Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Rhenium sapphyrins: Remarkable difference between the C_6F_5 and CF_3-substituted derivatives

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Instrumental Section

^{1}H and ^{19}F NMR spectra were recorded on Bruker Avance III 400 spectrometer (400 MHz for ^{1}H and 377 MHz for ^{19}F) and chemical shift are reported in ppm relative to residual hydrogen atoms of $CDCl_3$ solvent. Mass spectra were recorded on Brcker maXis impact using APCI positive method. Absorption spectra were recorded using Agilent Cary 8454 UV-visible spectrophotometer in Toluene. The fluorescence emission spectral data recorded on Fluorolog-3 spectrofluorometer equipped with a Xenon-arc and fluorescence decay measurements recorded using Time-correlated single photon counting (TCSPC) apparatus using 405±10 nm excitation wavelength. Quantum yield calculated at 450 nm excitation wavelength with respect to the $Ru(bpy)_3PF_6$ which gives 6.2% in acetonitrile[1] under argon atmosphere using following equation

$$\emptyset_f = \emptyset_{st}\frac{F}{F_{st}}\frac{A_{st}\eta^2}{A\,\eta_{st}^2}$$

f – fluorophore, st - standard, F-area of emission peak, A-absorbance, η-refractive index

The electrochemical measurements were recorded using a conventional three electrode system consisting of a glassy carbon working electrode, a platinum wire as counter electrode and Ag/AgCl reference electrode in DMF and acetonitrile solvent. Electrochemical measurements were recorded with an EmStat3+ electrochemical system. All the potentials are referenced vs the $Fc^{+/0}$ redox potential added as an internal standard ($E_{1/2}$ = 0.058 V in acetonitrile and 0.075 V in DMF).

Crystal structure determination of (tpfs)Re$(CO)_3$ and (tfs)Re$(CO)_3$

The single-crystal material immersed in Paratone–N oil and mounted on a APEX II Bruker diffractometer at low temperature. Data collection was performed using monochromated Mo Kα radiation, λ = 0.71073 Å, using φ and ω scans to cover the Ewald sphere. Accurate cell parameters were obtained with the amount of indicated reflections. Using Olex2,[2] the structure was solved with the olex2.solve[3] structure solution program using Charge Flipping and refined with the ShelXL[4] refinement package using Least Squares minimization. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Software used for molecular graphics: Mercury 3.10.1. The X-ray crystallographic coordinates for structure (tfs)Re$(CO)_3$ and (tpfs)Re$(CO)_3$ reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number CCDC 1949176 and 1949175 respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Experimental Section

Free base sapphyrins were prepared as reported in earlier literature.[5]

Synthesis of rhenium(I) sapphyrins

Free base sapphyrin (0.03 mM) dissolved in decalin and stirred at 175 °C followed by addition of $Re_2(CO)_{10}$ (10 equivalent) and continue the reaction at 175 °C under Ar atmosphere until reactant is fully consumed (about 1 hr). Load the reaction mixture on silica gel column and elute with pure hexane to remove decalin. The desired fraction of rhenium(I) sapphyrin is collected using 30%CH_2Cl_2:60% hexane mixture. Evaporate the solution and recrystallized the rhenium(I) sapphyrin by 25% CH_2Cl_2 in heptane solution. X-ray quality crystals of (tfs)Re$(CO)_3$ and (tpfs)Re$(CO)_3$ were obtained from THF/n-heptane and CH_2Cl_2/n-heptane solvent mixtures, respectively.

5,10,15,20-tetrakis(trifluoro-methyl)sapphyrinato tricarbonyl-rhenium(I) ((tfs)Re $(CO)_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 13.74 (s, 1H), 10.32 (d, 4.6 Hz, 1H), 10.16 (d, 5 Hz, 1H), 9.93-9.84 (m, 2H), 9.75-9.62 (m,3H), 9.40-9.36 (m, 1H)), -0.58 (s, 1H), -3.36 (d, 4.56 Hz, 1H), -4.75 (d, 4.44 Hz, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ = -36.44 (s, 3F), -41.08 (s, 3F), -45.97 (s, 3F), -48.66 (s, 3F). MS- (ACPI, positive mode) for $C_{31}H_{12}F_{12}N_5O_3Re$: m/z = 917.0306 (calculated), 917.0219 (observed). λ_{max} in Toluene (ε); 473(318000), 505(323000), 669(36000), 725(43000).

5,10,15,20-tetrakis(pentafluorophenyl)sapphyrinato tricarbonyl-rhenium(I) ((tpfs)Re $(CO)_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ =10.73 (d, 4.48 Hz, 1H), 10.65 (d, 4.6 Hz, 1H), 9.79 (t, 4.9 Hz, 2H), 9.62 (dd, 12.28, 4.9 Hz, 2H), 9.53 (d, 4.72 Hz, 2H), 9.22 (d, 4.72 Hz, 1H), 9.11 (d, 4.68 Hz, 1H), -1.05 (s, 1H), -3.11 (s, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ = -134.22 (dd, 26.4, 7.54 Hz, 1F), 135.20 (dd, 22.6, 7.54 Hz, 1F), -135.38 (dd, 22.6, 7.54 Hz, 1F), -135.82 (dd, 26.4, 7.54 Hz, 1F), -137.06 (dd, 22.6, 7.54 Hz, 1F), -137.56 (dd, 26.4, 7.54 Hz, 1F), -137.88 (dd, 22.6, 7.54 Hz, 1F), -150.17 (t, 20.7 Hz, 1F), -150.57 (t, 18.9 Hz, 1F), -151.08 (t, 20.7 Hz, 2F), -160.52 (td, 22.6, 7.54 Hz, 1F), -160.77 (td, 22.6, 7.54 Hz, 1F), -160.91-161.42 (m, 4F), -161.60 (td, 22.6, 7.54 Hz, 1F), -162.27 (td, 22.6 Hz, 7.54 Hz, 1F). MS- (ACPI, positive mode) for $C_{51}H_{12}F_{20}N_5O_3Re$: m/z = 1309.0178 (calculated), 1309.0024 (observed). λ_{max} in Toluene (ε x 10^{-5}); 457(660000), 497(331000), 640(79000), 736(45000)

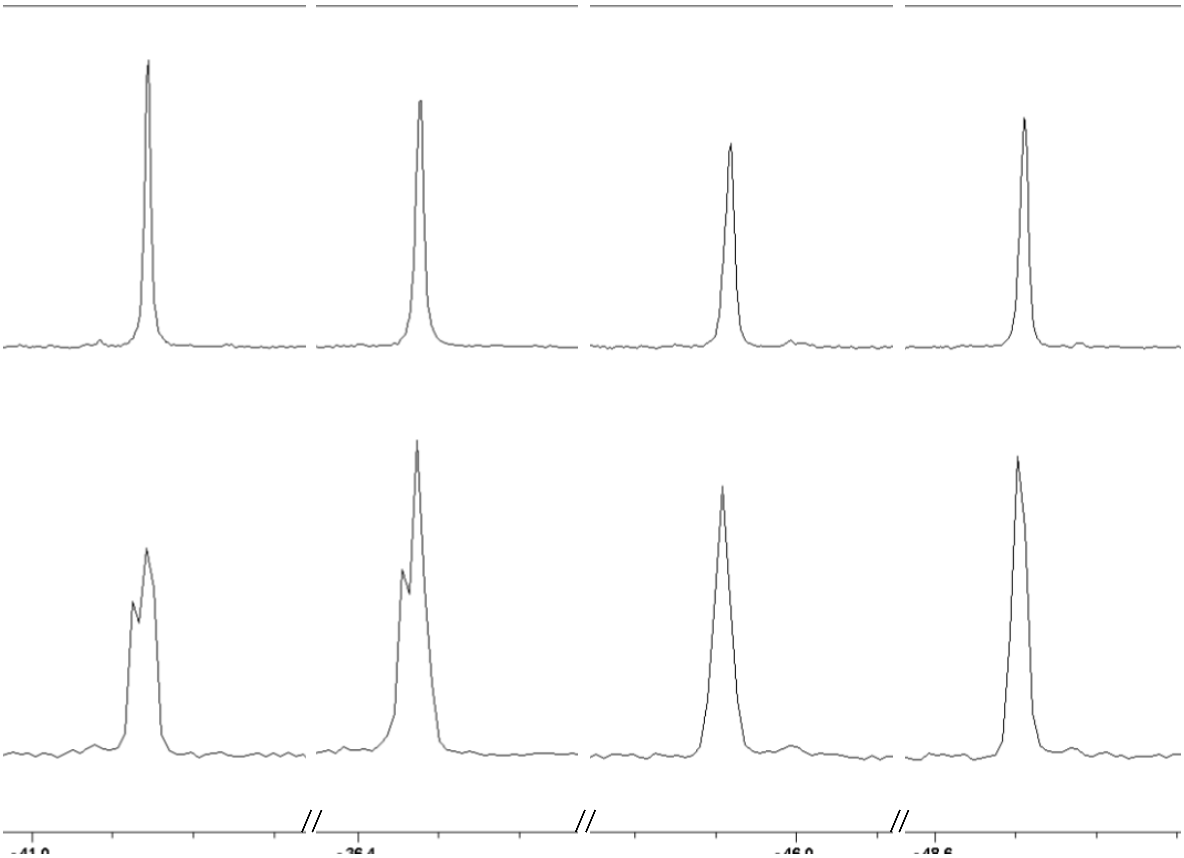

Figure S1 ^{19}F NMR of (tfs)Re$(CO)_3$ in $CDCl_3$, proton decoupled (top) and coupled (below).

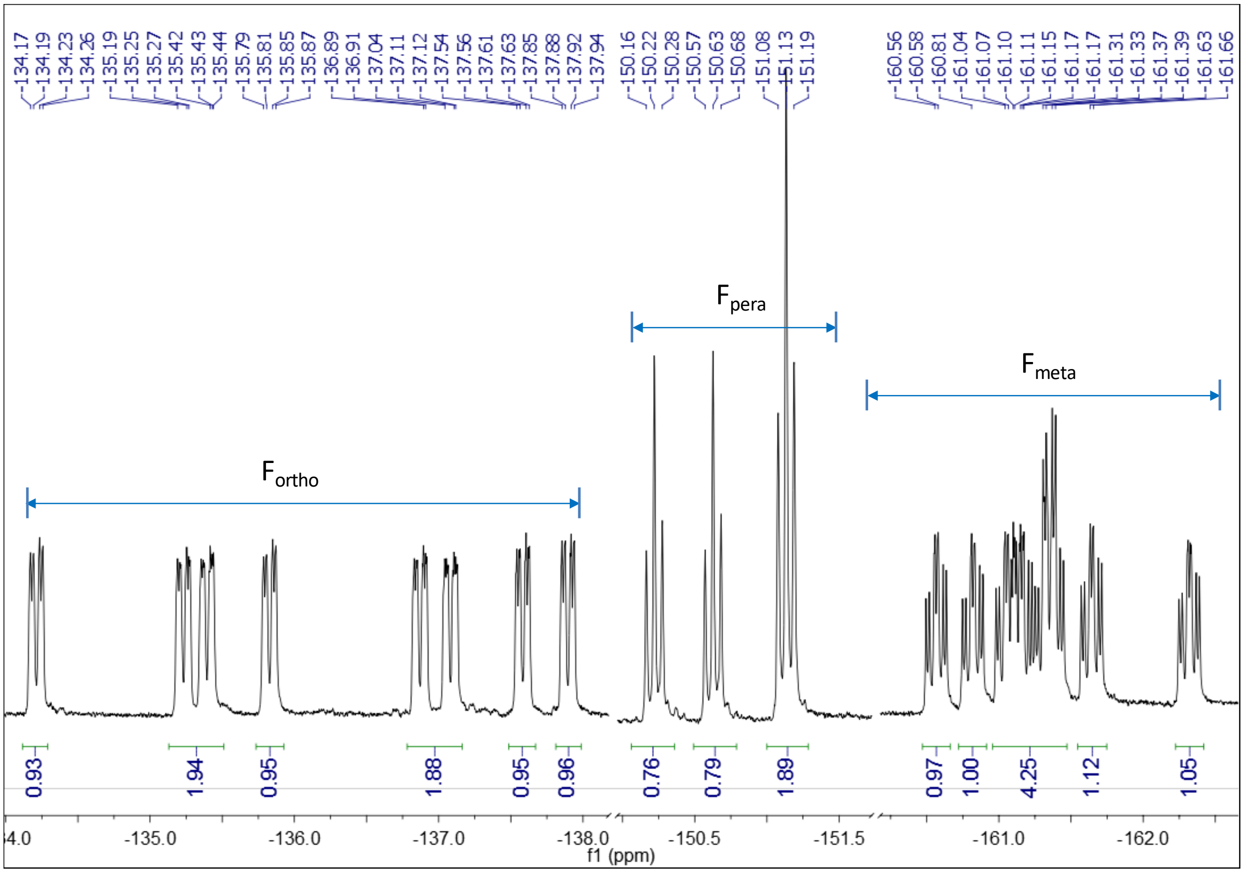

Figure S2 ^{19}F NMR of (tpfs)Re(CO)$_3$ in CDCl$_3$.

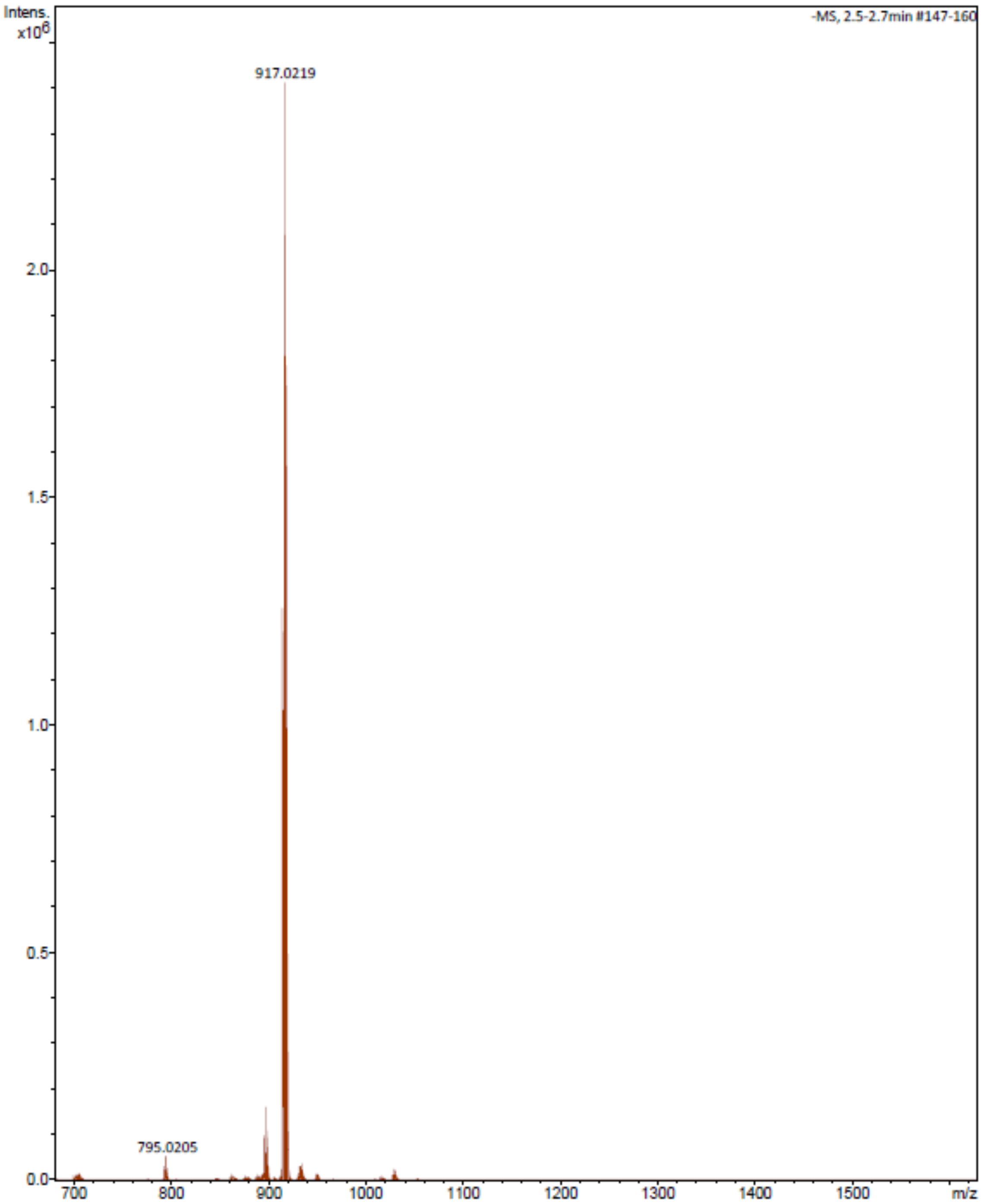

Figure S3 APCI-mass spectra of (tfs)Re(CO)$_3$ (917.0306, calculated) in positive ion mode.

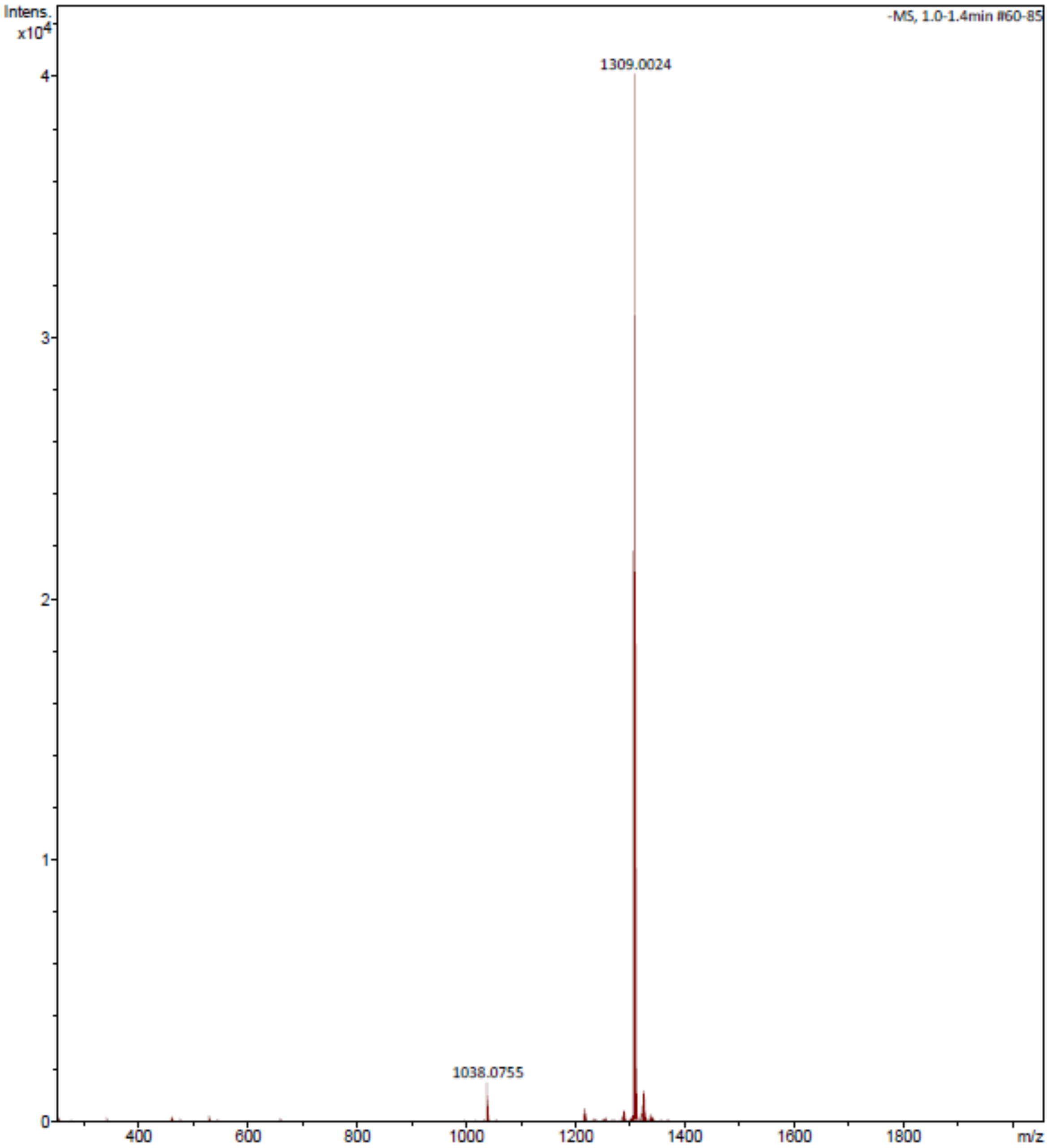

Figure S4 APCI-mass spectra of (tpfs)Re(CO)$_3$ (1309.0178, calculated) in positive ion mode.

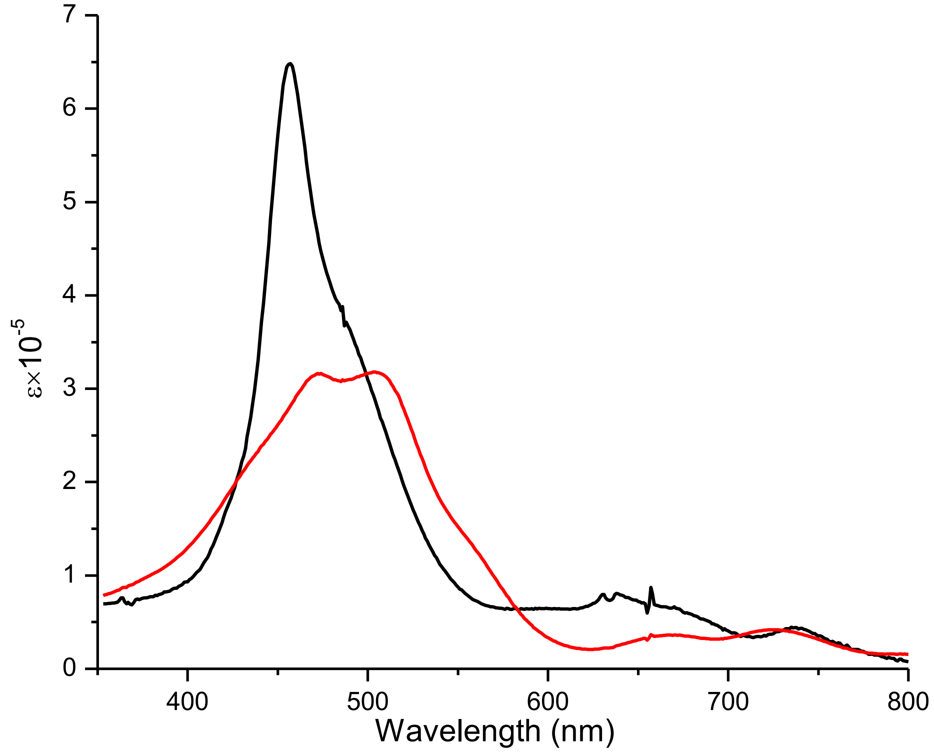

Figure S5 UV-Visible spectra of Re(H_2TpFS)$(CO)_3$-black and Re(H_2TFS)$(CO)_3$-red in toluene.

References

1. Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc*. **1983**, *105*, 5583-5590

2. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

3. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2015). Acta Cryst. A71, 59-75.

4. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

5. (a) Chen, Q. C.; Soll, M.; Mizrahi, A.; Saltsman, I.; Fridman, N.; Saphier, M.; Gross, Z. *Angew. Chem. Int. Ed*. **2018**, *57*, 1006-1010. (b) Simkhovich, L.; Rosenberg, S.; Gross, Z. *Tetrahedron Lett.* **2001**, *42*, 4929-4931