Dalton Transactions

COMMUNICATION

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Cite this: *Dalton Trans.*, 2021, **50**, 3479

Received 2nd December 2020, Accepted 23rd February 2021

DOI: 10.1039/d0dt04116e

rsc.li/dalton

[Re(CO)$_3$(5-PAN)Cl], a rhenium(I) naphthalimide complex for the visible light photocatalytic reduction of CO$_2$†

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A rhenium(I) naphthalimide complex [Re(CO)$_3$(5-PAN)Cl] (Re(5-PAN); 5-PAN = 1-(1,10-phenanthroline)-4-nitro-naphthalimide) was synthesized, characterized, and evaluated as a photocatalyst for CO$_2$ reduction. Characterization included use of MALDI-ToF mass spectrometry, FT-IR, RAMAN, ^{1}H and ^{13}C NMR, elemental analysis, electronic absorption and emission spectroscopy, single crystal X-ray diffraction, DFT and cyclic voltammetry. Photocatalytic (406 nm) reduction of ^{13}CO$_2$ to formate (H^{13}COO) in the presence of this catalyst was tracked *via* ^{13}C NMR. Results support Re5-PAN (φ = 0.021) functioning as a catalyst for the reduction of CO$_2$ (maximum turn-over 48–50 at 300 equiv. triethylamine as the sacrificial electron donor).

Increased levels of atmospheric, anthropogenic CO$_2$ and rapid consumption of fossil fuels present major challenges for society.[1–3] Inorganic–organic hybrid photocatalysts, especially those of rhenium(I), are a chemically versatile route to mitigating these problems.[4–6] The rhenium(I) tricarbonyl core has received significant attention for many years primarily as a precursor molecule to chemically relevant metal complexes that serve a host of purposes such as fluorochromes for cell imaging and catalytic reduction; these reductive catalytic properties are ideal for the conversion of the lower energy CO$_2$ to the higher energy, and more usable feedstock, CO.[7–9] The rhenium(I) tricarbonyl core is an ideal scaffold for catalytic rhenium complexes because it retains a kinetically inert d^6 electron configuration and allows mono-, bi-, and tridentate ligand binding modes with facile chemical synthesis from chloropentacarbonylrhenium(I) *via* a facile reflux in water to the air-stable triaquatricarbonylrhenium(I) precursor molecule (**1**) (whose aqua ligands exhibit ready substitution).[10,11]

While the rhenium(I) tricarbonyl core is ideal for carrying out the described reduction, the core does not confer a necessary level of photosensitization to produce a reductive potential greater than the −0.77 V required to reduce CO$_2$ to CO.[12] Photosensitizers, such as naphthalimides,[13–15] can also participate in multiple electron transfer (MET) processes[16] – a direct result of a largely conjugated π-orbital electron system – which is ideal given there is a substantial difference between the overpotential required for the one-electron reduction of CO$_2$ to CO$_2$$^{*-}$ ((−1.9) – (−2.1) V)[17–20] and the two electron reduction of CO$_2$ to CO and formate (−0.53 V).[21] It was hypothesized that a bidentate naphthalimide-derived bidentate ligand would serve as a photosensitizing ligand for the rhenium(I) tricarbonyl core, while also providing an open coordination site necessary for substrate binding.

We herein report on the synthesis and characterization of a naphthalimide ligand with bidentate metal coordination *via* a 1,10-phenanthroline unit (**2**), the complexation of **2** *via* reaction with **1** to produce [Re(CO)$_3$(5-PAN)Cl] (**3**), and the successful use of **3** in blue-light-dependent (450–460 nm) photocatalytic reduction of CO$_2$ to formate (HCOO$^-$) with comparable turnover relative to other catalysts of this type within the prescribed irradiation period of 0–2 h.

1. Experimental

1.1 Materials

Chloropentacarbonyl rhenium(I) (98%), 1,10-phenanthroline-5-amine (97%), 4-nitro-1,8-naphthalic anhydride (95%), potassium bromide (KBr), triethylamine (≥99%), CDCl$_3$ and DMSO-d_6 NMR solvents were all purchased through Sigma Aldrich. Acetonitrile, methanol, ethanol, sulfuric acid, diethyl ether and dichloromethane were purchased through Sigma Aldrich and subsequently dried over 3 Å molecular sieves in-house to remove excess water. Barium carbonate (^{13}C, 98%+) was pur-

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/d0dt04116e

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chased from Cambridge Isotope Laboratories, Inc. Reverse osmosis grade water was obtained in-house. 1 M H_2SO_4, **2**, **3**, and $[Re(CO)_3(phen)Cl]$ (**4**) were prepared in-house. A 12 W LED blue light (450–460 nm) was purchased from Abi, USA (Vernon, CA, USA).

1.2. Methods

Mass Spectrometry of $[Re(CO)_3(H_2O)_3]Cl$ and **2** were conducted on a Shimadzu 8040 mass spectrometer. Mass spectrometry of **3** was conducted on a Bruker AutoFlex III MALDI-ToF/ToF Mass Spectrometer and dilutions of **3** were made in 1 : 9 (v : v) MeOH/DCM in the presence of alpha-cyano-4-hydroxycinnamic acid (CHCA) matrix. $^1H/^{13}C$ NMR were conducted on a Bruker Avance III HD 400 MHz instrument and calibrated to the residual $CDCl_3$ signal at 7.24 ppm. FT-IR was carried out on a Nicolet Infrared Spectrophotometer utilizing potassium bromide (KBr) disks. Elemental Analysis was conducted by Intertek Pharmaceuticals (Whitehouse, NJ, 08888). Electronic absorption spectroscopy was conducted on a Varian 50 Bio spectrophotometer. Emission spectroscopy was conducted on an Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer. All samples that required centrifugation were centrifuged utilizing a Thermo Electronic Corporation Sorvall® Legend RT centrifuge and were centrifuged at 4000 rpm for 5–10 minutes. Crystals of **3** were attained by slowly diffusing diethyl ether into a solution of **3** in 1 : 9 (v : v) MeOH/DCM. Single crystal X-ray diffraction data was conducted at the European Synchrotron Radiation Facility in Grenoble, France – data were collected on an Arinax MD3Up using synchrotron radiation with $\lambda = 0.8726$ Å at 293(2) K. Cyclic voltammetry was performed on an Electrochemical Analyzer potentiostat model 600D from CH Instruments. CV solutions were prepared in acetonitrile and degassed by bubbling with nitrogen for about 10 min prior to scanning. Tetra(*n*-butyl)ammonium hexafluorophosphate ($TBAPF_6$; *ca.* 0.1 M in acetonitrile) was used as the supporting electrolyte. A Pt wire was used as the pseudo reference electrode; a Pt wire coil was used as the counter electrode and an Au disk electrode was used for the working electrode. The redox potentials are reported using the ferrocenium/ferrocene (Fc^+/Fc) redox couple as an internal reference.

1.3. Synthesis of rhenium(I) triaquatricarbonyl chloride ($[Re(CO)_3(H_2O)_3]Cl$) (1)

1 was synthesized in-house in quantitative yield using the synthesis reported by Zubieta *et al.*[11] and the product confirmed *via* ESI-MS (S1†) and ^{13}C NMR (S2†).

1.4 Synthesis of ($C_{24}H_{12}N_4O_4$) (2)

Synthesis of **2** (1-(1,10)-phenanthroline-5-(4-nitro-naphthalimide)), initially reported by Yarnell *et al.*,[22,23] was approached utilizing a new synthetic method. 0.429 g (2.2 mmol) of 1,10-phenanthroline-5-amine was suspended in 25 mL of anhydrous ethanol. Simultaneously, a second solution of 0.486 g (2 mmol) of 4-nitro-1,8-naphthalic anhydride was suspended in 25 mL of anhydrous ethanol. Both solutions were combined in a 100 mL round-bottom flask and heated to reflux under argon with stirring. The solution was refluxed for a period of 48 h and the solution was left to cool to room temperature, whereupon a tan colored precipitate was observed. Diethyl ether was then added to ensure complete precipitation of the product (**2**). The solution was filtered through a Gooch filter, washed three times with 20 mL of diethyl ether, each time centrifuged at 4000 rpm for 5 minutes, and the ether decanted off; **2** was then dried overnight *in vacuo* and was massed to 0.364 g (yield ≈44% based on 4-nitro-1,8-naphthalimide). This yield is less than the 67% reported by Yarnell in the presence of acetic acid.[23] **2** was confirmed *via* ^1H NMR (S3†), ^{13}C NMR (S4), ESI-MS (S5†), and FT-IR (S6†); subsequent electronic absorption and emission spectra were collected (S7 and S10†). MW = 420 g mol^{-1}, observed peak = 421 *m*/*z* (5-PAN + H^+). ^1H NMR (400 MHz, chloroform-d) δ 9.32–9.31 (dd, 1H), 9.28–9.26 (dd, 1H), 9.00–8.97 (dd, 1H), 8.86–8.84 (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).

1.5. Synthesis of $[Re(CO)_3(5\text{-}PAN)Cl]$ (3)

0.0814 g (0.25 mmol) of rhenium(I) triaquatricarbonyl chloride was dissolved in 5 mL of CH_3OH/DCM (1 : 9 v : v) in a 50 mL round-bottom flask. 0.105 g (0.25 mmol) of **2** was then dissolved in 15 mL of CH_3OH/DCM (1 : 9 v : v) and combined with the solution of rhenium(I) triaquatricarbonyl chloride; the solution was stirred at room temperature for 1.5 h. The MeOH/DCM (1 : 9 v : v) azeotrope was selected to aid in the solubility of **2**, which was not soluble in methanol alone, as is **1**. After stirring, a yellow solid was precipitated with diethyl ether and dried *in vacuo.* The presence of **3** was confirmed *via* MALDI-ToF MS (Fig. 1 and S8†), electronic absorption and emission spectroscopy (S9 and S10†), ^1H NMR (Fig. 3 and S12†), ^{13}C NMR (S13†) FT-IR (S14†), elemental analysis (Theo: C = 43.6, H = 1.90, N = 7.53; Calc: C = 43.3, H = 1.98, N = 7.10) (S15†), Raman spectroscopy (S16†) and single crystal X-ray diffraction (Fig. 3) – which indicated an octahedral geometry.

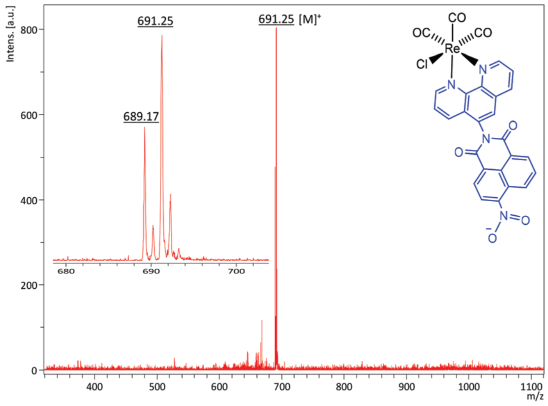

Fig. 1 MALDI-ToF mass spectrum of **3** with (inset) the predicted isotopic distribution pattern.

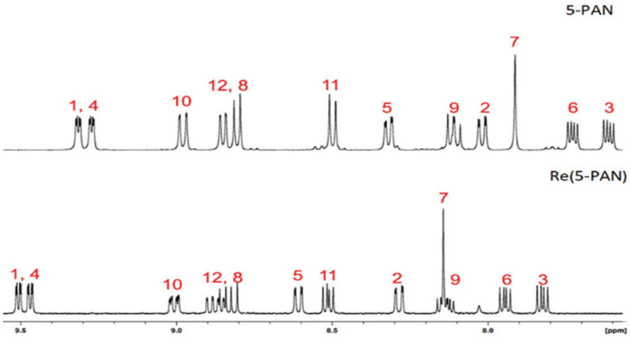

Fig. 2 ^{1}H NMR spectra of **2** (top) and **3** (bottom) in $CDCl_3$. Complexation was evidenced by the downshifting of proton signals adjacent to the chealation site.

Mass-to-charge of desired product was determined to be 691 *m*/*z* (Fig. 1). Further complex purity was confirmed utilizing ^{1}H/^{13}C NMR and elemental analysis. ^{1}H NMR (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) – Fig. 2.

2. Results

2.1. Evaluating the electrochemical properties of 3

Cyclic voltammetry (CV) was undertaken to discern the energies of the HOMO and LUMO of the complex, which is crucial for understanding its capacity to perform as a photocatalyst. The CV traces of **2** and **3** in acetonitrile and DMF are given in Fig. 4, and the relevant parameters obtained for the electrochemical experiments are summarized in Table 1.

The CV trace for **2** exhibits two reversible reduction waves and a third reduction wave close to the solvent window. **3** also exhibits two reversible reduction waves at modestly cathodically shifted potentials with respect to the ligand. This small shift is due to the charged metal ion which inductively withdraws electron density from the ligand, making it more capable of accepting electrons when coordinated to the metal. There is also a third, more anodically shifted, reversible reduction wave.

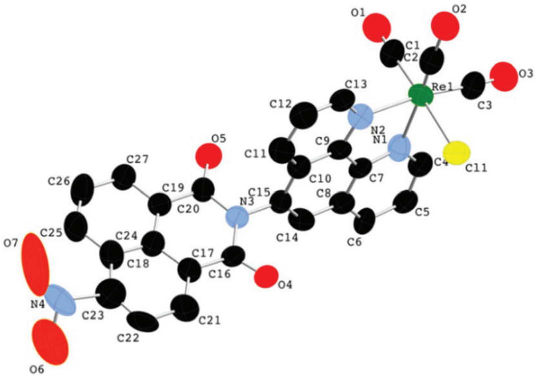

Fig. 3 Single-crystal X-ray structure of **3**. H-Atoms are omitted for clarity. Crystal data: $C_{27}H_{12}ClN_4O_7Re$, fw = 726.06, triclinic $P\bar{1}$, a = 9.126(2) Å, b = 11.822(2) Å, c = 13.096(3) Å, α = 7840(3)°, β = 80.69(3)°, γ = 85.97(3)°, V = 1364.8(5) Å^3, D_{calc} = 1.767 g cm^{-3}, μ = 4.602 (synchrotron, λ = 0.8726 Å), R1 = 0.0582, wR2 = 0.1464 (1785 reflections). Structure is shown for connectivity only.

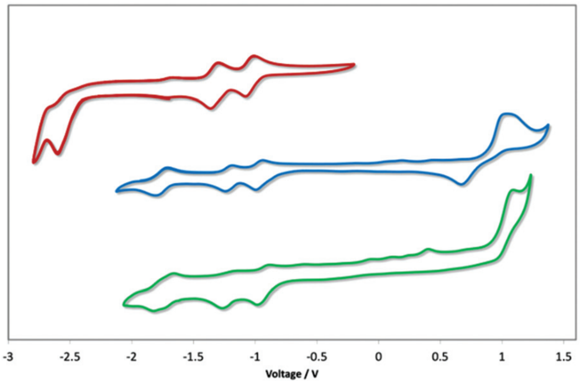

Fig. 4 Cyclic voltammograms of **2** in acetonitrile (red), **3** in acetonitrile (blue), and **3** in DMF (green).

Table 1 Relevant electrochemical data for **2** and **3**[a]

	Compound		
	5-PAN-[a]	Re(5-PAN)[a]	Re(5-PAN)[b]
$E_{\text{pa(ox)}}$ (V)	—	+0.84[c]	+0.95
$E_{1/2(\text{red1})}$ (V)	−1.03	−0.95	−0.92
$E_{1/2(\text{red2})}$ (V)	−1.31	−1.18	−1.08[d]
$E_{1/2(\text{red3})}$ (V)	−2.42[d]	−1.73	−1.73
E_{redox} [e] (V)	—	+1.70	+1.70
E_{HOMO} [f] (eV)	—	−5.64	−5.75
E_{LUMO} [f] (eV)	−3.86	−3.98	−4.11
$\Delta E_{\text{LUMO–HOMO}}$ (eV)	—	1.64	1.64

[a] Measurements were carried out in MeCN at a scan rate of 100 mV s^{-1} with Fc/Fc$^+$ employed as an internal standard and are reported *vs.* Fc/Fz+. [b] Measurements were carried out in DMF at a scan rate of 100 mV s^{-1} with Fc/Fc$^+$ employed as an internal standard and are reported *vs.* Fc/Fc+. [c] This wave is irreversible and the value reported is the onset of oxidation in the anodic scan direction. [d] This wave is irreversible and the value reported is the onset of reduction in the cathodic scan direction. [e] E_{redox} is defined as the difference in onset potential of the first oxidation [$E_{\text{pa(ox)}}$] and first reduction [$E_{\text{pc(red)}}$]. [f] $E_{\text{HOMO/LUMO}}$ = −[$E_{\text{ox/red}}$ *vs.* Fc/Fc + + 4.8] eV.[24]

No oxidation of **2** is observed, but **3** does exhibit a complex multi-electron oxidation process [$E_{\text{pc(ox)}}$ = +0.84 V] that is probably irreversible as the offset in potential of the return wave is too large for a typical reversible process. The oxidation potential and its irreversible nature is similar to other rhenium complexes reported in the literature [$E_{1/2(\text{ox})}$ = *ca.* +0.70–1.0 V],[25,26] although it is somewhat different from the structurally similar complex [Re(CO)$_3$(phen)(Cl)], for which the first irreversible oxidation is cathodically shifted in MeCN [$E_{\text{pa(ox)}}$ = +1.03 V].[27]

The multiple reduction processes observed for both **2** and **3** arises from the presence of the individual phenanthroline and nitro-naphthalimide moieties, both of which are capable of acting as electron sinks. A helpful comparison in ascribing the reduction processes is the complex [Re(CO)$_3$(phen-PNI)(Cl)], wherein PNI denotes a naphthalimide with a piperidinyl electron donating group.[28] In this complex, the two analogous reduction waves are anodically shifted [$E_{1/2(\text{red})}$ = −1.59, −1.73 V] compared to **3**.[28] DFT calculations ascribed the first wave to reduction of phenanthroline and the second to naphthalimide reduction, which is in line with destabilisation of both sets of orbitals but particularly the naphthalimide by the electron donating piperidine. However, in the case of **3**, the much more electron deficient nature of the nitro-naphthalimide stabilizes it such that it is the first reduction [$E_{1/2(\text{red})}$ = −0.95 V] while the second reduction [$E_{1/2(\text{red})}$ = −1.18 V] is reduction of the phenanthroline.

In order to characterise the nature of the oxidation, measurements were also conducted on **3** in DMF (Fig. 4) which is a poorly coordinating solvent. In the cathodic scan the CV profile of the complex in DMF was similar to that observed in MeCN, with three reduction waves, all of which appeared at similar potentials to those observed in MeCN, although the reduction waves are much less reversible. However, the oxidation of **3** in DMF has very different features. In the characterisation of the electrochemical oxidation of [Re(CO)$_3$(phen)(Cl)], the authors ascribe the first oxidation [$E_{\text{pa(ox)}}$ = +1.39 V] of this complex to loss of radical chlorine followed by rapid solvent coordination, while the second reversible oxidation [$E_{1/2(\text{ox})}$ = +1.79 V] is ascribed to the Re(I)/Re(II) redox couple.[27] Although the potentials of these processes are different to that observed for **2** in MeCN [$E_{\text{pa(ox)}}$ = +0.84 V], the combination of a multielectron process and return wave at *ca.* +0.7 V points towards a similar electrochemical phenomenon in effect here. The first oxidation is likely to be loss of chlorine radical, with the return wave likely to be due to electrochemical reaction with the free chlorine radical, and the second process constituting the metal centred oxidation. This is in contrast to the CV trace in DMF, where the poorer coordinating properties of DMF preclude the displacement of chlorine radical for solvent, resulting in a simpler oxidation process [$E_{\text{pa(ox)}}$ = +0.95 V] comprised of the one electron oxidation of Re(I) to Re(II). The very similar redox potentials for both the oxidation and reductions in MeCN and DMF point toward a molecule with a small dipole moment in the ground state, as the electronics of the system appear insensitive to solvent polarity. This is clearly evidenced by the complex exhibiting the same net electrochemical (DE) and HOMO–LUMO gaps in MeCN and DMF (DE = +1.70, |HOMOLUMO| = 1.64 eV) and DMF.

2.2. Determining the quantum yield of 3

The quantum yield of **3** was determined using a comparative emission method. After synthesizing **4**, in-house utilizing the method of Marti *et al.*,[29] emission experiments were conducted. Absorption spectra of both **3** and **4** were taken and the absorption intensities kept to between 0.1–0.2. Utilizing the $\lambda_{\max}$ values of the metal-to-ligand charge transfer MLCT absorption bands of both **3** and **4** ($\lambda_{\max}$ = 351 nm, $\lambda_{\max}$ = 361 nm, respectively) emission spectra were recorded and the integrations of the respective emission spectra were determined. After obtaining these values, eqn (1) was applied with the reported quantum yield of **4** (φ = 0.017),[29] producing a quantum yield for **3** of φ = 0.021 ± 0.003. This was calculated using eqn (1).

$$\varphi_{\text{Re(5-PAN)}} = \varphi_{\text{RePhen}}\left(\frac{(A_{\text{RePhen}})(I_{\text{Re(5-PAN)}})}{(A_{\text{Re(5-PAN)}})(I_{\text{RePhen}})}\right) \quad (1)$$

Equation utilized to calculate the quantum yield of Re(5-PAN) ($\varphi_{\text{Re(5-PAN)}}$). φ_{RePhen} is representative of the reported quantum yield of rhenium(I) tricarbonylphenanthroline chloride (RePhen) and A and I are the absorbance intensity and emission integration of the respective Re(5-PAN) and RePhen species.

2.2. Evaluation of the excited state of 3

To determine whether or not the MLCT being accessed during catalysis is a triplet ^{3}MLCT or a singlet ^{1}MLCT, the electron absorption spectrum of **3** was collected in both methanol and dichloromethane – if the accessible excited state of the **3** were a triplet ^{3}MLCT, there would be a bathochromic shift observable in the electronic absorption spectrum upon the utilization of the more polar methanol solvent. Upon collecting the electronic absorption spectrum of **3** in methanol there was a minimal (*ca.* 2 nm) bathochromic shift relative to the electronic absorption spectrum of **3** collected in dichloromethane (S11a†).

Subsequently, however, electronic absorption spectra for **3** were collected in aerated and degassed methanol at equimolar concentrations, analysis of which showed no change in absorption intensity (S11b†), which is consistent with singlet ^{1}MLCT fluorescence, as quenching of a singlet excited state by oxygen is unlikely relative to the ^{3}MLCT; if the excited state were a ^{3}MLCT, there would be an observable decrease in absorption intensity. The excited state being a ^{1}MLCT would be consistent with naphthalimides commonly acting as fluorophores, but to this end, the final excited state has not been assigned, as these results are inconclusive and further studies are required to confirm the final excited state.

2.3. Quantification of reduction of CO_2 to $HCOO^-$ *via* ^{13}C NMR

Complex **3** was evaluated for catalytic reduction of CO_2 to CO in the presence of blue light (450–460 nm) utilizing ^{13}C NMR tracking of $H^{13}COO^-$, which is a product of the catalytic reduction cycle (typical ^{13}C NMR included in S18†). In each sample tested, 13.5 mg (0.018 mmol) of **3** 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 (450–460 nm) at a constant distance from the reaction vessel (*ca.* 6 inches), and bubbled with $^{13}CO_2$ evolved *in situ* with a $Ba^{13}CO_3$ and 1 M H_2SO_4 drip, at constant flow, for 1.5 h.

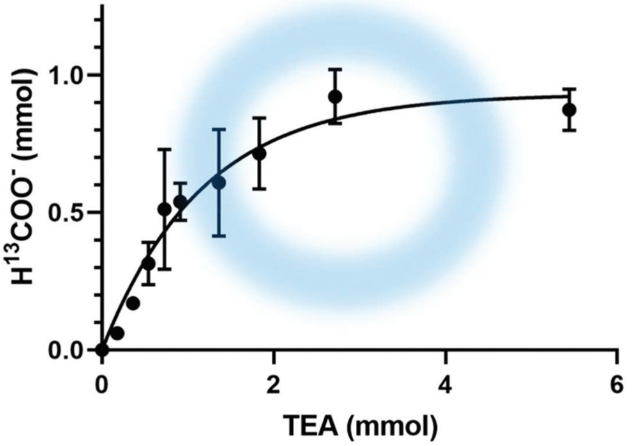

Fig. 5 A plot of $H^{13}COO^-$ (mol) *vs.* TEA (mmol) upon blue light (450–460 nm) irradiation in the presence of **3**. $H^{13}COO^-$ increases with an exponential curve fit with R^2 = 0.9682 and reaching a plateau at y = 0.87 mmol $H^{13}COO^-$.

Catalytic studies of **3** showed that reduction was completely dependent upon photoirradiation with 450–460 nm blue light – in the absence of blue light, no catalytic conversion of CO_2 was observed (S20†) – and that catalytic conversion was dependent on the **3** complex and not the **2** ligand alone (S19†). The catalytic capability of **3** to reduce $^{13}CO_2$ to $H^{13}COO^-$ was quantified with the integration of the $H^{13}COO^-$ peak at ~160 ppm on the ^{13}C NMR spectrum relative to the TEA peak (Fig. 5). This value was subsequently confirmed by developing a calibration curve of the integrations of known concentration of formate (S21†) that were within the range of catalytically produced formate.

Analysis of the catalytic data shows that the production of $H^{13}COO^-$ correlates with the addition of excess TEA in an exponential trend with R^2 = 0.9682. Catalytic saturation of the system is indicated by the plateau such that the maximum $H^{13}COO^-$ produced is 0.87 mmol, corresponding to a turnover number (TN = $[H^{13}COO^-]/[\mathbf{3}]$) of 48–50 at 300 equiv. TEA where the concentration of **3** is 3.62 mM in 5 mL. This value is in accordance with literature values ranging from 0–230 with irradiation time periods ranging from 30 minutes to 24 h hours.[30–45] More precisely, this value is comparable to the 48 TN reported by Hawecker *et al.* for a similar rhenium diamine bidentate complex utilizing bipyridine over a similar time scale.[30] Quantified formate values resulting from catalysis experiments were validated utilizing a calibration curve fit to a set of formate standards of concentrations from 0–0.2 M in 1 : 9 (v : v) MeOH/DCM and 100 eq. TEA, and the subsequent integration of the ^{13}C peak of formate with TEA set as an integration of 1 at $D1$ relaxation times of 1, 2, and 5 seconds – the calibration curve for $D1$ = 5 s showed an R^2 = 0.9978 (S21†); similar R^2 values were observed for $D1$ = 1 s and $D1$ = 2 s (S21†). The subsequent reported quantified formate TN values are extrapolated by multiplying the experimentally determined formate value by the scale factor of TEA (Fig. 5 and S22†). The reported turnover numbers at $D1$ = 1 s, 2 s, and 5 s are consistent with each other (S22†).

3. Conclusions

Herein, we report on the synthesis, structural characterization, electrochemistry, and photocatalytic activity of a novel rhenium(I) naphthalimide complex. Synthesis of the previously reported **2** ligand was conducted utilizing a novel synthetic approach using 1,10-phenanthroline-5-amine and 4-nitro-1,8-naphthalic anhydride starting materials in ethanol. Synthesis of **3** was conducted utilizing rhenium(I) triaquatricarbonyl chloride ($[Re(CO)_3(H_2O)_3]Cl$) starting material and **2** in a 1 : 9 (v : v) MeOH : DCM solvent mixture at room temperature for 1.5 hours. The ^1H NMR of **2** showed an integration of 12 (predicted integration = 12), and this integration was conserved after complexation of **2** to the rhenium(I) tricarbonyl core. Further evidence of complexation of **2** to the rhenium(I) tricarbonyl is presented in the downfield shifting of the **2** proton signals adjacent to the chelation site, which is expected given the electron dense rhenium(I) center (Fig. 3). Solid-state characterization of the **3** complex indicated an octahedral complex of formula $Re(CO)_3$(5-PAN)Cl with direct coordination of the chloride to the rhenium metal. As was previously reported by McAllister *et al.*, the Raman frequency of the Re–Cl bond is observed in the far infrared region at 292 cm^{-1}.[46] This same Raman frequency was observed upon in-house analysis, and the subsequent Re–Cl bond of **3** was also observed at 280 cm^{-1} – a slight shift to lower frequency as a result of the coordination of an electron-withdrawing **2** ligand; a trend also observed by Kalläne *et al.*[47] This shift to lower vibrational frequencies was also support by in-house DFT conducted *in silico* (S17†).

It should be noted, however, that solvent displacement of chloride in coordinative solvent is highly probable, and in this case confirmed *via* cyclic voltammetry. Electrochemical evaluation of **3** indicated sufficient reduction potential to reduce CO_2 to $HCOO^-$, and as such, catalytic experiments were undertaken – production of $H^{13}COO^-$ was evaluated in relation to the sacrificial electron-donor TEA *via* ^{13}C NMR and confirmed to be strictly dependent upon photoirradiation (S20†). Analysis of the catalytic data obtained for **3** indicated that production of $H^{13}COO^-$ increased with additional molar equivalents of TEA, and plateaued at 0.87 mmol $H^{13}COO^-$ at 150 equivalents TEA. This method was verified *via* comparison to the observed integration of a set of formate standards of known concentration and the subsequent calibration curves produced from this data, and confirms the method as a valid means of formate quantification. The reported quantified formate values are consistent at NMR relaxation times of $D1$ = 1 s, 2 s, and 5 s.

While **3** exhibits TN that are comparable to TN previously reported in the literature (Table S1† for summary), it exhibits similar turnover in a significantly reduced amount of time and with visible, and indeed blue light, irradiation. This suggests a much higher turnover frequency (TOF) for **3** that is most likely attributed to successful communication between the naphthalimide photosensitizing unit and the rhenium tricarbonyl core. This also suggests the utility of the naphthalimide ligand precursor as a photosensitizing unit in solar systems. The naphthalimide system used herein is readily derivatized with a variety of substituants, allowing for the modification of the lowest excited state of the complexes; the emissive, likely singlet ^{1}MLCT fluorescent state can be tuned by modification of the ancillary ligand and the identity of the leaving group X, but this excited state must first be confirmed and will be evaluated in the future utilizing time-dependent density functional theory (TD-DFT) experiments that will analyze excited state lifetime as an indicator of excited state identiy. Subsequently, derivitization of the bidentate-naphthalimide core *via* removal of the nitro group and the subsequent alteration of this moiety to significantly more conjugated and photosensitive ancillary units is of paramount importance. This should be a fruitful area of future development.

Funding

The authors wish to thank The Science Foundation Ireland (SFI PI Award 13/IA/1865 to TG), The Irish Research Council (IRC GOIPD/2018/162 to AFH) and TCD for financial support.

Conflicts of interest

There are no conflicts to declare.

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