General

All starting materials, reagents and solvents were purchased from commercial suppliers and used as supplied unless otherwise stated. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker DPX 400MHz at 400MHz for proton and 160MHz for carbon, unless otherwise reported. IR spectra were recorded on a Perkin Elmer 1600 FT IR as thin films or nujol mulls and are reported in wavenumbers, and mass spectra were recorded on a VG Fisons Platform II or at the EPSRC national mass spectrometry service in Swansea (HRMS). Elemental analyses were performed by Warwick Analytical Services (University of Warwick). $Re(bpy)(CO)_3Cl$ was prepared according to ref. 4) of the manuscript. Rhenium acetonitrile and triflate complexes were treated as reactive intermediates and only characterised by NMR before being used as prepared. Solvents were purified according to D.D. Perrin, W.L.F. Armarego, *Purification of Laboratory Chemicals*, Butterworth, 1996.

Pyridine-3-methyleneoxyoctanoate 1a.

3-Hydroxymethyl pyridine (0.70mL, 7.2mmol) was dissolved in DCM (25mL), subsequently octanoyl chloride (1.12mL, 6mmol) was added dropwise. The reaction mixture was then stirred for 3 hours, extracted with sodium bicarbonate solution (sat. aq., 3 x 10 ml) dried over $MgSO_4$ and the solvent was removed in vacuo to leave **1a** (0.90g, 3.83mmol, 53.23%) as a colourless oil.[1]

Pyridinemethylene-3-oxystearate 1b.

EDCI (2.2g, 11mmol) and DMAP (268mg, 2.2mmol) were dissolved in DCM (15mL). To this mixture was added a solution of myristic acid (1.37 g, 6mmol) in DCM (25mL) at 0 ºC. 15 minutes subsequent to the initial mixing, a solution of 3-hydroxymethyl pyridine (0.55cm^3, 6mmol) in DCM (10 mL) was added. The reaction mixture was then left at room temperature for 15 hours with continual stirring. Saturated NH_4Cl (25 mL) was then combined with the reaction mixture and the resultant aqueous layer was extracted with diethyl ether (4 x 25mL) dired with $MgSO_4$ and concentrated in vacuo. The remaining mixture was purified using column chromatography (40-60 petroleum ether: ethyl acetate, 1:1) to yield compound **1b** (1.18 g, 68%) as a white crystalline solid.[2]

Pyridinemethylene-3-oxystearate 1c.

EDCI (2.2g, 11mmol) and DMAP (268mg, 2.2mmol) were dissolved in DCM (15mL). To this mixture was added a solution of stearic acid (1.71g, 6mmol) in DCM (25mL) at 0 ºC. 15 minutes subsequent to the initial mixing, a solution of 3-(hydroxymethyl) pyridine (0.55cm^3, 6mmol) in DCM (10 mL) was added. The reaction mixture was then left at room temperature for 60 hours with continual stirring. Saturated NH_4Cl (25 mL) was then combined with the reaction mixture and the resultant aqueous layer was extracted with diethyl ether (4 x 25mL) dried with $MgSO_4$ and concentrated in vacuo. The remaining mixture was purified using column chromatography (40-60 petroleum ether: ethyl acetate, 1:1) to yield compound **1c** (2.023g, 5.4mmol, 90.03%) as a white crystalline solid.[3]

fac-$[Re(bpy)(CO)_3CH_3CN](BF_4)$ 3.

To a solution of $Re(bpy)(CO)_3Cl$ (243 mg, 0.5 mmol) in acetonitrile (100 ml) was added silver tetrafluoroborate (105 mg, 0.5 mmol). The mixture was heated at reflux under nitrogen atmosphere in the dark for 5 hours then the solvent was removed at high vacuum to give **3** as a yellow solid. (255 mg, 87.9%). δ_H ($CDCl_3$) 2.13 (s, 3H, CH_3), 7.57 (2H, m, bpy$H_{5,5'}$), 8.19 (2H, app. t, J = 6.4 Hz, bpy$H_{4,4'}$), 8.49 (2H, d, 2H, J = 8.3 Hz, bpy$H_{3,3'}$), 8.85 (2H, d, J = 5.4, bpy$H_{6,6'}$). ν_{max} (Nujol), (cm^{-1}): 2035s, 1918s, υ (CO).

Fac-$[Re(bpy)(CO)_3Py\text{-}3\text{-}CH_2O_2C(CH_2)_6CH_3$ 4a

3 (0.080g, 0.14mmol), and **1a** (0.075g, 0.42mmol) were dissolved in tetrahydrofuran (20mL) and heated at 50°C for 20 hours. The resultant solution was subsequently filtered through celite prior to the removal of the solvent in vacuo to afford **4a** as a bright yellow solid; δ_H ($CDCl_3$): 0.81 (m, 3H, H_i), 1.25 (10 H, br.s, CH_2), 2.24 (2H, m, COCH_2), 4.91 (2H, s, PyCH_2), 7.34 (1H, m, PyH_5), 7.69 (3H, m, PyH_4 and bpy$H_{5,5'}$), 7.90 (1H, d, *J* = 8.0 Hz, PyH_6), 8.29 (3H, m, PyH_2 and bpy$H_{3,3'}$ overlapping), 9.02 (2H, d, *J* = 4.7 Hz, bpy$H_{6,6'}$); δ_C ($CDCl_3$): 14.4, 22.9, 25.1, 29.2, 29.4, 32.0, 34.3, 62.4, 126.1, 127.5, 129.4, 136.1, 140.0, 142.1, 151.3, 151.9, 153.2, 156.1, 173.6, 195.8 br; *m/z* (ES) 660.2, ν_{max} (nujol mull) / cm^{-1} 2924, 2854, 2032, 1917 (broad), 1739, 1604, 1462, 1377, 1029; m/z (ESI) Theoretical isotope pattern 660.2 (58%), 661.2 (19%), 662.2 (100%), 663.2 (32%), 664.2 (6%), Actual isotope pattern 660.3 (56%), 661.3 (18%), 662.3 (100%), 663.3 (30%), 664.3 (6%); HRMS (ESI) $[M-BF_4]^+$ 660.1631 observed 660.1628.

***Fac*-[Re(bpy)(CO)$_3$Py-3-CH$_2$O$_2$C(CH$_2$)$_{12}$CH$_3$ 4b**

3 (0.161 g, 0.29 mmol) and **1b** (0.092 g, 0.29 mmol) were dissolved in tetrahydrofuran (20mL) and heated at 50°C for 20 hours. The resultant solution was subsequently filtered through celite and the product precipitated by the addition of petroleum ether to give **4b** as a yellow solid (0.156 g, 64 %) as a bright yellow solid. Mp 123-125 ^{o} C; ; δ_H ($CDCl_3$): 0.82 (3H, t, *J* = 3.5 Hz CH_3) 1.22 (20 H, br. s. 10 x CH_2) 2.24 (2H, t, *J*= 7.5 Hz, COCH_2) 4.95 (2H, s, Py-CH_2) 7.33 (1H, dd *J*= 7.5, 2.0 Hz PyH_5) 7.71 (3H, m, PyH_4 and bpy$H_{5,}H_{5'}$) 7.89 (1H, d, *J*= 7.0 Hz, PyH_6) 8.26 (3H, m, PyH_2 and bpy$H_{4,}H_{4'}$)8.65 (2H, d, *J*=8.0 Hz, bpy$H_{3,}H_{3'}$) 9.03 (2H, d, *J*=5.5 Hz, bpy$H_{6,}H_{6'}$). δ_c ($CDCl_3$) 14.5, 23.1, 25.2 29.4-30.1 multiple peaks, 32.3, 34.3, 52.4, 126.4, 127.6, 129.3, 137.3, 139.9, 142.5, 151.2, 151.8, 153.3, 156.6, 174.2. ν_{max} (nujol mull) 2928, 2856, 2037, 1938 br. m/z (ESI) $[M-BF_4]^+$ theoretical isotope pattern 744.3 (60%) 746.3 (100%) 747.3 (40 %) 748.3 (10%) observed isotope pattern 744.3 (60%) 746.3 (100%) 747.3 (40 %) 748.3 (10%) HRMS (ESI) $[M-BF_4]^+$ calculated mass 744.2570 observed 744.2567.

***Fac*-[Re(bpy)(CO)$_3$Py-3-CH$_2$O$_2$C(CH$_2$)$_6$CH$_3$ 4c**

3 (0.050g, 0.09mmol), and **1c** (0.101g, 0.27mmol) were dissolved in tetrahydrofuran (20mL) and heated at 50°C for 20 hours. The resultant solution was subsequently filtered through celite prior to the removal of the solvent in vacuo to furnish **4c** (0.067g, 0.075mmol, 83.44%) as a bright yellow solid, mp 109-110°C; δ_H ($CDCl_3$) 0.81 (3H, t, , *J* = 6.8 Hz, CH_3), 1.22, (, 28H, br.s, CH_2), 2.22, (2H, t, *J* = 7.6 Hz, COCH_2), 4.93 (2H, s, PyCH_2), 7.34 (1H, dd, , *J* = 7.5, 2.0 Hz, PyH_5), 7.67 (2H, t, *J* = 6.6 Hz, bpy$H_{5,}H_{5'}$), 7.74 (1H, d, H_d, *J* =8.1 Hz, PyH_4), 7.88 (1H, d, *J* = 5.8 Hz, PyH_6) 8.27 (3H, m, PyH_2 and bpy$H_{4,}H_{4'}$), 8.67 (2H, d, *J* = 8.2 Hz, bpy$H_{3,}H_{3'}$), 9.03 (2H, d, *J* = 5.4 Hz, bpy$H_{6,}H_{6'}$); δ_C ($CDCl_3$): 14.5, 23.1, 29.5-30.1 multiple peaks, 32.3, 34.4, 62.8, 126.5, 128.1, 129.1, 136.6, 140.8, 142.1, 151.3, 151.9, 152.8, 156.9, 178.6; ν_{max} (nujol mull) 2922, 2852, 1738; *m/z* (ESI) 800.3 [M+], Theoretical isotope pattern 800.3 (56%), 801.4 (25%), 802.3 (100%), 803.3 (42%), 804.3 (9%), Actual isotope pattern 800.4 (56%), 801.4 (25%), 802.5 (100%), 803.4 (39%), 804.4 (9%); HRMS (ESI) $[M-BF_4]^+$ 800.3196, observed 800.3201.

***fac*-[Re(bpy)(CO)$_3$PyCH$_2$OH](BF$_4$) 4d.**

3 (255 mg, 0.4 mmol) and 3-(hydroxymethyl)pyridine (0.45 ml, 4 mmol) in THF (175 ml) was heated at reflux under nitrogen atmosphere for 1.5 hour. After the solution had cooled, petroleum ether was added dropwise to precipitate **4** as a yellow solid. (178 mg, 62% yield), m.p. 200^{o}C, δ_H ($CDCN_3$) 3.33 (1H, s, OH), 4.38 (2H, s, CH_2), 7.18 (1H, m, PyH_5) 7.68-7.78 (3H, m, PyH_4 and bpy$H_{5,5'}$), 8.04 (1H, d, J = 5.5 Hz PyH_6), 8.12 (1H, s, PyH_2), 8.2 (2H, dd J=7.0, 8.5 Hz bpy$H_{4,4'}$), 8.30 (2H, d, J = 8.5 Hz, bpy$H_{3,3'}$), 9.18 (2H, d, J = 6.5 Hz, bpy$H_{6,6'}$). δ_C ($CDCN_3$) 59.6, 124.3, 125.8, 127.8, 137, 140.6, 140.8, 149.5, 150.0, 153.5, 155.4, 191.3, 195.4. ν_{max} (Nujol) : 2032s, 1915sb υ (CO), m/z (ESI) 536.1 $[MH]^+$, 427 [M-BF_4-$PyCH_2OH$; $ReC_{19}H_{15}O_4N_3BF_4$ requires C, 36.65; H, 2.41; N, 6.75., found C, 36.68; H, 2.30; N, 6.56.

$[(O_3SPh)_2Phen][Bu_4N]_2$ 5. An aqueous solution (1ml) of tetrabuthylammonium hydrogen sulfate (0.14 g, 0.42 mmol) was added to a solution of bathophenanthrolinedisulfonic acid disodium salt hydrate (0.10g, 0.18mmol) in the same solvent (1ml). The resulting pink solution was extracted with DCM (4 x 2ml)and then dried with $MgSO_4$. The removal of the solvent at high vacuum afforded $[Bu_4N]_2[(O_3SPh)_2(Phen)]$ as a pink solid (0.172 g, 95% yield); mp 58 °C. m/z(ESI) 732 (MBu_4N^-, 18%), 491 (MH^+, 48%), 245 (Bu_4N^+, 39%)

***fac*-$[Re\{(O_3SPh)_2Phen\}(CO)_3Cl](Bu_4N)_2$ 6a.** To a suspension of $Re(CO)_5Cl$ (31 mg, 0.085 mmol) in dry toluene (2ml) was added **5** (88 mg, 0.085 mmol). The mixture was heated for 2h hours under N_2 atmosphere to afford an orange gel. The solvent was decanted and the gel formed was washed several times with diethyl ether until it became solid which was then dried under vacuum to give *fac*-$[Re\{(O_3SPh)_2Phen\}(CO)_3Cl](Bu_4N)_2$ **6a** as a yellow solid (92 mg, 84.4% yield). mp. 105° C. δ_H (CD_3CN) 9.40 (2H, m, phen$_{2,9}$), 8.02-7.85 (6H, m, 4xPh(-o-SO_3)*H*+phen*H* $_{5,6}$), 7.62 (4H, m, 4 x Ph(m-SO_3)*H*), 7.25 (2H, m, phen$H_{3,8}$), 3.09 (16H, m, 8 x NCH_2), 1.60 (16H, m, 8 x NCH_2CH_2) 1.35 (16H, m, 8 x CH_2CH_3), 0.98 (24H, m, 8 x CH_3). δ_C (MeCN) 197.5 (2CO), 190.0 (CO), 152.4 , 150.1 (2C), 147.0, 146.0 (2C), 136.1, 135.1, 130.7, 130.6, 129.4 (2C), 128.7, 128.5, 128.4, 128.3, 127.8, 126.8 (2C), 126.7, 126.1 (2C), 125.2 (2C) 57.9 , 22.9, 18.9, 12.5. ν_{max} (nujol) 2018, 1910, 1883. m/z (ESI) 1038.3 $[M+Bu_4N]^-$.

***fac*-$[Re(O_3SPh)_2(Phen))(CO)_3CF_3SO_3](Bu_4N)_2$ 6b.**

To a solution of **5** (100 mg, 0.07 mmol) in DCM (3 ml) was added 10.45 equivalents of trifluoromethylsulfonic acid (0.07 ml, 0.8 mmol) and the mixture was stirred for one hour under nitrogen atmosphere, then n-hexane was added using a pressure funnel until a yellow precipitate was formed. The solvent was removed *via* cannula and this operation was repeated twice in order to eliminate residual triflic acid. Finally, the solid was dried under vacuum to give *fac*-$[Re(O_3SPh)_2(Phen))(CO)_3CF_3SO_3](Bu_4N)_2$ **6b** as a yellow powder (0.123 mg, 99.55%) δ_H (MeOD) 9.52 (2H, d, J = 5.4 Hz, phen$H_{2,9}$), 8.15-7.63 (12H, m, phenH_{3-8} + 8 x Ph*H*), 3.13 (16H, m, 8xNCH_2), 1.56 (m, 16H, 8 x NCH_2CH_2) 1.32 (16H, m, 8 x CH_2CH_3), 0.95 (24H, m, 8 x CH_3). ν_{max} (nujol) 2030, 1926, 1902,

***fac*-$[Re(O_3SPh)_2(Phen))(CO)_3Py](NH_4)$ 6y.**

To a solution of **6b** (0.1g, 0.07 mmol) in CH_3CN (7 ml) was added diisopropylethylammine (0.7 ml, 0.4 mmol) and pyridine (0.06 ml, 0.7 mmol). After refluxing for five days under a nitrogen atmosphere the solvent was removed and the yellow solid was redisolved in the smallest possible volume of methanol. Dry diethyl ether was added until a precipitate formed then the supernatant liquid was removed *via* cannula and the remaining yellow solid was dried under high vacuum. The yellow solid was dissolved in the smallest possible volume of methanol and it was passed through an ion exchange column (Amberlite IR120 H resin as NH_4^+ form) which had been previously washed with aqueous ammonia eluting with methanol. The yellow coloured fraction which elutes immediately was collected and evaporated and dried under vacuum to give **6y** as a yellow solid (26 mg, 43 %) mp > 150 °C,. δ_H (MeOD) 9.72 (2H, m, phen$H_{2,9}$), 8.47 (2H, dd, J=3.62, 3.18, Py$H_{2,6}$) 8.09-7.92 (8H, m, 8 x Ph*H*) 7.73 (1H, m, PyH_4), 7.69-7.55 (4H, m, phen$H_{3,8}$) 7.25 (2H, m, Py$H_{3,5}$). δ_C (MeOD) 197.1 (2CO), 193.3 (CO), 155.0, 153.7, 153.6 (2C), 148.9, 148.5 (2C), 147.1 (2C), 141.6, (2C), 138.8, 137.2, 133.1 (2C), 131.5 (2C), 130.9 (3C), 130.8 (2C), 129.1, 129.0, 128.7, 128.4, 128.2, 127.6 (2C). ν_{max} (nujol) 3401, 2026, 1893 br. m/z FAB 840.1 $[MH_2]^+$. 100%. HRMS (ESI-) calculated $[M]^-$ = 838.0098, measured $[M]^-$ = 838.0093.

***fac*-[Re{$(O_3SPh)_2$Phen}$(CO)_3$PyCH2OH] [H_4N] 6z.**

3-(Hydroxymethyl)pyridine (0.02 ml, 0.195 mmol) and **6b** (40 mg, 0.03 mmol) were heated at reflux in THF (5 ml) under a nitrogen atmosphere for a week followed by stirring for 2 more days. The solvent was removed under vacuum and the residue dissolved in the smallest volume possible of methanol to give a yellow solution. Dry diethyl ether was added until a precipitate formed then the supernatant liquid was removed *via* cannula and the remaining yellow solid was dried under high vacuum. The yellow solid was dissolved in the smallest possible volume of methanol and it was passed through an ion exchange column (Amberlite IR120 H resin as NH_4^+ form) which had been previously washed with aqueous ammonia eluting with methanol. The yellow coloured fraction which elutes immediately was collected and evaporated and dried under vacuum to give **6z** as a yellow solid (20 mg, 46.4%), mp > 150 °C. (NH_4) δ_H (MeOD) 9.71 (2H, d, J=4.83, phen$H_{2,9}$), 8.38 (1H, s, PyH_2), 8.32 (1H, d, J=4.95, PyH_6), 8.05 (2H, d, J=5.1, ½ x 4 x PhH(o-SO_3)) 7.95-8.01 (3H, m, PyH_4 + phen$H_{5,6}$), 7.93 (2H, d, J=6.7 Hz, ½ x 4 x PhH(o-SO_3)) 7.55-7.7 (6H, m, phen$H_{3,8}$ 4 x PhH(m-SO_3), 7.18 (1H, t, J=6.47 Hz, PyH_5), 4.38 (2H, s, PyCH_2O). δ_C (MeOD) 195.6 (2CO), 191.4 (CO), 154.4, 150.0 (2C), 150.7, 150.0, 147.4 (2C),, 146.8, 146.4 (2C), 141.2, 138.2 137.2, 135.7, 131.6, 130.0 (2C), 129.3 (3C), 129.2 (2C), 127.5, 127.4, 127.1, 126.6, 126.2, 126.1 (2C), 60.2. ν_{max} (nujol) 3414, 2028, 1906 br. m/z (FAB) 870.2 $[MH_2]^+$A HRMS calculated $[M^-]$ = 868.0203, measured $[M]^-$ = 868.0204.

References.

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