

Details of the synthesis of the Co complex (**3**).

4'-(6-acetylthiohexyloxy)-2,2';6',2''-terpyridine (7)

To a solution of 2,6-*bis*-(pyrid-2-yl)-4-pyridone¹ (**5**) (8mmol, 2g) in DMF was added 6-acetylthio-1-bromohexane² (**6**) (14,6mmol, 3,5g). The solution was heated to 70°C for 20 hours and poured into water (200mL). After extraction with dichloromethane (2 x 80 mL) the pooled extracts were dried with sodium sulfate, and concentrated *in vacuo*. The resulting crystals were recrystallised from ethanol (99,5%) affording 2,7g of 4'-(6-acetylthiohexyloxy)-2,2';6',2''-terpyridine (**7**) as white crystals (83% yield).

Mp: 82.0-82.7°C. Anal. Calcd. for C₂₃H₂₅N₃O₂S: C, 67.79; H, 6.18; N, 10.31; S, 7.87. Found: C, 67.71; H, 6.30; N, 9.97; S, 7.86. ¹H NMR (400 MHz, CDCl₃): δ 1.50 (m, 4H), 1.63 (m, 2H), 1.85 (q, *J* = 6Hz, 2H), 2.32 (s, 3H), 2.90 (t, *J* = 6Hz, 2H), 4.22 (t, *J*=6Hz, 2H), 7.32 (dd, *J*₁=6, *J*₂=1, 2H), 7.84 (dt *J*₁=6, *J*₂=1, 2H), 8.01 (s, 2H), 8.62 (d, *J*=6 Hz, 2H), 8.69 (td, *J*₁=6, *J*₂=1, 2H). ¹³C NMR (400 MHz, CDCl₃): δ 25.44, 28.34, 28.77, 28.94, 29.34, 30.53, 67.97, 107.38, 121.29, 123.68, 136.76, 148.79, 155.93, 156.77, 167.20, 195.80. MS: FAB⁺, matrix *m*-nitrobenzoicacid (*m/z*, relative intensity): 408 (*M*+1, 100), 250(40). HRMS Calcd for C₂₃H₂₆N₃O₂S: 408.1746, found 408.1743.

4'-(6-acetylthiohexyloxy)-2,2';6',2''-terpyridine-terpyridine-cobalt(III)trihexafluorophosphate (3)

4'-(6-acetylthiohexyloxy)-2,2';6',2''-terpyridine (**7**) (0.15mmol, 61.1mg) in 1mL DMF and monoterpyridine-cobalt(II)chloride¹ (**4**) (0.15mmol, 57.2mg) suspended in 1.5mL DMF were mixed in a test tube. Hydrogenperoxide (35% in water) was added and the dark brown solution was stirred for 5min. 4mL KPF₆ (0.2M in H₂O) was added and the heteroleptic complex (**5**) precipitated. The reaction mixture was centrifuged at 3800g and the supernatant removed. The precipitate was washed 3 times with milliQ water and 3 times with ether. The precipitate contained approximately -90-95% of the heteroleptic complex and 5-10% of symmetric complexes, based on the intensities in ESI-MS. In order to get the pure heteroleptic complex, the precipitate was purified using column chromatography (80cm silica column, eluent acetone/KPF₆ (0.25g/100mL), r.f. $\approx$ 0.9). Evaporation of the solvent and washing with water and ether followed by drying in vacuo afforded 4'-(6-acetylthiohexyloxy)-2,2';6',2''-terpyridine-terpyridine-cobalt(III)trihexafluorophosphate (**3**) as a light brown powder (75 mg corresponding to 39% yield).

Mp: 193.0-195.2°C. Anal. Calcd for C₃₈H₃₆CoF₁₈N₆O₂P₃S: C, 40.23; H, 3.20; N, 7.41. Found: C, 40.31; H, 3.22; N, 7.41. MS: ESI⁺: 989(1) (M⁺-

PF₆), 844(2) (M⁺-2PF₆), 349.6(100) (M²⁺-3PF₆). ¹H NMR (400 MHz, acetone-d₆): δ 1.5–1.7 (m, 8H), 2.32 (s, 3H), 2.95 (t, J=6, 2H), 4.15 (t, J=6, 2H), 7.54-7.62 (m, 4H), 7.80 (dd, J=7, J=9, 2H), 7.89 (dd, J=7, J=9, 2H), 8.34-8.44 (m, 4H), 8.92-8.98 (m, 5H), 9.28-9.41 (several peaks, 3H).

References:

1. E. C. Constable, M. D. Ward, J. Chem. Soc. Dalton Trans 1990, 1405-1409.
2. F. P. Sun, T. Darbre, Helv. Chim. Acta 2002, **85**, 3002-3018.