

Supplementary Information to

A TRLFS study on the complexation of Cm(III) and Eu(III) with 4-*t*-butyl-6,6'-bis-(5,6-diethyl-1,2,4-triazin-3-yl)-2,2'-bipyridine in water/2-propanol mixture

Sascha Trumm, Georg Lieser, Mark R. S. J. Foreman, Petra J. Panak, Andreas Geist and Thomas Fanghänel

Synthesis of ^tBu-C2-BTBP

All organic reagents required for the synthesis of the *t*-Bu-C2-BTBP were purchased from Acros or Aldrich, while inorganic reagents required for the preparation of ^tBu-C2-BTBP were obtained from either BDH or Aldrich.

Synthesis of 4-tert-butyl-2,2'-bipyridine

A solution of *N,N*-dimethyl-2-aminoethanol (8 mL) in petroleum ether (150 mL of the 60–80 °C fraction) was placed in a 1 L three necked flask and was cooled to -78 °C, before the addition of 2 M butyl lithium dissolved in hexanes (80 mL). The mixture was seen to occasionally change colour momentary to yellow during this addition. The cooling bath was removed and the mixture allowed returning to room temperature over the course of 60 min. The mixture was recooled to -78 °C before the drop wise addition of 4-*tert*-butylpyridine (16 mL) dissolved in petroleum ether (50 mL of the 60 to 80 °C fraction). This addition was performed over the course of twenty minutes, the colour of the mixture changed to red. The mixture was allowed to stir for one hour at -78 °C before the flask was transferred to an ice/water bath. After one hour within this 0 °C bath the flask was transferred back into the -78 °C bath. After cooling for ten minutes a mixture of tributyl tin chloride (30 mL) in tetrahydrofuran (100 mL) was added drop wise over a thirty minute time period. The mixture was allowed to stir for a further 150 min before being allowed to slowly return to room temperature. The next day the mixture was cooled to 0 °C before the careful addition of water (150 mL). The organic layer was separated from the aqueous layer. The organic layer was then concentrated using a rotary evaporator, before being treated with petroleum ether (250 mL of the 60–80 °C fraction) and anhydrous sodium sulfate. After removal of the sodium sulphate the solution was concentrated again using the rotary evaporator. The unchanged starting materials were removed by distillation under reduced pressure to leave a mixture of 4-*tert*-butyl-2-tributylstannanyl-pyridine and other polybutyl tin compounds as an involatile residue.

MS (CI+) 426 (z/m). Molecular ion found at 426.2189 amu, ¹²C₂₁¹H₄₀¹⁴N¹²⁰Sn requires 426.2183 (error of 1.5 ppm).

After cooling the residue from the still pot was dissolved in toluene (240 mL) before the addition of 2-bromopyridine (8 mL). After removal of atmospheric oxygen, *tetrakis*-(triphenyl phosphine) palladium (1.76 g) was added. The resulting mixture was heated under reflux (24 h). After allowing the mixture to cool before the removal of toluene by means of a rotary evaporator. The resulting oily residue was dissolved in petroleum ether (150 mL of the 60–80 °C fraction) and extracted four times with 1.2 M hydrochloric acid (100 mL). The combined aqueous extracts were washed twice with petroleum ether (30 mL of the 60–80 °C fraction) before the addition of sodium hydroxide pellets (24 g). After the sodium hydroxide

had dissolved and the mixture had returned to room temperature the aqueous mixture was extracted with diethyl ether (5×50 mL). The combined ethereal extracts were treated with anhydrous sodium sulfate, before removal of the drying agent by filtration and the removal of the solvent using the rotary evaporator. The resulting oil (18 g) was subject to chromatography using silica (180 g). The column was eluted with dichloromethane, followed by 10 % (v/v) ethyl acetate in dichloromethane and finally 10% (v/v) ethanol in dichloromethane as the mobile phase. Note that the presence and location of 4-*tert*-butyl-2,2'-bipyridine upon silica TLC plates can be rapidly revealed (by the formation of a deep red colour) by dipping the plates in a dilute aqueous iron(II) chloride solution. Those fractions which were judged by TLC to contain 4-*tert*-butyl-2,2'-bipyridine were combined and concentrated to furnish the title compound as a solid. (9.3 g)

MS (CI+) 213 and 197 (z/m). Molecular ion found at 213.1394 amu, $^{12}\text{C}_{14}^1\text{H}_{17}^{14}\text{N}_2$ requires 213.1392 (error of 1.0 ppm).

Synthesis of 4-tert-butyl-2,2'-bipyridine-N,N'-dioxide

4-*tert*-butyl-2,2'-bipyridine (9.31 g) was dissolved in acetic acid (40 mL) before the addition of 35 % (w/w) aqueous hydrogen peroxide solution (25 mL). The resulting mixture was heated (80 °C) for 24 h before the addition of 35 % (w/w) aqueous hydrogen peroxide solution (40 mL). After a further 24 h of heating the mixture was allowed to cool before the careful addition of 12 M aqueous sodium hydroxide solution (50 mL). The resulting cloudy mixture was extracted with dichloromethane (4×40 mL), the resulting organic extracts were combined and treated with anhydrous sodium sulfate. After removal of the sodium sulfate by filtration and the dichloromethane by rotary evaporation a semi-solid residue remained. This was treated with acetone (10 mL) to furnish a solid. The solid (4.95 g) was collected by filtration and washed twice with cold acetone (10 mL) before being allowed to dry in air.

δ_{H} 8.34 (1H, m), 8.27 (1H, dd, 6.9 and 0.4 Hz), 7.66 (1H, m), 7.62 (1H, m), 7.34 (3H, m) and 1.34 (9H, s) ppm. δ_{C} 150.01 (quat), 143.01 (quat), 141.55 (quat), 140.57, 139.67, 128.98, 126.84, 125.68, 125.29, 124.27, 35.06 and 30.90 ppm. MS (CI+) 244 (z/m). Molecular ion found at 244.1208 amu, $^{12}\text{C}_{14}^1\text{H}_{16}^{14}\text{N}_2^{16}\text{O}_2$ requires 244.1212 (error of 1.3 ppm).

Synthesis of 4-tert-butyl-6,6'-dicyano-2,2'-bipyridine

4-*tert*-butyl-2,2'-bipyridine-*N,N'*-dioxide (4.95 g) was dissolved in dichloromethane (90 mL) before being treated with trimethylsilyl cyanide (6.8 mL) and dimethyl carbonyl chloride (4.7 mL). After allowing the mixture to stand for three days trimethylsilyl cyanide (7.0 mL) and dimethyl carbonyl chloride (7.0 mL) were added to the mixture. After a further five days the reaction mixture was evaporated down to a mixture of a white solid and a liquid. This was treated with methanol (50 mL) and the solid (4.33 g) was collected by filtration, before being washed with methanol (2×15 mL) and being allowed to dry in air.

δ_{H} 8.71 (1H, m), 8.69 (1H, m), 8.01 (1H, dd, 7.9 and 7.9 Hz), 7.77 (2H, m) and 1.43 (9H, s) ppm. δ_{C} 163.83, 156.39, 155.71, 138.68, 133.65, 129.35, 127.04, 125.23, 122.08, 117.94, 35.93 and 30.80 ppm. MS (CI+) 263, 262 and 247 (z/m). Molecular ion found at 263.1216 amu, $^{12}\text{C}_{16}^1\text{H}_{14}^{14}\text{N}_4$ requires 262.1218 (error of 0.8 ppm). Molecular ion found at 263.1289 amu, $^{12}\text{C}_{16}^1\text{H}_{15}^{14}\text{N}_4$ requires 263.1297 (error of 3.0 ppm).

Synthesis of 4-tert-butyl-2,2'-bipyridyl-6,6'-dicarbamidrazone

To a suspension of 4-*tert*-butyl-6,6'-dicyano-2,2'-bipyridine (650 mg) in ethanol (60 ml) was added hydrazine hydrate (6 ml) and the resulting mixture was stirred for seventeen days before being collected upon a P3 sintered glass disk. After washing with ethanol (3 x 25 ml) the solid (613 mg) was dried in air.

δ_{H} (DMSO) 8.58 (1H, dd, 7.5 and 1.0 Hz), 8.48 (1H, d, 1.8 Hz), 7.91 (3H, m), 5.94 (2H, s broad), 5.90 (2H, s broad), 5.39 (4H, s broad) and 1.37 (9H, s) ppm. δ_{C} (DMSO) 160.85 (quat), 153.94 (quat), 153.58 (quat), 151.79 (quat), 151.74 (quat), 143.77 (quat), 143.56 (quat), 137.52, 120.60, 119.75, 117.20, 116.12, 35.20 (quat) and 30.67 ppm.

Synthesis of 6,6'-bis-(5,6-diethyl-[1,2,4]triazin-3-yl)-4-tert-butyl-[2,2']bipyridinyl

To a suspension of 4-*tert*-butyl-2,2'-bipyridyl-6,6'-dicarbamidrazone (683 mg) in tetrahydrofuran (40 mL) was added hexane-3,4-dione (6 mL). Within two minutes the mixture became yellow and homogenous, triethylamine (2 mL) was added and the resulting mixture heated under reflux (2 h). After cooling the mixture was filtered through (Celite) before the volatile solvents were removed by rotary evaporation. The resulting oil (4.7 g) was treated with methanol (20 mL), after tituration the yellow solid (685 mg, 68 %) was collected by filtration, washed with methanol (10 mL), washed with diethyl ether (10 mL) and dried in air.

δ_{H} 8.95 (1H, d, $^4\text{J } ^1\text{H}-^1\text{H} = 1.8 \text{ Hz}$), 8.89 (1H, dd, $^3\text{J } ^1\text{H}-^1\text{H} = 7.9 \text{ Hz}$ and $^4\text{J } ^1\text{H}-^1\text{H} = 1.0 \text{ Hz}$), 8.68 (1H, d, $^4\text{J } ^1\text{H}-^1\text{H} = 1.8 \text{ Hz}$), 8.63 (1H, dd, $^3\text{J } ^1\text{H}-^1\text{H} = 7.9 \text{ Hz}$ and $^4\text{J } ^1\text{H}-^1\text{H} = 1.0 \text{ Hz}$), 8.06 (1H, dd, $^3\text{J } ^1\text{H}-^1\text{H} = 7.9 \text{ Hz}$ and $^3\text{J } ^1\text{H}-^1\text{H} = 7.9 \text{ Hz}$), 3.10 (8H, m), 1.50 (12H, m). MS (CI+) 483, 373 and 263 (z/m). Molecular ion found at 483.2976 amu, $^{12}\text{C}_{28}^{1}\text{H}_{35}^{14}\text{N}_8$ requires 483.2976 (error of 1.8 ppm).