

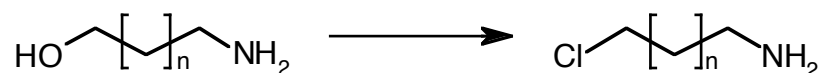
Luminescent, water-soluble gold nanoparticles functionalised with ³MLCT emitting rhenium complexes

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Experimental

All reactions were performed with the use of vacuum line and Schlenk techniques. Reagents were commercial grade and were used without further purification. ¹H and ¹³C-{¹H} NMR spectra and were run on a NMR-FT Bruker Avance DPX-400 spectrometer and were recorded in CDCl₃ or D₂O. ¹H and ¹³C{¹H} NMR chemical shifts were determined relative to internal TMS and are given in ppm. Infrared spectra were run on a Perkin-Elmer FT-1600 spectrometer as CH₂Cl₂ solutions. Mass spectra were carried out by the staff of the Chemical Analysis Service of Cardiff University on a Waters LCT Premier XE ESI/APCI mass spectrometer. High resolution accurate mass determinations of the rhenium complexes were performed at the EPSRC National Mass Spectrometry Service at Swansea University. UV-Vis studies were performed on a Jasco V-570 spectrophotometer.

Synthesis of ligands

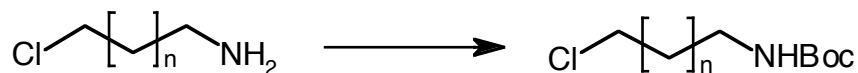


Compound 1a

SOCl₂ (5.3 ml, 72.97 mmol) in CHCl₃ (30 ml) was added dropwise to 3-amino-1-propanol (4.5 ml, 59.19 mmol) at 0 °C. The mixture was allowed to reach room temperature and then heated at reflux for 3 h. A light brown precipitate formed which was filtered and washed with CHCl₃. Yield = 6.903 g (90 %). ¹H NMR (400 MHz, D₂O) δ = 3.61 (2H, t, ³J_{H-H} = 6 Hz, CH₂), 3.08 (2H, t, ³J_{H-H} = 7 Hz, CH₂), 2.07 (2H, m, CH₂). ¹³C{¹H} NMR (101 MHz, D₂O) δ = 41.9, 37.5, 29.7. EI MS found *m/z* 93.0, calculated *m/z* 93.6 for [M]⁺.

Compound 1b

SOCl₂ (1.4 ml, 19.19 mmol) in CHCl₃ (25 ml) was added dropwise to 6-amino-1-hexanol (2.037 g, 17.38 mmol) at 0 °C. The mixture was allowed to reach room temperature and then heated at reflux for 3 h. The solvent was removed under reduced pressure to give the product as an oily solid. Yield = 2.827 g (96 %). ¹H NMR (400 MHz, CDCl₃) δ = 8.17 (3H, br s, NH₃⁺), 3.49 (2H, t, ³J_{H-H} = 7 Hz, CH₂), 2.93 (2H, m, CH₂), 1.74 (4H, m, 2 x CH₂), 1.41 (4H, m, 2 x CH₂). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ = 45.2, 40.2, 32.6, 27.7, 26.6, 26.2. ES MS found *m/z* 136.1 and 177.1, calculated *m/z* 136.6 and 177.7 for [M + H]⁺ and [M + MeCN + H]⁺ respectively.

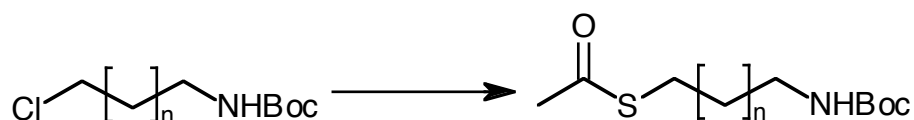


Compound 2a

Compound 1a (6.903 g, 53.03 mmol) and Et₃N (7.8 ml, 55.96 mmol) were stirred in CH₂Cl₂ (40 ml) at room temperature for 30 min. Di-*tert*-butyldicarbonate (12.014 g, 55.05 mmol) in CH₂Cl₂ (30 ml) was then added dropwise at 0 °C. The mixture was allowed to reach room temperature and stirred for 2 h before being washed with 0.1 M HCl (40 ml), water (40 ml) and brine (40 ml). The solution was dried over MgSO₄, filtered and the solvent removed under reduced pressure. Yield = 9.550 g (99 %). ¹H NMR (400 MHz, CDCl₃) δ = 4.61 (1H, br, NH), 3.53 (2H, t, ³J_{H-H} = 6 Hz, CH₂), 3.21 (2H, m, CH₂), 1.90 (2H, t, ³J_{H-H} = 6 Hz, CH₂), 1.38 (9H, s, ^tBu). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ = 156.4, 79.6, 42.7, 38.2, 33.0, 28.7. EI MS found *m/z* 193.1, calculated *m/z* 193.7 for [M]⁺.

Compound 2b

Compound 1b (2.827 g, 16.62 mmol) and Et₃N (2.6 ml, 18.65 mmol) were stirred in CH₂Cl₂ (30 ml) at room temperature for 30 min. Di-*tert*-butyldicarbonate (4.007 g, 18.36 mmol) in CH₂Cl₂ (30 ml) was then added dropwise at 0 °C. The mixture was allowed to reach room temperature and stirred for 2 h before being washed with 0.1 M HCl (30 ml), water (30 ml) and brine (30 ml). The solution was dried over MgSO₄, filtered and the solvent removed under reduced pressure. Yield = 3.917 g (100 %). ¹H NMR (400 MHz, CDCl₃) δ = 4.47 (1H, br, NH), 3.03 (2H, t, ³J_{H-H} = 7 Hz, CH₂), 2.78 (2H, m, CH₂), 2.25 (3H, s, OCCH₃), 1.50 (4H, m, 2 x CH₂), 1.38 (9H, s, ^tBu), 1.28 (4H, m, 2 x CH₂). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ = 196.3, 156.4, 79.4, 40.8, 31.0, 30.3, 29.8, 29.4, 28.8, 28.7, 26.7. EI MS found *m/z* 235.1, calculated *m/z* 235.8 for [M]⁺.

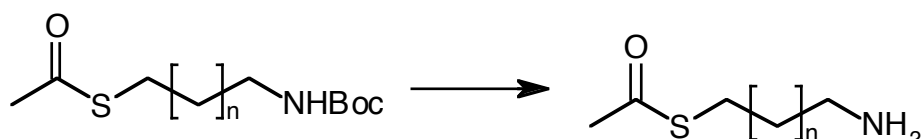


Compound 3a

Compound 2a (6.613 g, 36.40 mmol) and an excess of potassium thioacetate (4.648 g, 40.70 mmol) were heated at 80 °C in NMP (35 ml) for 16 h. Toluene (50 ml) was added and the mixture washed with water (2 x 50 ml) and brine (50 ml). The solution was dried over MgSO₄, filtered and the solvent removed under reduced pressure. Yield = 7.371 g (87 %). ¹H NMR (400 MHz, CDCl₃) δ = 4.71 (1H, br, NH), 3.09 (2H, br, CH₂), 2.85 (2H, t, ³J_{H-H} = 7 Hz, CH₂), 2.28 (3H, s, OCCH₃), 1.70 (2H, m, CH₂), 1.38 (9H, s, ^tBu). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ = 196.6, 156.3, 79.5, 39.3, 30.9, 30.3, 28.7, 26.6. AP MS found *m/z* 234.1, 251.2, 467.3 and 484.3, calculated *m/z* 234.3, 251.4, 467.7 and 484.7 for [M+H]⁺, [M+NH₄]⁺, [2M+H]⁺ and [2M+NH₄]⁺ respectively.

Compound 3b

Compound 2b (3.917 g, 16.61 mmol) and an excess of potassium thioacetate (3.612 g, 31.63 mmol) were heated at 80 °C in NMP (35 ml) for 16 h. Toluene (50 ml) was added and the mixture washed with water (2 x 50 ml) and brine (50 ml). The solution was dried over MgSO₄, filtered and the solvent removed under reduced pressure. Yield = 4.553 g (99 %). ¹H NMR (400 MHz, CDCl₃) δ = 4.47 (1H, br, NH), 3.03 (2H, m, CH₂), 2.78 (2H, t, ³J_{H-H} = 7 Hz, CH₂), 2.25 (3H, s, OCCH₃), 1.50 (4H, m, 2 x CH₂), 1.38 (9H, s, ^tBu), 1.28 (4H, m, 2 x CH₂). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ = 196.3, 156.4, 79.4, 40.8, 31.0, 30.3, 29.8, 29.4, 28.8, 28.7, 26.7. ES MS found *m/z* 276.2, calculated *m/z* 276.4 for [M + H]⁺.

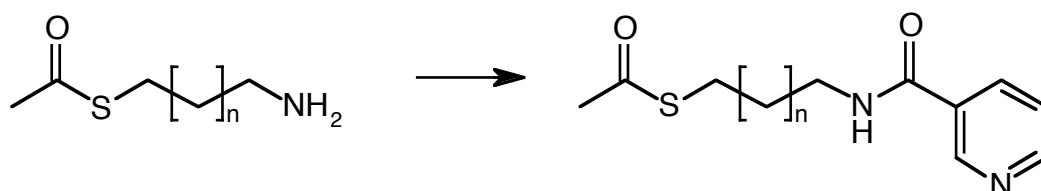


Compound 4a

Trifluoroacetic acid (8 ml, 103.84 mmol) was added dropwise to a stirring solution of compound 3a (7.346 g, 31.48 mmol) in CH₂Cl₂ (15 ml) and stirred at room temperature for 16 hours. The product was extracted into water (50 ml) and washed with CH₂Cl₂ (2 x 25 ml). The water was removed under reduced pressure to give the product as a light brown oil. Yield = 7.705 g (99 %). ¹H NMR (400 MHz, CDCl₃) δ = 7.91 (3H, br s, NH₃⁺), 3.08 (2H, m, CH₂), 2.97 (2H, t, ³J_{H-H} = 7 Hz, CH₂), 2.37 (3H, s, OCCH₃), 2.01 (2H, m, CH₂). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ = 201.8, 38.4, 30.2, 27.1, 25.7. ES MS found *m/z* 134.0, 175.1 and 267.1, calculated *m/z* 134.2, 175.3 and 267.4 for [M+H]⁺, [M+MeCNH]⁺ and [2M+H]⁺ respectively.

Compound 4b

Trifluoroacetic acid (8 ml, 103.84 mmol) was added dropwise to a stirring solution of compound 3b (4.553 g, 16.53 mmol) in CH₂Cl₂ (15 ml) and stirred at room temperature for 14 hours. The product was extracted into water (40 ml) and washed with CH₂Cl₂ (2 x 20 ml). The water was removed under reduced pressure to give the product as a light brown oil. Yield = 4.752 g (99 %). ¹H NMR (400 MHz, CDCl₃) δ = 2.83 (2H, t, ³J_{H-H} = 7 Hz, CH₂), 2.76 (2H, t, ³J_{H-H} = 7 Hz, CH₂), 2.21 (3H, s, OCCH₃), 1.50 (2H, m, CH₂), 1.44 (2H, m, CH₂), 1.25 (4H, m, 2 x CH₂). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ = 202.5, 39.7, 30.3, 29.0, 28.7, 27.6, 26.9, 25.4. ES MS found *m/z* 176.1, 217.1 and 351.2 calculated *m/z* 176.3, 217.3 and 351.6 for [M + H]⁺, [M + MeCN + H]⁺ and [2M + H]⁺ respectively.



Ligand 1

Solid nictinoyl chloride hydrochloride (0.332 g, 1.86 mmol) was added slowly to a solution of 4a (0.540 g, 1.87 mmol) and EtN^tPr₂ (1.62 ml, 9.30 mmol) in MeCN (10 ml) and stirred at room temperature for 3 hours. The solvent was removed under

reduced pressure and the crude product dissolved in CH₂Cl₂ (30 ml) and washed with water (2 x 30 ml) and brine (30 ml). The solution was dried over MgSO₄, filtered and the solvent removed under reduced pressure to give a light brown oil. Yield = 0.500 (96 %). ¹H NMR (400 MHz, CDCl₃) δ = 9.14 (1H, s, PyH), 8.75 (1H, d, ³J_{H-H} = 4 Hz, PyH), 8.12 (1H, d, ³J_{H-H} = 5 Hz, PyH), 7.47 (1H, dd, J_{H-H} = 4 Hz and 5 Hz, PyH), 6.02 (1H, br s, NH), 3.28 (2H, m, CH₂), 3.09 (2H, m, CH₂), 1.97 (3H, s, OCCH₃), 1.81 (2H, m, CH₂). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ = 191.6, 170.9, 154.3, 148.8, 135.0, 132.9, 124.0, 38.2, 30.0, 26.6, 23.8. IR: (CH₂Cl₂, cm⁻¹) ν = 1670(s), 1586(w), 1518(m). EI MS found *m/z* 238.1, calculated *m/z* 238.3 for [M]⁺.

Ligand 2

Solid nictinoyl chloride hydrochloride (0.500 g, 2.81 mmol) was added slowly to a solution of 4b (0.699 g, 2.83 mmol) and EtNⁱPr₂ (2.50 ml, 14.35 mmol) in MeCN (10 ml) and stirred at room temperature for 3 hours. The solvent was removed under reduced pressure and the crude product dissolved in CH₂Cl₂ (30 ml) and washed with water (2 x 30 ml) and brine (30 ml). The solution was dried over MgSO₄, filtered and the solvent removed under reduced pressure to give yellow oil. Yield = 0.629 (94 %). ¹H NMR (400 MHz, CDCl₃) δ = 8.92 (1H, br s, PyH), 8.61 (1H, br s, PyH), 8.08 (1H, d, ³J_{H-H} = 8 Hz, PyH), 7.32 (1H, br, pyH), 6.53 (1H, br s, NH), 3.39 (2H, m, CH₂), 2.79 (2H, m, CH₂), 2.25 (3H, s, OCCH₃), 1.54 (4H, m, 2 x CH₂), 1.34 (4H, m, 2 x CH₂). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ = 196.7, 166.0, 152.2, 148.2, 135.8, 131.0, 124.0, 40.4, 31.1, 29.8, 29.4, 29.2, 28.6, 26.7. IR: (CH₂Cl₂, cm⁻¹) ν = 1672(s), 1522(m). AP MS found *m/z* 281.1, calculated *m/z* 281.4 for [M+H]⁺.

Synthesis of rhenium complexes

fac-[Re(CO)₃(bipy)(NCMe)][OTf] was prepared according to literature procedures.¹

Re-1

Ligand 1 (0.025 g, 0.11 mmol) and *fac*-[Re(CO)₃(bipy)(NCMe)][OTf] (0.060 g, 0.10 mmol) in CHCl₃ (10 ml) were heated at reflux for 16 h. The mixture was concentrated under reduced pressure (*c.a.* 2 ml) and precipitated by slow addition of diethyl ether (25 ml). Yield = 0.072 g (91 %). ¹H NMR (400 MHz, CDCl₃) δ = 9.09 (3H, m, 2 x bipyH and PyH), 8.73 (2H, d, ³J_{H-H} = 8 Hz, 2 x bipyH), 8.51 (1H, d, ³J_{H-H} = 8 Hz, PyH), 8.23 (3H, m, 2 x bipyH and PyH), 7.78 (1H, t, J_{H-H} = 8 Hz, PyH), 7.36 (2H, t, J_{H-H} = 8 Hz, 2 x bipyH), 6.69 (1H, br s, NH), 3.27 (2H, m, CH₂), 3.09 (2H, m, CH₂), 1.95 (3H, s, OCCH₃), 1.83 (2H, m, CH₂). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ = 191.2, 186.5, 169.4, 154.7, 152.8, 151.9, 148.0, 147.4, 141.0, 136.6, 133.6, 128.2, 126.8, 126.3, 125.1, 36.9, 28.6, 25.2, 22.3. IR: (CH₂Cl₂, cm⁻¹) ν = 2037(s), 1933(s br), 1673(w), 1606(m), 1516(w). ES MS found *m/z* 665.1, calculated *m/z* 664.7 for [M-OTf]⁺. HR ES MS found *m/z* 666.0938, calculated *m/z* 666.0941 for [M+H-(OTf)]⁺.

Re-2

Ligand 2 (0.052 g, 0.19 mmol) and *fac*-[Re(CO)₃(bipy)(NCMe)][OTf] (0.097 g, 0.18 mmol) in CHCl₃ (10 ml) were heated at reflux for 16 h. The mixture was concentrated under reduced pressure (*c.a.* 2 ml) and precipitated by slow addition of diethyl ether (25 ml). Yield = 0.125 g (93 %). ¹H NMR (400 MHz, CDCl₃) δ = 9.16 (2H, d, ³J_{H-H} = 4 Hz, 2 x bipyH), 8.52 (1H, s, PyH), 8.46 (2H, d, ³J_{H-H} = 8 Hz, 2 x bipyH), 8.30 (1H,

¹ J. V. Caspar and T. J. Meyer, *J. Phys. Chem.*, 1983, **87**, 952.

d, $^3J_{\text{H-H}} = 8$ Hz, PyH), 8.19 (3H, m, 2 x bipyH and PyH), 7.87 (1H, t, $^3J_{\text{H-H}} = 8$ Hz, PyH), 7.76 (2H, t, $^3J_{\text{H-H}} = 8$ Hz, 2 x bipyH), 7.29 (1H, br s, NH), 3.23 (2H, m, CH₂), 2.75 (2H, t, $^3J_{\text{H-H}} = 7$ Hz, CH₂), 2.24 (3H, s, OCCH₃), 1.45 (4H, m, 2 x CH₂), 1.24 (4H, m, 2 x CH₂). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ = 196.7, 195.4, 191.2, 154.7, 163.4, 156.1, 153.7, 153.2, 151.6, 141.8, 138.9, 134.1, 129.5, 127.0, 125.6, 40.5, 31.1, 29.8, 29.4, 29.3, 28.7, 26.7. IR: (CH₂Cl₂, cm⁻¹) ν = 2037(s), 1933(s br), 1675(w), 1605(w), 1544(w), 1523(w). ES MS found *m/z* 707.2, calculated *m/z* 706.8 for [M-(OTf)]⁺. HR ES MS found *m/z* 707.1327, calculated *m/z* 707.1332 for [M-(OTf)]⁺.

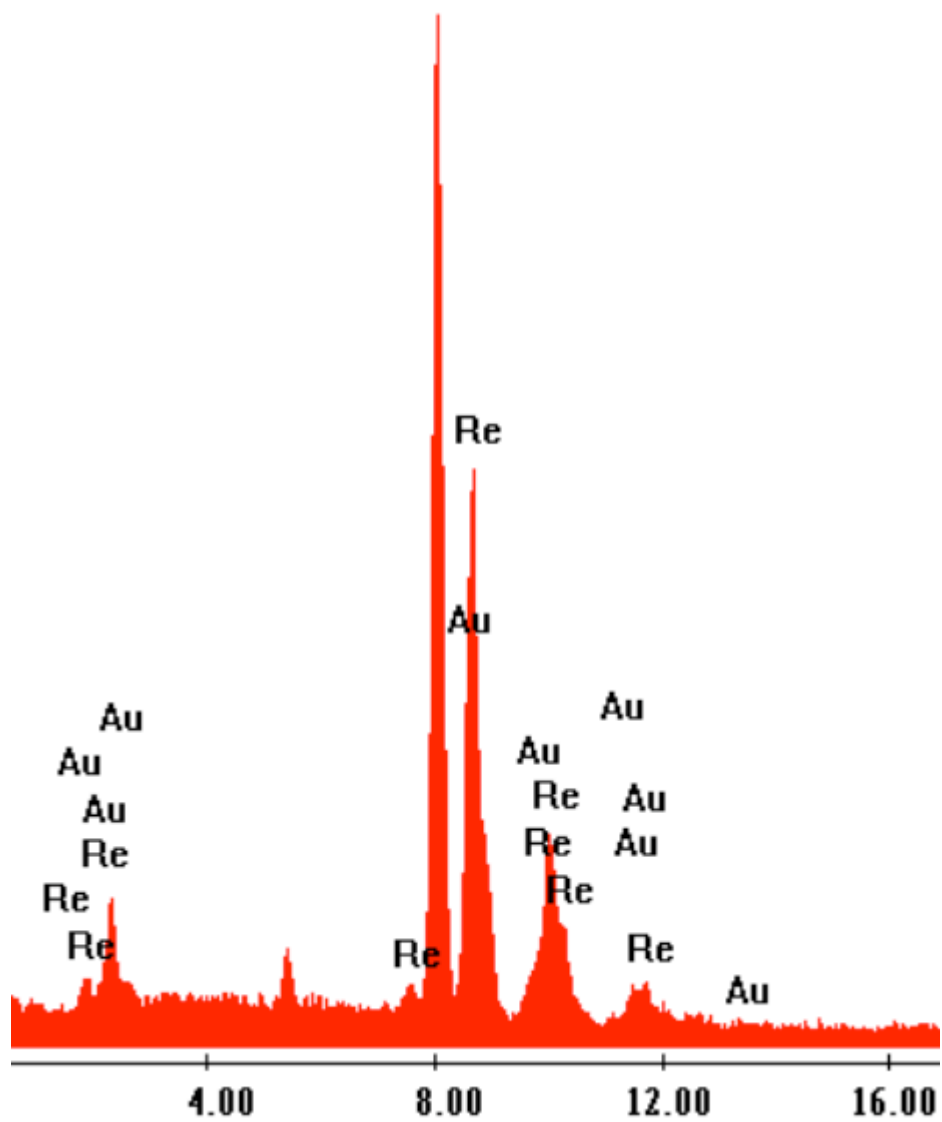
Synthesis of GNPs

A solution of HAuCl₄ (0.1g, 0.3 mmol) and the MPEGSH (Me(OCH₂CH₂)₁₆SH) capping agent 590mg in methanol (50ml) was treated with triethylamine (70 μ l, 0.3mmol) to form a neutral solution. The reaction mixture was then treated with a solution of sodium borohydride (35.8mg 0.942mmol) in 4ml methanol. The particles were isolated by removal of the solvent under vacuum. The solid was extracted with DCM, the DCM was removed under vacuum and the particles precipitated from methanol by using diethylether to give the particles as a waxy dark solid. Yield ~ 45% based on gold.

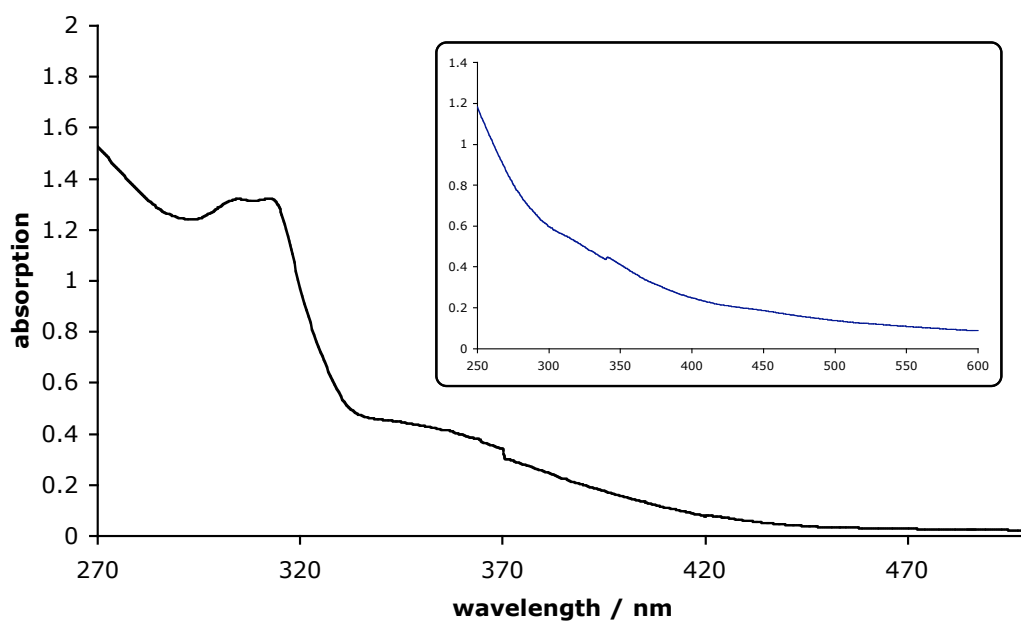
Co-ordination of rhenium complexes to nanoparticles

Re-2-GNP

Gold nanoparticles (0.012 g, 27 % Au by weight) and complex **Re-2** (0.042 g, 0.05 mmol) were stirred in MeOH (2.5 ml) at room temperature for 24 h. The solvent was removed under reduced pressure and water (20 ml) and CH₂Cl₂ (20 ml) were added. The aqueous phase was collected and extracted once more with CH₂Cl₂ (10 ml).



EDX Characterisation of Re-2-GNP



Main: UV-vis absorption spectrum of Re-2-GNP in water. Inset: GNPs in methanol