Supplementary Information

Experimental

Compound 3: 1, 4-Methyl-2,2′-bipyridine-4′-carboxylicacid (1 g, 4.668 mmol) was suspended in dichloromethane (10cm^3) and $SOCl_2$ (10 cm^3) added dropwise whilst stirring. The mixture was stirred at room temperature for 6 h and then evaporated to dryness *in vacuo* giving a white residue. This crude acid chloride derivative was then reacted without further purification. The residue was redissolved in dry acetonitrile (10 cm^3) with triethylamine (1 cm^3) under a nitrogen atmosphere and an acetonitrile (5 cm^3) solution of **2**, *N*-*tert*-butoxycarbonylethylenediamine (0.748 g, 4.668 mmol) added dropwise *via* syringe. The mixture was allowed to stir at room temperature for 24 h. The solvents were removed *in vacuo* and the product redissolved in dichloromethane and submitted to aqueous washings. The organic layers were collected and evaporated to dryness yielding a light brown solid. This crude product was then introduced to a silica column and eluted initially with dichloromethane/methanol (99:1) and then 95:5. The main yellow band was collected giving the product as a very pale pink (indicative of trace Fe(II) contamination), mildly hygroscopic solid (yield 1.21 g, 73 %). IR (solid) ν_{max} = 3343, 3296, 3053, 2983, 2940, 1691, 1644, 1594, 1536, 1446, 1387, 1362, 1335, 1269, 1251, 1169, 1098, 1070, 1037 cm^{-1}. ES$^+$ MS (MeCN): *m/z* 379 {M + Na}$^+$, 357 {M + H}$^+$. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K) δ_H = 1.45 (9H, s, *tert*-Bu), 2.35 (3H, s), 3.3 (2H, q, CH_2), 3.6 (2H, q, CH_2), 5.1 (1H, s br, NHboc), 7.15 (1H, s, bipyH^5), 7.65 (1H, s, NH), 7.7 (1H, d, bipyH^2), 8.2 (1H, s, bipyH^4), 8.5 (1H, d, bipyH^6), 8.65 (1H, s, bipyH^3), 8.7 (1H, d, bipyH^1). Found C, 62.79; H, 7.00; N, 15.04; calc. for $C_{19}H_{24}N_4O_3.0.5CH_3OH$: C, 62.88; H, 7.04; N, 15.04 %.

***fac*-[ReCl(CO)$_3$(3)]** **3** (0.1 g, 0.281 mmol) and $ReCl(CO)_5$ (0.101 g, 0.281 mmol) were dissolved in chloroform (15 cm^3) and heated to reflux for 6 h. The mixture was then evaporated to dryness *in vacuo* giving an orange residue. This crude product was purified on an alumina column and eluted with dichloromethane/methanol (99:1). The main yellow band was collected giving the desired product as a light orange-yellow solid (yield 0.134g, 72 %). IR (solid) ν_{max} = 3334 (br), 3051, 2978, 2936, 2017 (CO), 1939 (CO), 1913 (CO), 1867, 1766, 1716, 1669, 1645, 1623, 1517, 1485, 1451, 1409, 1365, 1309, 1236, 1163, 1029 cm^{-1}. ES$^-$ MS (MeCN): *m/z* 660 {M – H}$^-$. ^{1}H NMR (400 MHz, CDCl$_3$, 300 K) δ_H = 1.45 (9H, s, *tert*-Bu), 2.4 (3H, s, Me), 3.4 (2H, dd, CH$_2$), 3.55 (2H, m, CH$_2$), 5.1 (1H, t, br, NHboc), 7.35 (1H, d, bipyH^5), 7.9 (1H, d, bipyH^2), 8.15 (1H, s, bipyH^4), 8.35 (1H, s, NH), 8.65 (1H, s, bipyH^3), 8.85 (1H, d, bipyH^6), 9.10 (1H, d, bipyH^1). Found C, 39.79; H, 3.22; N, 8.19; calc. for $C_{22}H_{24}N_4O_6ReCl$: C, 39.91; H, 3.65; N, 8.46 %.

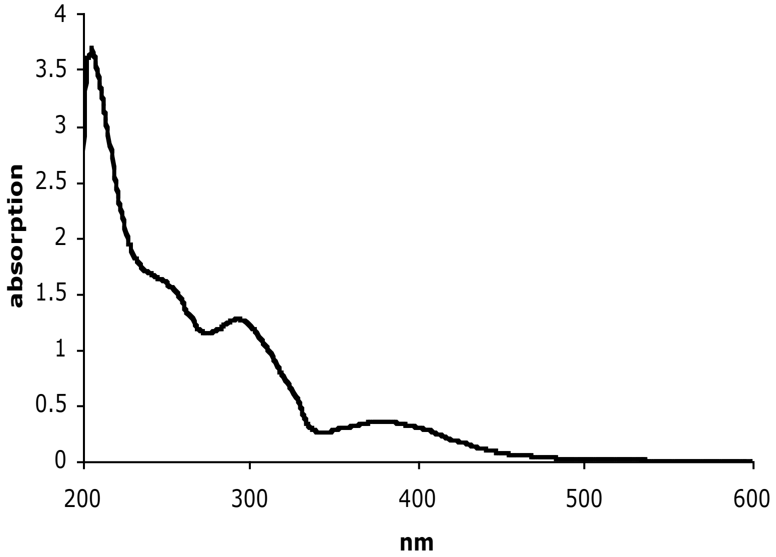
***fac*-[ReCl(CO)$_3$(4-methyl-4′-amido-(2-aminoethyl)-2,2′-bipyridine)]** *fac*-ReCl(CO)$_3$(**3**) (0.05 g, 7.55 × 10^{-5} mol) was dissolved in dichloromethane (5 cm^3) and trifluoroacetic acid (2 cm^3) added dropwise. The mixture was stirred at room temperature for 2 h. The solvents were removed *in vacuo* and the product precipitated from acetone with diethyl ether and filtered using Schlenk apparatus giving the trifluoroacetic acid adduct (yield 0.049 g, 89 %). IR (solid) ν_{max} = 3074 (v br), 2019 (CO), 1915 (br, CO), 1867, 1769, 1671, 1623, 1551, 1484, 1449, 1412, 1336, 1307, 1280, 1238, 1198, 1130, 1109, 1076, 1030 cm^{-1}. UV-vis (CH$_3$OH) λ_{max} (ε/mol^{-1}dm^{3}cm^{-1}) = 381 (2300), 297 (8400), 240 sh (12400) nm. ES$^+$ MS (MeCN): *m/z* 568 {M – Cl + CH$_3$CN}$^+$, 527 {M – Cl}$^+$. ^{1}H NMR (400 MHz, CO(CD$_3$)$_2$, 300 K) δ_H = 2.65 (3H, s, CH$_3$), 3.8-4.0 (2H, m, CH$_2$), 4.1 (2H, dd, CH$_2$), 7.65 (1H, d, bipyH^5), 8.20 (1H, dd, bipyH^2), 8.80 (1H, s, bipyH^4), 8.95 (1H, d, bipyH^3), 9.20 (1H, d, bipyH^6), 9.30 (1H, s, bipyH^1). Found C, 32.57; H, 2.09; N, 8.14; calc. for $C_{17}H_{15}N_4O_4ReCl$. 1.5 CF_3CO_2H: C, 32.82; H, 2.27; N, 7.65 %.

{*fac*-ReCl(CO)$_3$}$_2$L *fac*-[ReCl(CO)$_3$(bipy-NH$_2$)](CF$_3$CO$_2$H)$_{1.5}$ (0.05 g, 6.8 × 10^{-5} mol) was dissolved in dry acetonitrile (5 cm^3) with a few drops of NEt$_3$ and 0.5 equivalents of diethylenetriaminepentaacetic anhydride (0.012 g, 3.4 × 10^{-5} mol) and stirred at room temperature for 24 h. The solution was concentrated and the hygroscopic product precipitated with the addition of diethyl ether (yield 0.042 g, 84 %). IR (solid) ν_{max} = 3273 (br), 3054, 2980, 2019 (CO), 1885 (br, CO), 1717, 1623 (br), 1543, 1483, 1383, 1308, 1236, 1198, 1137, 1033 cm^{-1}. UV-vis (CH$_3$OH) λ_{max} (ε/mol^{-1}dm^{3}cm^{-1}) = 378 (5000), 292 (17100), 243 sh (22400) nm. MALDI MS (alpha/methanol): *m/z* 1446 {M – Cl}$^+$, 1411 {M – 2Cl}$^{2+}$, 1382 {M – 2Cl – CO}$^{2+}$, 1358 {M – 2Cl – 2CO}$^{2+}$. ^{1}H NMR (400 MHz, CD$_3$OD, 300 K) 2.51 (6H, s, CH$_3$), 2.9-3.7 (26H, m, CH$_2$), 7.41 (2H, d, bipyH^5), 7.88 (2H, m, bipyH^2), 8.44 (2H, s, bipyH^4), 8.67 (2H, d, bipyH^3), 8.83 (2H, d, bipyH^6), 9.01 (2H, d, bipyH^1). Found C, 37.87; H, 3.70; N, 9.76; calc. for $C_{48}H_{51}N_{11}O_{16}Re_2Cl_2.H_2O$: C, 38.45; H, 3.43; N, 10.28 %.

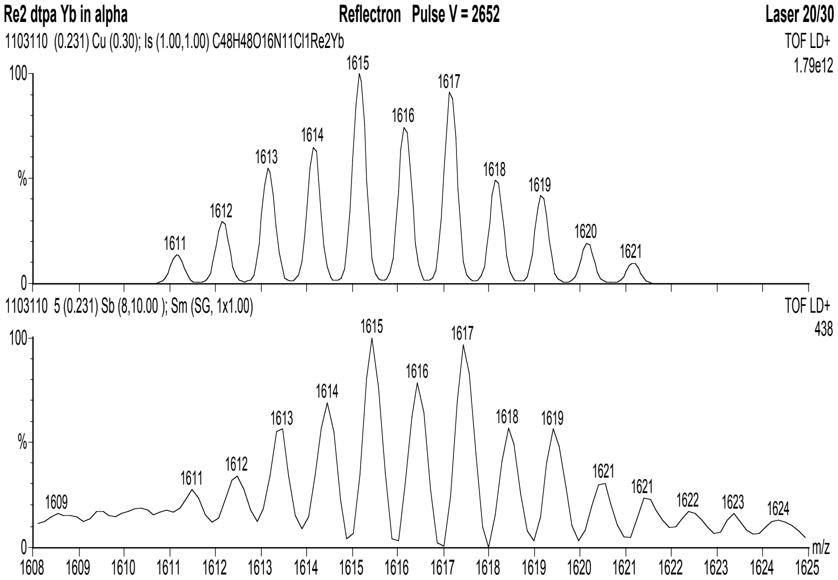
{*fac*-ReCl(CO)$_3$}$_2$L-Nd {*fac*-ReCl(CO)$_3$}$_2$L (0.02 g, 1.35 □ 10^{-5} mol) was dissolved in methanol (10 cm^3) and one equivalent of Nd(OTf)$_3$ (0.008 g, 1.35 □ 10^{-5} mol) added. The mixture was stirred at 50 °C for 24 h. The solvent volume was then reduced to a minimum and diethyl ether added inducing precipitation of the desired complex (yield 0.019 g, 87 %). IR (solid) □$_{max}$ = 3292, 3078, 2980, 2023 (CO), 1893 (br, CO), 1624, 1579, 1553, 1485, 1442, 1410, 1276, 1236, 1164, 1118, 1098, 1027 cm^{-1}. UV-vis (CH_3OH) □$_{max}$ (□/mol^{-1}dm^{3}cm^{-1}) = 379 (3200), 296 (10800), 242 (15200) nm. MALDI MS (alpha/methanol): *m/z* broad clusters at 1587 {M – Cl}$^+$, 1555 {M – 2Cl}$^{2+}$, 1446 {M – Cl – Nd}$^+$. ^{1}H NMR (500 MHz, CD_3OD, 300K): -2 (br), +1.2, +2-3 (m, br), +3.2, +3.3-4.5 (m, br), +7-11 (m, br) ppm.

{*fac*-ReCl(CO)$_3$}$_2$L-Er Method as for {*fac*-ReCl(CO)$_3$}$_2$L-Nd, but using Er(OTf)$_3$ (0.008 g, 1.35 □ 10^{-5} mol) (yield 0.02 g, 90 %). IR (solid) □$_{max}$ = 3294, 3089, 2967, 2022 (CO), 1890 (br, CO), 1624, 1586, 1550, 1484, 1442, 1410, 1275, 1235, 1224, 1163, 1096, 1027 cm^{-1}. UV-vis (CH_3OH) □$_{max}$ (□/mol^{-1}dm^{3}cm^{-1}) = 380 (4100), 296 (13800), 241 (19500) nm. MALDI MS (alpha/methanol): *m/z* broad clusters at 1609 {M – Cl}$^+$, 1577 {M – 2Cl}$^{2+}$, 1446 {M – Cl – Er}$^+$. ^{1}H NMR (500 MHz, CD_3OD, 300K): -62, -54, -40, -34, -28, -26, -20, +24, +28, +30, +33, +35, +42, +54, +58, +63, +80, +114 ppm.

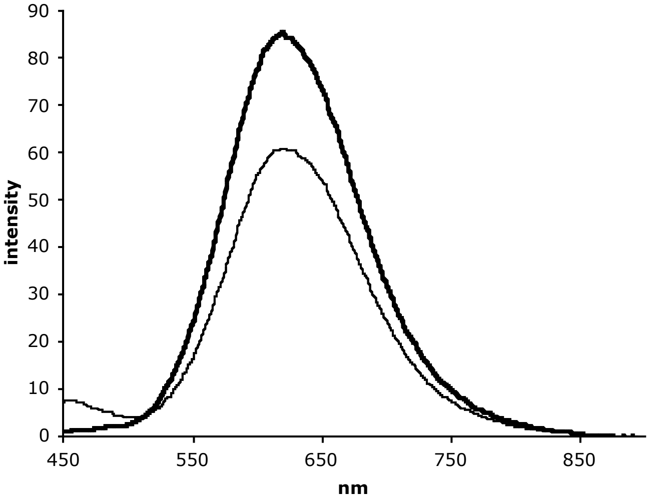
{*fac*-ReCl(CO)$_3$}$_2$L-Yb Method as for {*fac*-ReCl(CO)$_3$}$_2$L-Nd, but using Yb(OTf)$_3$ (0.008 g, 1.35 □ 10^{-5} mol) (yield 0.021 g, 94 %). IR (solid) □$_{max}$ = 3293 (br), 3088, 2954, 2022 (CO), 1889 (br, CO), 1624, 1586, 1550, 1484, 1441, 1410, 1274, 1236, 1162, 1098, 1027 cm^{-1}. UV-vis (CH_3OH) □$_{max}$ (□/mol^{-1}dm^{3}cm^{-1}) = 379 (3800), 295 (12500), 243 (17900) nm. MALDI MS (alpha/methanol): *m/z* broad clusters at 1615 {M – Cl}$^+$, 1583 {M – 2Cl}$^{2+}$, 1446 {M – Cl – Yb}$^+$. ^{1}H NMR (500 MHz, CD_3OD, 300K): -59, -56, -55, -47, -28, -24, -22, -17, -16, -14, -6, +13, +21, +23, +25, +27, +28, +32, +36, +40, +43, +45, +48, +61, +66, +100 ppm.



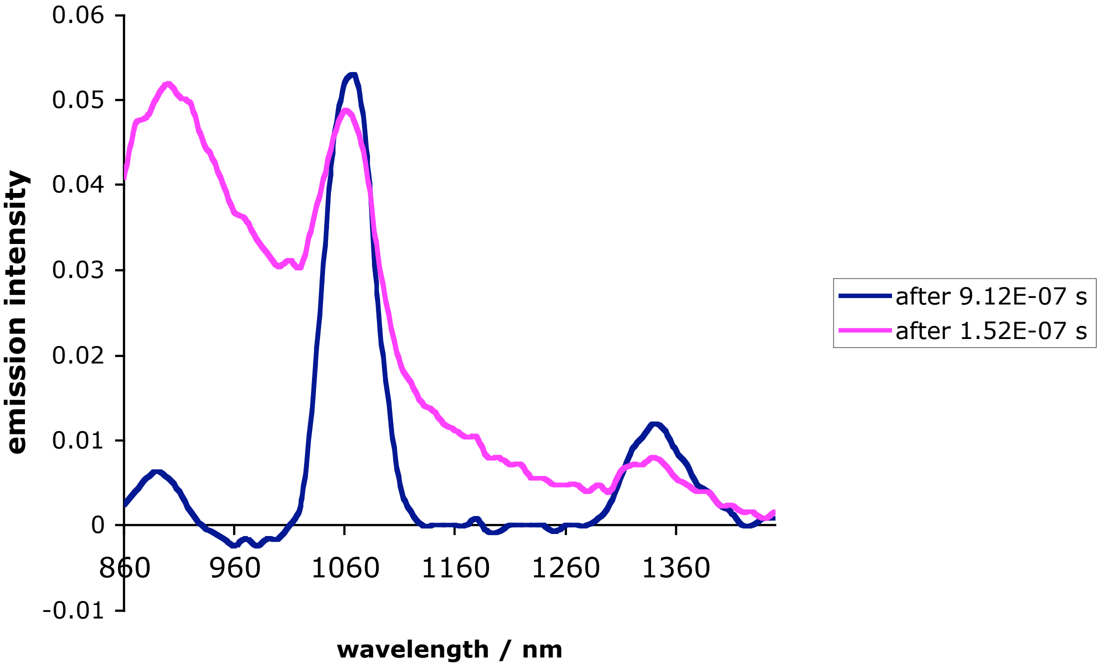
Supplementary Figure 1:UV-visible absorption spectrum of a solution of {*fac*-ReCl$(CO)_3\}_2$L in methanol.



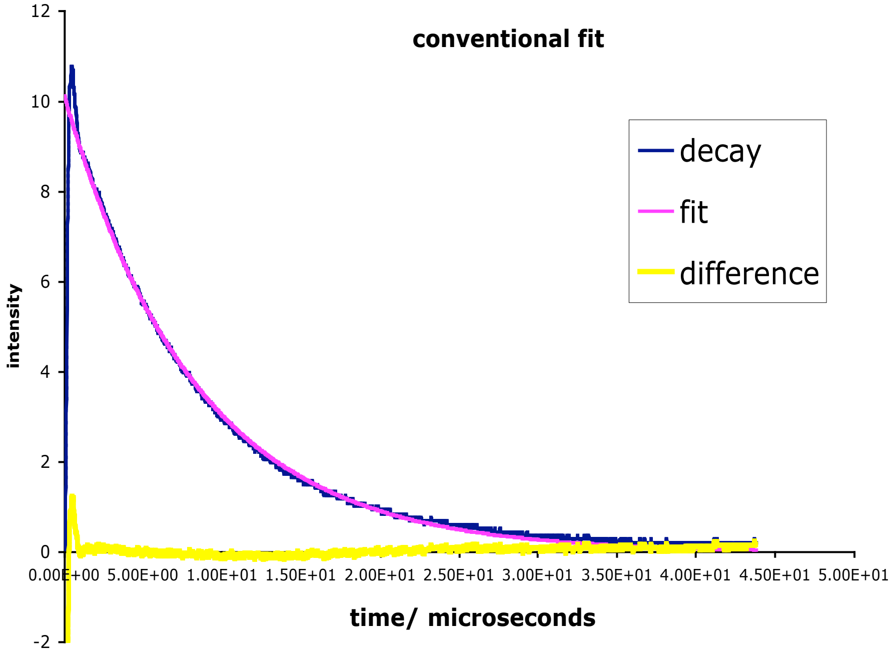
Supplementary Figure 2. MALDI mass spectrum (alpha) of $\{M - Cl\}^+$ (where M = {*fac*-$ReCl(CO)_3\}_2$L-Yb). Top: theoretical isotopic distribution. Bottom: actual.



Supplementary Figure 3. Visible emission spectra of {*fac*-ReCl(CO)$_3$}$_2$L in methanol (thick line) and = {*fac*-ReCl(CO)$_3$}$_2$L-Nd) (thin line), showing the partial quenching of the rhenium MLCT emission by the lanthanide centre.



Supplementary Figure 4. Emission spectra of $\{fac\text{-ReCl(CO)}_3\}_2$L-Nd. Note the grow-in of the neodymium based signal (1055 and 1340 nm) and disappearance in rhenium based emission after 9.12E-07 seconds.



Supplementary Figure 5.: Fitted decay for the complex {*fac*-ReCl(CO)$_3$}$_2$L-Yb in CD_3OD (λ_{ex} = 337 nm, λ_{em} = 980 nm). The fit was obtained by fitting the tail of the emission and ignoring the early datapoints, where the signal is convoluted with the detector response.