₁₈N₈O₆S₂ + H]⁺ 627.0863.

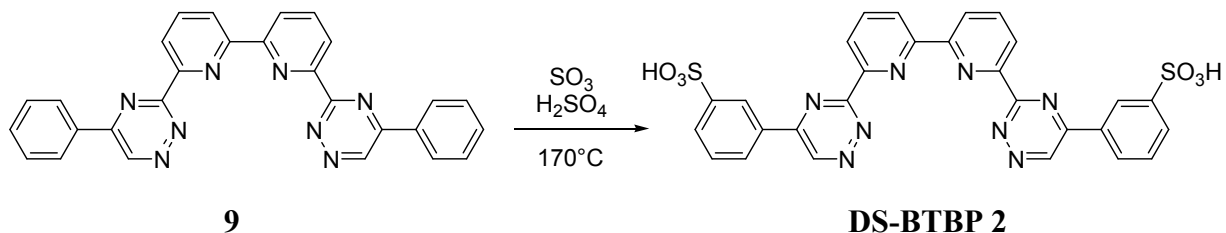
3,3'-[3-(2,2'-Bipyridine-6,6'-diyl)-1,2,4-triazine-5,5-diyl]dibenzenesulfonic acid **DS-BTBP 2**

Method A:



The starting material **11** (0.50 g, 0.755 mmol) was placed in a round bottomed flask and water (70 mL) was added. The mixture was heated under reflux for 3 days. The resulting mixture was allowed to cool to room temperature and was then evaporated to afford the title compound **DS-BTBP 2** as a green solid (0.42 g, 89 %).

Method B:

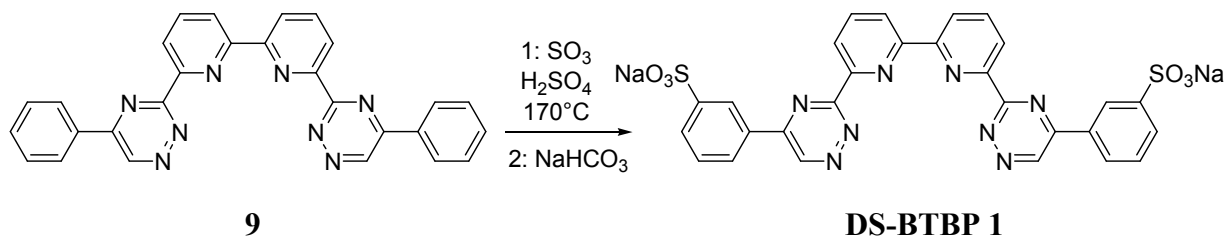


The starting material **9** (0.12 g, 0.257 mmol) was placed in a round bottomed flask and oleum (5 mL, 20 % SO₃ in H₂SO₄) was added. The solution was stirred at 170 °C for 3 h. The solution was allowed to cool to room temperature and acetone (100 mL) was added. The precipitated solid was filtered, washed with acetone (100 mL) and was allowed to dry in air to afford the title compound **DS-BTBP**

2 as a light green solid (0.16 g, 99 %). Mp 258–262 °C (decomposed); Found: C, 53.28; H, 3.14; N, 17.65; S, 10.07 %; C₂₈H₁₈N₈O₆S₂ requires C, 53.67; H, 2.90; N, 17.87; S, 10.23 %; IR ν_{\max} (N) 3406, 3176, 3080, 1682, 1618, 1581, 1543, 1506, 1435, 1366, 1321, 1288, 1163 (SO₂), 1125 (SO₂), 1030 (SO₂), 992, 907, 880, 822, 786, 764, 737, 687, 670, 653, 610 cm⁻¹; ¹H NMR (400.1 MHz, DMSO-*d*₆) δ : 7.68 (t, *J* = 7.7, 2H, 2 × ArSO₃H 5-H), 7.95 (app d, *J* = 7.7, 2H, 2 × ArSO₃H 4-H), 8.36 (t, *J* = 7.7, 2H, 4-H and 4'-H), 8.49 (app d, *J* = 7.8, 2H, 2 × ArSO₃H 6-H), 8.67 (app d, *J* = 7.7, 2H, 3-H and 3'-H), 8.76 (app s, 2H, 2 × ArSO₃H 2-H), 8.87 (app d, *J* = 7.7, 2H, 5-H and 5'-H), 10.18 (s, 2H, 2 × HC=N) ppm; ¹³C NMR (100.6 MHz, DMSO-*d*₆) δ : 122.7 (C-5 and C-5'), 124.5 (C-3 and C-3'), 124.9 (2 × ArSO₃H C-2), 128.2 (2 × ArSO₃H C-6), 129.0 (2 × ArSO₃H C-5), 129.8 (2 × ArSO₃H C-4), 132.8 (2 × ArSO₃H C-3), 138.9 (C-4 and C-4'), 146.0 (2 × HC=N), 149.4 (2 × quat), 152.5 (2 × quat), 154.7 (2 × quat), 155.2 (2 × ArSO₃H C-1), 162.0 (2 × quat) ppm; HRMS (CI) *m/z* 627.0867: calculated for [C₂₈H₁₈N₈O₆S₂ + H]⁺ 627.0863.

Disodium 3,3'-[3-(2,2'-bipyridine-6,6'-diyl)-1,2,4-triazine-5,5-diyl]dibenzenesulfonate DS-BTBP 1

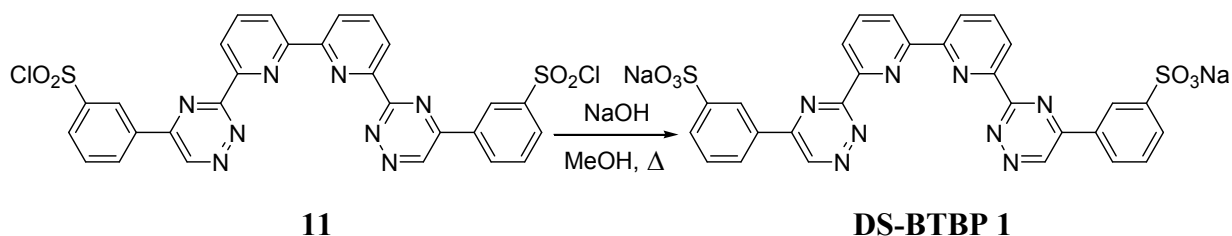
Method A:



The starting material **9** (0.10 g, 0.214 mmol) was placed in a round bottomed flask and oleum (5 mL, 20 % SO₃ in H₂SO₄) was added. The solution was stirred at 170 °C for 4 h. The solution was allowed to cool to room temperature and carefully poured onto ice (ca. 100 mL). Solid sodium hydrogen carbonate was added to the resulting mixture until the evolution of CO₂ had ceased, and the insoluble

solids were filtered. The filtrate was evaporated to yield an off-white solid that was triturated with hot MeOH (40 mL). The insoluble solids were filtered and washed with hot MeOH (40 mL) and the filtrate was evaporated to afford the title compound **DS-BTBP 1** as a light yellow solid (0.12 g, 85 %).

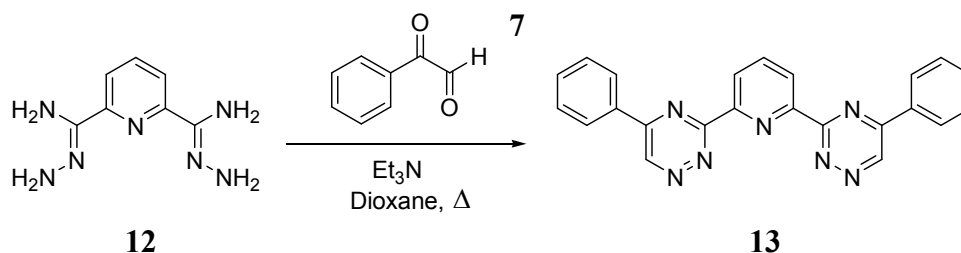
Method B:



The starting material **11** (0.31 g, 0.467 mmol) was suspended in MeOH (50 mL) and a solution of finely powdered NaOH (0.074 g, 1.868 mmol, 4 eq) in MeOH (20 mL) was added. The mixture was heated under reflux for 2 days. The mixture was allowed to cool to room temperature and excess NaOH was neutralized by the dropwise addition of HCl (ca. 1 mL, 2 M) until the pH was neutral. The insoluble solid was then filtered and washed with MeOH (50 mL) and allowed to dry in air to afford the title compound **DS-BTBP 1** as a light yellow solid (0.24 g, 76 %). Mp above 300 °C (from MeOH); Found: C, 49.77; H, 2.62; N, 16.54; S, 9.73 %; C₂₈H₁₆N₈O₆S₂Na₂ requires C, 50.15; H, 2.40; N, 16.70; S, 9.56 %; IR ν_{\max} (N) 3105, 1626, 1592, 1547, 1511, 1442, 1421, 1365, 1317, 1293, 1258, 1185 (SO₂), 1127 (SO₂), 1083, 1034 (SO₂), 994, 911, 826, 784, 742, 694, 668, 636, 614 cm⁻¹; ¹H NMR (400.1 MHz, DMSO-*d*₆) δ : 7.67 (t, *J* = 7.7, 2H, 2 × ArSO₃Na 5-H), 7.94 (dt, *J* = 7.7 and 1.2, 2H, 2 × ArSO₃Na 4-H), 8.36 (t, *J* = 7.8, 2H, 4-H and 4'-H), 8.48 (dt, *J* = 7.8 and 1.2, 2H, 2 × ArSO₃Na 6-H), 8.67 (dd, *J* = 7.8 and 0.8, 2H, 3-H and 3'-H), 8.74 (t, *J* = 1.4, 2H, 2 × ArSO₃Na 2-H), 8.88 (dd, *J* = 7.8 and 0.8, 2H, 5-H and 5'-H), 10.18 (s, 2H, 2 × HC=N) ppm; ¹³C NMR (100.6 MHz, DMSO-*d*₆) δ : 122.8 (C-5 and C-5'), 124.5 (C-3 and C-3'), 124.8 (2 × ArSO₃Na C-2), 128.2 (2 ×

ArSO₃Na C-6), 129.0 (2 × ArSO₃Na C-5), 129.8 (2 × ArSO₃Na C-4), 132.8 (2 × ArSO₃Na C-3), 139.0 (C-4 and C-4'), 146.0 (2 × HC=N), 149.3 (2 × quat), 152.5 (2 × quat), 154.6 (2 × quat), 155.1 (2 × ArSO₃Na C-1), 161.9 (2 × quat) ppm; HRMS (CI) *m/z* 627.0861 (as disulfonic acid): calculated for [C₂₈H₁₈N₈O₆S₂ + H]⁺ 627.0863.

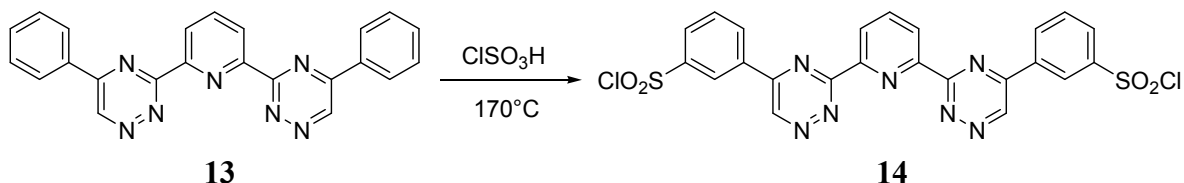
2,6-Bis(5-phenyl-1,2,4-triazin-3-yl)pyridine **13**



The starting material **12** (0.65 g, 3.367 mmol) was suspended in 1,4-dioxane (75 mL) and phenylglyoxal **7** (1.12 g, 7.409 mmol, 2.2 eq) was added. Triethylamine (6 mL) was added and the mixture was heated under reflux for 3 days. The mixture was allowed to cool to room temperature and the precipitated solid was filtered and washed with ether (150 mL). The solid was allowed to dry in air to afford the title compound **13** as a yellow solid (1.29 g, 98 %). Mp 240–245 °C (from 1,4-dioxane); Found: C, 70.71; H, 3.97; N, 24.94 %; C₂₃H₁₅N₇ requires C, 70.94; H, 3.88; N, 25.18 %; IR ν_{\max} (N) 3059, 1651, 1598, 1548, 1508, 1439, 1404, 1368, 1354, 1323, 1286, 1261, 1180, 1161, 1123, 1091, 1049, 1027, 1002, 992, 914, 872, 847, 831, 762, 745, 685, 670, 642, 630 cm⁻¹; ¹H NMR (400.1 MHz, CDCl₃, Me₄Si) δ : 7.63–7.68 (m, 6H, 4 × *m*-ArH and 2 × *p*-ArH), 8.22 (t, *J* = 7.8, 1H, 4-H), 8.41–8.44 (m, 4H, 4 × *o*-ArH), 8.90 (d, *J* = 7.8, 2H, 3-H and 5-H), 9.78 (s, 2H, 2 × HC=N) ppm; ¹³C NMR (100.6 MHz, CDCl₃, Me₄Si) δ : 125.9 (C-3 and C-5), 128.0 (4 × *o*-ArC), 129.4 (4 × *m*-ArC), 132.8 (2 × *p*-ArC), 133.3 (2 × quat), 138.4 (C-4), 145.3 (2 × HC=N), 153.7 (2 × quat), 155.8

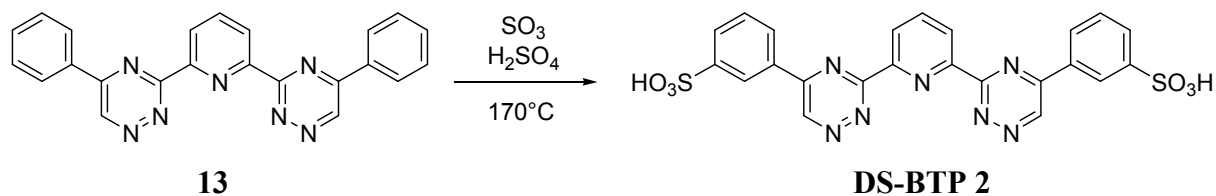
(2 × quat), 162.6 (2 × quat) ppm; HRMS (CI) m/z 390.1465: calculated for $[C_{23}H_{15}N_7 + H]^+$ 390.1462.

3,3'-[3-(Pyridine-2,6-diyl)-1,2,4-triazine-5,5-diyl]dibenzenesulfonyl chloride **14**



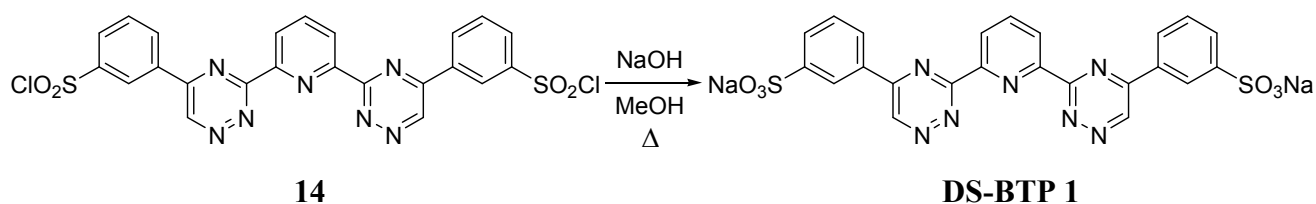
The starting material **13** (0.60 g, 1.542 mmol) was placed in a round bottomed flask and chlorosulfonic acid (10 mL) was added. The solution was stirred at 170 °C for 3 h. The solution was allowed to cool to room temperature and then carefully poured onto ice (ca. 100 mL). The precipitated solid was filtered and washed with water (300 mL) and allowed to dry in air to afford the title compound **14** as a green solid (0.88 g, 97 %). Mp above 300 °C (from H₂O); Found: C, 46.78; H, 2.52; N, 16.55 %; C₂₃H₁₃N₇O₄S₂Cl₂ requires C, 47.11; H, 2.23; N, 16.72 %; IR ν_{\max} (N) 3073, 1599, 1588, 1573, 1537, 1455, 1418, 1373, 1352, 1321, 1288, 1255, 1165 (SO₂), 1138 (SO₂), 1103, 1028 (SO₂), 991, 910, 812, 784, 770, 750, 711, 683, 656, 608 cm⁻¹; ¹H NMR (400.1 MHz, DMSO-*d*₆) δ : 7.69 (t, J = 7.7, 2H, 2 × ArSO₂Cl 5-H), 7.93 (dt, J = 7.9 and 1.2, 2H, 2 × ArSO₂Cl 4-H), 8.42 (t, J = 7.8, 1H, 4-H), 8.47 (dt, J = 7.8 and 1.2, 2H, 2 × ArSO₂Cl 6-H), 8.68 (t, J = 1.6, 2H, 2 × ArSO₂Cl 2-H), 8.76 (d, J = 7.8, 2H, 3-H and 5-H), 10.18 (s, 2H, 2 × HC=N) ppm; ¹³C NMR (100.6 MHz, DMSO-*d*₆) δ : 124.8 (2 × ArSO₂Cl C-2), 125.9 (C-3 and C-5), 128.4 (2 × ArSO₂Cl C-6), 129.1 (2 × ArSO₂Cl C-5), 129.8 (2 × ArSO₂Cl C-4), 132.8 (2 × ArSO₂Cl C-3), 139.0 (C-4), 146.1 (2 × HC=N), 149.3 (2 × quat), 153.5 (2 × quat), 154.8 (2 × ArSO₂Cl C-1), 162.1 (2 × quat) ppm; HRMS (CI) m/z 550.0614 (as disulfonic acid): calculated for $[C_{23}H_{15}N_7O_6S_2 + H]^+$ 550.0603.

3,3'-[3-(Pyridine-2,6-diyl)-1,2,4-triazine-5,5-diyl]dibenzenesulfonic acid DS-BTP 2



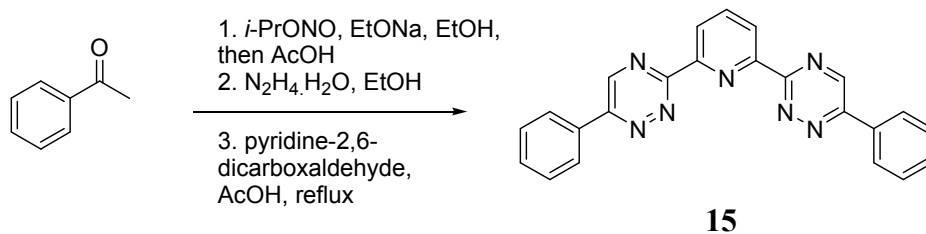
The starting material **13** (0.12 g, 0.308 mmol) was placed in a round bottomed flask and oleum (5 mL, 20 % SO₃ in H₂SO₄) was added. The solution was stirred at 170 °C for 3 h. The solution was allowed to cool to room temperature and acetone (100 mL) was added. The precipitated solid was filtered, washed with acetone (100 mL) and was allowed to dry in air to afford the title compound **DS-BTP 2** as a grey solid (0.16 g, 94 %). Mp above 300 °C (from acetone); Found: C, 49.96; H, 3.05; N, 17.68; S 11.81 %; C₂₃H₁₅N₇O₆S₂ requires C, 50.27; H, 2.75; N, 17.83; S 11.67 %; IR ν_{\max} (N) 3076, 1708, 1609, 1580, 1536, 1459, 1420, 1375, 1351, 1331, 1221, 1162 (SO₂), 1135 (SO₂), 1025 (SO₂), 989, 890, 864, 835, 810, 772, 711, 684, 656 cm⁻¹; ¹H NMR (400.1 MHz, DMSO-*d*₆) δ : 7.69 (t, *J* = 7.7, 2H, 2 × ArSO₃H 5-H), 7.94 (app d, *J* = 7.9, 2H, 2 × ArSO₃H 4-H), 8.43 (t, *J* = 7.8, 1H, 4-H), 8.48 (app d, *J* = 7.8, 2H, 2 × ArSO₃H 6-H), 8.69 (t, *J* = 1.5, 2H, 2 × ArSO₃H 2-H), 8.76 (d, *J* = 7.8, 2H, 3-H and 5-H), 10.19 (s, 2H, 2 × HC=N) ppm; ¹³C NMR (100.6 MHz, DMSO-*d*₆) δ : 124.8 (2 × ArSO₃H C-2), 125.8 (C-3 and C-5), 128.3 (2 × ArSO₃H C-6), 129.1 (2 × ArSO₃H C-5), 129.7 (2 × ArSO₃H C-4), 132.8 (2 × ArSO₃H C-3), 139.0 (C-4), 146.1 (2 × HC=N), 149.2 (2 × quat), 153.4 (2 × quat), 154.8 (2 × ArSO₃H C-1), 162.0 (2 × quat) ppm; HRMS (CI) *m/z* 548.0430: calculated for [C₂₃H₁₄N₇O₆S₂]⁻ 548.0441.

Disodium 3,3'-[3-(pyridine-2,6-diyl)-1,2,4-triazine-5,5-diyl]dibenzenesulfonate DS-BTP 1



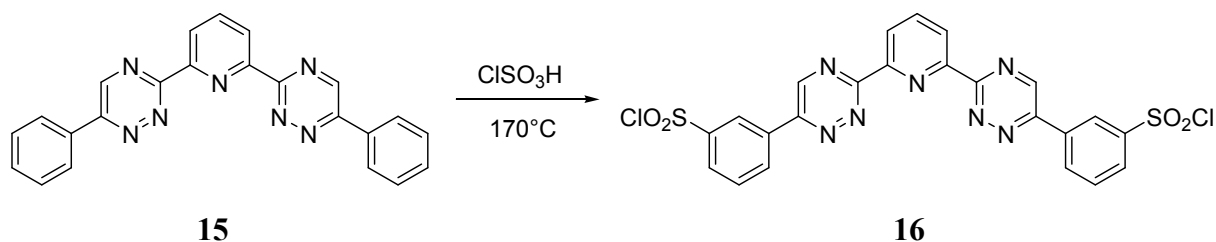
The starting material **14** (0.60 g, 1.023 mmol) was suspended in MeOH (50 mL) and a solution of finely powdered NaOH (0.163 g, 4.095 mmol, 4 eq) in MeOH (30 mL) was added. The mixture was heated under reflux for 5 h. The solution was allowed to cool to room temperature and the excess NaOH was neutralized by the dropwise addition of HCl (ca. 1 mL, 2 M) until the pH was neutral. The insoluble solid was filtered and washed with MeOH (120 mL) and allowed to dry in air to afford the title compound **DS-BTP 1** as a light yellow solid (0.39 g, 65 %). Mp above 300 °C (from MeOH); Found: C, 46.48; H, 2.59; N, 16.85; S, 10.67 %; C₂₃H₁₃N₇O₆S₂Na₂ requires C, 46.55; H, 2.21; N, 16.52; S, 10.80 %; IR ν_{\max} (N) 3071, 1630, 1599, 1546, 1508, 1483, 1412, 1373, 1355, 1318, 1297, 1266, 1183 (SO₂), 1125 (SO₂), 1086, 1054, 1032 (SO₂), 1007, 995, 909, 865, 846, 811, 784, 750, 715, 689, 673, 662, 645, 607 cm⁻¹; ¹H NMR (400.1 MHz, DMSO-*d*₆) δ : 7.69 (t, *J* = 7.7, 2H, 2 × ArSO₃Na 5-H), 7.94 (dt, *J* = 7.9 and 1.2, 2H, 2 × ArSO₃Na 4-H), 8.45 (t, *J* = 7.8, 1H, 4-H), 8.48 (dt, *J* = 7.8 and 1.2, 2H, 2 × ArSO₃Na 6-H), 8.69 (t, *J* = 1.5, 2H, 2 × ArSO₃Na 2-H), 8.78 (d, *J* = 7.8, 2H, 3-H and 5-H), 10.20 (s, 2H, 2 × HC=N) ppm; ¹³C NMR (100.6 MHz, DMSO-*d*₆) δ : 124.8 (2 × ArSO₃Na C-2), 125.8 (C-3 and C-5), 128.2 (2 × ArSO₃Na C-6), 129.0 (2 × ArSO₃Na C-5), 129.8 (2 × ArSO₃Na C-4), 132.7 (2 × ArSO₃Na C-3), 139.1 (C-4), 146.1 (2 × HC=N), 149.4 (2 × quat), 153.4 (2 × quat), 154.8 (2 × ArSO₃Na C-1), 162.0 (2 × quat) ppm; HRMS (CI) *m/z* 548.0444 (as disulfonic acid monoanion): calculated for [C₂₃H₁₃N₇O₆S₂ + H]⁻ 548.0441.

2,6-Bis(6-phenyl-1,2,4-triazin-3-yl)pyridine **15**¹⁷



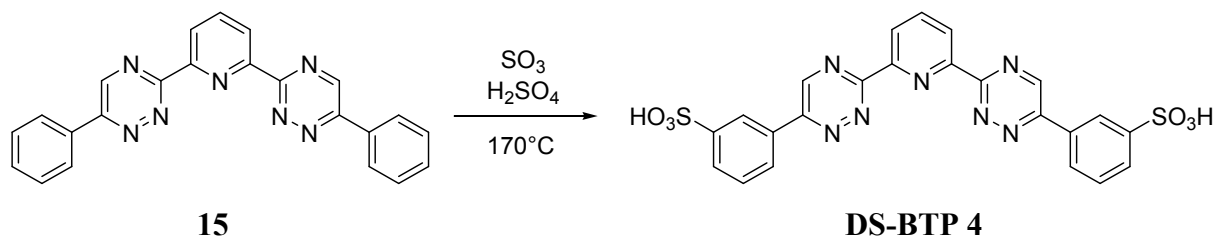
BTP **15** was synthesized from acetophenone as described previously in the literature¹⁷ and had: ¹H NMR (399.7 MHz, CDCl₃, Me₄Si) δ: 7.59–7.64 (m, 6H, 4 × *m*-ArH and 2 × *p*-ArH), 8.19–8.21 (m, 4H, 4 × *o*-ArH), 8.22 (t, *J* = 7.9, 1H, 4-H), 8.91 (d, *J* = 7.9, 2H, 3-H and 5-H), 9.27 (s, 2H, 2 × HC=N) ppm.

3,3'-[3-(Pyridine-2,6-diyl)-1,2,4-triazine-6,6-diyl]dibenzenesulfonyl chloride **16**



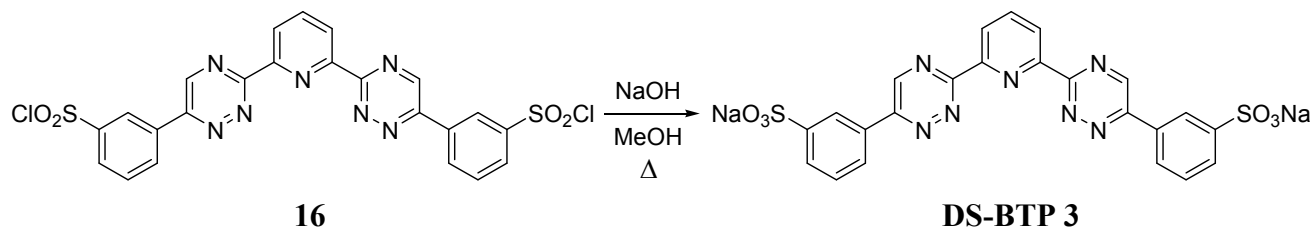
The starting material **15** (0.20 g, 0.514 mmol) was placed in a round bottomed flask and chlorosulfonic acid (8 mL) was added. The solution was stirred at 170 °C for 3 h. The solution was allowed to cool to room temperature and then carefully poured onto ice (ca. 100 mL). The precipitated solid was filtered and washed with water (100 mL) and allowed to dry in air to afford the title compound **16** as a light yellow solid (0.25 g, 83 %). Mp above 300 °C (from H₂O); Found: C, 46.65; H, 2.63; N, 16.48 %; C₂₃H₁₃N₇O₄S₂Cl₂ requires C, 47.11; H, 2.23; N, 16.72 %; IR ν_{max} (N) 3057, 1620, 1575, 1446, 1399, 1330, 1172, 1144, 1039, 935, 847, 798, 785, 766, 716, 688 cm⁻¹; ¹H NMR (399.7 MHz, DMSO-*d*₆) δ: 7.59 (t, *J* = 7.5, 2H, 2 × ArSO₂Cl 5-H), 7.79–7.84 (m, 2H, 2 × ArSO₂Cl 4-H), 8.22–8.27 (m, 2H, 2 × ArSO₂Cl 6-H), 8.32 (t, *J* = 7.9, 1H, 4-H), 8.52 (t, *J* = 1.5, 2H, 2 × ArSO₂Cl 2-H), 8.71 (d, *J* = 7.9, 2H, 3-H and 5-H), 9.59 (s, 2H, 2 × HC=N) ppm; ¹³C NMR not visible; HRMS (CI) *m/z* 550.0609 (as disulfonic acid): calculated for [C₂₃H₁₅N₇O₆S₂ + H]⁺ 550.0603.

3,3'-[3-(Pyridine-2,6-diyl)-1,2,4-triazine-6,6-diyl]dibenzenesulfonic acid DS-BTP **4**



The starting material **15** (0.18 g, 0.462 mmol) was placed in a round bottomed flask and oleum (8 mL, 20 % SO₃ in H₂SO₄) was added. The solution was stirred at 170 °C for 3 h. The solution was allowed to cool to room temperature and acetone (100 mL) was added. The precipitated solid was filtered, washed with acetone (100 mL) and was allowed to dry in air to afford the title compound **DS-BTP 4** as a grey solid (0.14 g, 56 %). Mp above 300 °C (from acetone); Found: C, 49.88; H, 3.02; N, 17.78 %; C₂₃H₁₅N₇O₆S₂ requires C, 50.27; H, 2.75; N, 17.83 %; IR ν_{\max} (N) 3126, 1715, 1679, 1630, 1575, 1557, 1461, 1445, 1423, 1358, 1164, 1122, 1033, 994, 802, 737, 688, 672 cm⁻¹; ¹H NMR (399.7 MHz, DMSO-*d*₆) δ : 7.51 (t, *J* = 7.6, 2H, 2 × ArSO₃H 5-H), 7.77–7.82 (m, 2H, 2 × ArSO₃H 4-H), 8.21–8.25 (m, 2H, 2 × ArSO₃H 6-H), 8.32 (t, *J* = 7.9, 1H, 4-H), 8.52 (app s, 2H, 2 × ArSO₃H 2-H), 8.71 (d, *J* = 7.9, 2H, 3-H and 5-H), 9.59 (s, 2H, 2 × HC=N) ppm; ¹³C NMR not visible; HRMS (CI) *m/z* 548.0422: calculated for [C₂₃H₁₄N₇O₆S₂]⁻ 548.0441.

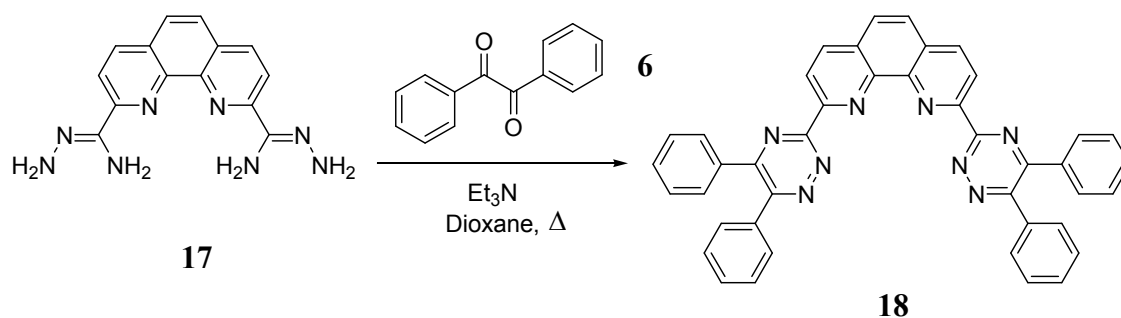
Disodium 3,3'-[3-(pyridine-2,6-diyl)-1,2,4-triazine-6,6-diyl]dibenzenesulfonate DS-BTP 3



The starting material **16** (0.50 g, 0.853 mmol) was suspended in MeOH (40 mL) and a solution of finely powdered NaOH (0.136 g, 3.413 mmol, 4 eq) in MeOH (20 mL) was added. The mixture was heated under reflux for 6 h. The solution was allowed to cool to room temperature and stirring was

continued overnight. The excess NaOH was neutralized by the dropwise addition of HCl (ca. 0.8 mL, 2 M) until the pH was neutral. The insoluble solid was filtered and washed with MeOH (100 mL) and allowed to dry in air to afford the title compound **DS-BTP 3** as a light green solid (0.24 g, 48 %). Mp above 300 °C (from MeOH); Found: C, 46.47; H, 2.56; N, 16.41 %; C₂₃H₁₃N₇O₆S₂Na₂ requires C, 46.55; H, 2.21; N, 16.52 %; IR ν_{\max} (N) 3478, 1660, 1605, 1556, 1446, 1389, 1301, 1279, 1193, 1125, 1038, 995, 872, 766, 719, 668 cm⁻¹; ¹H NMR (399.7 MHz, DMSO-*d*₆) δ : 7.59 (t, *J* = 7.6, 2H, 2 × ArSO₃Na 5-H), 7.80–7.83 (m, 2H, 2 × ArSO₃H 4-H), 8.22–8.24 (m, 2H, 2 × ArSO₃H 6-H), 8.33 (t, *J* = 7.9, 1H, 4-H), 8.54 (app s, 2H, 2 × ArSO₃H 2-H), 8.73 (d, *J* = 7.9, 2H, 3-H and 5-H), 9.59 (s, 2H, 2 × HC=N) ppm; ¹³C NMR (100.5 MHz, DMSO-*d*₆) δ : 124.5 (2 × ArSO₃Na C-2), 126.0 (C-3 and C-5), 127.7 (2 × ArSO₃Na C-6), 128.8 (2 × ArSO₃Na C-5), 129.4 (2 × ArSO₃Na C-4), 132.9 (2 × quat), 139.6 (C-4), 148.6 (2 × HC=N), 150.0 (2 × quat), 153.5 (2 × quat), 155.9 (2 × ArSO₃Na C-1), 161.7 (2 × quat) ppm; HRMS (CI) *m/z* 548.0453 (as disulfonic acid monoanion): calculated for [C₂₃H₁₃N₇O₆S₂ + H]⁻ 548.0441.

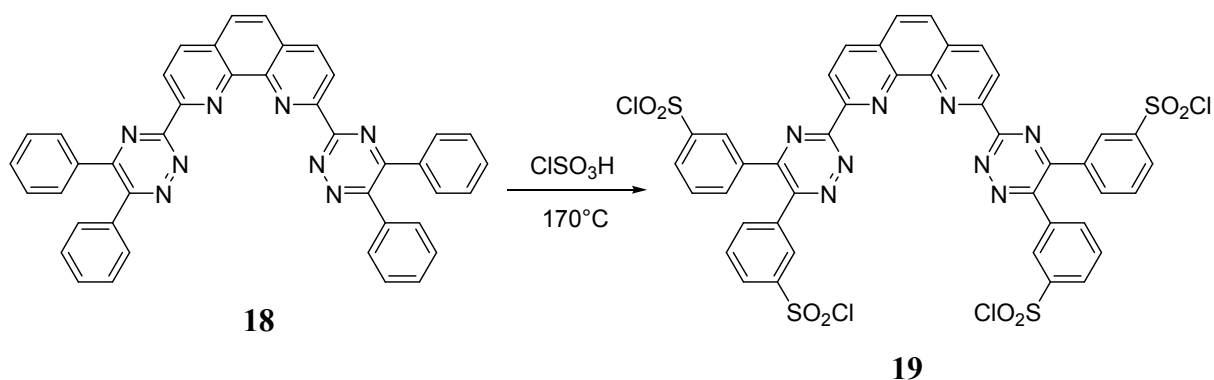
2,9-Bis(5,6-diphenyl-1,2,4-triazin-3-yl)-1,10-phenanthroline **18**



The starting material **17** (0.10 g, 0.340 mmol) was suspended in 1,4-dioxane (20 mL) and benzil **6** (0.157 g, 0.748 mmol, 2.2 eq) was added. Triethylamine (2 mL) was added and the mixture was heated under reflux for 4 days. The mixture was allowed to cool to room temperature and the

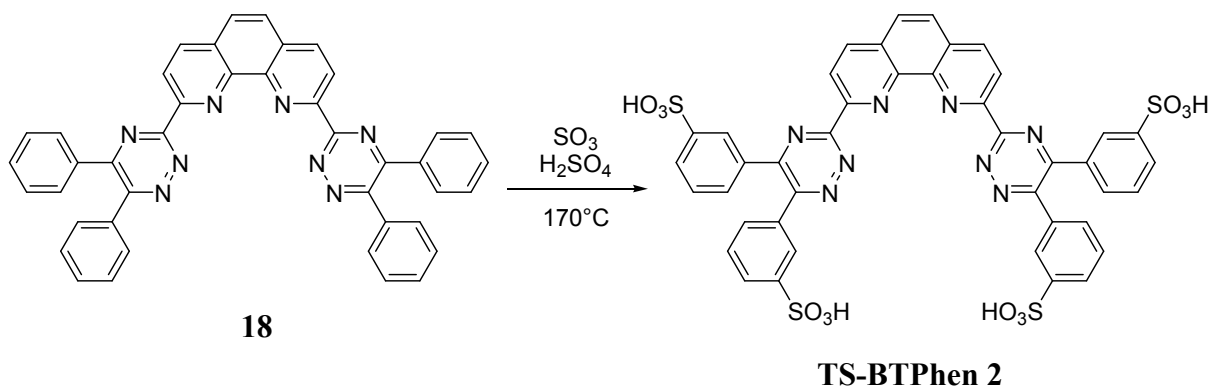
solvents were evaporated. The solid residue was triturated with MeOH (30 mL) and the insoluble solid was filtered and washed with MeOH (50 mL) and ether (25 mL). The solid was allowed to dry in air to afford the title compound **18** as a yellow solid (0.10 g, 48 %). Mp 289–293 °C (from 1,4-dioxane); Found: C, 78.34; H, 3.98; N, 17.81 %; C₄₂H₂₆N₈ requires C, 78.49; H, 4.08; N, 17.43 %; IR ν_{\max} (N) 3053, 1619, 1600, 1583, 1552, 1489, 1444, 1377, 1362, 1308, 1216, 1198, 1180, 1147, 1133, 1102, 1074, 1049, 1026, 1008, 919, 872, 842, 768, 751, 726, 697, 690, 637, 594, 564 cm⁻¹; ¹H NMR (400.1 MHz, CDCl₃, Me₄Si) δ : 7.35–7.49 (m, 12H, 8 \times *m*-ArH and 4 \times *p*-ArH), 7.74 (app d, *J* = 6.8, 4H, 4 \times *o*-ArH), 7.94 (app d, *J* = 6.8, 4H, 4 \times *o*-ArH), 8.00 (s, 2H, 5-H and 6-H), 8.53 (d, *J* = 8.3, 2H, 4-H and 7-H), 9.03 (d, *J* = 8.3, 2H, 3-H and 8-H) ppm; ¹³C NMR (100.6 MHz, CDCl₃, Me₄Si) δ : 123.2 (C-3 and C-8), 127.6 (C-5 and C-6), 128.6 (4 \times *m*-ArC), 128.6 (4 \times *m*-ArC), 129.6 (4 \times *o*-ArC), 129.7 (2 \times *p*-ArC), 130.4 (4 \times *o*-ArC), 130.7 (2 \times *p*-ArC), 135.5 (2 \times quat), 135.6 (2 \times quat), 137.2 (C-4 and C-7), 146.6 (2 \times quat), 153.1 (2 \times quat), 156.0 (2 \times quat), 156.3 (2 \times quat), 160.9 (2 \times quat), 165.2 (2 \times quat) ppm; HRMS (CI) *m/z* 643.2338: calculated for [C₄₂H₂₆N₈ + H]⁺ 643.2353.

3,3',3'',3'''-[3-(1,10-Phenanthroline-2,9-diyl)-1,2,4-triazine-5,5,6,6-tetrayl]tetrabenzenesulfonyl chloride **19**



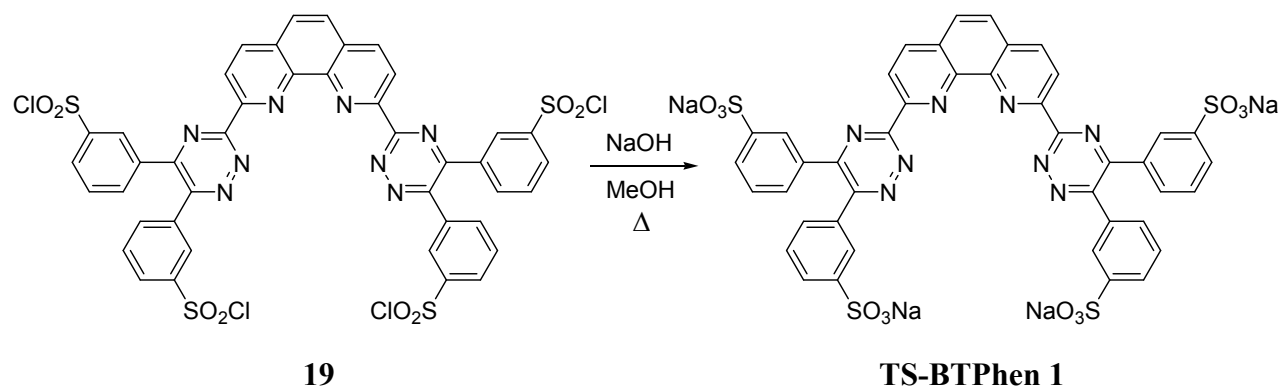
The starting material **18** (0.51 g, 0.794 mmol) was placed in a round bottomed flask and chlorosulfonic acid (10 mL) was added. The solution was stirred at 170 °C for 3 h. The solution was allowed to cool to room temperature and then carefully poured onto ice (ca. 100 mL). The precipitated solid was filtered and washed with water (50 mL) and allowed to dry in air to afford the title compound **19** as a yellow solid (0.71 g, 86 %). Mp 286–290 °C (decomposed); Found: C, 48.32; H, 2.47; N, 10.65 %; $C_{42}H_{22}N_8O_8S_4Cl_4$ requires C, 48.66; H, 2.14; N, 10.81 %; IR ν_{max} (N) 3092, 1625, 1593, 1577, 1541, 1532, 1474, 1420, 1307, 1219 (SO₂), 1167 (SO₂), 1118 (SO₂), 1098, 1024 (SO₂), 992, 851, 803, 791, 745, 677 cm⁻¹; ¹H NMR (400.1 MHz, DMSO-*d*₆) δ : 7.29–7.47 (m, 6H, 6 \times ArH), 7.64–7.77 (m, 6H, 6 \times ArH), 8.21–8.31 (m, 4H, 4 \times ArSO₂Cl 2-H), 8.35 (s, 2H, 5-H and 6-H), 8.92 (d, *J* = 8.4, 2H, 4-H and 7-H), 9.02 (d, *J* = 8.4, 2H, 3-H and 8-H) ppm; ¹³C NMR (100.6 MHz, DMSO-*d*₆) δ : 123.9 (C-4 and C-7), 125.8 (2 \times ArC), 126.4 (2 \times ArC), 126.8 (2 \times ArC), 127.0 (2 \times ArC), 127.8 (2 \times ArSO₂Cl C-2), 128.1 (2 \times ArC), 128.1 (2 \times ArC), 129.0 (C-5 and C-6), 130.0 (2 \times ArC), 134.6 (2 \times ArSO₂Cl C-3), 134.7 (2 \times ArSO₂Cl C-3), 139.4 (C-3 and C-8), 143.6 (2 \times quat), 146.5 (2 \times quat), 148.7 (2 \times quat), 149.2 (2 \times quat), 151.9 (2 \times quat), 155.6 (2 \times quat), 159.6 (2 \times quat), 164.5 (2 \times quat) ppm; HRMS (CI) *m/z* 963.0658 (as tetrasulfonic acid): calculated for [C₄₂H₂₆N₈O₁₂S₄ + H]⁺ 963.0631.

3,3',3'',3'''-[3-(1,10-phenanthroline-2,9-diyl)-1,2,4-triazine-5,5,6,6-tetrayl]tetrabenzenesulfonic acid TS-BTPhen 2



The starting material **18** (0.35 g, 0.545 mmol) was placed in a round bottomed flask and oleum (10 mL, 20 % SO₃ in H₂SO₄) was added. The solution was stirred at 170 °C for 3 h. The solution was allowed to cool to room temperature and acetone (500 mL) was added. The precipitated solid was filtered, washed with acetone (150 mL) and was allowed to dry in air to afford a solid that was dried at 70 °C for 30 min to afford the title compound **TS-BTPhen 2** as a brown solid (0.50 g, 95 %). Mp 230–235 °C (decomposed); Found: C, 51.96; H, 3.13; N, 11.72; S 13.68 %; C₄₂H₂₆N₈O₁₂S₄ requires C, 52.39; H, 2.72; N, 11.63; S 13.32 %; IR ν_{max} (N) 3069, 1708, 1640, 1619, 1595, 1534, 1498, 1365, 1328, 1138 (SO₂), 1116 (SO₂), 1023 (SO₂), 992, 872, 804, 768, 730, 680, 610 cm⁻¹; ¹H NMR (400.1 MHz, D₂O) δ : 6.28–7.10 (m, 8H, 8 \times ArH), 7.21–7.42 (m, 2H, 2 \times ArH), 7.56–7.82 (m, 4H, 4 \times ArH), 7.87–8.03 (m, 2H, 2 \times ArH), 8.17–8.27 (m, 2H, 2 \times ArH), 8.65–9.02 (m, 4H, 4 \times ArH) ppm; ¹H NMR (400.1 MHz, DMSO-*d*₆) δ : 7.35–7.58 (m, 6H, 6 \times ArH), 7.66–7.80 (m, 6H, 6 \times ArH), 8.20–8.29 (m, 4H, 4 \times ArSO₃H 2-H), 8.36 (s, 2H, 5-H and 6-H), 8.91–8.98 (m, 2H, 4-H and 7-H), 9.02–9.08 (m, 2H, 3-H and 8-H) ppm; ¹³C NMR (100.6 MHz, DMSO-*d*₆) δ : 124.0 (C-4 and C-7), 125.7 (2 \times ArC), 126.5 (2 \times ArC), 126.9 (2 \times ArC), 127.1 (2 \times ArC), 128.0 (2 \times ArSO₃H C-2), 128.3 (2 \times ArC), 129.2 (C-5 and C-6), 130.0 (2 \times ArC), 130.3 (2 \times ArC), 134.4 (2 \times ArSO₃H C-3), 134.5 (2 \times ArSO₃H C-3), 140.3 (C-3 and C-8), 142.4 (2 \times quat), 148.1 (2 \times quat), 148.1 (2 \times quat), 148.7 (2 \times quat), 151.0 (2 \times quat), 156.1 (2 \times quat), 156.4 (2 \times quat), 158.8 (2 \times quat) ppm; HRMS (CI) *m/z* 961.0479 (as tetrasulfonic acid monoanion): calculated for [C₄₂H₂₅N₈O₁₂S₄]⁻ 961.0469.

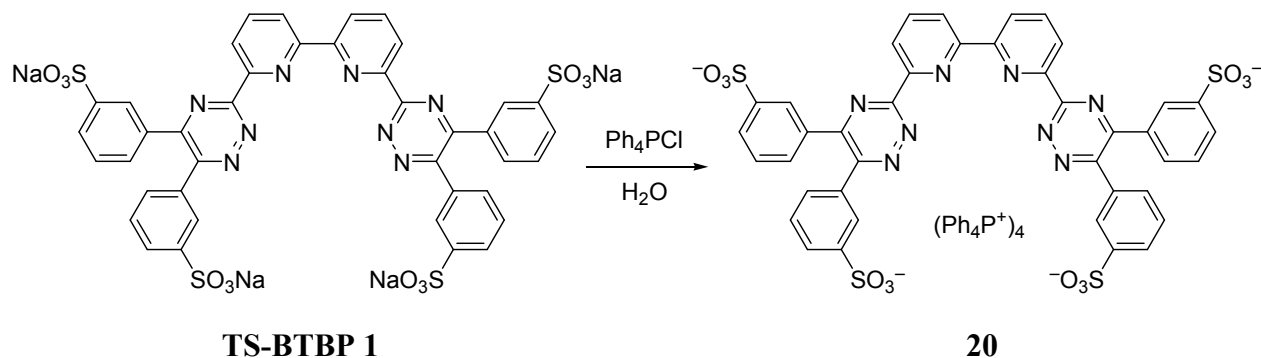
Tetrasodium 3,3',3'',3'''-[3-(1,10-phenanthroline-2,9-diyl)-1,2,4-triazine-5,5,6,6-tetrayl]tetrabenzenesulfonate TS-BTPhen 1



The starting material **19** (0.55 g, 0.532 mmol) was suspended in MeOH (80 mL) and a solution of finely powdered NaOH (0.127 g, 3.191 mmol, 6 eq) in MeOH (30 mL) was added. The mixture was heated under reflux for 3 h. The solution was allowed to cool to room temperature and was filtered. Excess NaOH in the filtrate was neutralized by the dropwise addition of HCl (ca. 1.5 mL, 2 M) until the pH was neutral. The filtrate was then diluted with acetone (1000 mL) and the precipitated solid was filtered and washed with MeOH (10 mL) and acetone (200 mL). The solid was allowed to dry in air and then dried at 70 °C for 30 min to afford the title compound **TS-BTPhen 1** as a green solid (0.51 g, 91 %). Mp above 300 °C (from MeOH); Found: C, 48.13; H, 2.31; N, 10.32; S, 11.87 %; $C_{42}H_{22}N_8O_{12}S_4Na_4$ requires C, 48.00; H, 2.11; N, 10.66; S, 12.20 %; IR ν_{max} (N) 3431, 1632, 1498, 1423, 1380, 1314, 1188 (SO₂), 1157, 1123, 1036 (SO₂), 996, 871, 802, 732, 687, 617 cm⁻¹; ¹H NMR (400.1 MHz, D₂O) δ : 6.22–6.38 (m, 4H, 4 \times ArH), 6.81–6.98 (m, 4H, 4 \times ArH), 7.15–7.23 (m, 2H, 2 \times ArH), 7.34–7.40 (m, 2H, 2 \times ArH), 7.50–7.72 (m, 4H, 4 \times ArH), 7.79–7.85 (m, 2H, 2 \times ArH), 8.36–8.53 (m, 4H, 4 \times ArH) ppm; ¹H NMR (400.1 MHz, DMSO-*d*₆) δ : 7.29–7.41 (m, 6H, 6 \times ArH), 7.67–7.82 (m, 6H, 6 \times ArH), 8.35–8.48 (m, 6H, 6 \times ArH), 9.00–9.08 (m, 4H, 4 \times ArH) ppm; ¹³C NMR (100.6 MHz, DMSO-*d*₆) δ : 123.1 (2 \times ArC), 125.8 (2 \times ArC), 126.6 (2 \times ArC), 126.9 (2 \times ArC), 127.1 (2 \times ArC), 127.6 (2 \times ArSO₃Na C-2), 128.1 (2 \times ArC), 129.0 (2 \times ArC), 129.5 (2 \times ArC), 130.2 (2 \times ArC), 134.4 (2 \times ArSO₃Na C-3), 134.6 (2 \times ArSO₃Na C-3), 139.3 (C-3 and C-8), 144.9 (2 \times quat), 145.4 (2 \times quat), 149.0 (2 \times quat), 149.2 (2 \times quat), 151.5 (2 \times quat), 155.8 (2 \times

quat), 156.6 (2 × quat), 159.0 (2 × quat) ppm; HRMS (CI) m/z 1026.9911: calculated for $[\text{C}_{42}\text{H}_{22}\text{N}_8\text{O}_{12}\text{S}_4\text{Na}_3]^-$ 1026.9928.

Tetrakis(tetraphenylphosphonium) 3,3',3'',3'''-[3-(2,2'-bipyridine-6,6'-diyl)-1,2,4-triazine-5,5,6,6-tetrayl]tetrabenzenesulfonate 20

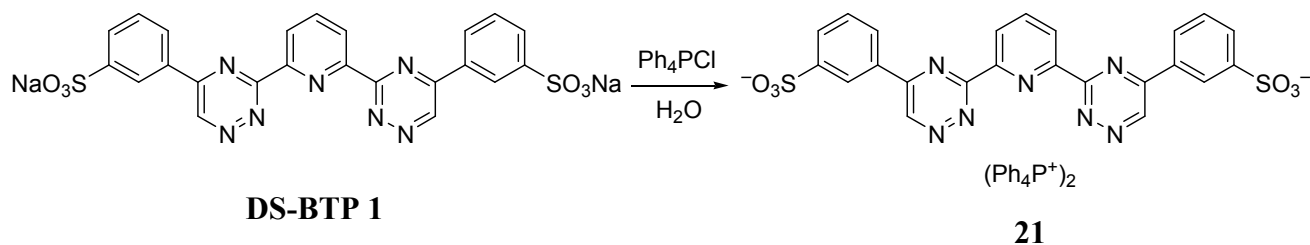


The starting material **TS-BTBP 1** (0.21 g, 0.204 mmol) was dissolved in distilled water (10 mL) in a conical flask. In a separate flask, tetraphenylphosphonium chloride (0.61 g, 1.637 mmol, 8 eq) was dissolved in distilled water (15 mL). This solution was added to the solution of the starting material **TS-BTBP 1**, and the resulting cloudy suspension was extracted with DCM (2 × 50 mL). The combined organic extracts were washed with distilled water (2 × 30 mL), dried over sodium sulfate and evaporated to afford the title compound **20** as a light green solid (0.34 g, 72 %). Mp 219–224 °C (from DCM); Found: C, 70.82; H, 4.85; N, 4.76; S, 5.12; P, 5.69 %; $\text{C}_{136}\text{H}_{102}\text{N}_8\text{O}_{12}\text{S}_4\text{P}_4$ requires C, 71.25; H, 4.48; N, 4.89; S 5.59; P, 5.40 %; IR ν_{max} (N) 3415, 3063, 1617, 1585, 1483, 1436, 1375, 1318, 1203 (SO_2), 1105 (SO_2), 1032, 995, 802, 760, 719, 687, 614 cm^{-1} ; ^1H NMR (400.1 MHz, CD_3CN) δ : 7.23 (t, $J = 7.7$, 2H, 2 × ArSO_3^- 5-H), 7.28 (t, $J = 7.7$, 2H, 2 × ArSO_3^- 5-H), 7.31–7.34 (m, 4H, 4 × ArSO_3^- 4-H), 7.65–7.71 (m, 32H, 32 × Ph_4P^+ *m*-ArH), 7.73–7.78 (m, 32H, 32 × Ph_4P^+ *o*-ArH), 7.82–7.86 (m, 4H, 4 × ArSO_3^- 6-H), 7.90–7.95 (m, 16H, 16 × Ph_4P^+ *p*-ArH), 8.08 (t, $J = 7.8$, 2H, 4-H and 4'-H), 8.25 (t, $J = 1.3$, 2H, 2 × ArSO_3^- 2-H), 8.43 (t, $J = 1.3$, 2H, 2 × ArSO_3^- 2-H), 8.55

(dd, $J = 7.8$ and 0.9 , 2H, 3-H and 3'-H), 8.77 (dd, $J = 7.8$ and 0.9 , 2H, 5-H and 5'-H) ppm; ^{13}C NMR (100.6 MHz, CD_3CN) δ : 117.4 (d, $^1J_{\text{C-P}} = 95.1$, $16 \times \text{Ph}_4\text{P}^+$ *ipso*-ArC), 122.3 (C-5 and C-5'), 124.0 (C-3 and C-3'), 126.4 ($2 \times \text{ArSO}_3^-$ C-2), 126.6 ($2 \times \text{ArSO}_3^-$ C-2), 127.0 ($2 \times \text{ArSO}_3^-$ C-6), 127.3 ($2 \times \text{ArSO}_3^-$ C-6), 127.4 ($2 \times \text{ArSO}_3^-$ C-5), 127.7 ($2 \times \text{ArSO}_3^-$ C-5), 129.3 ($2 \times \text{ArSO}_3^-$ C-4), 129.4 ($2 \times \text{ArSO}_3^-$ C-4), 130.0 (d, $^2J_{\text{C-P}} = 12.7$, $32 \times \text{Ph}_4\text{P}^+$ *o*-ArC), 134.3 (d, $^3J_{\text{C-P}} = 10.5$, $32 \times \text{Ph}_4\text{P}^+$ *m*-ArC), 134.8 ($2 \times \text{quat}$), 135.0 (d, $^4J_{\text{C-P}} = 3.0$, $16 \times \text{Ph}_4\text{P}^+$ *p*-ArC), 135.2 ($2 \times \text{quat}$), 138.1 (C-4 and C-4'), 149.0 ($2 \times \text{quat}$), 149.2 ($2 \times \text{quat}$), 152.3 ($2 \times \text{quat}$), 155.4 ($2 \times \text{quat}$), 155.6 ($2 \times \text{quat}$), 156.2 ($2 \times \text{quat}$), 160.3 ($2 \times \text{quat}$) ppm; ^{31}P NMR (161.8 MHz, CD_3CN) δ : 22.9 (s, $4 \times \text{Ph}_4\text{P}^+$) ppm; HRMS (CI) m/z 937.0436 (as triprotonated tetraanion): calculated for $[\text{C}_{40}\text{H}_{25}\text{N}_8\text{O}_{12}\text{S}_4]^-$ 937.0474.

Bis(tetraphenylphosphonium) 3,3'-[3-(pyridine-2,6-diyl)-1,2,4-triazine-

5,5-diyl]dibenzenesulfonate **21**



The starting material **DS-BTP 1** (0.12 g, 0.202 mmol) was dissolved in distilled water (10 mL) in a conical flask. In a separate flask, tetraphenylphosphonium chloride (0.30 g, 0.809 mmol, 4 eq) was dissolved in distilled water (10 mL). This solution was added to the solution of the starting material **DS-BTP 1**, and the resulting cloudy suspension was extracted with DCM (2×50 mL). The combined organic extracts were washed with distilled water (2×30 mL), dried over sodium sulfate and evaporated to afford the title compound **21** as a light yellow solid (0.23 g, 93 %). Mp 168–172 °C (from DCM); Found: C, 69.02; H, 4.61; N, 7.74; S, 4.87; P, 5.16 %; $\text{C}_{71}\text{H}_{55}\text{N}_7\text{O}_6\text{S}_2\text{P}_2$ requires C, 69.43; H, 4.51; N, 7.98; S 5.22; P, 5.04 %; IR ν_{max} (N) 3434, 3058, 1585, 1540, 1502, 1483, 1436,

1316, 1207 (SO₂), 1106 (SO₂), 1031, 994, 839, 790, 757, 720, 688, 666, 642, 612 cm⁻¹; ¹H NMR (400.1 MHz, CDCl₃) δ: 7.49 (t, *J* = 7.7, 2H, 2 × ArSO₃⁻ 5-H), 7.56–7.62 (m, 16H, 16 × Ph₄P⁺ *m*-ArH), 7.74–7.79 (m, 16H, 16 × Ph₄P⁺ *o*-ArH), 7.86–7.91 (m, 8H, 8 × Ph₄P⁺ *p*-ArH), 8.17 (t, *J* = 7.8, 1H, 4-H), 8.21 (dt, *J* = 7.7 and 1.4, 2H, 2 × ArSO₃⁻ 4-H), 8.48 (dt, *J* = 7.7 and 1.4, 2H, 2 × ArSO₃⁻ 6-H), 8.77 (t, *J* = 1.5, 2H, 2 × ArSO₃⁻ 2-H), 8.82 (d, *J* = 7.8, 2H, 3-H and 5-H), 9.68 (s, 2H, 2 × HC=N) ppm; ¹³C NMR (100.6 MHz, CDCl₃) δ: 117.4 (d, ¹*J*_{C-P} = 89.4, 8 × Ph₄P⁺ *ipso*-ArC), 125.6 (2 × ArSO₃⁻ C-2), 125.9 (C-3 and C-5), 128.5 (2 × ArSO₃⁻ C-6), 129.0 (2 × ArSO₃⁻ C-5), 130.8 (d, ²*J*_{C-P} = 12.8, 16 × Ph₄P⁺ *o*-ArC), 131.0 (2 × ArSO₃⁻ C-4), 132.4 (2 × quat), 134.4 (d, ³*J*_{C-P} = 10.3, 16 × Ph₄P⁺ *m*-ArC), 135.8 (d, ⁴*J*_{C-P} = 2.9, 8 × Ph₄P⁺ *p*-ArC), 138.4 (C-4), 145.3 (2 × HC=N), 148.8 (2 × quat), 153.8 (2 × quat), 155.6 (2 × ArSO₃⁻ C-1), 162.5 (2 × quat) ppm; ³¹P NMR (161.8 MHz, CDCl₃) δ: 23.0 (s, 2 × Ph₄P⁺) ppm; HRMS (CI) *m/z* 548.0437 (as monoprotonated dianion): calculated for [C₂₃H₁₄N₇O₆S₂]⁻ 548.0441.

2: Solvent Extraction Studies

General procedures

The approximate solubilities of the tested ligands in 0.5 mol L⁻¹ HNO₃ were determined, and are shown in Table 1. The solubilities of the ligands were determined by stepwise dissolution of a known mass of the ligand. The diluent was then added incrementally in 100 μL aliquots followed by shaking after each addition until a clear aqueous solution was obtained.

For the measurements of distribution ratios, the aqueous solutions were prepared by spiking 1.18 mL of nitric acid solutions (0.25 – 1 mol L⁻¹) containing 10 mmol L⁻¹ of the tested ligand with 10 μL of working solutions of ²⁴¹Am and with 10 μL of working solutions of ¹⁵²Eu tracers. The organic phase solutions consisted of 0.2 mol L⁻¹ TODGA dissolved in 5 % vol. 1-octanol in kerosene. In each case before contacting with the organic phase, an aliquot of 200 μL was taken from the labeled aqueous phases to measure activity of americium and europium to allow for activity balance calculations. Each organic phase (1 mL) was shaken with each of the aqueous phases (1 mL) for 6 hours at a thermostatted temperature of 22 °C, using a horizontal GFL 3005 Orbital Shaker (250 min⁻¹).

After phase separation by centrifugation (1 minute, 6000 rot/min), two parallel 200 μL aliquots of each phase were withdrawn into glass ampoules for the analysis. The walls of the glass ampoules were washed with 1 mL of distilled water or 5 % vol. 1-octanol in kerosene and ampoules were covered with a piece of parafilm. Activity measurements of ²⁴¹Am and ¹⁵²Eu were performed with a γ-ray spectrometer EG&G Ortec with a PGT HPGe detector. The γ-lines at 59.5 keV, and 121.8 keV were examined for ²⁴¹Am and ¹⁵²Eu, respectively. The errors given in the figures, throughout the text and in the supporting information are 1 σ and are based on the counting statistics.

Table 1. Solubilities of disulfonated and tetrasulfonated ligands in 0.5 M HNO₃.

Ligand	Solubility (mol/L)
TS-BTBP 1	> 0.11
TS-BTBP 2	> 0.11
TS-BTPhen 1	> 0.11
TS-BTPhen 2	> 0.11
DS-BTBP 1	< 0.01
DS-BTBP 2	< 0.01
DS-BTP 1	> 0.11
DS-BTP 2	> 0.11
DS-BTP 3	< 0.005
DS-BTP 4	≥ 0.005

2.1 Extraction of Am(III) and Eu(III) by TODGA in the absence and presence of sulfonated ligands

Table 2. Extraction of Am(III) and Eu(III) from 0.28 M nitric acid by TODGA (0.2 M dissolved in 5 vol. % octanol in kerosene) in the absence and presence of sulfonated ligands in the aqueous phase.

Ligand (0.01 M)	[HNO ₃]	D_{Am}	D_{Eu}	$SF_{Eu/Am}$
None	0.28 M	9.4 ± 0.4	58 ± 7	6.2 ± 0.8
TS-BTBP 1	0.28 M	0.003 ± 0.001	2.1 ± 0.1	707 ± 312
TS-BTBP 2	0.28 M	— ^a	— ^a	— ^a
TS-BTPhen 1	0.28 M	0.012 ± 0.003	5.8 ± 0.2	482 ± 110
TS-BTPhen 2	0.28 M	0.007 ± 0.002	6.5 ± 0.3	934 ± 233
DS-BTBP 1	0.28 M	— ^a	— ^a	— ^a
DS-BTBP 2	0.28 M	— ^a	— ^a	— ^a
DS-BTP 1	0.28 M	— ^a	— ^a	— ^a
DS-BTP 2	0.28 M	— ^a	— ^a	— ^a
DS-BTP 3	0.28 M	— ^a	— ^a	— ^a
DS-BTP 4^b	0.28 M	4.2 ± 0.1	29.8 ± 1.9	7.1 ± 0.5

^a Not measured. ^b Ligand concentration was 0.005 M.

Table 3. Extraction of Am(III) and Eu(III) from 0.5 M nitric acid by TODGA (0.2 M dissolved in 5 vol. % octanol in kerosene) in the absence and presence of sulfonated ligands in the aqueous phase.

Ligand (0.01 M)	[HNO ₃]	D_{Am}	D_{Eu}	$SF_{Eu/Am}$
None	0.5 M	46 ± 4	162 ± 37	3.5 ± 0.9
TS-BTBP 1	0.5 M	0.121 ± 0.009	74 ± 21	616 ± 178
TS-BTBP 2	0.5 M	0.18 ± 0.01	83 ± 24	458 ± 132
TS-BTPhen 1	0.5 M	0.25 ± 0.001	79 ± 19	321 ± 79
TS-BTPhen 2	0.5 M	0.30 ± 0.01	76 ± 22	256 ± 77
DS-BTBP 1	0.5 M	38 ± 3	150 ± 30	7.75 ± 1.1
DS-BTBP 2	0.5 M	32 ± 3	144 ± 32	5 ± 1
DS-BTP 1	0.5 M	24.3 ± 1.4	139 ± 18	5.7 ± 0.8
DS-BTP 2	0.5 M	27 ± 3	98 ± 27	4 ± 1
DS-BTP 3	0.5 M	— ^a	— ^a	— ^a
DS-BTP 4^b	0.5 M	24.1 ± 4.9	111 ± 33	4.6 ± 1.6

^a Not measured. ^b Ligand concentration was 0.005 M.

Table 4. Extraction of Am(III) and Eu(III) from 0.77 M nitric acid by TODGA (0.2 M dissolved in 5 vol. % octanol in kerosene) in the absence and presence of sulfonated ligands in the aqueous phase.

Ligand (0.01 M)	[HNO ₃]	D_{Am}	D_{Eu}	$SF_{Eu/Am}$
None	0.77 M	103 ± 14	543 ± 302	5.3 ± 3.0
TS-BTBP 1	0.77 M	0.71 ± 0.03	184 ± 70	260 ± 99
TS-BTBP 2	0.77 M	0.63 ± 0.02	172 ± 86	271 ± 136
TS-BTPhen 1	0.77 M	1.22 ± 0.03	169 ± 65	138 ± 54
TS-BTPhen 2	0.77 M	1.46 ± 0.04	207 ± 96	142 ± 66
DS-BTBP 1	0.77 M	— ^a	— ^a	— ^a
DS-BTBP 2	0.77 M	47 ± 5	192 ± 119	4 ± 3
DS-BTP 1	0.77 M	— ^a	— ^a	— ^a
DS-BTP 2	0.77 M	74 ± 8	487 ± 292	7 ± 4
DS-BTP 3	0.77 M	— ^a	— ^a	— ^a
DS-BTP 4^b	0.77 M	54.5 ± 4.7	178 ± 32	3.3 ± 0.7

^a Not measured. ^b Ligand concentration was 0.005 M.

Table 5. Extraction of Am(III) and Eu(III) from 1.04 M nitric acid by TODGA (0.2 M dissolved in 5 vol. % octanol in kerosene) in the absence and presence of sulfonated ligands in the aqueous phase.

Ligand (0.01 M)	[HNO ₃]	D_{Am}	D_{Eu}	$SF_{Eu/Am}$
None	1.04 M	175 ± 31	385 ± 243	2.2 ± 1.4
TS-BTBP 1	1.04 M	2.23 ± 0.06	282 ± 164	127 ± 73
TS-BTBP 2	1.04 M	— ^a	— ^a	— ^a
TS-BTPhen 1	1.04 M	4.7 ± 0.2	144 ± 60	31 ± 13
TS-BTPhen 2	1.04 M	4.2 ± 0.1	274 ± 94	65 ± 22
DS-BTBP 1	1.04 M	— ^a	— ^a	— ^a
DS-BTBP 2	1.04 M	— ^a	— ^a	— ^a
DS-BTP 1	1.04 M	— ^a	— ^a	— ^a
DS-BTP 2	1.04 M	— ^a	— ^a	— ^a
DS-BTP 3	1.04 M	— ^a	— ^a	— ^a
DS-BTP 4^b	1.04 M	88.2 ± 9.6	207 ± 56	2.4 ± 0.7

^a Not measured. ^b Ligand concentration was 0.005 M.

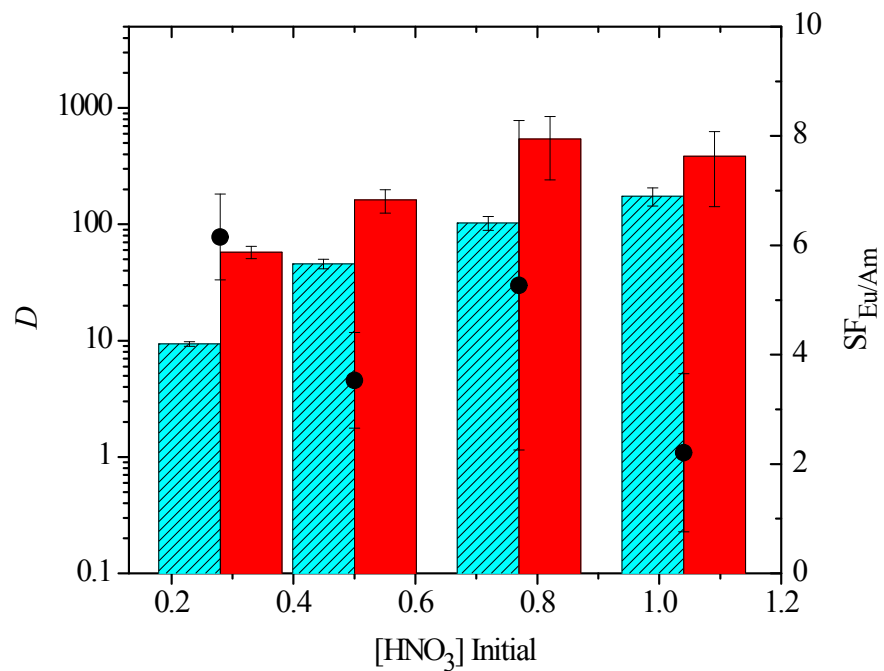


Figure 1. Extraction of Am(III) and Eu(III) from nitric acid by TODGA (0.2 M dissolved in 5 vol. % octanol in kerosene) in the absence of tetrasulfonated BTBP and BTPPhen ligands (0.01 M) in the aqueous phase as a function of initial nitric acid concentration (D = distribution ratio, SF = separation factor, dashed bars = D_{Am} , clear bars = D_{Eu} , ● = $SF_{Eu/Am}$, mixing time: 360 min., temperature: 22 °C ± 1 °C).

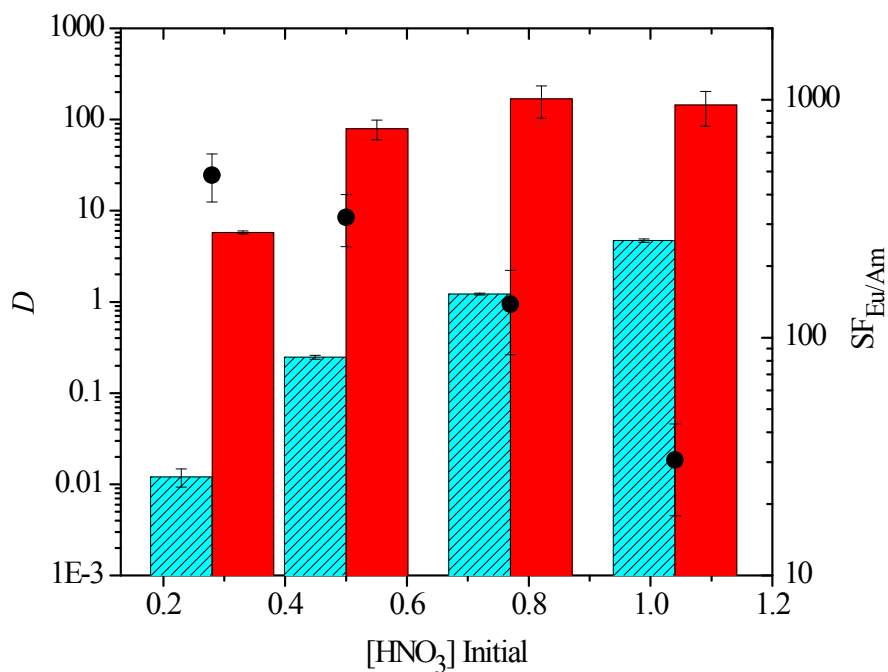


Figure 2. Extraction of Am(III) and Eu(III) from nitric acid by TODGA (0.2 M dissolved in 5 vol. % octanol in kerosene) in the presence of tetrasulfonated BTPPhen ligand **TS-BTPPhen 1** (0.01 M) in the aqueous phase as a function of initial nitric acid concentration (D = distribution ratio, SF = separation factor, dashed bars = D_{Am} , clear bars = D_{Eu} , \bullet = $SF_{Eu/Am}$, mixing time: 360 min., temperature: 22 °C \pm 1 °C).

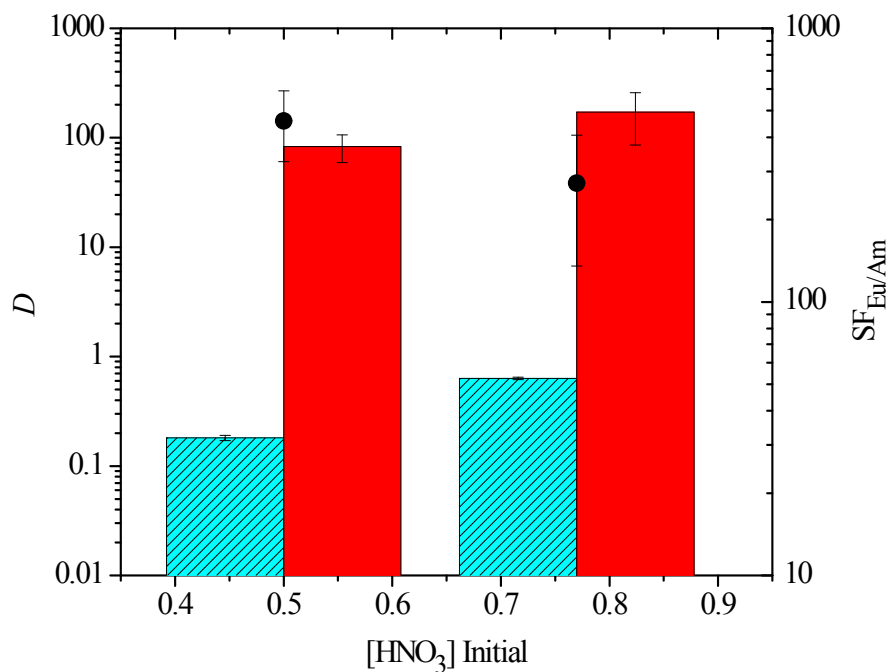


Figure 3. Extraction of Am(III) and Eu(III) from nitric acid by TODGA (0.2 M dissolved in 5 vol. % octanol in kerosene) in the presence of tetrasulfonated BTBP ligand **TS-BTBP 2** (0.01 M) in the aqueous phase as a function of initial nitric acid concentration (D = distribution ratio, SF = separation factor, dashed bars = D_{Am} , clear bars = D_{Eu} , \bullet = $SF_{Eu/Am}$, mixing time: 360 min., temperature: 22 °C \pm 1 °C).

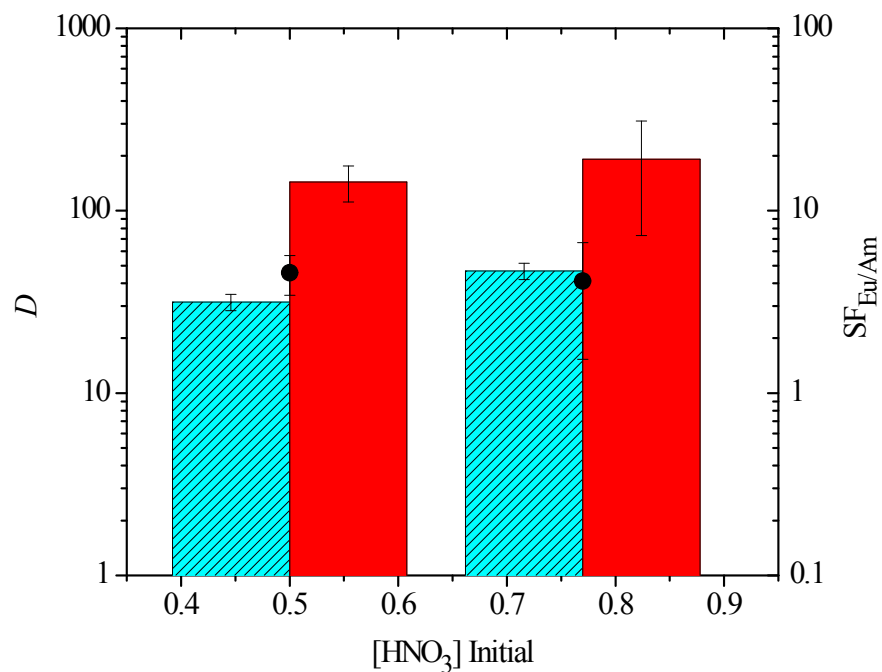


Figure 4. Extraction of Am(III) and Eu(III) from nitric acid by TODGA (0.2 M dissolved in 5 vol. % octanol in kerosene) in the presence of disulfonated BTBP ligand **DS-BTBP 2** (0.01 M) in the aqueous phase as a function of initial nitric acid concentration (D = distribution ratio, SF = separation factor, dashed bars = D_{Am} , clear bars = D_{Eu} , \bullet = $SF_{Eu/Am}$, mixing time: 360 min., temperature: 22 °C \pm 1 °C).

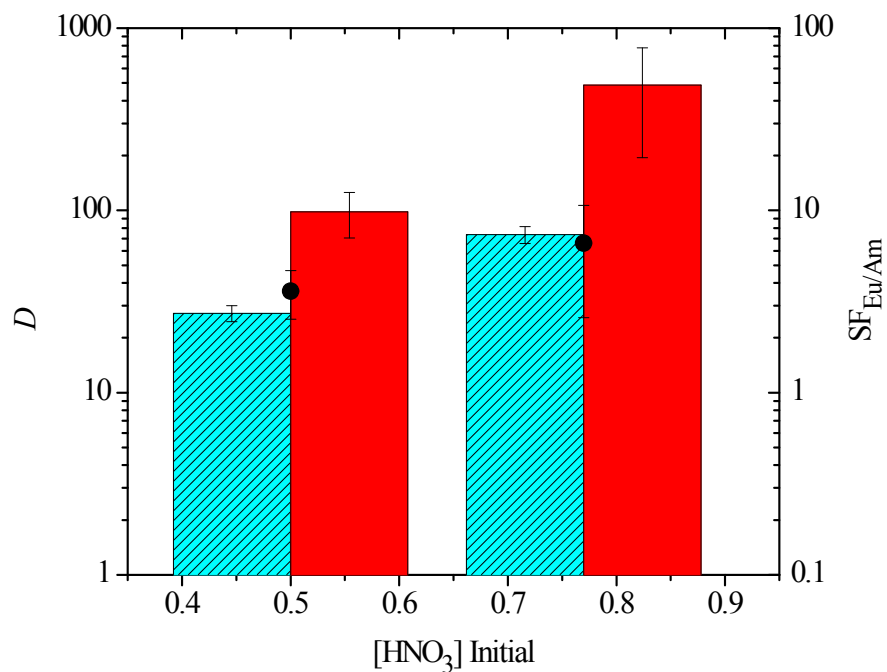


Figure 5. Extraction of Am(III) and Eu(III) from nitric acid by TODGA (0.2 M dissolved in 5 vol. % octanol in kerosene) in the presence of disulfonated BTP ligand **DS-BTP 2** (0.01 M) in the aqueous phase as a function of initial nitric acid concentration (D = distribution ratio, SF = separation factor, dashed bars = D_{Am} , clear bars = D_{Eu} , ● = $SF_{Eu/Am}$, mixing time: 360 min., temperature: 22 °C ± 1 °C).

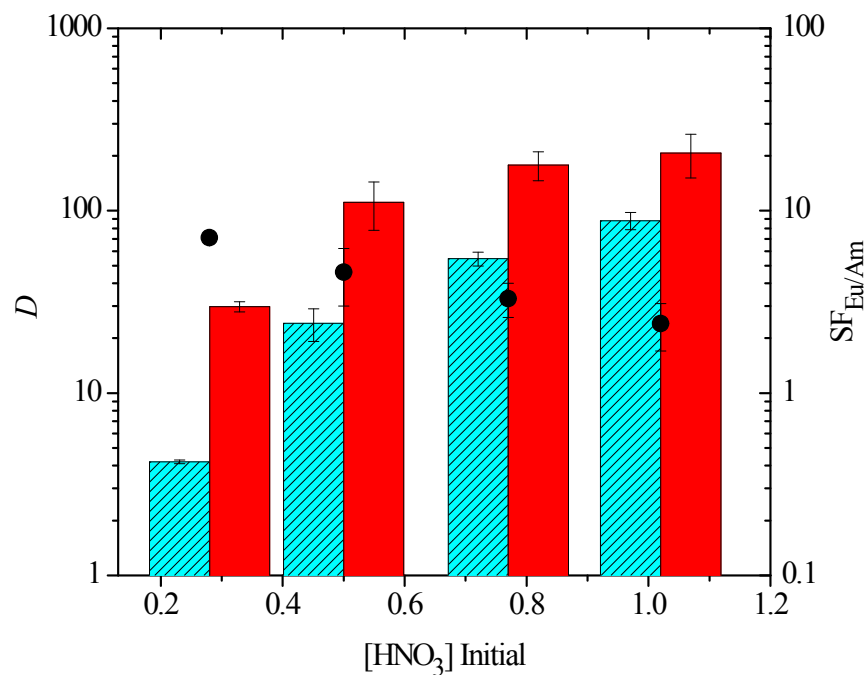


Figure 6. Extraction of Am(III) and Eu(III) from nitric acid by TODGA (0.2 M dissolved in 5 vol. % octanol in kerosene) in the presence of disulfonated BTP ligand **DS-BTP 4** (0.005 M) in the aqueous phase as a function of initial nitric acid concentration (D = distribution ratio, SF = separation factor, dashed bars = D_{Am} , clear bars = D_{Eu} , ● = $SF_{Eu/Am}$, mixing time: 360 min., temperature: 22 °C ± 1 °C).

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