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Supplementary Material

$[Re(CO)_3(5\text{-PAN})Cl]$, A Rhenium(I) Naphthalimide Complex for the Visible Light Photocatalytic Reduction of CO_2

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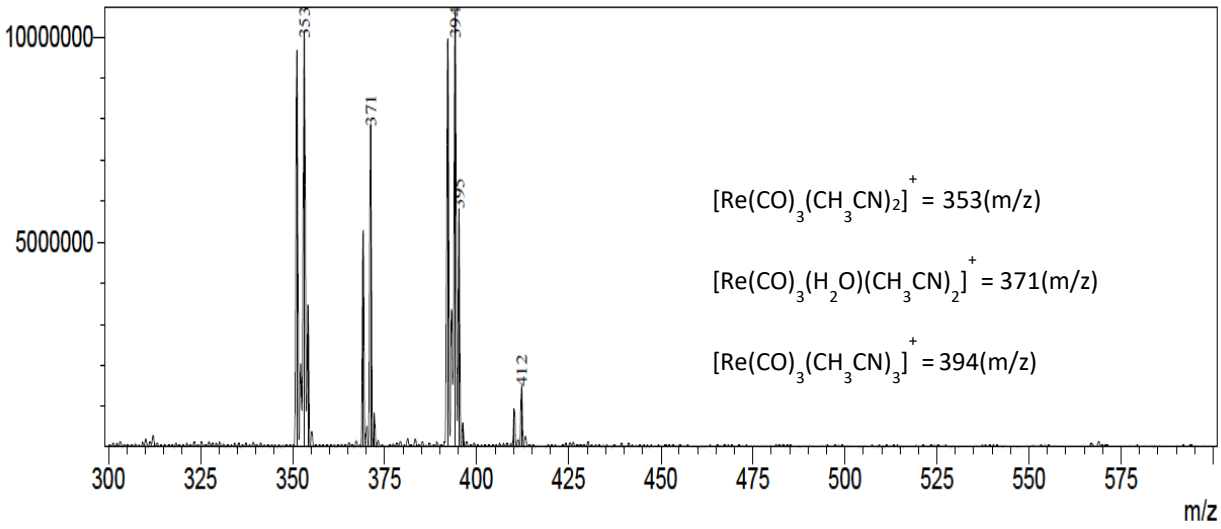
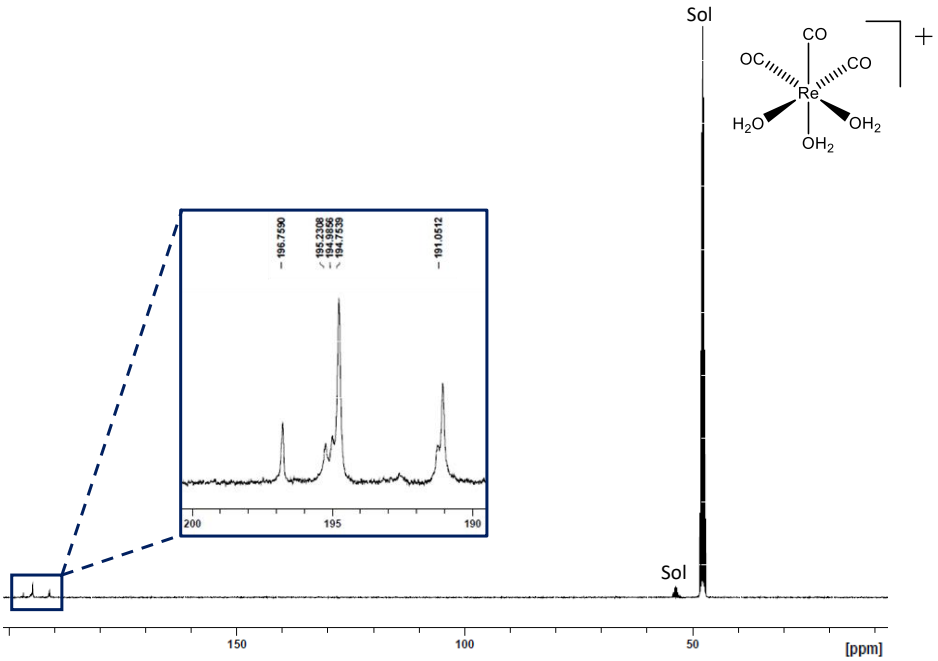
1. Synthesis and Characterization of 5-PAN, $[Re(CO)_3(H_2O)_3]Cl$, and Re(5-PAN)

Synthesis of $[Re(CO)_3(H_2O)_3]Cl$

Chloropentacarbonyl rhenium(I) (8.45 mmol, 3.0551 g) was dissolved in 50 mL of water in a 100 mL round bottom flask. The solution was left to reflux and monitored via TLC (70/30 hexanes/ethyl acetate) until full conversion was observed. The reflux of chloropentacarbonyl rhenium (I) can take up to four days for full conversion. The solvent was removed and the solid dried *in vacuo*. The white/green solid was obtained in ~93% yield (2.5451 g).



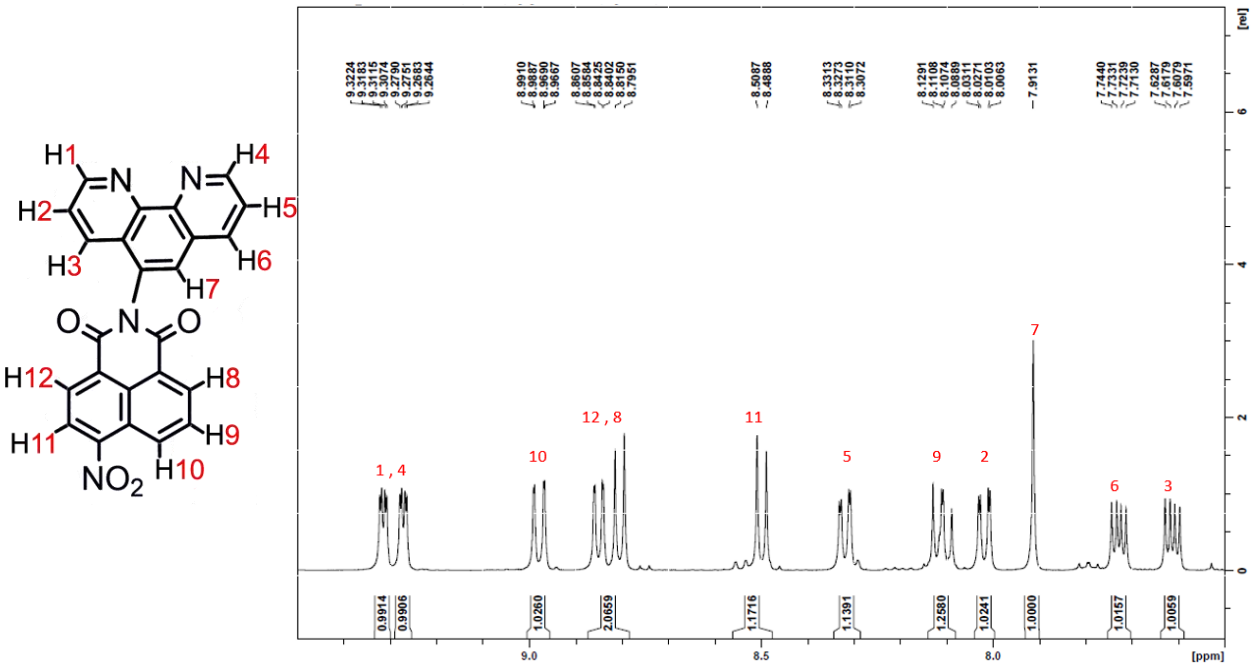
S1. Electrospray. $[Re(CO)_3(H_2O)_3]^+$ was dissolved in methanol and characterized via ESI-MS in the presence of acetonitrile and water with 0.1% TFA. Both the di- and trisubstituted acetonitrile adducts were observed at 353, 371, and 394 m/z, respectively. Expected mass = 324 g/mol.



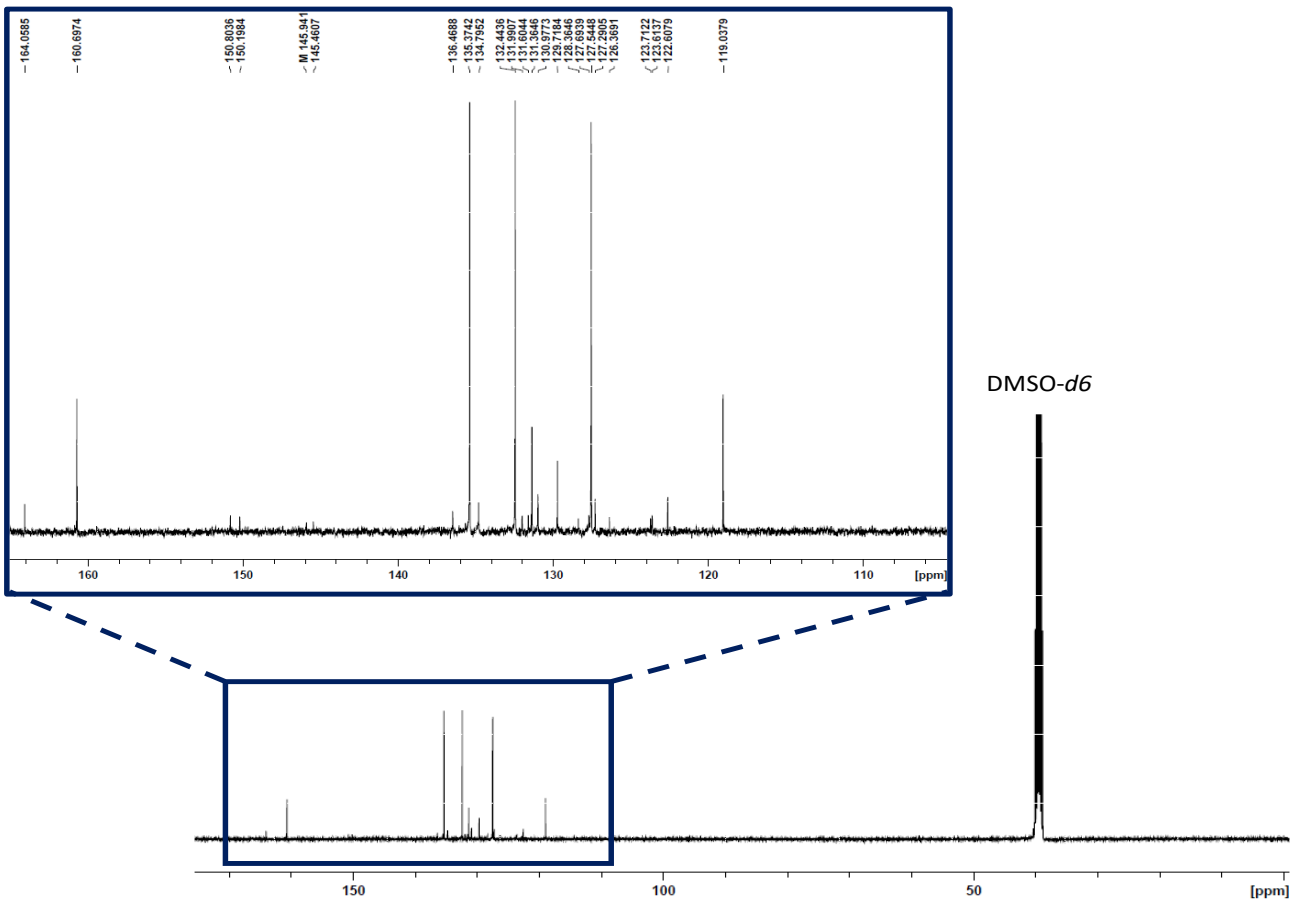
S2. ^{13}C NMR of $[Re(CO)_3(H_2O)_3]Cl$ in deuterated methanol (CD_3OD) showing distinct carbonyl peaks between 190 – 200ppm.

*Synthesis of **5-PAN***

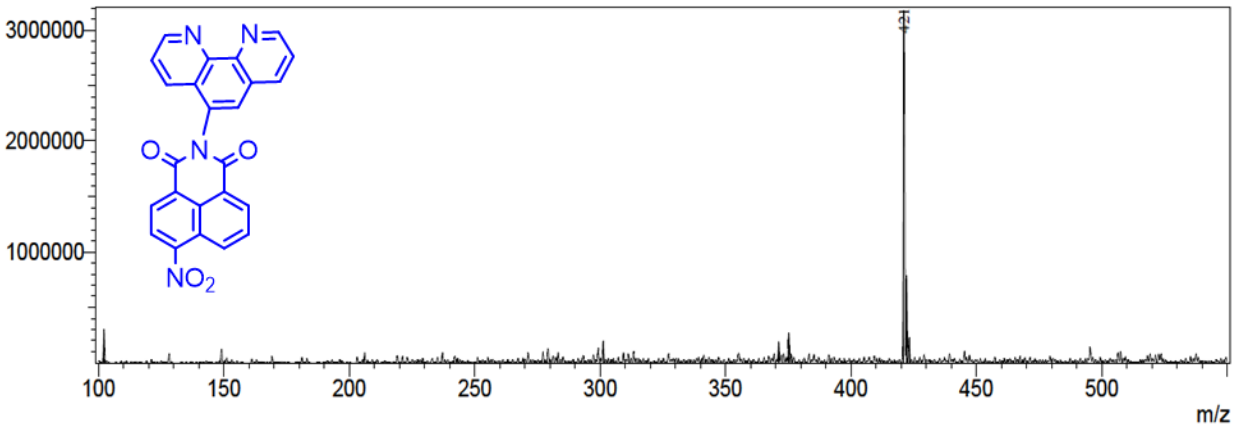
1,10-phenanthroline-5-amine (2 mmol, 390 mg) and 4-nitro-naphthalic anhydride (2 mmol, 486 mg) were each placed in a 50 mL round bottom flask with 20 mL of anhydrous ethanol. Each were placed in a sand bath to reach 65°C after which, the solutions were combined and set to reflux under argon for 48 hours. The solvent was reduced in volume by half *in vacuo* and diethyl ether was added to further precipitate the product. The mixture was centrifuged, and the ether decanted. The tan solid was washed with methanol and acetonitrile and dried overnight under vacuum. **5-PAN** was obtained in ~44% yield (276 mg).



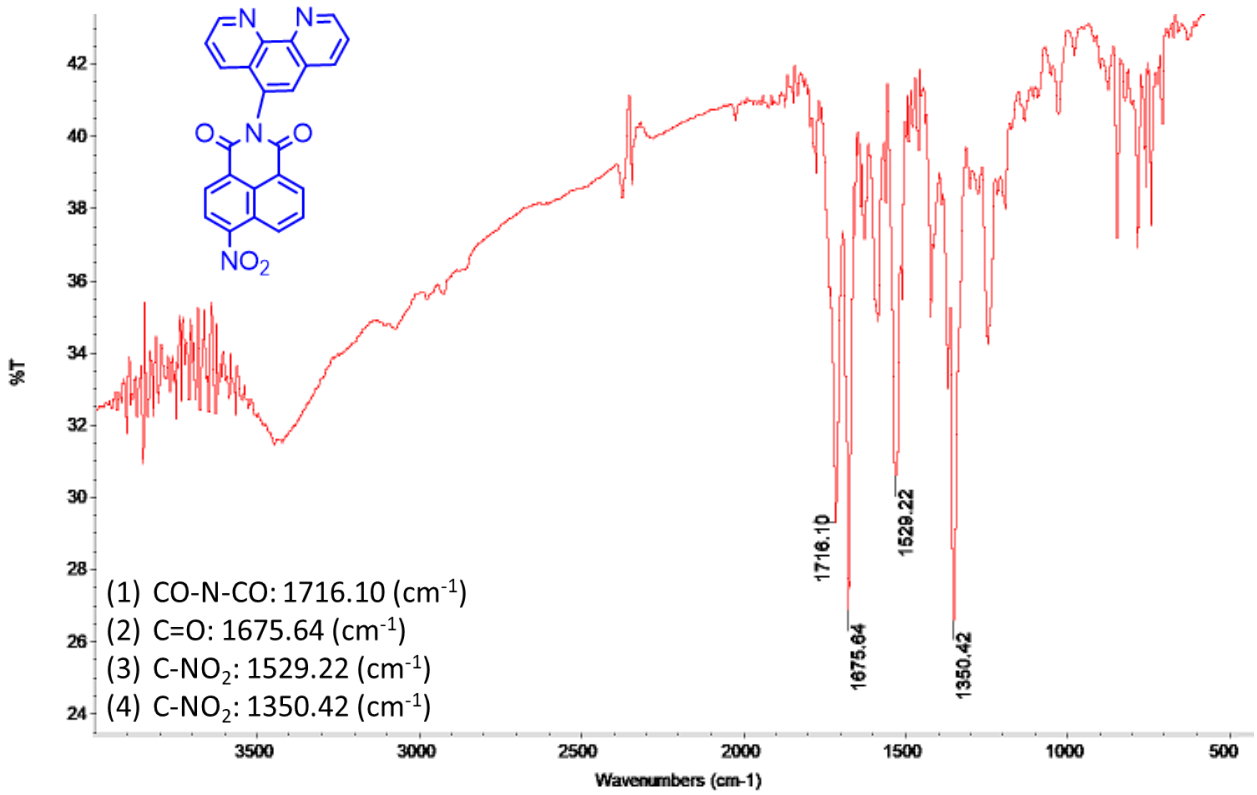
S3. ^{1}H NMR spectrum of **5-PAN** with zoomed in aromatic region (400 MHz, chloroform-d) δ 9.32-9.31 (dd, 1H), 9.28-9.26 (dd, 1H), 9.00-8.97 (dd, 1H), 8.86-.84 (dd, 1H), 8.82-8.80 (d, *J* = 8.0 Hz, 1H), 8.51-8.49 (d, *J* = 8.0 Hz, 1H), 8.33-8.31 (dd, 1H), 8.13-8.09 (dd, 1H), 8.03-8.00 (dd, 1H), 7.91 (s, 1H), 7.74-7.71 (dd, 1H), 7.63-7.60 (dd, 1H).



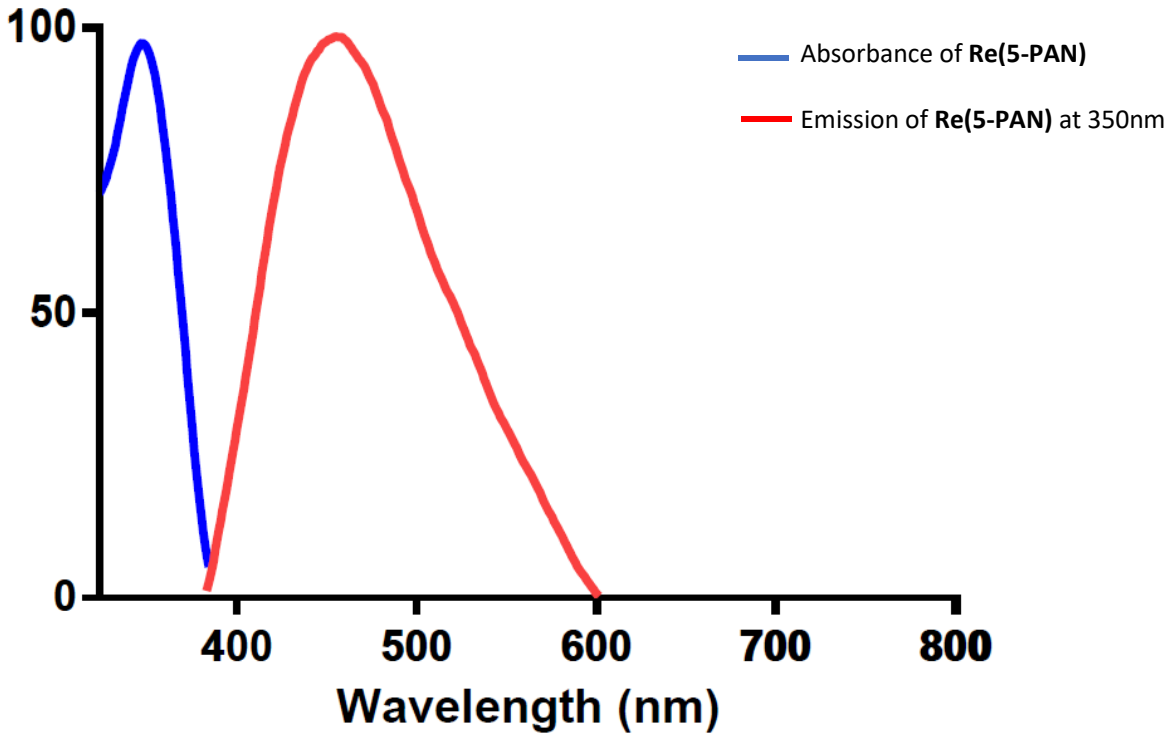
S4. ^{13}C NMR of the free **5-PAN** ligand acquired in DMSO-*d6* showing the appropriate number of 24 carbon signals with the signals beyond 160 being assigned to ketone carbons of the naphthal core. Unlike the **Re(5-PAN)** complex, there is no presence of the rhenium tricarbonyl core carbons.



S5. Electrospray mass spectrometry **5-PAN** was dissolved in DCM and run in the presence of methanol. Expected mass was 420 g/mol.



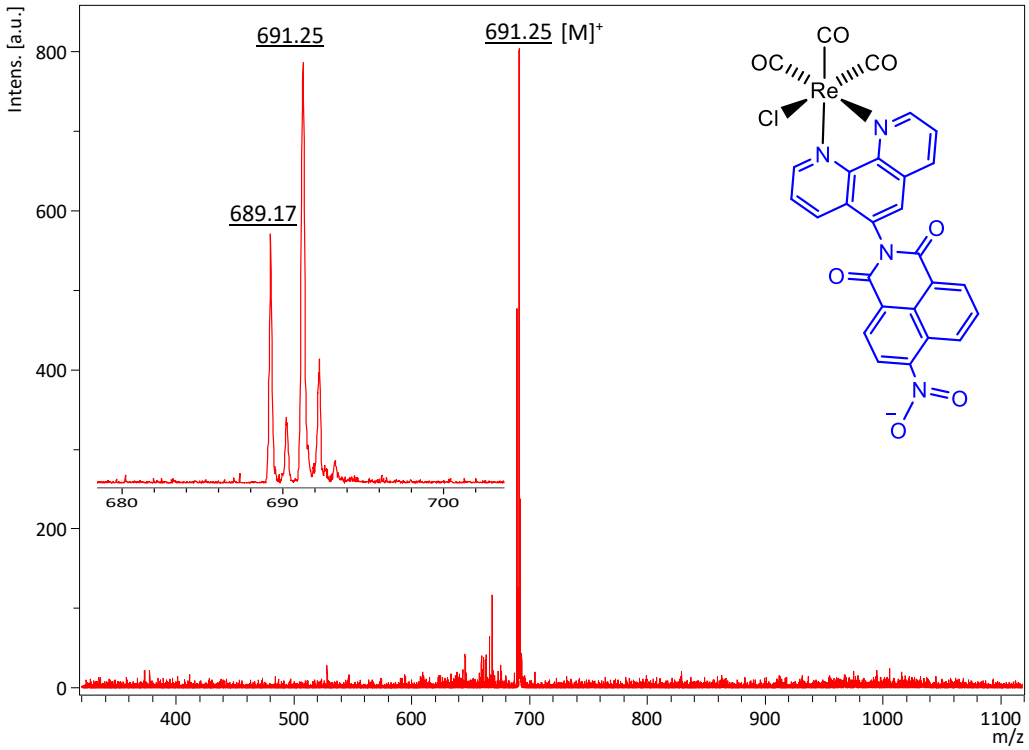
S6. FT-IR of **5-PAN** (KBr, cm^{-1}) CO-N-CO: 1716.10, C=O: 1675.64, C-NO_2: 1529.22, C-NO_2: 1350.42



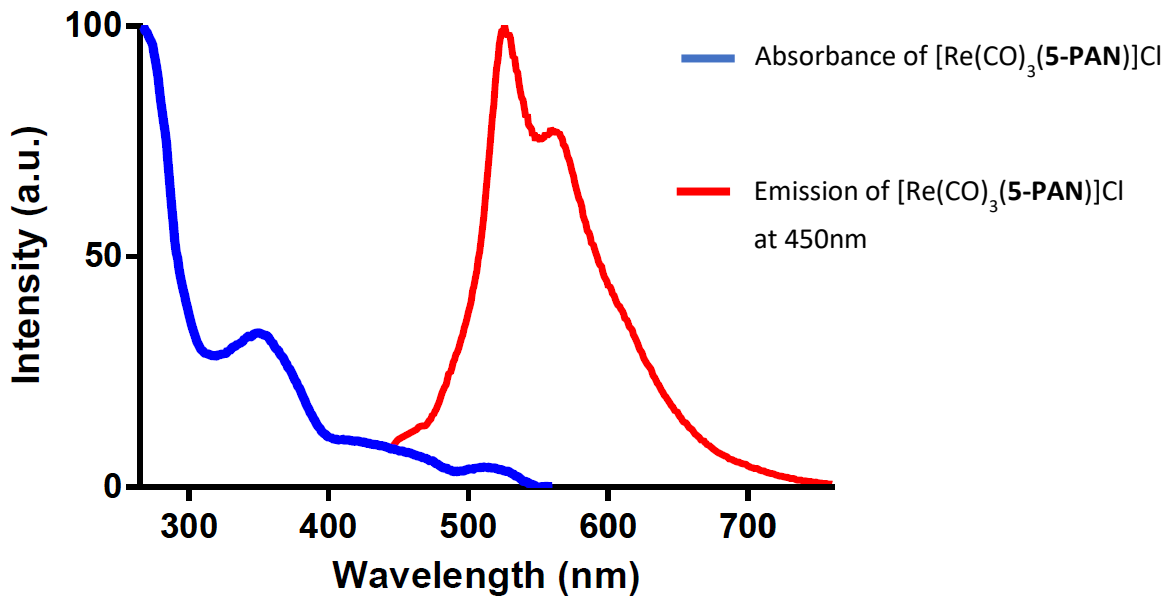
S7. Absorption-emission spectra **5-PAN** in 1:9 (v:v) MeOH/DCM showing an excitation λmax of 350 nm and an emission λmax of 456 nm for a subsequent Stokes shift of 106 nm.

*Synthesis of (**Re(5-PAN)**)*

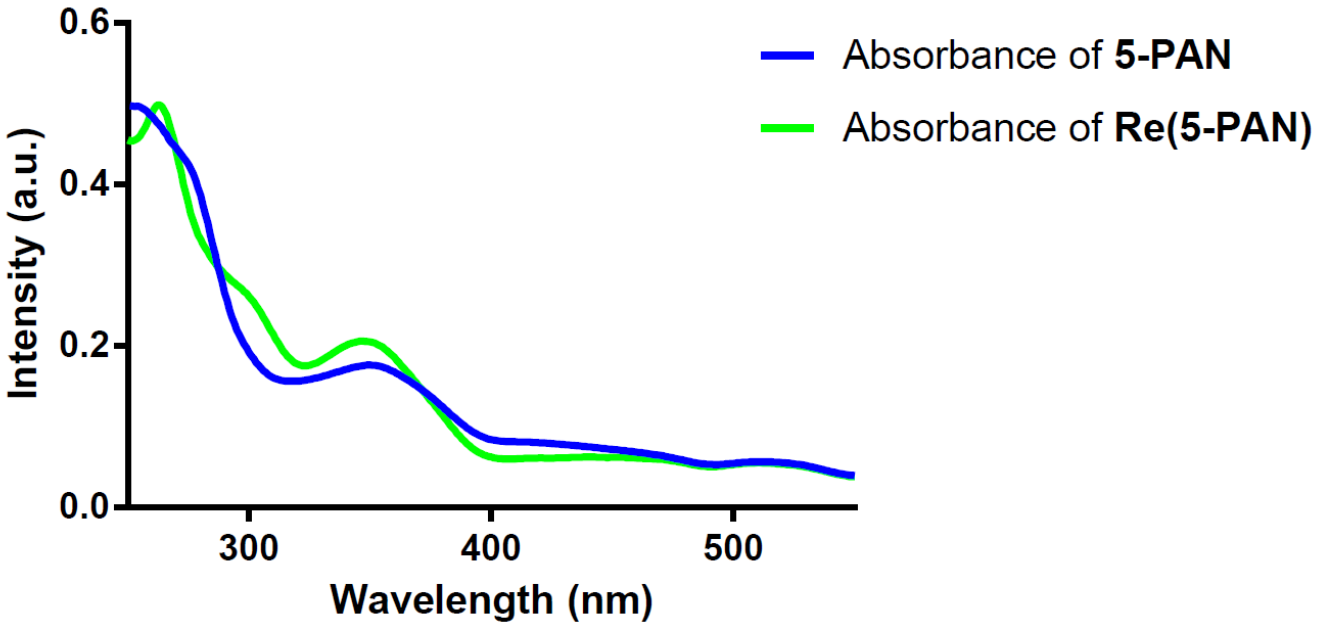
$Re(CO)_3(H_2O)_3Cl$ (0.26 mmol, 94.12 mg) and **5-PAN** (0.26 mmol, 110 mg) were each added to a 50 mL round bottom flask along with 15 mL of MeOH/DCM (1:9 v:v). After completely dissolved, the two were combined, put under argon, and stirred for 1.5 hours. The solution volume was reduced to half and diethyl ether was added to precipitate the product. The mixture was centrifuged, and the ether decanted. The yellow solid was collected and dried under vacuum overnight.



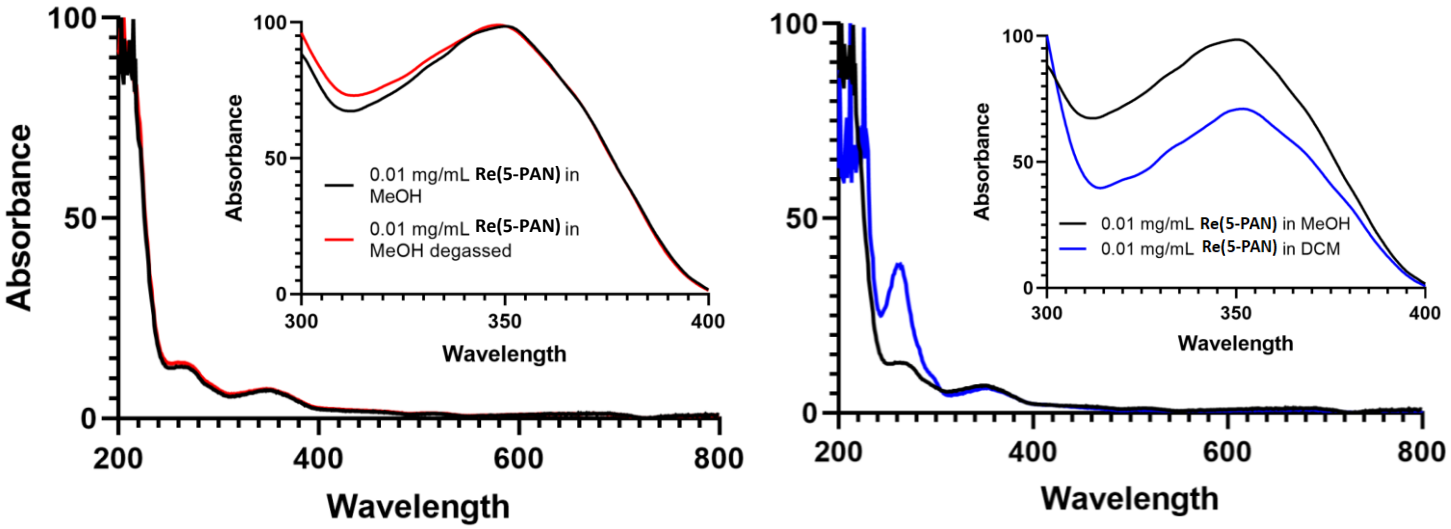
S8. MALDI-ToF spectrum of **Re(5-PAN)** Expected peak = 691 (m/z) for **Re(5-PAN)** without the Cl^- anion and water solvate.



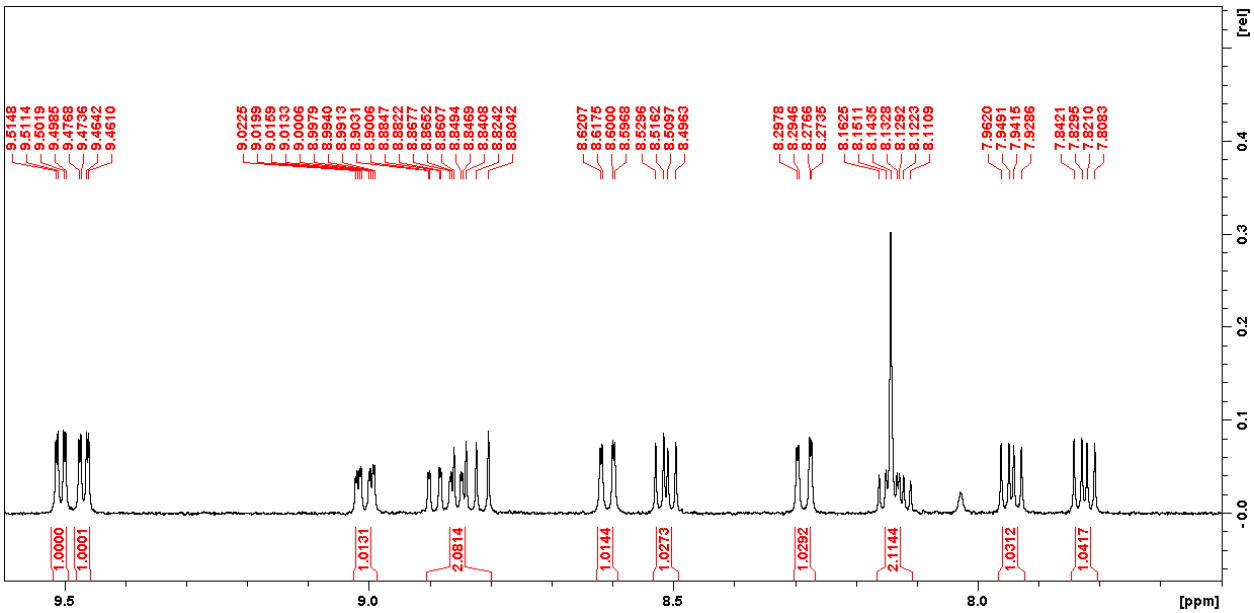
S9. Electronic absorption (blue) and emission (red) spectra of **Re(5-PAN)** for determination of achievable excitation with blue light was collected in a solution of 1:9 (v:v) MeOH/DCM. λmax = 526nm when excited at 450nm.



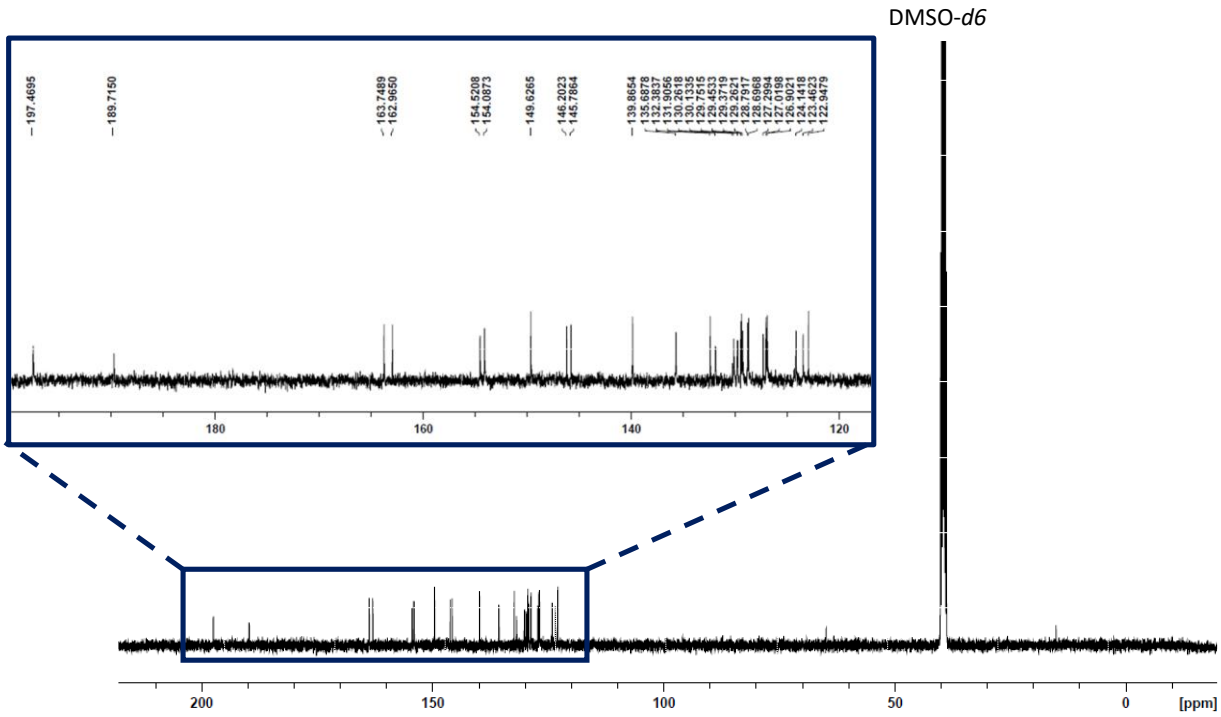
S10. Electronic absorption spectra of both **5-PAN** and **Re(5-PAN)** conducted in 1:9 (v:v) MeOH/DCM collected at equimolar concentration showing a broadening of the λmax value of **5-PAN** upon coordination to rhenium and a shift in absorbance toward blue wavelengths.



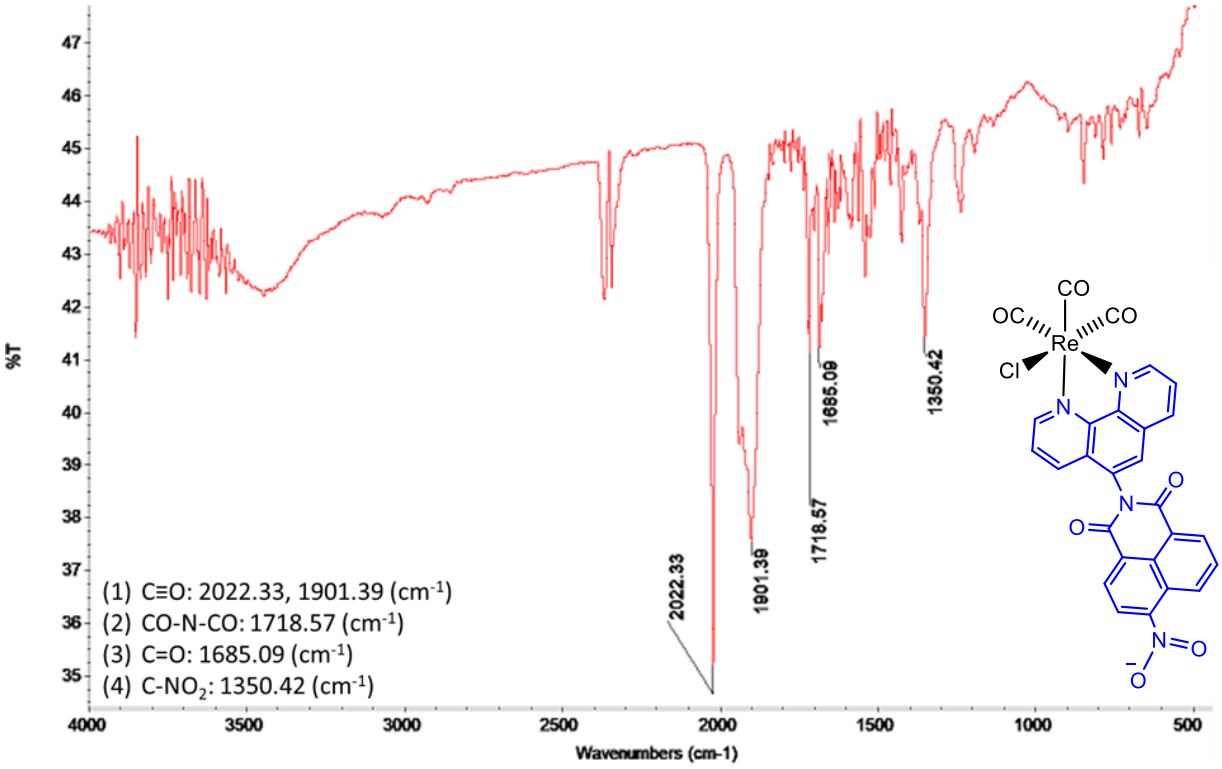
S11. Electronic absorption spectrum of **Re(5-PAN)** conducted in both methanol and dichloromethane (right) showing a minimal red shift (2nm) of the absorption spectrum of **Re(5-PAN)** in a less polar solvent. Also depicted is the electronic absorption spectrum of **Re(5-PAN)** in both methanol and degassed methanol (left) – electronic absorption spectrum was collected utilizing samples of equimolar concentration of 0.0134 µM. Insets show a zoom of the region of interest containing the MLCT band from 300 – 400 nm.



S12. ^{1}H NMR spectrum of **Re(5-PAN)** with zoomed in aromatic region (400 MHz, Chloroform-d) δ 9.51-9.50 (dd, 1H), 9.48-9.46 (dd, 1H), 9.02-9.00 (ddd, 1H), 8.90-8.80 (2H, overlapped), 8.62-8.60 (dd, 1H), 8.53-8.50 (dd, 1H), 8.30-8.27 (dd, 1H), 8.16-8.11 (2H, overlapped), 8.00-7.92 (dd, 1H), 7.84-7.81 (dd, 1H).



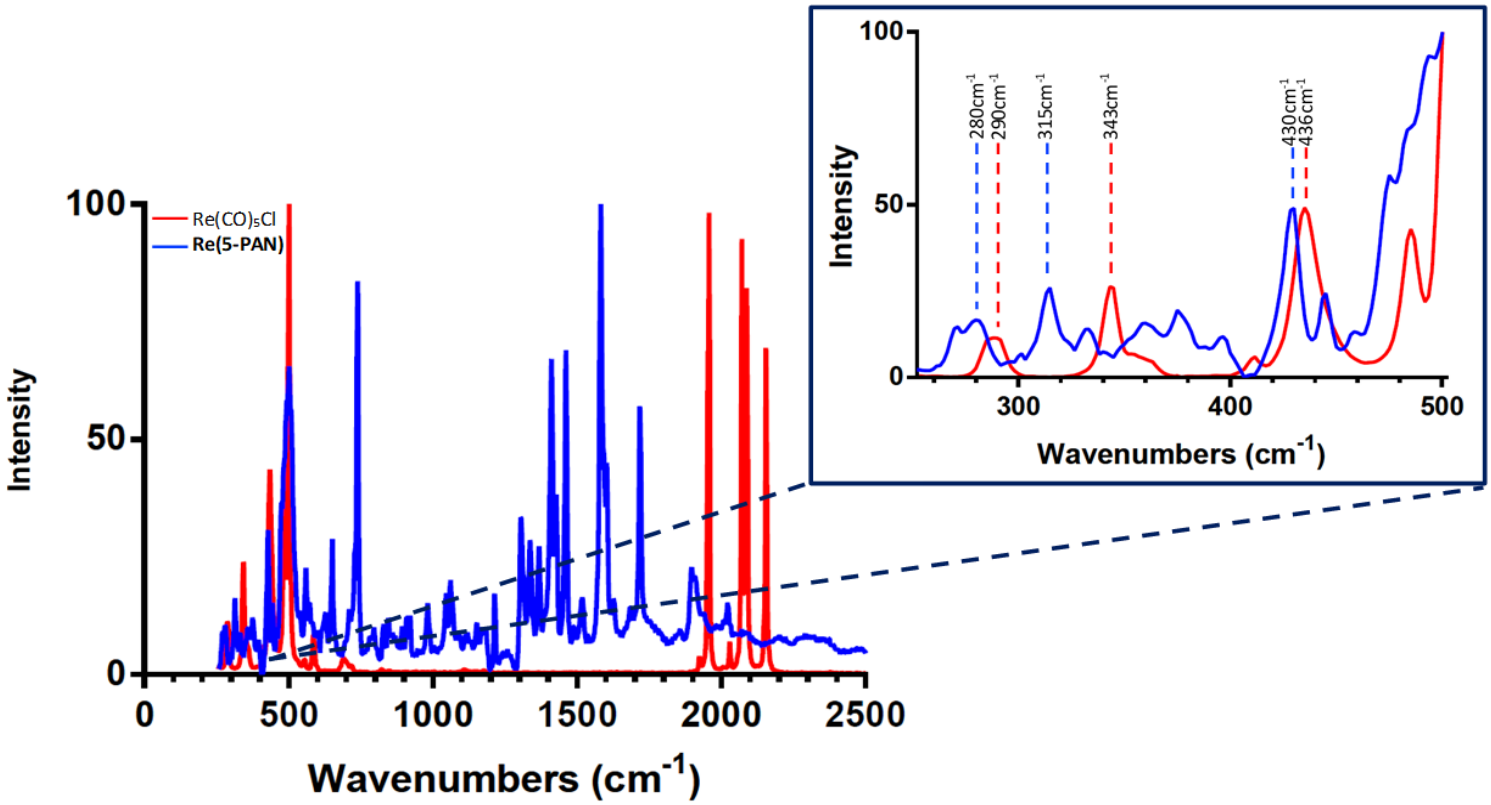
S13. ^{13}C NMR spectrum of the **Re(5-PAN)** complex, acquired in DMSO-*d6*, exhibiting the appropriate number of carbon signals – with the carbon signals at 189ppm and 197ppm, respectively, assigned as the carbonyl carbons of the rhenium tricarbonyl core.



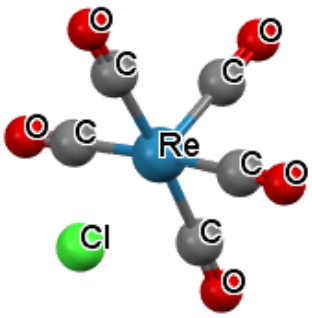
S14. FT-IR of **Re(5-PAN)** (KBr, cm^{-1}) C≡O: 2022; 1901, CO-N-CO: 1716, C=O: 1685.09, C-NO_2: 1350

Elemental Analysis of $[Re(CO)_3(5\text{-PAN})Cl]$			
$[Re(CO)_3(5\text{-PAN})Cl]$	%C	%H	%N
Theoretical	44.08	1.66	7.62
Sample 1	44.08	1.79	7.07
Sample 2	42.58	2.16	7.12
Average	43.33	1.98	7.10
Error	-0.75	0.32	-0.52

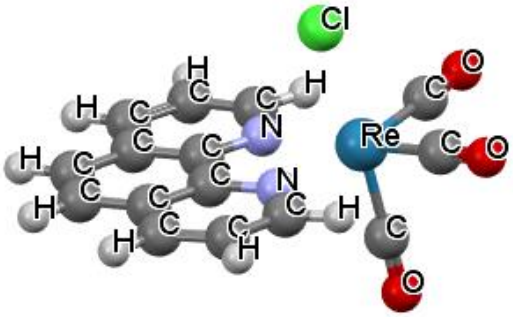
S15. Elemental Analysis of **Re(5-PAN)** performed by Intertek (Whitehouse, NJ, USA).



S16. Raman spectra of previously reported starting material chloropentacarbonyl rhenium (I) (**$Re(CO)_5Cl$** - red) and **Re(5-PAN)** (blue) highlighting the solid-state rhenium-chloride bonds at 290 and 280 cm^{-1}, respectively. Raman spectra were collected using a fiber-coupled i-Raman Plus spectrometer (B&W Tek, Newark DE) with an excitation wavelength of 785 nm. Final spectra are the product of 100 averages of 1 s integration windows and have a spectral resolution of ~4 cm^{-1}. The Raman spectral intensities have been normalized to one. In the case of **Re(5-PAN)**, the Raman spectrum showed a significant fluorescence background with well-defined Raman peaks on top of this. An approximate polynomial baseline representing the fluorescence interference was subtracted from the final data shown here. See also DFT calculations in Figure S17.



$Re(CO)_5Cl$



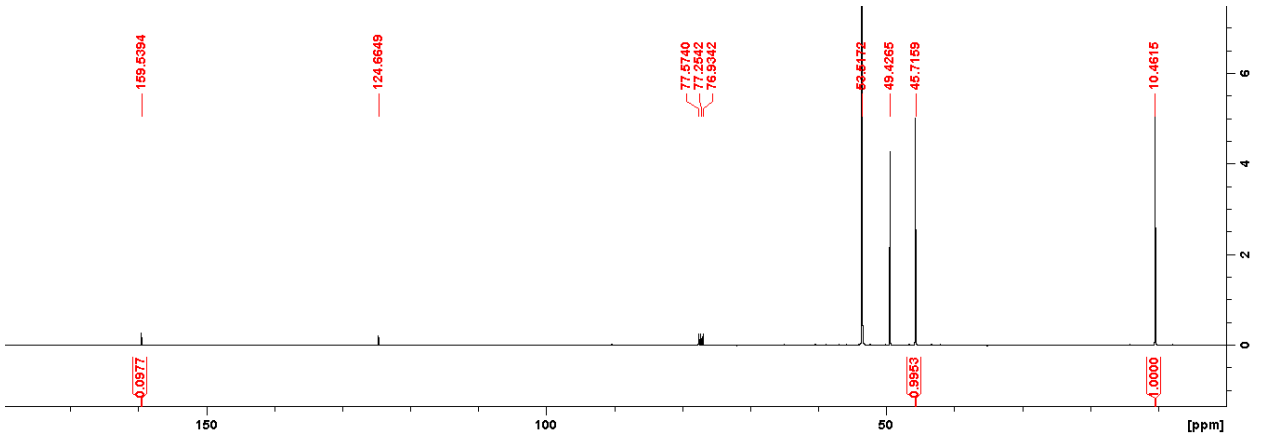
$Re(CO)_3(Phen)Cl$

S17. *In silico* determination of the predicted rhenium-chloride vibrational frequencies of **$Re(CO)_5Cl$** and a **Re(5-PAN)** analog (**$Re(CO)_3(Phen)Cl$**) (Reindicating shift to a lower vibrational frequency. Density functional theory simulations of the monomeric molecular structures and vibrational frequencies of $Re(CO)_5Cl$ and $Re(C_{12}H_8N_2)(CO)_3Cl$ were performed with the Gaussian 16 (Revision A.03) software package. The calculations utilized the B3LYP density functional and def2-TZVP basis set for all atoms. Point group symmetry was utilized in both species, with $Re(CO)_5Cl$ in C_{4v} and $Re(C_{12}H_8N_2)(CO)_3Cl$ (**$Re(CO)_3(Phen)Cl$**) in C_s. Convergence quality was increased from the default configuration using program settings of integral (grid=superfine) and opt=verytight. Harmonic vibrational frequency analyses of the optimized structures revealed no imaginary eigenvalues, verifying each structure to represent an energetic minimum on the potential energy surface. For $Re(CO)_5Cl$: Re-Cl (Exp.) = 2.515 Å, Re-Cl (DFT) = 2.500 Å. DFT Re-Cl stretching frequency = 296.65 cm^{-1}. For $Re(C_{12}H_8N_2)(CO)_3Cl$: Re-Cl (Exp.) = 2.500 Å, Re-Cl (DFT) = 2.495 Å. DFT Re-Cl stretching frequency = 281.08 cm^{-1}. [1,2]

2. Detailed CO_2RR procedure

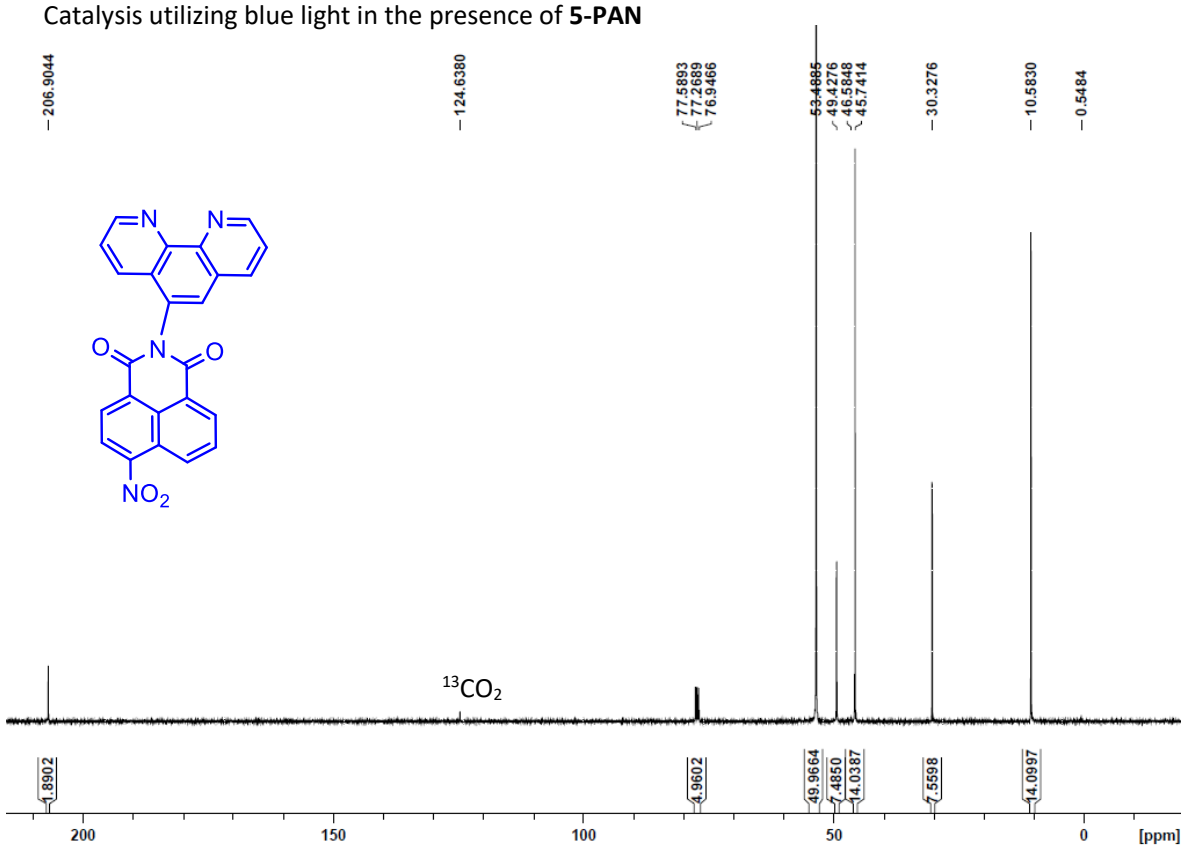
Re(5-PAN) was evaluated for catalytic reduction of CO_2 to CO in the presence of blue light (450nm) utilizing ^{13}C NMR tracking of $H^{13}COO^{-1}$ - a product of the catalytic reduction cycle. In each sample tested, 13.5 mg (0.018 mmol) of **Re(5-PAN)** was dissolved in approximately 5 mL of CH_3OH/DCM (1:9 v:v) and supplemented with 0 – 300 equiv. of triethylamine (TEA, 0 – 5.44 mmol) as a sacrificial donor. All samples were kept at 5 mL total reaction volume, irradiated with blue light at a constant distance from the reaction vessel, and bubbled with $^{13}CO_2$ evolved in-situ with 0.500 g $Ba^{13}CO_3$ and 1M H_2SO_4 drip for 1.5 hours. For each trial, the drip rate was set such that the Schlenk flask holding the $Ba^{13}CO_3$ was full at the end of 1.5 hr and the H_2SO_4 was well in excess. Runs were done at least in triplicate.

At the end of each trial, 500 µL of the reaction solution and 100 µL of $CDCl_3$ was added to an NMR tube and wrapped in aluminum foil until it was ready to be loaded into the NMR. The TEA peaks at ~10.46 and ~45.71 ppm were integrated and set to 1. The $H^{13}COO^{-1}$ peak at ~160 ppm was integrated and with the known moles of TEA, the relative moles of $H^{13}COO^{-1}$ was calculated.

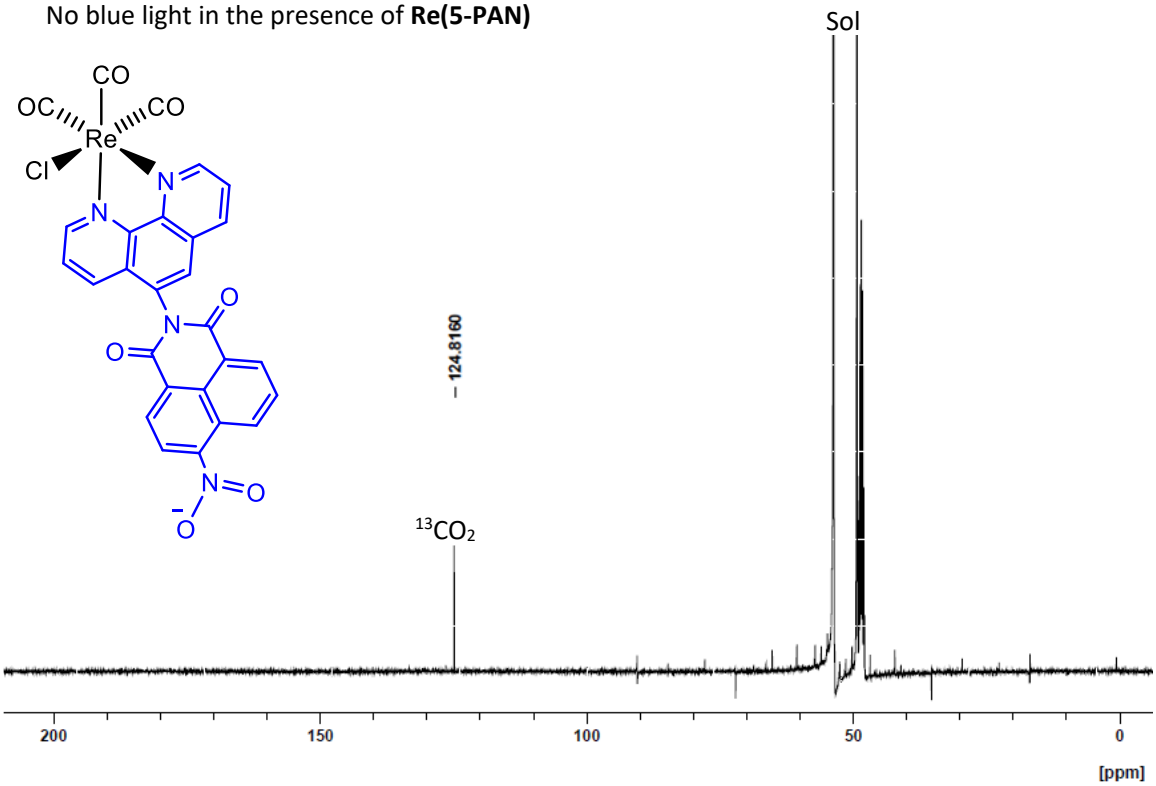


S18. ^{13}C NMR for **Re(5-PAN)** and 150 equiv. TEA. The TEA peaks are at 10.4615 and 45.7159 ppm. Methanol peak is at 49.4265 ppm. DCM peak is at 53.5172 ppm. $CDCl_3$ peaks are at 76.9342, 77.2542, and 77.5740 ppm. $^{13}CO_2$ peak is at 124.6649 ppm. $H^{13}COO^{-1}$ 159.5394 ppm.

Catalysis utilizing blue light in the presence of **5-PAN**



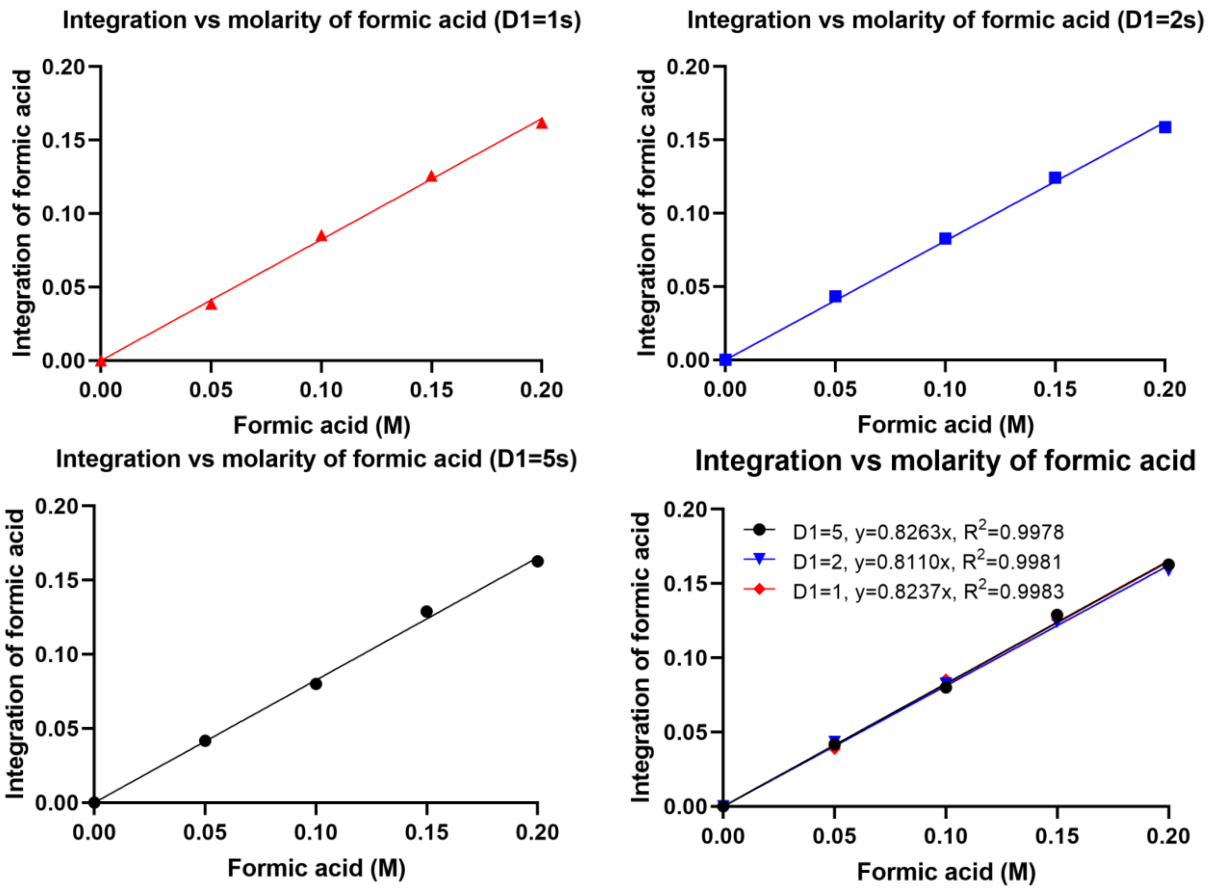
S19. ^{13}C NMR of a CO_2/**5-PAN** solution in 1:9 (v:v) MeOH/DCM indicating only the presence of $^{13}CO_2$ when photoirradiated at 450 – 460 nm – suggesting no catalysis without the **Re(5-PAN)** complex. All other peaks are attributed to solvent, including a minor acetone impurity as noted by the peaks at 30 and 207ppm, respectively, or sacrificial donor TEA.



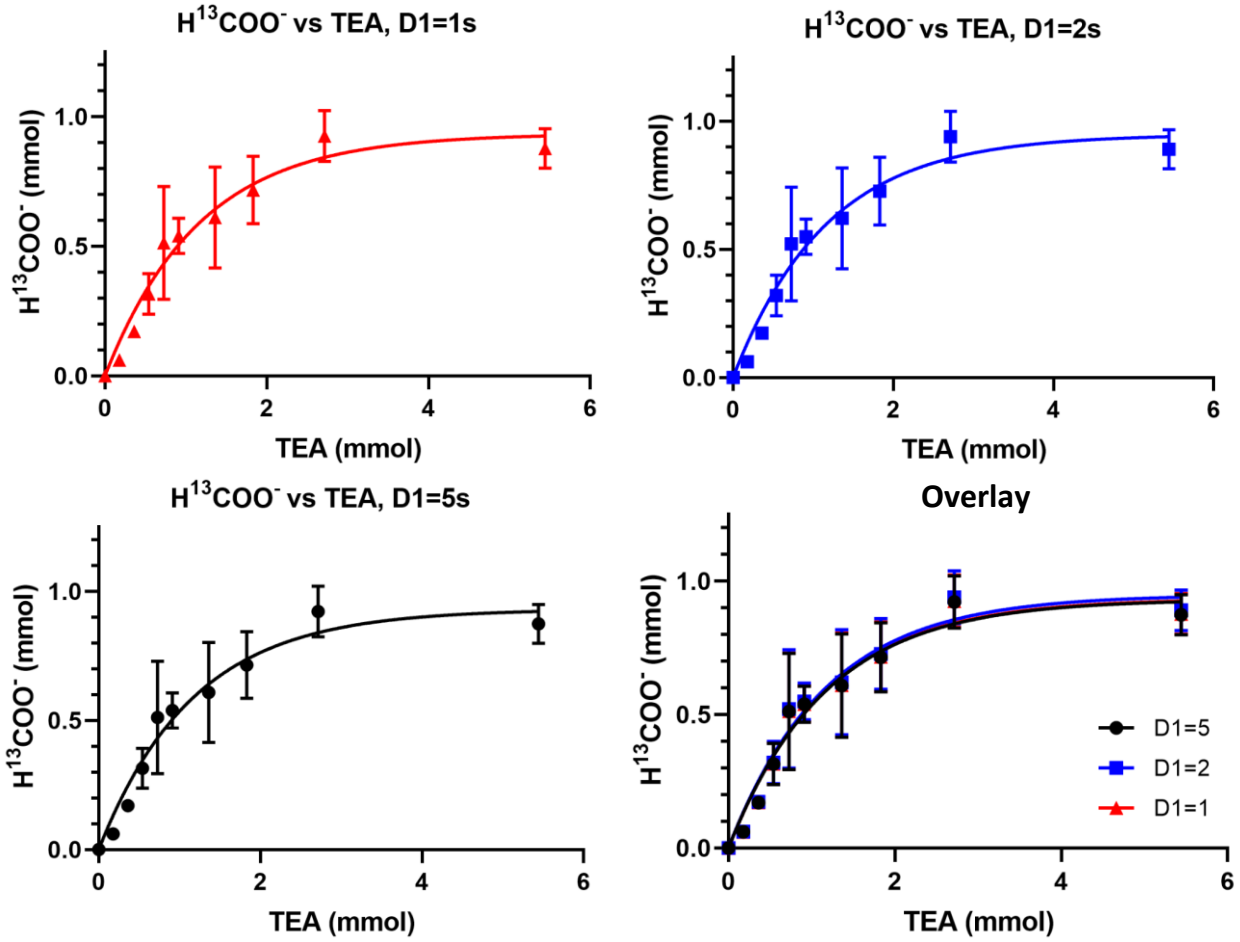
S20. ^{13}C NMR of a CO_2/**Re(5-PAN)** solution in 1:9 (v:v) MeOH:DCM indicating only the presence of $^{13}CO_2$ when not photoirradiated at 450 – 460 nm.

Complex	Time (hr)	TN	Catalyst Concentration (mM)	Wavelength of Irradiation	Reference
fac-[Re(bpy)$(CO)_3$Cl] (1-Cl)	24	15	2.5	<330nm	3
fac-[Re(bpy)$(CO)_3$(NCS)]	24	30	2.5	<330nm	3
[Re(4,4′ -H_2bpy)$(CO)_3P(OEt)_3]^+$	13	6.2	2.6	365nm	4
Re(bpy) $(CO)_3${$P(OEt)_3$}] SbF_6	16	7.5	0.51	365nm	5,6
cis,trans-[Re(dmbpy)$(CO)_2$ (P*p*-FPh_3)(P*p*-FPh_3)]$^+$	16	17.3	0.5	365nm	7
fac-[Re(phen-dione)$(CO)_3$Cl]	0-24	25.5 - 34	0.2	365nm	8
[ReSCN(bipy)$(CO)_3$]	0.5	4.9	1	< 400nm	9
CPOP-30-Re	4	17.3	10mgs of catalyst in 10mLs total volume	390nm filter	10
[ReSCN(bipy)$(CO)_3$]	2	26.4	1	< 400nm	9
[Re(BB2)$(CO)_3$Cl]	17hr	0	1.5	>400nm or 495nm	11
Re-TXP-H_2	24	13	-	>450	12
[Re(4,4′-H_2-bpy)$(CO)_2(PR_3)PPh_3$]	6	16.5	1	>400nm	13
[Re(Me-bpy)$(CO)_3$Cl]−Phenyl	17	22	1.5	>430	14
Re(pyridylNHC-CF_3)$(CO)_3$X	4	0-40	0.1	Solar Simulator	15
Anthryl-Re	a	16-43	0.05	"Irradiated with a solar simulator"	16
Re(5-PAN)	1.5	48	3.6	450 - 460nm	*This Paper*
Re(bipy)$(CO)_3$Cl + NEt_4Cl	4	48	0.87	>400nm	17
[Re(TPSbpy)$(CO)_3$Cl	6	230	0.05	"In The Visible Region"	18

Table S1. Overview of Re(I) based mononuclear complexes reported to catalyze the reduction of carbon dioxide.



S21. Linear regression of the ^{13}C NMR integration of $H^{13}COO^-$ supplemented with an internal standard of 100eq. TEA at D1 relaxation times of D1 = 1s **(top left)**, 2s (**top right**), and 5s (**bottom left**). Also displayed is an overlay of all of the independent linear regression at the previously described relaxations (**bottom right**).



TEA equiv.	TN (D1=5)	TN (D1=2)	TN (D1=1)
0	0	0	0
10	3.33	3.39	3.34
20	9.41	9.59	9.44
30	17.32	17.65	17.38
40	28.21	28.75	28.30
50	29.77	30.33	29.86
75	33.48	34.11	33.59
100	39.10	39.84	39.23
150	50.96	51.92	51.12
300	48.34	49.25	48.49

S22. Turnover numbers for **Re(5-PAN)** calculated from the linear regression of D1 = 1s **(top left)**, 2s (**top right**), and 5s (**bottom left**). Also displayed is an overlay of all of the independent TN plots at the previously described relaxations (**bottom right**) showing similar R^2 values consistent about 0.96.

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